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PEAT AND COMPOST FILTERS FOR THE SEPARATION OF HAZARDOUS WASTES FROM WATER

CDR grant No. TA-MOU-C12-050

FINAL REPORT

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INTRODUCTION

This work represents a joint effort of two teams, from Poland and from Israel, to develop a low cost filter for industrial wastewater

Industrial wastewater originating from large and modern industries is usually well treated and the effluents meet stringent environmental standards

The level of treatment is much lower in small-scale industries, or workshops

In our surveys, we found numerous small metal finishing workshops, each employing a few workers, with no one trained and able to control and maintain an up to date waste water treatment facility In addition, the price of running a wastewater treatment device in workshops with an average output of a few litters per day, is very high The other alternative, of shipping all the wastewater to a hazardous materials dump is also expensive and difficult

The practical goal of this work was to develop a low cost, sturdy, simple and reliable system that can be placed in such workshops, systems that will bring the effluents to a level that it can be disposed safely into the municipal waste stream

Our basic hypothesis was that organic materials or residues, such as peat, composts or sewage sludge have the adsorptive capacity and are suitable to serve as a cheap adsorber

This report summarizes our efforts and our approach toward the goal of having a system that can be utilized in the industry

The work was conducted jointly by the two teams During the course of this work we had mostly very good and productive cooperation However, this cooperation was not free of problems The Polish team had problems associated with the transfer of funds, problems that slowed down the work during the first half of this project In addition, we did have problems with the write up of this last report, that unfortunately was not timely submitted Due to the last minute submission and to the fact that it was written separately in the two countries, we submit two separate reports

We do hope that regardless of the difficulties, this work has and will contribute to the scientific infrastructure of the two countries and that it will contribute to the solution of important environmental problems

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(our no 150-708)

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1. ABSTRACT

Industrial wastewater originating from large and modern industries is usually well treated and the effluents meet stringent environmental standards The level of treatment is much lower in small-scale industries, or workshops In our surveys, we found numerous small metal finishing workshops, each employing a few workers, with no one trained and able to control and maintain an up to date waste water treatment facility In addition, the price of running a wastewater treatment device in workshops with an average output of a few litters per day, is very high The other alternative, of shipping all the wastewater to a hazardous materials dump is also expensive and difficult The practical goal of this work was to develop a low cost, sturdy, simple and reliable system that can be placed in such workshops, systems that will bring the effluents to a level that it can be disposed safely into the municipal waste stream

Work done during the first half of this project has revealed the high adsorptive capacity of residual humic compounds, i e composts and sewage sludge toward metals These materials are available in Israel and had better adsorption properties as compared with our local peat Adsorption of metals from pure solutions as well as from mixed actual industrial wastewater was studied In addition, it was found that release of the adsorbed metals under acidic conditions is very effective

Our first practical approach was aimed at the development of exchange columns, to be leached with the industrial waste water in the adsorption phase and subsequently leached with acid to get the metals back, in a concentrated stream The major problem associated with this was the inability to maintain good hydraulic conductivity of the column The column was clogged due to gas formation, swelling and dispersion of the different tested organic substrates

Different column operation such as upstream flow patterns did not drastically improved the ability to use the column system

The next and final stage was to develop a batch operation reactor The reactor worked properly in the laboratory and was scaled up to a scale that can be operative in a small workshop The experimental pilot reactor has a volume of 120 l and was shown to effectively reduce the concentrations of metals in raw industrial wastewater from a metal finishing plant The treated effluents can be released to the municipal waste water system and the metals are concentrated in an easily separated sludge that has a volume of less than 10% of the original waste water

We believe that the proposed method will become operative in the near future

2. BACKGROUND AND RATIONALE

The treatment of effluents that contain hazardous materials posses a series of problems, both in regard to the technical aspects and price of the water treatment as well as in regard to the reuse of the water
An intrinsic problem is the fact that very often, the hazardous material is present in the effluents in minute concentration and a large volume of water has to be treated, biologically or chemically, to degrade or detoxify the target compound The ability to separate the hazardous compound from the water at the source is an advantage as to the water treatment and reuse technology

Our working hypothesis is based upon the fact that peat, or related substrates (composts from municipal solid waste or other organic waste material) has a unique capacity for the adsorption of an array of compounds Over the past years, peat has received increasing attention due to the potential to act as an effective agent either for metal ions removal from wastewater or for retrospective monitoring of their migration and accumulation in the environment (e g Wieder et al 1990, Stack et al 1993, Allen, 1996) These substrates have favorable physical properties They are made of colloids that have a high specific surface area, essential to adsorption, yet are aggregated in a way as to have a high hydraulic conductivity, needed for a filtering material These substrates can be disposed when they are saturated by incineration, or treated biologically so as to degrade organic hazardous materials Finally, these substrates are inexpensive and available, in one form or the other all over

Peat has been used in the past as a filter for municipal waste water and was shown to adsorb phosphorus and nitrogen Humic compounds, such as peat or compost are known to have a high chelating capacity and thus to reduce the heavy metal concentration in the solution It is well known that plants grown in peatlands suffer from trace metal deficiency, due to the strong sequestering of these metals by the humic material The humic materials are made of aromatic groups and are, to a large extent hydrophobic Thus, they will efficiently and selectively adsorb aromatic compounds and other non-polar compounds from the aqueous phase (An example for this property is the common use of compost as a filter of organic odorous materials from the air) A computerized literature survey that was conducted revealed a rather large number of reports on the use of peat for the treatment of waste water and of the industrial residues These reports are presented in literature from all over the world, especially from China, Japan and the East European countries The Vast majority of these works are empirical

Most reports describe the use of peat to remove heavy metals from waste water (Cullen & Siviour 1982, Dissanayake & Weerasooriya 1981, Chistova et al 1990, Lapakko 1988, Brown et al 1992, Allen 1996), It is reported that a very high removal of heavy metal (ca 99%) is achieved at pH values higher than 4 One example for such system may be cited from the work of Chaney & Hundemann (1979) "A method for reducing effluent Cd from industrial wastewater to levels equal or below those normally found in domestic wastewater was examined A synthetic oxidized Cd plating solution (100 mg/l Cd) was adjusted to levels of pH and carbonate which would cause low equilibrium dissolved Cd, 560 μg/l Cd remained soluble because of slow precipitation The solution was added in 1 1 increments (14 times) to 60 cm columns of peat or peat + $CaCO_3$ Effluent Cd was measured for each 1 1 addition Cd in the peat columns was analyzed at various depths at the end of the leaching Results showed that was both an excellent physical filter of Cd precipitates and also an effective material for dissolved Cd Effluents averaged 2 μg/l Cd for peat columns and 24 μg/l Cd for peat + $CaCO_3$ Column analysis showed that most of the Cd was present in the upper few cm of the column Thus peat appears to be an effective and inexpensive method for removing Cd from pH and carbonate adjusted industrial wastewater free of strong chelating agents"

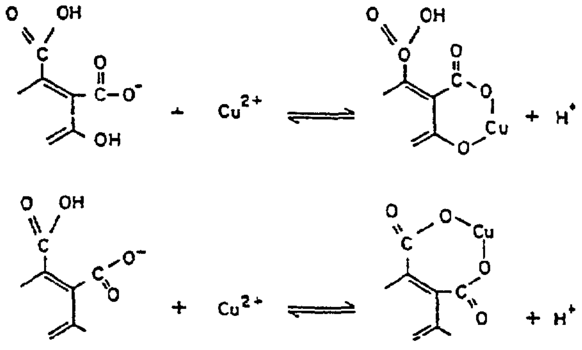
The metals that are adsorbed on peat can be later eluted by leaching with acids The use of peat to remove organic pollutants is also mentioned (Pierre & Cohen 1980, Spivakova& Stadnic 1979) Humic compounds are known to bind heavy metals The ability of humic substances to form stable complexes with metal ions can be attributed to their high content of oxygen containing functional groups, including COOH, phenolic-, alcoholic- and enolic-OH and C=O structures of various types Results given in Table 1 show that the total acidities of fulvic acids (640-1420 meq/100 gr) are considerably higher than for humic acids (560-890 meq/100 gr) Both COOH an acidic OH groups (phenolic OH) contribute to the acidic nature of these substances, with COOH being the most important

Table No. 1 - Oxygen Containing Functional groups in humic and fulvic acids (all values in meq/100 gr)

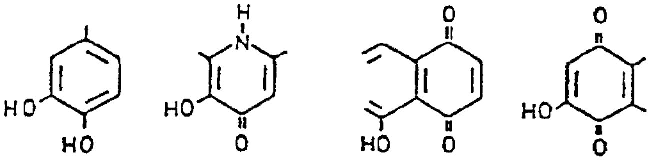
Material	**Total acidity**	**COOH**	**Acidic OH**	**weakly acidic + alcoholic OH**	**C=O**
Humic acids	560-890	150-570	210-570	20-496	10-560
Fulvic acids	640-1420	520-1120	30-570	260-950	120-420

Schnitzer (1969) and Gamble et al (1970) concluded that two types of reactions are involved in metal fulvic acid interactions, the most important one involving both phenolic OH and COOH groups A reaction of lesser importance involved COOH groups only

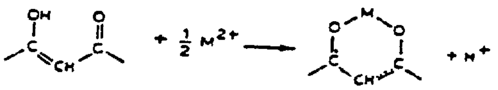
The two reactions are



The formation of phthalate-type complexes (bottom reaction) is likely because humic acids have been shown to contain COOH groups that are located on adjacent positions of aromatic rings (Stevenson 1982) Positive proof for the formation of salicilate-like ring structures (top reaction) has yet to be achieved Other structures considered to be present in humic substances, and that have the potential for binding with metal ions, include the following



Results of IR spectroscopy studies have confirmed that COOH groups, or more precisely carboxylate (COO⁻), play a prominent role in the complexing of metal ions by humic and fulvic acids (Boyd et al 1981, Piccolo et al 1981, Vinkler et al 1976) Some evidence indicates that OH, C=O, and NH groups are also involved (Boyd et al 1979, Piccolo et al 1981, Vinkler et al 1976) Complexes may be formed with conjugated structures, according to the following reactions (Piccolo et al 1981)



Results of electron spin resonance spectroscopy (ESR) studies have also been inconclusive Lacatos et al (1977) reported that Cu^{+2} was bound to humic acid by a nitrogen donor atom and two carboxylates On the other hand, Mcbride (1978) concluded that only oxygen donors (COO) were involved , furthermore, a single bond was formed between Cu^{+2} and humic acid Boyd et al (1981,1983) obtained evidence indicating that Cu^{+2} formed two equatorial bonds with oxygen donor atoms of humic acids, such as would be formed by the reactions shown above Goodman & Cheshire (1973,1976) obtained evidence suggesting that Cu retained by peat humic acid after washing with acid was coordinated to porphrin groups, from which they concluded that a small fraction of Cu in peat was strongly fixed in the form of porphyrin-type complexes In contrast, spectra obtained by Bloom & McBride (1979) for acid washed peat failed to show the participation of groups other than COO$^-$ in binding of Cu^{+2} Approaches used to determine the binding capacities of humic substances for metal ions include coagulation (Rashid 1971), proton release (Stevenson 1976, Stevenson 1977, van Dijk 1971) metal ion retention was determined by competition with a cation-exchange resin (Crosser & Allen 1977, Zunino et al 1972), dialysis (Zunino & Martin 1977) anodic stripping volammetry (Guy & Chakrabarti 1976, O'shea & Mancy 1976) and ion-selective electrode measurements (Bresnahan et al 1978, Buffle et al 1977), The maximum amount of any given metal ion that can be bound was found to be approximately equal to the content of COOH groups The COOH content generally fall within the range of 1 5-5 0 meq/g (e g 48-160 mg Cu/gr humic acid)

For adsorbent characterization and the strength of adsorbed metal binding estimation is of great importance for evaluation either of metal potential for remobilization and recovery of bound metals along with regeneration/repeated reuse of the adsorbent For this purpose, assessment of metal fractionation with respect to binding strength, apart from the mechanism of binding, may give the most valuable information, which would enable optimum adsorbent use, reuse and efficient metal recovery
sequential extraction- a method developed primary for defining chemical "forms" of metal binding is conventionally used to differentiate between the exchangeable, carbonatic, easily reducible (hydrous Mn-oxides), moderately reducible (amorphous Fe-oxides), oxidizable (sulphides and organic phases) and residual fractions in different substrates, mostly in soil and sediments, but also in sewage sludge (Forstner and Kersten, 1988) In this study, pattern of sequential extraction by Tessier *et al,* 1979, modified by Kersten and Forstner, 1988, comprising 7 steps, was applied The use of this sequential leach procedure for the environmental studies, as well as, with some modifications, for geochemical applications, e g for characterizing different types of surficial geochemical anomalies, including identification of the sulphide phase within the insoluble organic residue of humus (Hall *et al,* 1996, Kaszycki and Hall, 1996) and its high precision tested on 10 different international CRMs i e soils, marine mud, lake sediments and the till samples (Hall et al ,1996 ab) proved it to be an extremely useful and reliable tool

Nevertheless, different chemical extraction sequences being in use are still subject to arguments concerning among others the chemical "forms" of binding and redistribution of metals among phases during fractionation (e g Tessier and Campbell, 1991, Tack and Verloo, 1996) In the case of humic-rich matters the direct application of this procedure for the identification of binding mechanisms may be questionable In substrate such as peat, consisting mainly of organic matter, where the mineral fraction content usually does not exceed 10-12 % wt , the binding mechanisms can differ from the mentioned above This was already pointed out with respect to peat matter (Twardowska and Kyziol, 1996)

Assuming influencing the quantity of metal ions bound by humic substances include pH, ionic strength, molecular weight and functional group content (Fitch and Stevenson 1983, Stevenson & Fitch 1981) For any given pH and ionic strength trivalent cations are bound in greater amounts than divalent cations Cations forming strong coordination complexes (e g Cu) will be bound to a greater extent than weakly coordinated ones (e g Ca or Mg)
Avnimelech & Raveh (1979, 1982) have shown that iron hydroxide solubility is raised by orders of magnitude in municipal solid waste effluents, due to the binding of iron to soluble organic complexes The solubility of the metal-humic complexes is thus an essential feature of any proposed filter
A number of processes effect the solubility characteristic of metal-humate and metal-fulvate complexes A major factor is the extent to which the complex is saturated with metal ions Other factors affecting solubility include pH, adsorption of the complex to mineral matter and biodegradation Under proper pH conditions, trivalent cations, and to some extent divalent cations, are effective in precipitating humic substances from very dilute solutions Monovalent cations are generally effective only at relatively high particle concentrations
Humic substances are insoluble in organic-rich horizons of mineral soils, as well as peat, which can be attributed to intermolecular associations involving H-bonding and polymerization through bridging by polyvalent cations Organic adsorbents are known to adsorb organic pollutants, Thus it is well established that pesticides in the soil are specifically adsorbed to the organic matter in the soil

The general procedure widely used in batch sorption studies, also on peat (e g Wieder, 1990, Allen et al , 1992), was used in this study, in order to evaluate the effects of the listed conditions

In general, sorption capacity evaluated experimentally is the most reliable, direct source of information Langmuir model is assumed a better fit to the experimental data than the Freundlich model for peat metal ion systems (Wieder, 1990, Allen, 1996)

The term Peat was used all along the previous discussion Peat is a natural product produced as a decomposition product of vegetation, when this decomposition is limited either due to flooding and lack of oxygen, or due to climatic conditions (low temperature) The decomposition product under such conditions is an array of humic compounds, Different peat sources differ by the percentage of organic matter, the ratio of humic to fulvic acids, the particle size (from colloidal size to cm scale) and by the presence of nutrients and salts A different group of similar materials is the variable group of composts A compost is the stable decomposition product of organic waste materials Usually the definition of composts is limited to aerobically stabilized residues The more available organic substrates are degraded along the compostation process and the residues are made mostly of stable humic compounds The stability (maturity) of the compost can be adjusted by the length of the active compostation stage and that of the maturation stage Composition of different composts is different according to the source of the residue The most common composts are made of municipal solid wastes, sewage sludge, manure, food industry wastes and agricultural wastes Particle size of the compost depends, to a large extent on the particle size of the parent materials and on the presence of stable or inert particles in the parent material In addition, compost plant usually sieves the product and thus different distribution size of particles is available

3. SUMMARY OF RESEARCH WORK IN FIRST AND SECOND YEAR

3.1 General Methods

in this research, a number of major procedures were used in order to study and understand the adsorption ability of the substrates in different conditions The following methods were used

A. Adsorption Isotherms

The isotherms were aiming to show the ability of the substarte to adsorb metals in a constant pH The isotherms were analysed according to the Langmuir theory, and from that data obtained the constants -
M- the maximal metal adsorption capacity of the adsorbent
E- the factor related to free energy of adsorption

A.1 Materials

A.1.1. Chemicals

Stock Solutions, having a metal concentration of 1000 mg/L, were prepared by dissolving separately 2 744 g $ZnSO_4*H_2O$ and 3 292 g $CuSO_4*5H_2O$ in 1000 ml H_2O

Working solutions were made from the stock solutions, by diluting to concentrations 0-500 mg/L

Acetate Buffer was prepared by mixing 12 5 ml 2 M acetic acid and 87 5 ml 2 M Na-acetate and adding distilled H_2O up to 1000 ml

A.1.2 Adsorbents

Peat from the Hula vally Israel, commercialy sold North European peats, Compost from municipal waste and an aerobically digested sewage sludge were tested as Cu and Zn adsorbing materials

A.2. Methods

A 2.1. Instruments

Atomic adsorption spectrophotometer "Varian - Spectra 300 plus", pH meter "Metrohm 654", Centrifuge, Conductivity meter, Shaker were used during the work

A.2.2. Sample Preparation

Adsorbents were tested at constant pH in either status nascendi or after washing with Hcl or H_2O In washing pre-treatment Whatman #1 or #42 was placed into wide Buchner funnel to which one to three l of a material was added the material was slowly leached with distilled H_2O or Hcl, water to solid ratio (w/w was 5 to 1 eached sample was vacuum dried and kept in refrigerator at 5°C
Determination of buffer mixtures for constant ph place 10 g of peat into suitable glass and add different amount (0-50 ml) of 0 5 N Hcl Make final volume of samples to 50 ml using acetate buffer Put on shaker (100 RPM) and shake overnight Measure pH in sample An acid addition that yields desured pH is used in subsequent experiments

A.2.3. Method for Elucidation of Adsorption Isitherm on Peat and Materials Alike

Mixture of acetate Buffer and Hcl (50 ml) was added to 10 g of an adsorbing material Suspention was pre-equilibrated for 16 hrs Immediately thereafter 50 ml of either Cu or Zn working solution of known concentartion C was added to suspention The suspension was shaked for additional 20 hrs, and then filtered through Whatman #1

Metal concentration, C_O = metal concentration at 0 time and C_{eq} = metal concentration in equilibrium after 20 hrs adsorption, were determined by atomic adsorption

B. Binary Systems

Experiments were conducted with the binary system of Zn-Cd and Pb-Cu both in equal and varying concentrations. This set of experiment was designated to examine the effect of the presence of one metal ion on the adsorption of another.

B.1. Materials

B.1.1. Chemicals

Stock Solutions, having a metal concentration of 2000 mg/L, were prepared by dissolving separately
3.2 gr $Pb(NO_3)_2$,
7.86 gr $CuSO_4$,
5.49 gr $ZnSO_4{*}H_2O$ and
4.58 gr $CdSO_4$ in 1000 ml acetate buffer at pH=5.5

Working solution was made from stock solution by diluting it to concentrations 0-1000 mg/L.

Acetate Buffer was prepared by mixing 88 ml 0.2 M acetic acid and 412 ml 0.2 M Na-acetate and adding distilled H_2O up to 1000 ml.

B.1.2. Adsorbents

Compost from municipal waste and an aerobically digested sewage sludge were tested as Zn and Cd adsorbing materials.

B.2. Methods

B.2.1. Instruments

Atomic adsorption spectrophotometer "Varian - Spectra 300 plus", pH meter "Metrohm 654", Centrifuge, Shaker, Hot plate were used during the work.

B.2.2. Sample Preparation

Substrates were pre-treated with H_2O and acetate buffer Washing with H_2O, water to solid ratio 3 1, as described in our annual report 1993-1994 chapter 3 2 2 [2]
Conditioning with acetate buffer by shaking 500 gr of washed substrate with 1500 ml buffer overnight, then filtering through Whatman #1 filter paper

Two series were applied to evaluate adsorption in binary systems:

B.3. Metals in Equal Concentrations

10 gr samples of pre-treated substrate were placed into suitable glass vials
Mixtures of acetate buffer and metals stock solutions in different ratios were added to the substrates
The suspension was shaked for additional 20 hrs, and then filtered through Whatman #1

Metals concentration, C_o = both metals concentration at 0 time and C_{eq} = each metal concentration in equilibrium after 20 hrs adsorption, were determined by atomic adsorption

B.4. Metals in Varying Concentrations

10 gr samples of pre-treated substrate were placed into suitable glass vials
Mixtures of acetate buffer and metals stock solutions in different ratios were added to the substrates
Ratios were calculated so that in each isotherm one of the metals will be kept in constant concentration, while the other varies For each metal there were four Such constant concentrations
The suspension was shaked for additional 20 hrs, and then filtered through Whatman #1

Metals concentration, C_o = first metal concentration at 0 time, C_{const} = second metal concentration in equilibrium and C_{eq} = each metal concentration in equilibrium after 20 hrs adsorption, were determined by atomic adsorption

C. Sequential Extraction

In this chapter of the work an attempt to look into the pattern of adsorption was made The sequential adsorption procedure provided a tool to characterize the adsorption of each and every metal on the different substrates and to compare them

C.1. Materials

C.1.1 Chemicals

1 1 M NH_4NO_3 at pH=7 - prepared by dissolving 40 02 gr of NH_4NO_3 in 1000 ml distilled H_2O

2 Acetate Buffer at pH=4 5 - prepared by mixing 30 5 ml of Acetic acid (0 2 M) and 19 5 ml of NaOAc 0 2 M, diluting to total volume of 1000 ml

3 0 04 M $NH_2OH*HCl$ in 25% acetic acid - prepared by dissolving 3 61 gr of $NH_2OH*HCl$ in 1000 ml of acetic acid

4 0 01 M nitric acid

5 H_2O_2 30%

C.1.2. Substrates

the method was implied on two different substrates, with three different pre-treatments

1 No adsorption at all, only washing with water and buffer

2 adsorption of metal from a solution of 500 ppm

3 adsorption of metal from a solution of 1000 ppm

The metals were adsorbed on the substrates in the procedure described in our former report [1]

C.2. Methods

C.2 1. Instruments

Atomic adsorption spectrophotometer "Varian - Spectra 300 plus", pH meter "Metrohm 654", Centrifuge, Shaker, Hot plate were used during the work

C.2.2 Method

Selective Sequential dissolution Technique was adapted from Han & Banin (1)

a *Soluble and exchangeable elements (EXC)* One gram of substrate was weighed into 50 ml polycarbonate centrifuge tube, and 25 ml of 1 M NH_4NO_3 (sol #1) was added to it The suspension was shaken for 30 min at 25^{o}C and then centrifuged at 10,000 rpm for 10 min The supernatant was decanted for analysis and the substrate residue was kept for the next step The same centrifugation decantation procedure was used after each extraction step in the following procedure, although in many cases centrifugation was not needed for the separation

b *Carbonate bound (CARB)* 25 ml of NaOAc-HOAc buffer solution (sol #2) were added to the substrate residue from previous step The mixture was agitated for 16 hrs at 25^{o}C Excess CO_2 was released by frequent opening of the tube cap during the first 6 hrs Then the centrifugation-decantation was repeated

c *Bound to easily-reducible oxides (ERO)* 25 ml of $NH_2OH*HCl$ (sol #3) were added to the residue from previous step and agitated for 30 min (We think that the name of this fraction is wrong It was found that the same amounts of metal are extracted when the reducing agent $NH_2OH*HCl$ is omitted from the acidic extraction solution (see appendix II as an example) Fraction *c* is probably a fraction that is solubilized when the acidic extraction is stronger than that used to extract fraction *b*)

d *Bound to organic matter (OM)* the residue from previous step was transferred to a Pyrex glass test tube using 3 ml of nitric acid (sol #4) 55 ml of 30% H_2O_2 (sol #5) were added, and the suspension was digested at 80^{o}C for 2 hrs An additional 2 ml of 30% H_2O_2 were added, and heating was continued for another one hr The mixture was allowed to cool to room temperature and 15 ml of nitric acid (sol #4) were added After agitation for 10 min, the supernatant was separated as described above

e *Bound to reducible oxides (RO)* 25 ml of 0 04 M $NH_2OH*HCl$ (sol #3) were added to the residue, and the mixture was digested at 90^{o}C for 3 hrs, then cooled, and the supernatant separated as described above

D. Desorption

In order to determine the pheasability of reusing the adsorbent after acidifying, the pattern of desorption as a function of pH was examined

D.1. Materials

D.1.1 Chemicals

To control the pH, 0 5 N HCl solution was used

D.1.2. Adsorbents

Working Substrates, compost and sewage sludge, were equilibrated with all metals - Zn, Cd, Cu, Pb, Fe and Cr in the same method as described in our former report [1]

D.2. Method

D.2.1. instruments

The instruments used for this work are the same as described in ch 2 1 2 1

D 2.2. Method for desorption of metals

10 gr samples of substrate, with metal adsorbed on it, were placed into suitable glass vial, and a mixture of HCl and water in different ratios was added The total volume was 100 ml

After 24 hrs shaking, pH was measured and the suspension was filtered through Whatman #1 filter paper

In order to determine the amount of metal desorbed from virgin material in the different pH values, the procedure was applied to a sample of compost and sludge, and was examined for any traces of metals

E. Column Work

Some work has been done on columns, containing compost or sludge
Through the column a metal solution was passed, and the rate of flow was measured Those columns were in fact a small scale pilot plant to determine the efficiency of adsorption in continuous flow The columns were tested both with sinthetic solutions and with industrial wastewater

E.1. Materials

E.1.1. Chemicals

Stock Solutions, having a metal concentration of 2000 mg/L, were prepared by dissolving separately
7 86 gr $CuSO_4$,
5 49 gr $ZnSO_4*H_2O$ and
4 58 gr $CdSO_4$ in 1000 ml distilled water

Working solution was made from stock solution by diluting it to concentrations 0-1000 mg/L

Industrial wastewater collected from the metal plating plant, and measyred for pH and metal concentrations

E.1.2. Adsorbents

Compost from municipal waste and an aerobically digested sewage sludge were tested as Zn and Cd adsorbing materials

E.2. Method

E.2.1. instruments

Glass Columns, as described in appendix I (ch 2 3)
The column having active length of 20 cm and diameter of 4 cm
Constant head bottles, having volume of 2 litters
The instruments used for determining metals concentrations are the same as described in ch 2 1 2 1

E.2.2. Method of work

The column was filled with a thin layer of glass wool, sand (washed and dried) and a constant volume of adsorbent Due to low Hydraulic conductivity of sludge, we used 95 gr of compost (aprox 200 ml), and 45 gr of sludge

In order to reach saturation in the column we followed a thumb rule according to which 2 litters of distilled water were passed through the column before introducing the working solution

Experiments were done using 3 metals in different concentrations and different flow rates

4. EXPERIMENTAL WORK - 3RD YEAR

4 1. Plan of Work

The main and most important purpose of this year's work was to built a small scale facility that will determine the feasibility of actual treatment column for metal plating workshops

for this purpose we tried to find a representing composition of waste solution of several metal processing workshop, and to accommodate a proper treatment to each case

The conclusion of this year was to evaluate if and under what conditions will this treatment facility work

4.2. Work Done So Far

In the passing year, we worked on two main subjects At the first few months of the year we conducted a survey on metal processing facilities in Israel, and the type of waste water they produce

After characterizing the desired waste type, we contacted a small workshop in the Haifa region, and sampled its waste stream We checked the waste for pH, metal concentrations and flow rate on more than one occasion, and started to work with these wastes

We determined the adsorption isotherms of these wastes on sludge and compost in their natural conditions (pH, metal concentration and metal concentration ratio)

The second part of the year was dedicated to column work aimed to determine the feasibility of commercial use of the columns In this context we conducted a series of column experiments in varying conditions to reach an optimal degree of adsorption and recovery in minimal cost All experiments were conducted on sludge and later compost columns, and with the industrial waste water

All methods and research activities are given in chapters 2 1-2 3

4 2.1. Metals Concentrations in Metal Processing Industry Waste Water

In order to try and determine a typical composition of waste streams from different metal processing facilities, we have tried to collect data involving waste streams of typical metal processing workshops in Israel

Our sources were mainly two - The ministry of environment of Israel, the Tel-Aviv region, and the “Shafdan”, which is the treatment authority for waste water in the Dan district

As a first step, we collected the main metal processes used in Israel, and characterized the main pollutants in their waste stream (table 2)

As can be seen from this table, there is no common denominator between the large variety of processes described

TABLE NO. 2 - MAIN METAL PROCESSING WASTE STREAMS (from MoE, 1995)

process	waste stream main components
Chemical nickel plating	nickel sulfate, sodium hypophosphite, complex former and buffering agents, stabilizers, dimethylaminoborane, accelerators
Chemical coppering	copper sulfate, complex former, sodium hydroxide, stabilizers
Iron posphating	sodium biphosphate, chlorate, nitrates/nitrites, molibden salts, complex formers, polyphosphoric acids, surfactants
Zinc posphating	phosphoric acid, zinc salts, nitric acid, hydrofluoric acid, nitrates/nitrites, chlorate, chromate, nickel
Chromating - Aluminum	sodium carbonate, sodium chromate, chromic acid, sodium dichromate, sodium fluoride, phosphoric acid
Chromating - Aluminum	chromic acid, nitric acid, hydrofluoric acid, sodium dichromate, calcium fluoride, chromic acid, fluorides, nitric acid

TABLE NO. 2 -continuation

process	waste stream main components
Degreasing	paraffin oils, molybdenum sulfides?, propene, butane, propylene, graphites?, asphalt?
Degreasing with organic solvents	trichloroeyhylene, perchloroethylene, trichloroethane, methylene chloride, trifluorotrichloroethane, stabilizers
kerosine, white spirits, petrolium spirits, mineral terpentine containing	toluene, ethyl acetate, ethanol, xylene, trimethylbenzene, isopropylbenzene, methyl isopropylbenzene, ethylbenzene, diethylbenzene
Water-based degreasing	sodium hydroxide, sodium carbonate, sodium phosphate, sodium pyrophosphate, sodium metasilicates, sodium tetraborate, sodium tetraborate, sodium gluconates, non-ion-active tensides, anion-active tensides, organic complex former, fatty acids, alcohols, antioxidants, biocides, corrosion inhibitors, wetting agents
Ultrasonic degreasing	trifluorotrichloroethane, methylene chloride, water, emulsifiers, tensides
Emulsion degreasing	solvents, water, emulsifiers
Electrolytic degreasing	sodium hydroxide, trisodium phosphate, sodium carbonate, wetting agents
Pickling	sulfuric acid, nitric acid, hydrochloric acid, hydrofluoric acid, chromic acid, sodium carbonate, sodium chloride, sodium fluoride, hydrogen peroxide
Hard chromium-plating	chromic acid, sulfuric acid, sugar, strontium sulfate, potassium hexafluorosilicate
Decorative chromium plating	chromic acid, sulfuric acid, sugar, strontium sulfate, potassium hexafluorosilicate
Black chromium-plating	chromic acid, ammonium metavanadate, acetic acid, barium carbonate
Electrolytic gilding	gold cyanide, sodium cyanide, sodium carbonate, sodium phosphate, gold, ammonium nitrate, nickel, cobalt sulfate
Electrolytic polishing	phosphoric acid, sulfuric acid, chromic acid, fluoboric acid, hydrofluoric acid

TABLE NO. 2 -continuation

process	waste stream main components
Electrolytic galvanizing	sodium cyanide, sodium hydroxide, gluconate, borate, ammonium chloride, zinc chloride, aluminium sulfate, boric acid, glossing agents, wetting agents, surfactants, surface smoothers, nickel fluoroborate, ammonium chloride
Tinning	tin (II) sulfate, sulfuric acid, cresol sulfuric acid, resorcinol, pheno sulfuric acid, betanaphtol, phenol, formaldehyde, tin fluoborate, tin, fluoboric acid, sodium stannate, nickel chloride, tin chloride, ammonium hydrogen fluoride, ammonia, ammonium chloride, cadmium sulfate, zinc cyanide, sodium cyanide
Cadmium coating	sodium cyanide, cadmium oxide, sodium hydroxide, glossing agents, wetting agents, cadmium
Coppering	copper sulfate, sulfuric acid, glossing agents, copper fluoborate, fluoboric acid, copper cyanide, sodium cyanide, sodium carbonate, potassium cyanide, sodium hydroxide, copper
Brass plating	copper cyanide, potassium zinc cyanide, sodium cyanide, sodium carbonate, ammonia, copper, zinc
Silvering	sodium cyanide, silver cyanide, sodium carbonate, silver, sodium hydroxide
Lead plating	lead fluoborate, fluoboric acid, lead, sodium hydroxide
Anodizing	chromic acid, sulfuric acid, phosphoric acid, oxalic acid, pigments, sulphosalicilic acid, sulphophtalic acid, maleic acid
Hot-dip galvanizing	flux (zinc ammonium chloride), wetting agents, lead, aluminium-zinc alloy, nickel, zinc
Oxidation of steel	sodium hydroxide, sodium nitrate, sodium nitrite, copper sulfate, zinc sulfate, mercury chloride, ferric nitrate

The next thing we tried to do was to determine the most problematic metals in the stream

Table no 3 shows the maximal concentrations of heavy metals in waste water, allowed for biological water treatment facilities

TABLE NO. 3 - LEVEL CONCENTRATIONS OF HEAVY METALS IN WATER TREATMENT FACILITIES (PPM)
(from MoE, 1995)

Metal (concentrations in ppm)	**nitrification**	**activated sludge**	**anaerobic treatment**
Cd	0 01-15	1	5
Cu	4-150	1	5
Cr	10-118	10	5
Pb	0 5-20	0 1	0 5
Hg	1-150	0 1	13
Ni	0 1-10	1	0 25
Zn	10	3	400

From these Data it is possible to calculate the concentrations of metals allowed in the waste stream

The EPA (United States Environmental Protection Agency) distinguish four types of typical waste water streams (EPA, 1983) The metal processes are classified according to the type of waste they produce The four types of waste streams are described on table 4

TABLE NO. 4 - TYPICAL WASTE STREAMS OF THE METAL PROCESSING INDUSTRY.
(EPA, 1983)

Type of stream	Process producing
common metals	Electroplating of aluminum, brass, bronze, cadmium, acid copper, fluoborate copper and copper pyrophosphate, iron, lead, nickel, solder, tin and zinc
Precious metals	Electroplating of gold, silver, rhodium, palladium, platinum, indium, ruthenium, iridium and osmium
Cyanide wastes	cyanide plating of copper, cadmium, zinc, brass, gold, silver, indium, iridium
Hexavalent chromium wastes	chromium plating

Our work will be related to the first category - common metals Table no 5 shows the concentration of various pollutants found in the waste stream of "common metals processes", based on a survey conducted by the EPA (EPA, 1983)

TABLE NO. 5 - POLLUTANT CONCENTRATIONS FOUND IN THE COMMON METALS RAW WASTE STREAM
(average daily value, ppm)
(EPA, 1983)

Toxic pollutant	**min**	**max**	**mean**
Antimony	0	0 43	0 007
Arsenic	0	0 064	0 005
Beryllium	0	0 044	0 008
Cadmium	0	21 5	0 613
Chromium	0	35 4	2 1
Copper	0	500	14 2
Cyanide	0	2370	42 1
Lead	0	42 3	1 25
Mercury	0	0 4	0 005
Nickel	0	415	19 4
Selenium	0	0 06	0 007
Silver	0	0 08	0 006
Thallium	0	0 062	0 008
Zinc	0	10500	312
Aluminum	0	200	27 4
Barium	0	0 017	0 0032
Boron	1 67	4	31 4
Calcium	25 0	76 2	51 4
Cobalt	0	0 023	0 007
Fluorides	0	36 1	4 31
Iron	0	13100	500
Magnesium	5 6	31 1	16 1
Manganese	0 059	0 5	0 233
Molybdenum	0	0 3	0 102
Phosphorous	0	76 7	7 72
Sodium	16 7	310	151
Tin	0	14 7	1 04
Titanium	0	4 3	0 493
Vanadium	0	0 216	0 066
Yttrium	0	0 02	0 010
Oil & Grease	4 70	802000	40700

Trying to define the most common metals in waste streams of this kind, table no 6 shows a questionnaire spread to more then a thousand metal finishing workshops throughout the US (EPA, 1983)

TABLE NO. 6 - COMMONNESS OF METALS IN WASTE STREAMS (EPA, 1983)

Metal	**total answers**	**KTBP**	**BTBP**	**KTBA**	**PTBA**
Antimony	990	33	37	696	200
Arsenic	996	39	18	689	226
Beryllium	986	33	37	685	208
Cadmium	1012	272	56	479	179
Copper	1038	577	105	248	82
Chromium	1048	633	96	219	74
Lead	1017	280	84	477	150
Mercury	1002	88	25	630	233
Nickel	1039	531	110	276	98
Selenium	990	37	28	686	215
Silver	1007	185	54	562	182
Zinc	1032	520	74	304	112

KTBP - known to be present
BTBP - believed to be present
KTBA - known to be absent
BTBA - believed to be absent

The metals shaded are the ones most common, that appear in a large number of plants

Any attempt to find detailed information about the metal finishing industry in Israel had reached a dead end due to lack of cooperation from the workshops themselves, and the confidentiality of information collected by the authorities From the information we were able to get concerning facilities in the Dan and Tel-Aviv region, we can draw several conclusions The results of the survey are summarized in table no 7

TABLE NO. 7 - COMMONNESS OF METALS IN WASTE WATER IN THE DAN DISTRICT, ISRAEL

(information supplied by the Shafdan)

Composition	No of plants
Cu alone	1
Cr (only total checked)	3
Ni alone	2
Cd alone	1
Zn and Fe	1
Cu and Cr (+6)	1
Cu and Ni	6
Cr (+6) and total Cr	17
Cr (total) and Ni	3
Cr (total) and Al	2
Ni and Cd	1
Zn, Cu and Cr (total)	1
Zn, Cu and Ni	3
Ni and Cr (+6) and total	4
Cr (total), Ni and boron	1
Pb, Al, As and Mo	1
Zn, Cu, Cr (total) and Cd	1
Zn, Cu, Cr (total) and Al	1
Zn, Cr (total) Ni, Ag and B	1
Zn, Cr (total) Cd and Fe	1
Cu, Ni, Cr (+6) and total	5
Ni, Cd, Cr (+6) and total	1
Al, Fe, Cr (+6) and total	1
Cr (total), Ni, Cd, Ag, Co, Mo and Mg	1
Ni, Pb, Fe and Sn	1
Zn, Cu, Cr (total), Ni and Cd	5
Cu, Ni, Cd, Cr (+6) and total	17
Cu, Cr (total), Ni, Cd, Ag	1
Cu, Cr (total), Ni, Cd, Pb, Fe	1

The shaded compositions are the most common ones It is important to notice the high number of facilities with waste water containing Cr (+6 and total) alone these are most likely tannery workshops, which are very common in this specific industrial zone The other frequent combination is that of the four metals - Cu, Ni, Cd and Cr This will also be in accordance with the data given on table 6

From all the information gathered and shown to this point, it is clear that the most common composition found in waste streams of metal processing plants is that of 4 or 5 metals - usually Cd, Cr, Ni and Cu and in some cases also Zn Different combinations of these metals can be found, but it is clear that the most general and interesting case is that of the five metals mixed together, in different ratios and probably different levels of pH

4.2.2. Characterization of the Waste Water Used in This Research

After defining the type of waste stream that will interest us most, we tried to find small workshops in the Haifa region that will fit the former description We specifically tried to find one that will deal with zinc plating and maybe other similar processes, will not have a high flow rate - so it will be practical to built a pilot plant in his yard, and also with a varying composition of metals concentration, to be able to conclude general conclusions from it's examination

At this point in our research we ran into some trouble trying to persuade commercial workshops to cooperate with us The fear from the authorities and constant examination of their waste water caused many of them to refuse our request Eventually, we contacted two workshops, and started sampling their waste Due to our promise to confidentiality, they will be marked here as A and B

TABLE NO. 8 - DESCRIPTION OF THE METAL FINISHING PLANTS

	plant A	**plant B**
process	hard chromium plating, silvering, cadmium, tin and zinc plating	zinc plating with caustic soda
waste stream flow rate	Apr 9 ton water / year	1 ton sludge / year
current treatment	no treatment removal to hazardous waste facility ???	reduction of chromate, precipitation and neutralizing pH ???

From a brief look at the data presented in table no 8 concerning the two facilities it seemed that they were both "interesting" from the scientific and practical point of view The next stage was to sample the waste stream of these plants, and try to characterize the nature of these streams

4 2.2.1. Sampling Procedure

In both facilities waste water solutions are kept in closed flasks of about 1 cubic meter, outdoors

Samples from plant B were taken from the storage flask placed in front of the treatment process
In both plants, flasks were mixed to the best of our ability, and 5 liter samples were taken from the middle of the flask
The samples were immediately taken to the lab for pH determination
After pH measurement samples were filtered through a double layer of Whatman #1 filter paper
The metals concentration was then determined with the use of an ICP

4.2.2 2. Instruments

pH meter "El-Hama", Inductively Coupled Plasma Atomic Emission Spectrometer "Perkin Elmer" Optima 3000-DV

4.2.2.3. Adsorbents

Working Substrates, compost and sewage sludge, were equilibrated with all solutions in the same method as described in our former reports (Avnimelech & Twardowska, 1995)

4.2.2 4. Methods

Sequential Extraction - as described in chapter 3 1 C
the method was implied on two different substrates, with two different pre-treatments
1 Raw material, No adsorption at all, only washing with water
2 Final stage, Maximum adsorption of waste water solution

The solutions were adsorbed on the substrates in the procedure described in our former reports (Avnimelech & Twardowska, 1995) with the waste water as sampled from the plants

Adsorption Isotherms - as described in chapter 3 1 A

Working solutions were made from the stock solution as sampled, by diluting it with acetate buffer to different concentrations The dilution was made in order to avoid the changing of concentrations ratio among the metals in the solution

Desorption Ability - as described in chapter 3 1 D

4.2.2.5 Results and Discussion

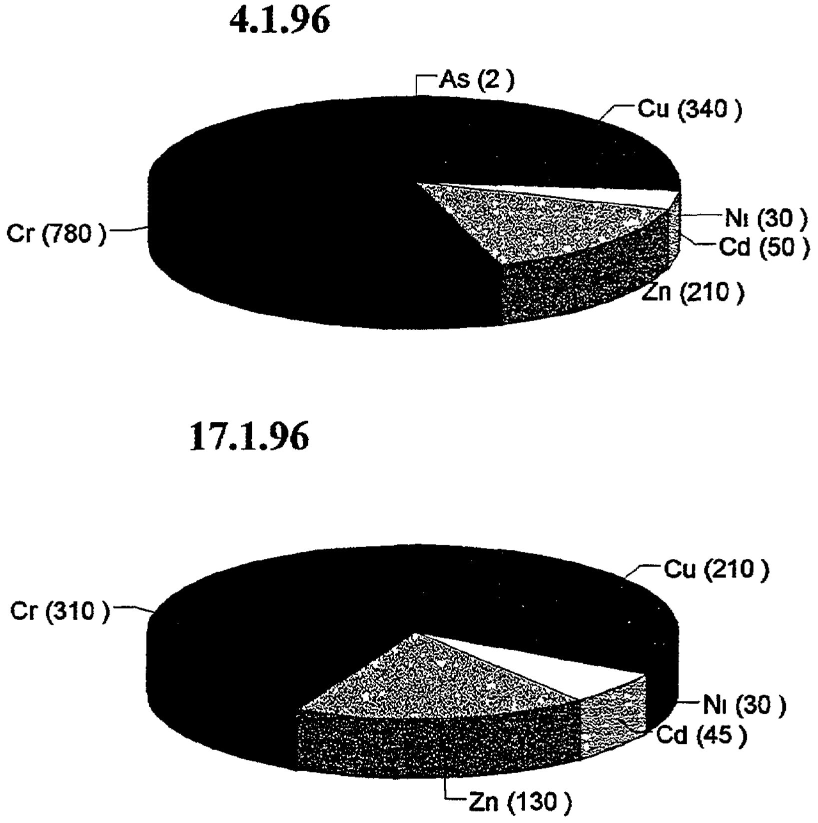
The results of sampling, executed through January 1996 are given in table no 9 and on figures 1-2

TABLE NO. 9 - COMPOSITION OF METALS IN INDUSTRIAL WASTE WATER

	Plant A		plant B	
date of sampling	4 1 96	17 1 96	8 1 96	24 1 96
pH	3 5	3 6	5 0	6 9
As (ppm)	2	-	-	-
Cu (ppm)	340	210	-	-
Ni (ppm)	30	30	-	-
Cd (ppm)	50	45	-	-
Zn (ppm)	210	130	4	1 5
Cr total (ppm)	780	310	-	-
Mn (ppm)	-	-	4	1 5
Mg (ppm)	-	-	260	250

As can be seen already from these primary results - the waste concentrations of plant B waste water are very poor in “interesting” metals The metal concentrations are relatively low, and only Mg appears in significant levels Mg was not one of the metals concerning us in this research, and therefor we decided to continue our research on the waste water of **plant A**

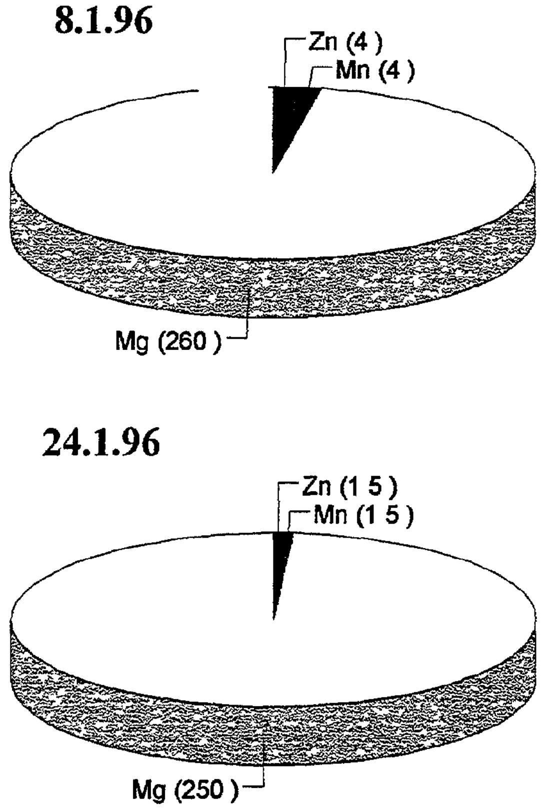
Figure 1 - Plant A waste water concentrations in ppm



4.1.96

17.1.96

Figure 2 - Plant B waste water concentrations in ppm



In addition to measurements and chemical analyses of the waste water, we have performed a few tests on adsorption of metals from the waste water We have derived the adsorption isotherm of the solution with accordance to the method described in chapter 3 1 A and performed sequential extraction on the sludge, as described in chapter 3 1 C

All the results of the adsorption isotherms are given on figures 3 to 13
Adsorption isotherm was plotted for each of the metals in the solution, in the presence of all other metals, as collected in site.
Equilibrium adsorption capacities and maximal adsorption energies were calculated in the same manner as for the single-metal-system, by performing linear regression analysis on the experimental data using the rearranged form of Langmuir isotherm, as described in our former reports (Avnimelech & Twardowska, 1995)
The rearranged form of Langmuir isotherm is given as.

$$1/Y = 1/b + (1/(b*a)) * (1/X)$$

where
Y = the mass of metal adsorbed per mass of adsorbent at equilibrium
X = measured metal concentration in solution at equilibrium
a and b = constants

$b = M$ = the maximal metal adsorption capacity of adsorbent
$a = E$ = the factor related to free energy of adsorption $\approx e^{(-\partial G/RT)}$

The results are given in table no 10.

In some cases, regresion was not possible since the shape of the curve in the tested concentrations was not typical Langmuir.
In those cases we gave a freehand estimation to the maximal adsorption capacity, from the results that were measured in the experiment

TABLE NO 10 - RESULTS OF LINEAR REGRESSION FOR ADSORPTION ISOTHERMS

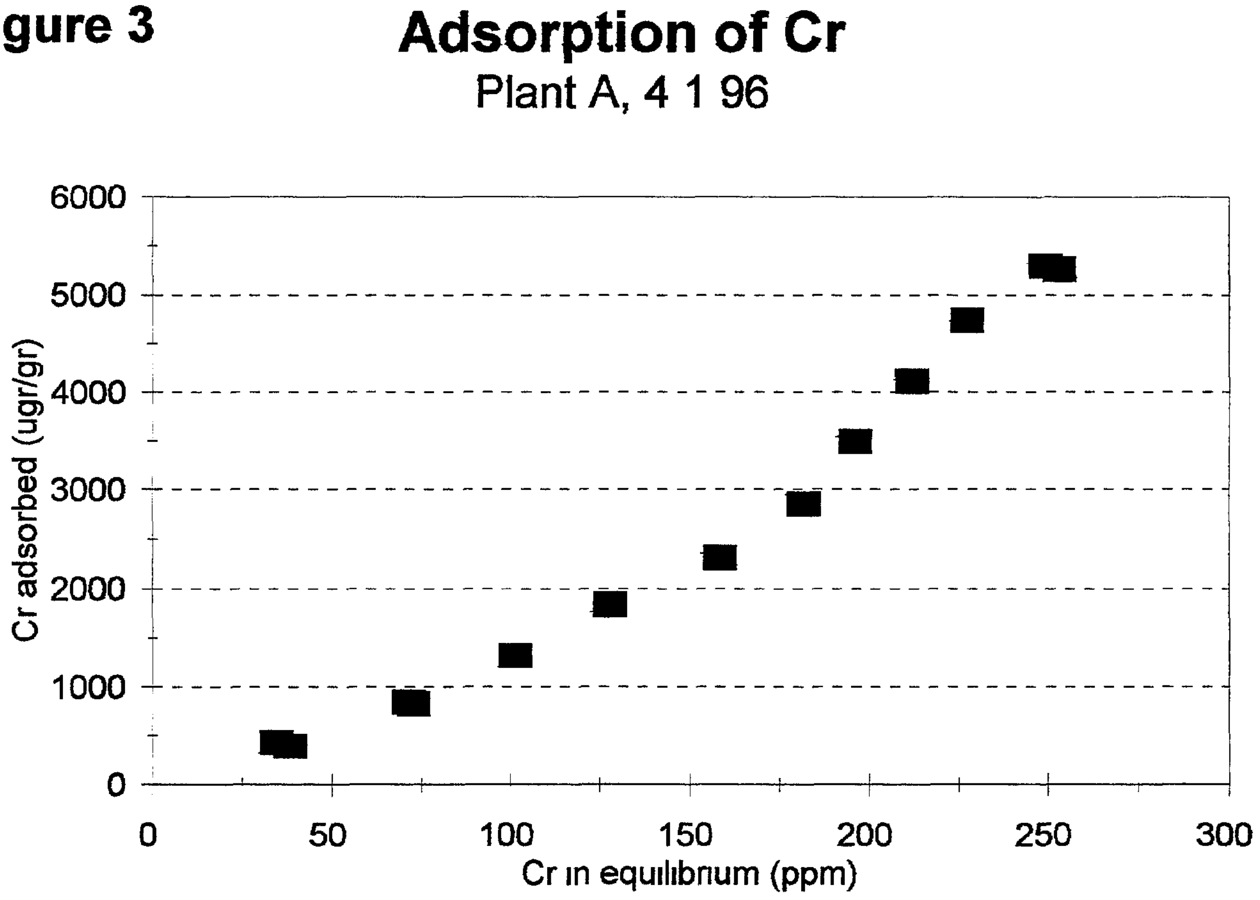
Metal	**Sampling date**	**1/b (constant)**	**M maximal adsorption**	**1/ab (x coefficient)**	**E energy factor**	**R^2**
Cr	4 1 96	estimated-	6000			
Zn	"	0.000418	2392	0.00055	0.76	0 911
Cd	"	0 00276	362	8 5E-5	32 5	0 765
As	"	estimated-	>12			
Cu	"	0 000122	8197	0 00253	0 0048	0 962
Ni	"	0 000654	1529	0 00212	0 31	0 969
Cr	17 1 96	estimated-	>2000			
Zn	"	0 000733	1364	0 000524	1 4	0 89
Cd	"	estimated-	>600			
Cu	"	estimated-	>2500			
Ni	"	0 00283	353	0 00195	1 45	0 917

Results of the sequential extraction are given on figures 14 to 16
The amount of metal adsorbed on the substrate was calculated from the concentrations of stock solutions and effluent remained after equilibrium.
The amount of metal released in each step was calculated as percent from the total desorption.

From the results it is clear that there was a major difference in the adsorption parameters in the two samples.
The adsorption capacity - In the second sampling (17/1/97, Fig 15) it is clear that adsorption was higher
The adsorption energy - for all metals the adsorption sites are more stable then in the first sampling (4/1/97, Fig 14)
The difference could be a result of a change in adsorption condition, or in the solution itself The overall composition of the solutions (organic matter, oils, fats and so on) was not checked and a difference in those conditions could result in a change in the adsorption pattern.

The results of desorption experiments are given on figures 17 to 26.
In each figure the desorption is presented as precent of the total metal adsorbed (recovery) and the blank release of virgin sludge in the same conditions is shown on the same scale [(μgr/gr metal released from clean sludge) / (μgr/gr metal released from adsorbed sludge) *100]
The results here show, as in the sequential extraction, that the adsorption in the socond sampling was stronger and "deeper" than in the first one At the same pH, less metal was desorbed at the second sampling (see Fig 17 vs. Fig 22, and so on)

Figure 3



Adsorption of Cr

Plant A, 4 1 96

Figure 4

Adsorption of Zn

Plant A, 4 1 96

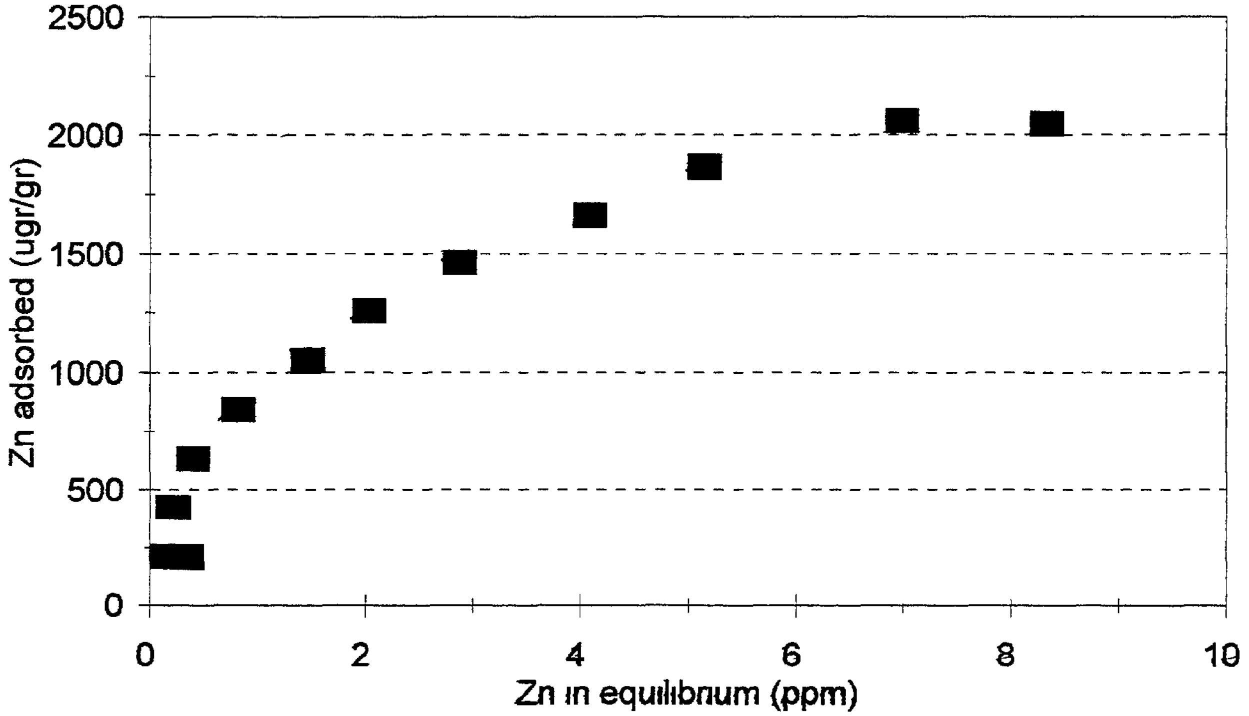
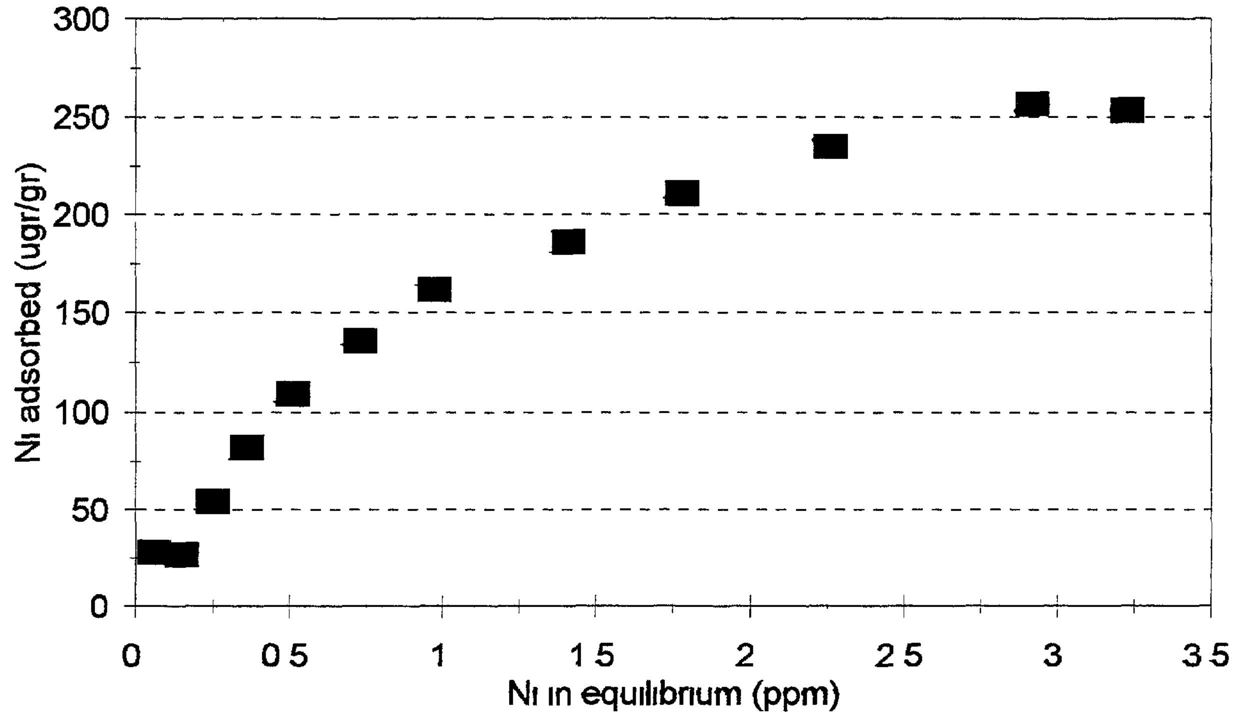


Figure 5



Adsorption of Ni

plant A, 4 1 96

Figure 6

Adsorption of Cd

Plant A, 4 1.96

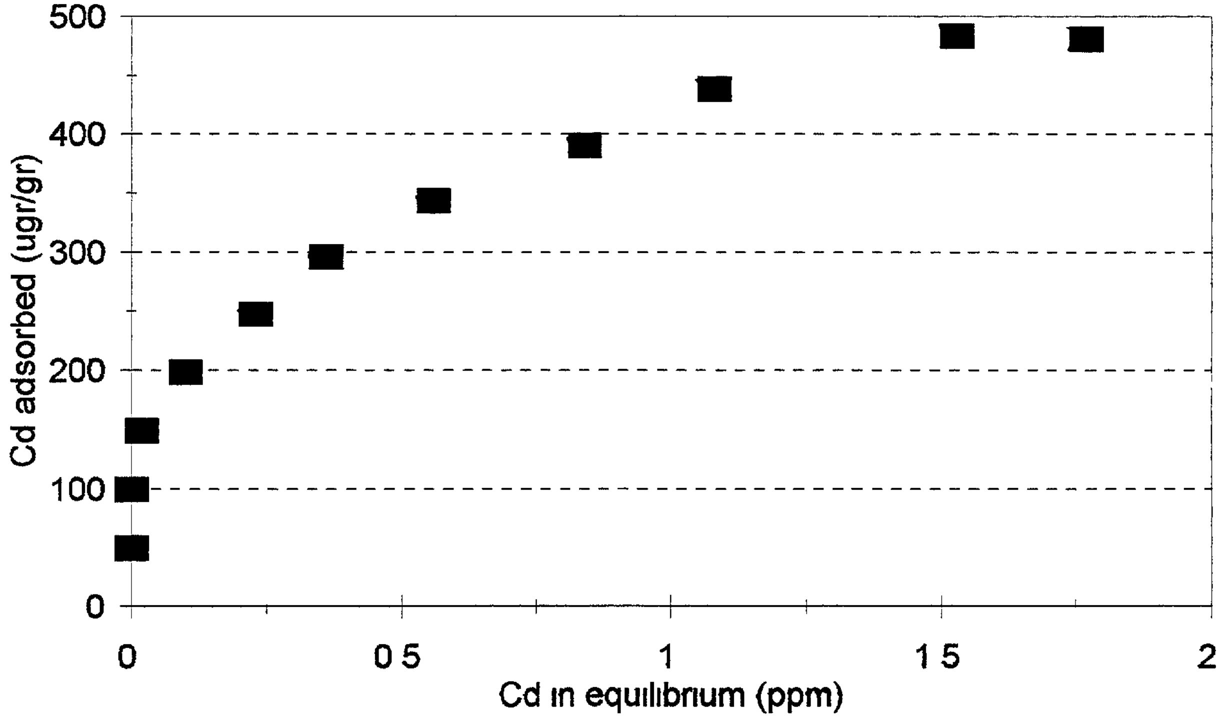


Figure 7

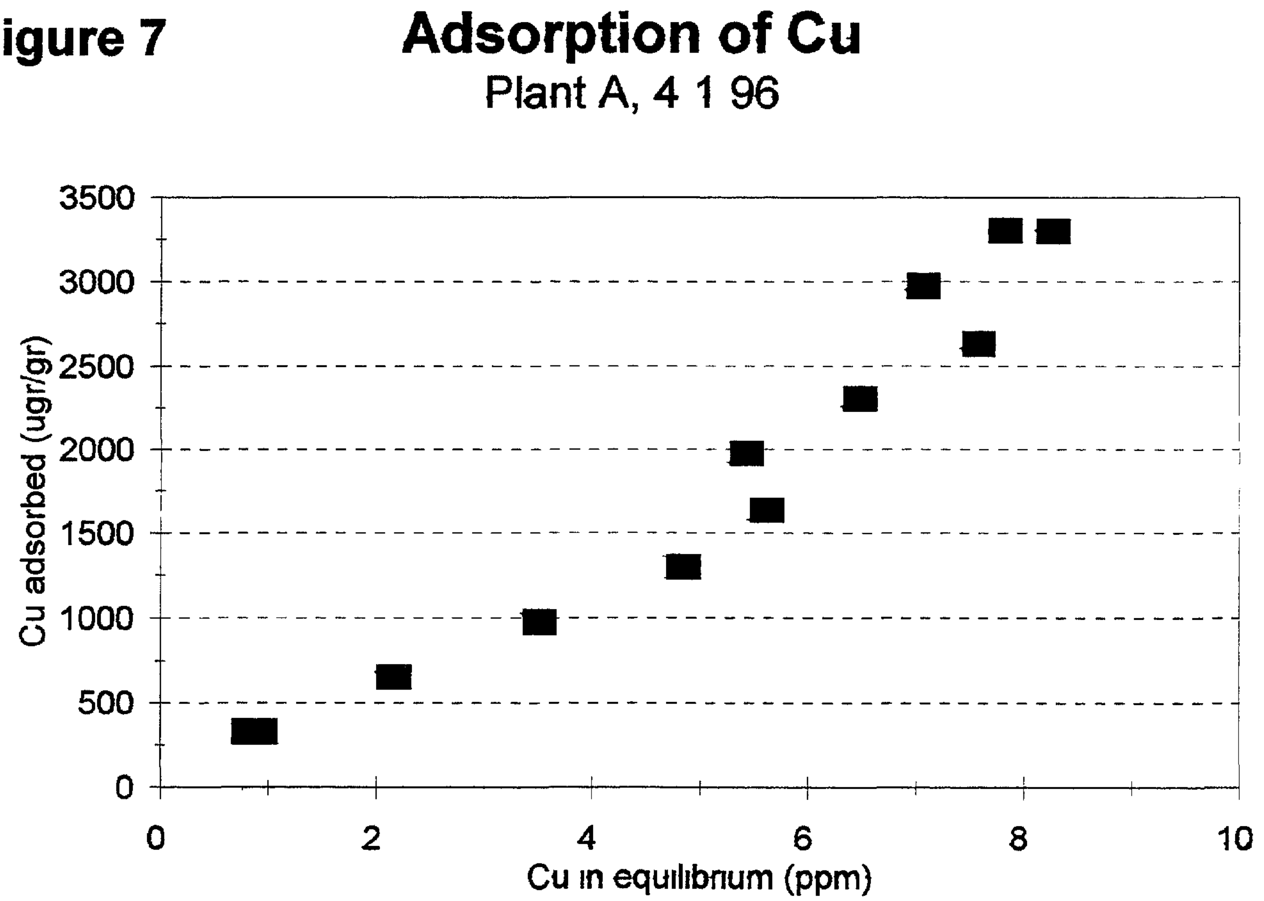

Adsorption of Cu
Plant A, 4 1 96
Cu adsorbed (ugr/gr)
3500
3000
2500
2000
1500
1000
500
0
0
2
4
6
8
10
Cu in equilibrium (ppm)

Figure 8

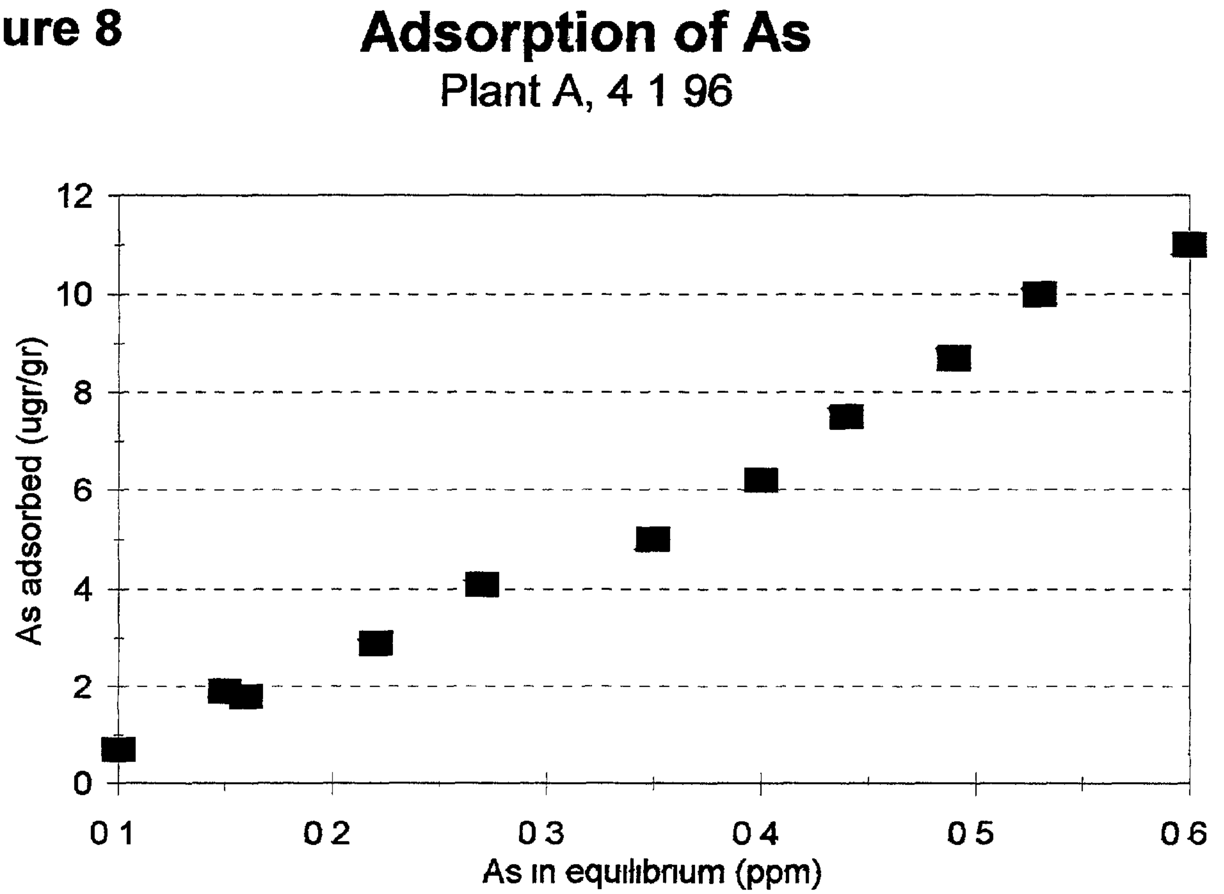

Adsorption of As
Plant A, 4 1 96
As adsorbed (ugr/gr)
0
2
4
6
8
10
12
0 1
0 2
0 3
0 4
0 5
0 6
As in equilibrium (ppm)

Figure 9

Adsorption of Cr

Plant A, 17 1 96

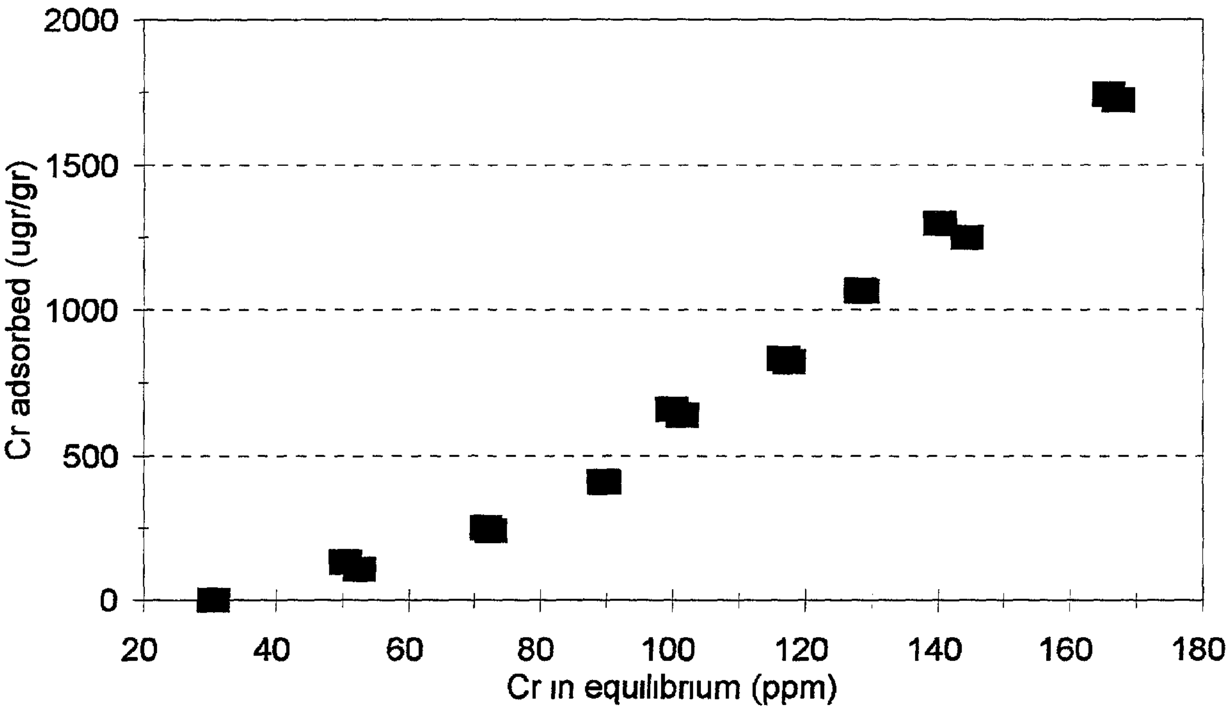


Figure 10

Adsorption of Zn

Plant A, 17 1 96

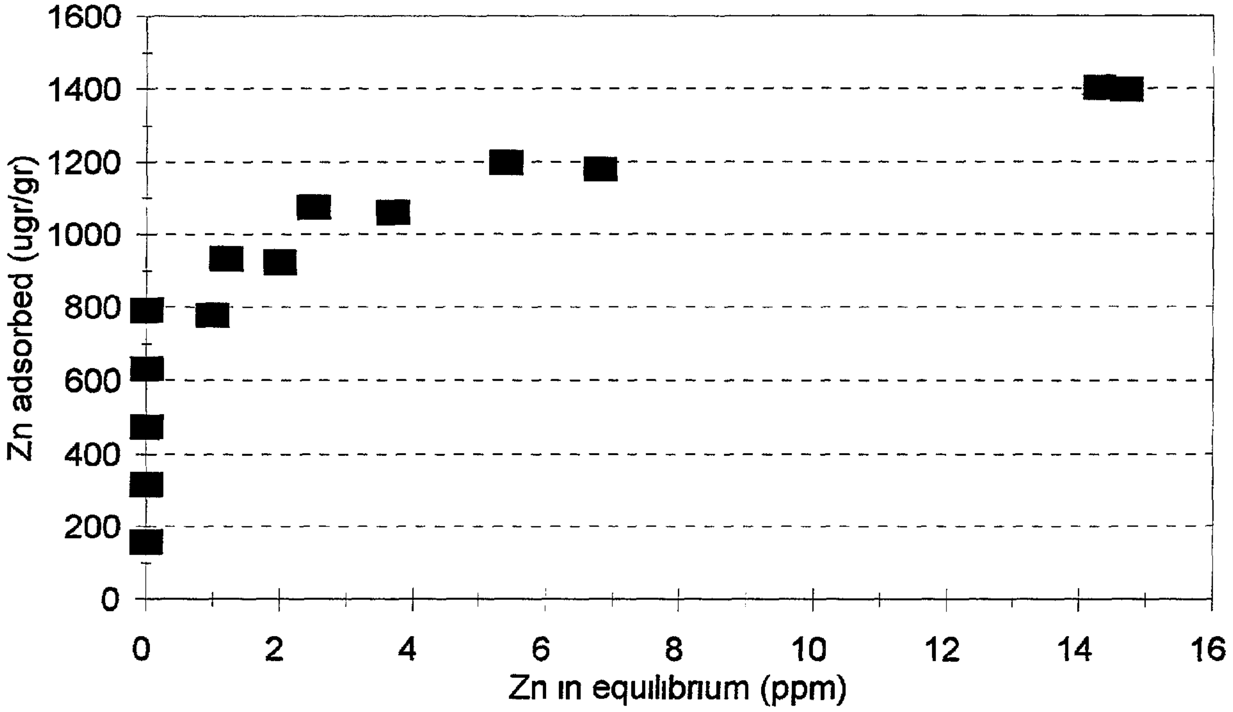


Figure 11

Adsorption of Ni

Plant A, 17 1 96

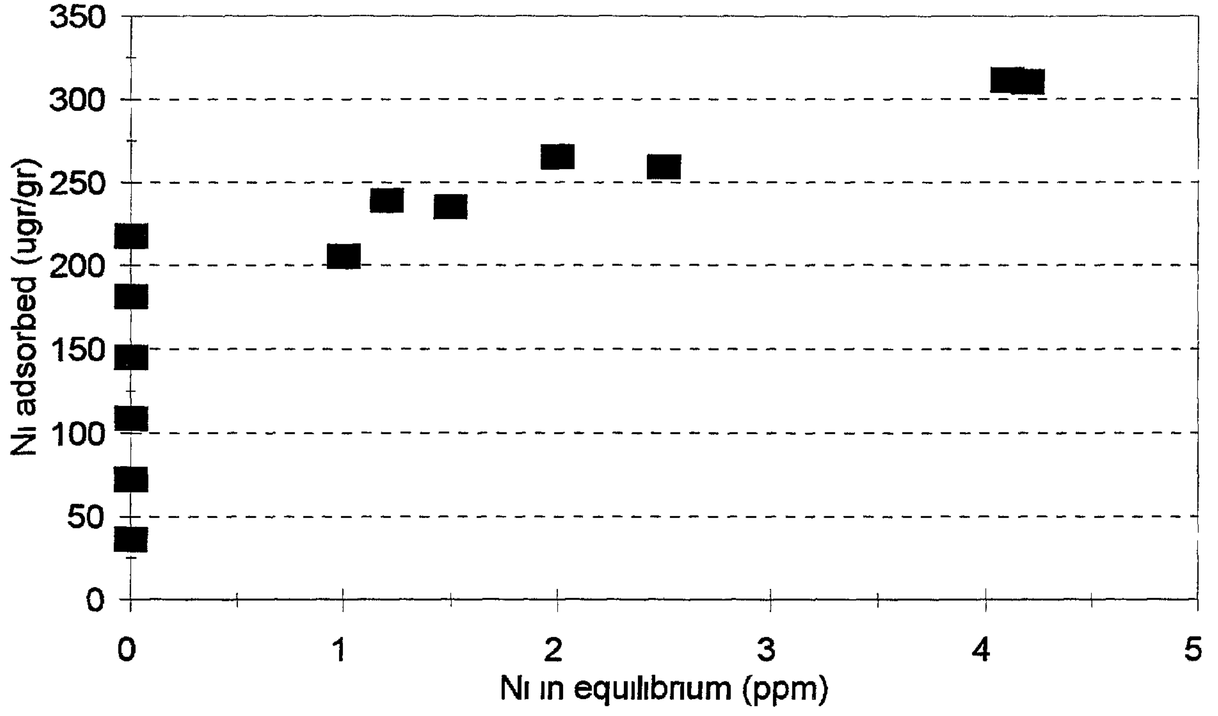
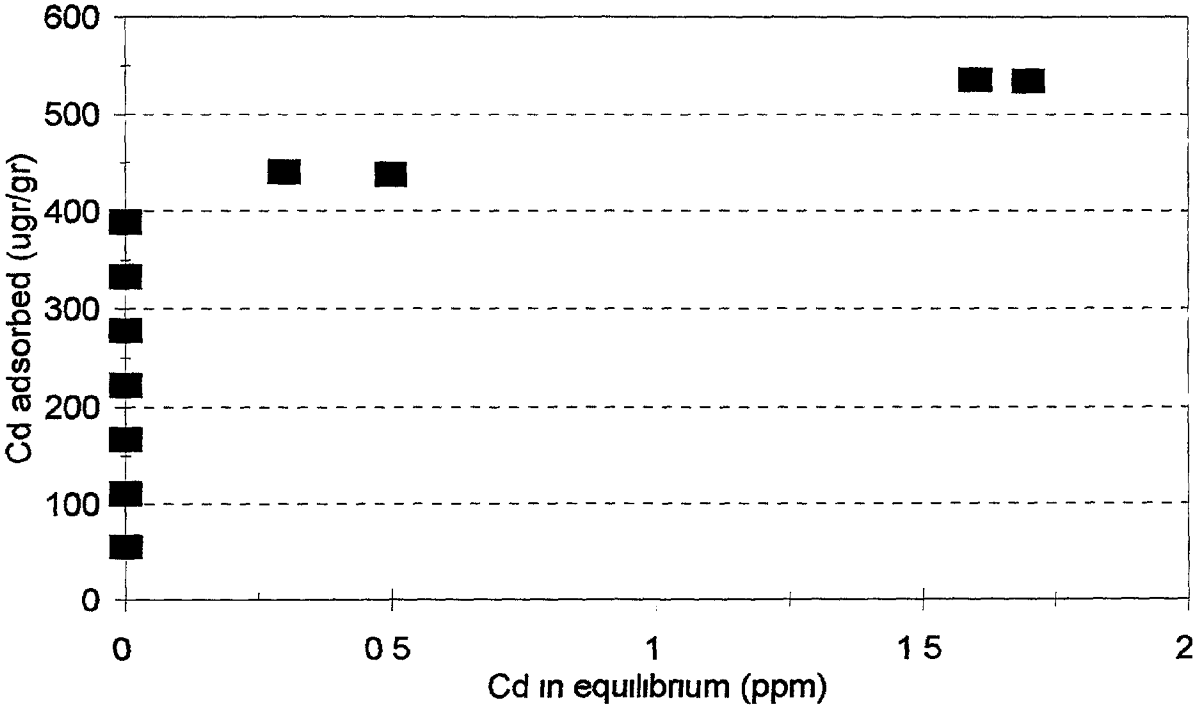


Figure 12



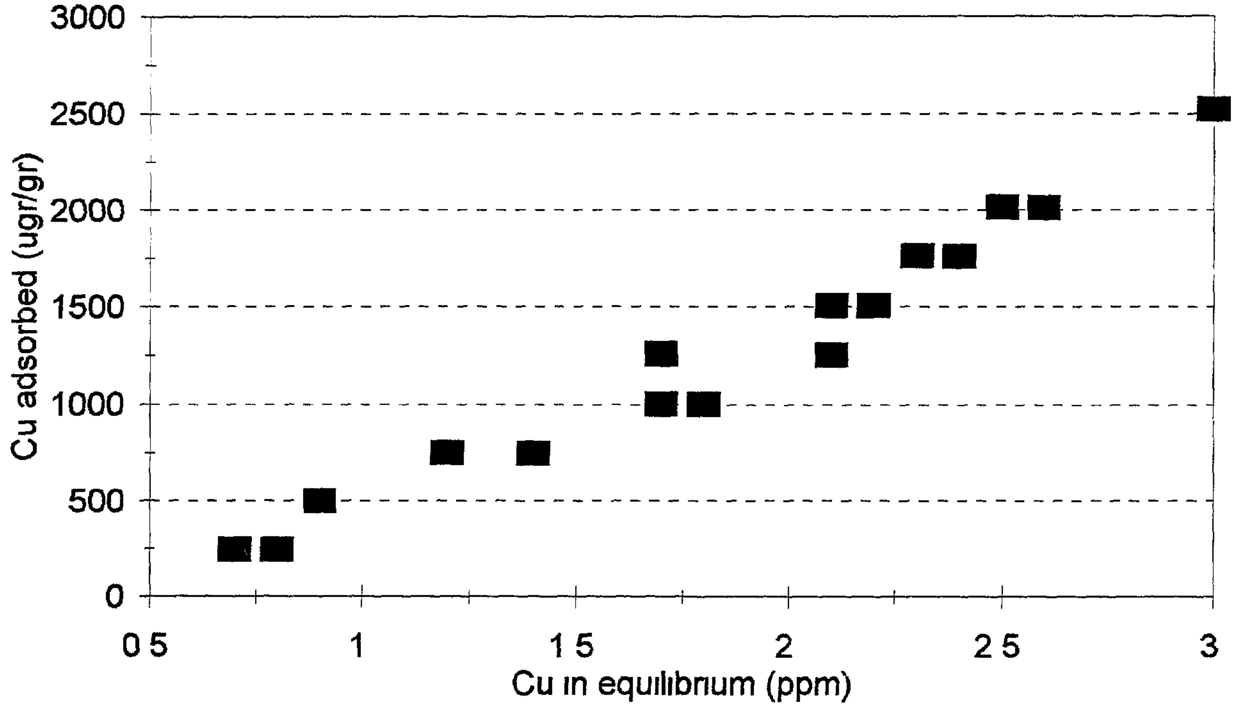
Adsorption of Cd

Plant A, 17 1 96

Figure 13

Adsorption of Cu

Plant A, 17 1 96



4

Figure 14 **Metals extraction from sludge**

Plant A, 4/1/96

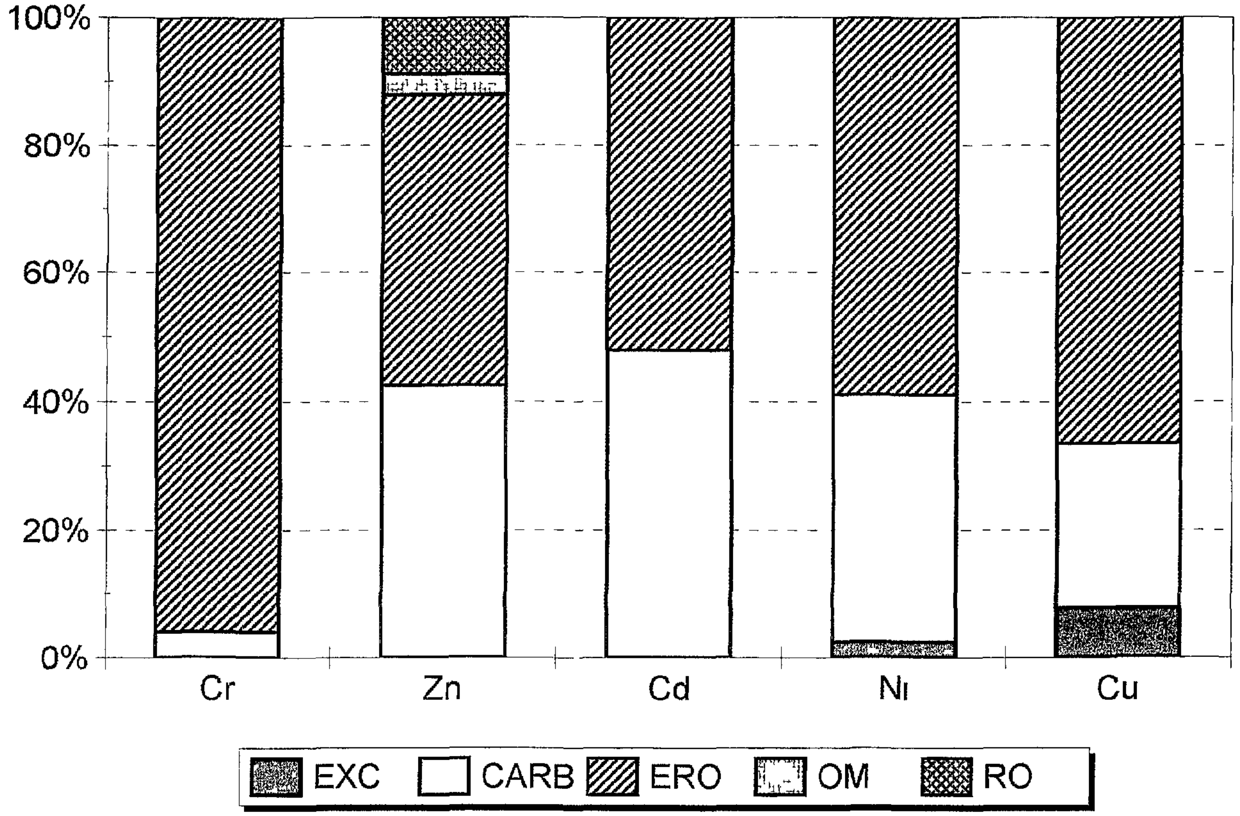


Figure 15

Metals extraction from sludge

Plant A, 17/1/96

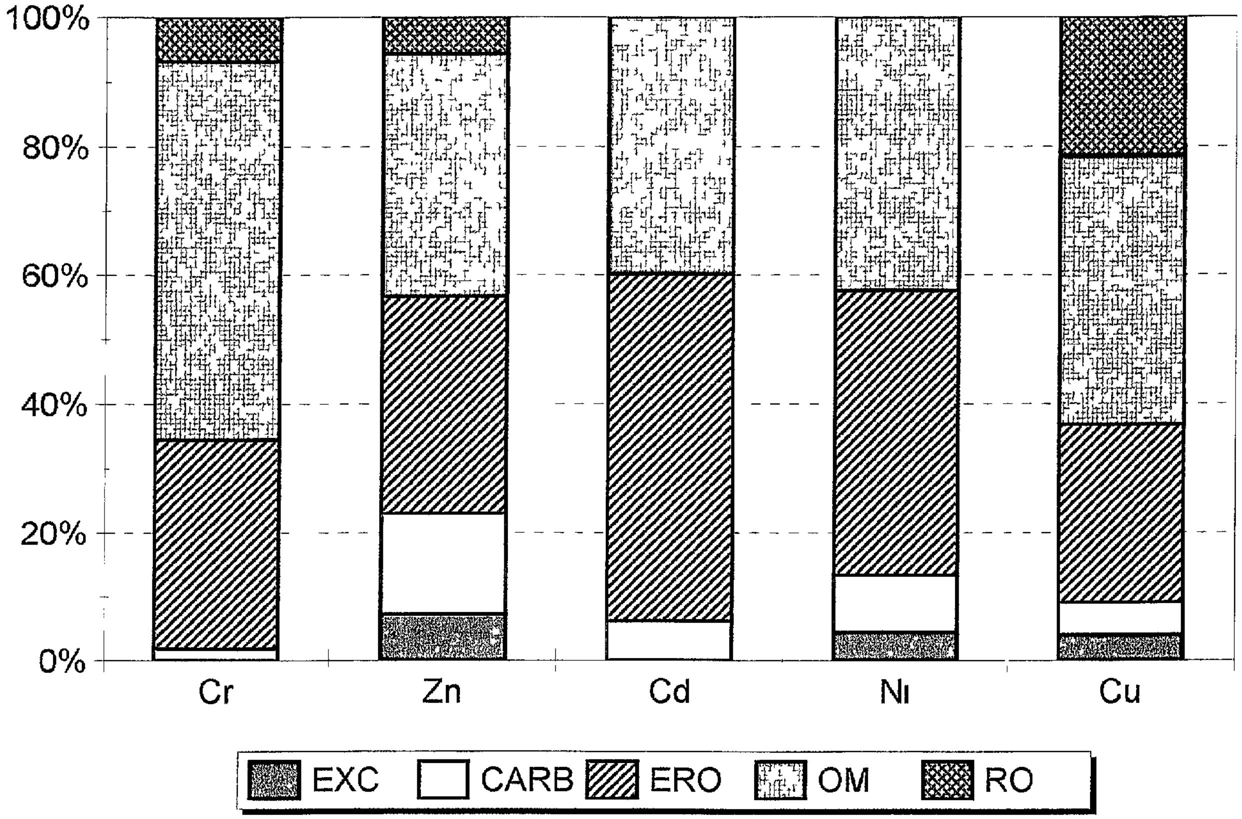
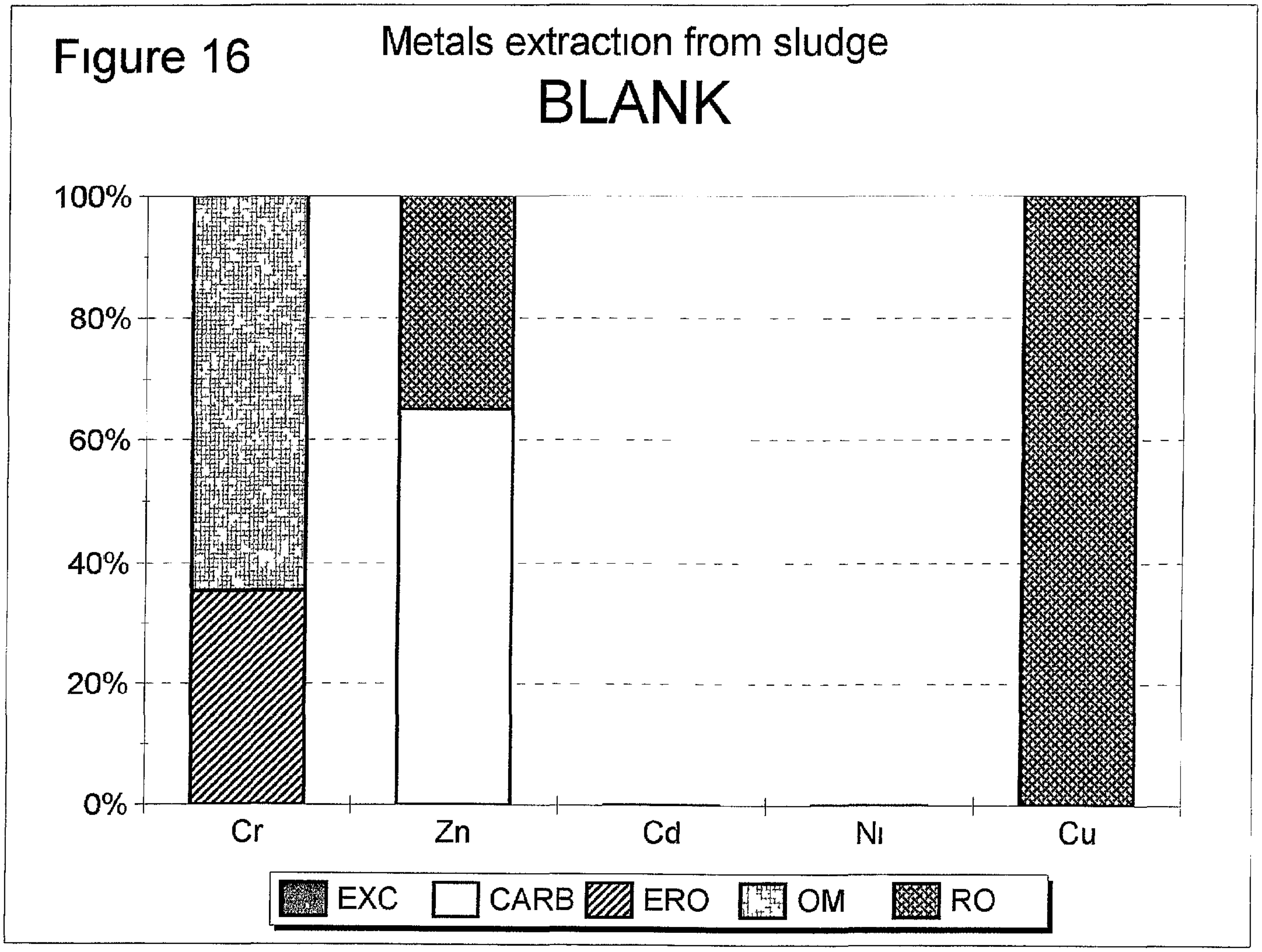


Figure 16


Metals extraction from sludge
BLANK
100%
80%
60%
40%
20%
0%
Cr
Zn
Cd
Ni
Cu
EXC
CARB
ERO
OM
RO

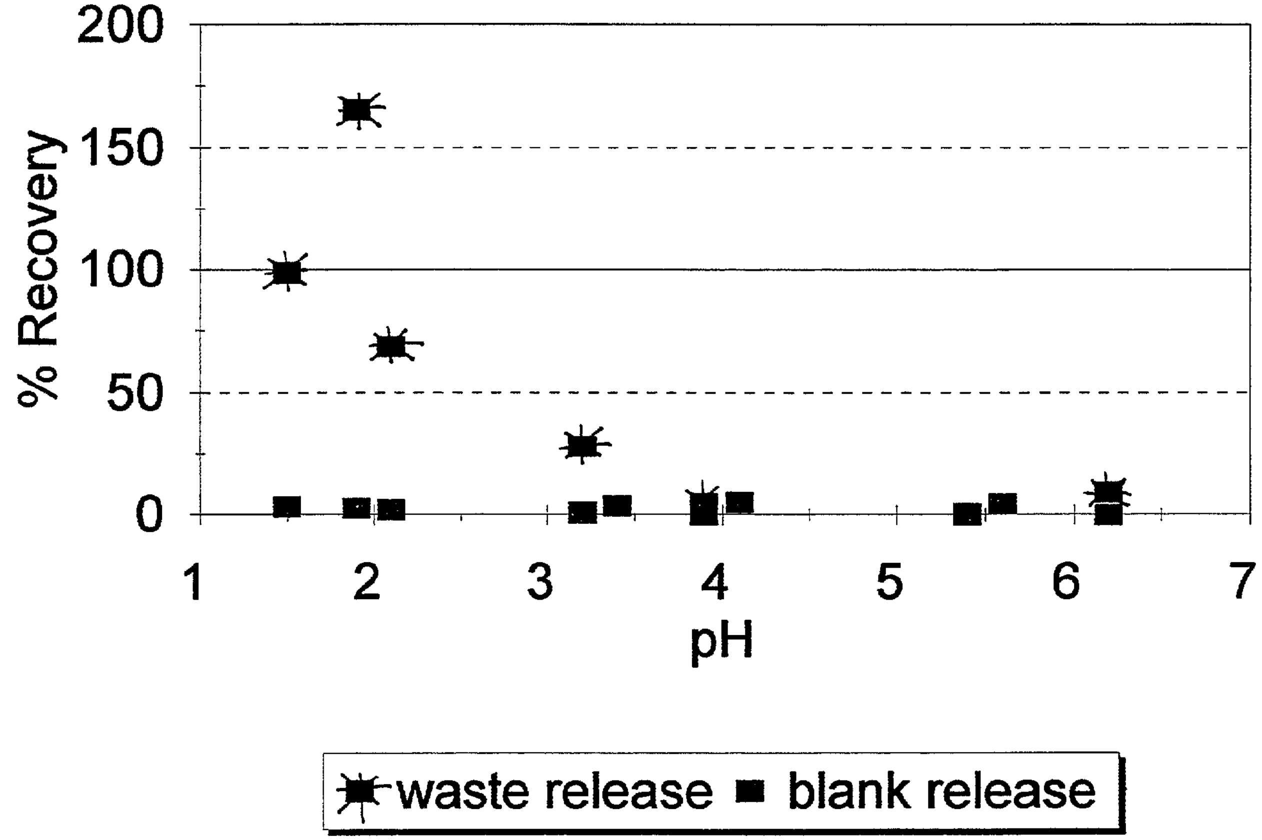


Figure 17 **Desorption of Cr from sludge**

Plant A, 4/1/96

Figure 18 **Desorption of Zn from sludge**

Plant A, 4/1/96

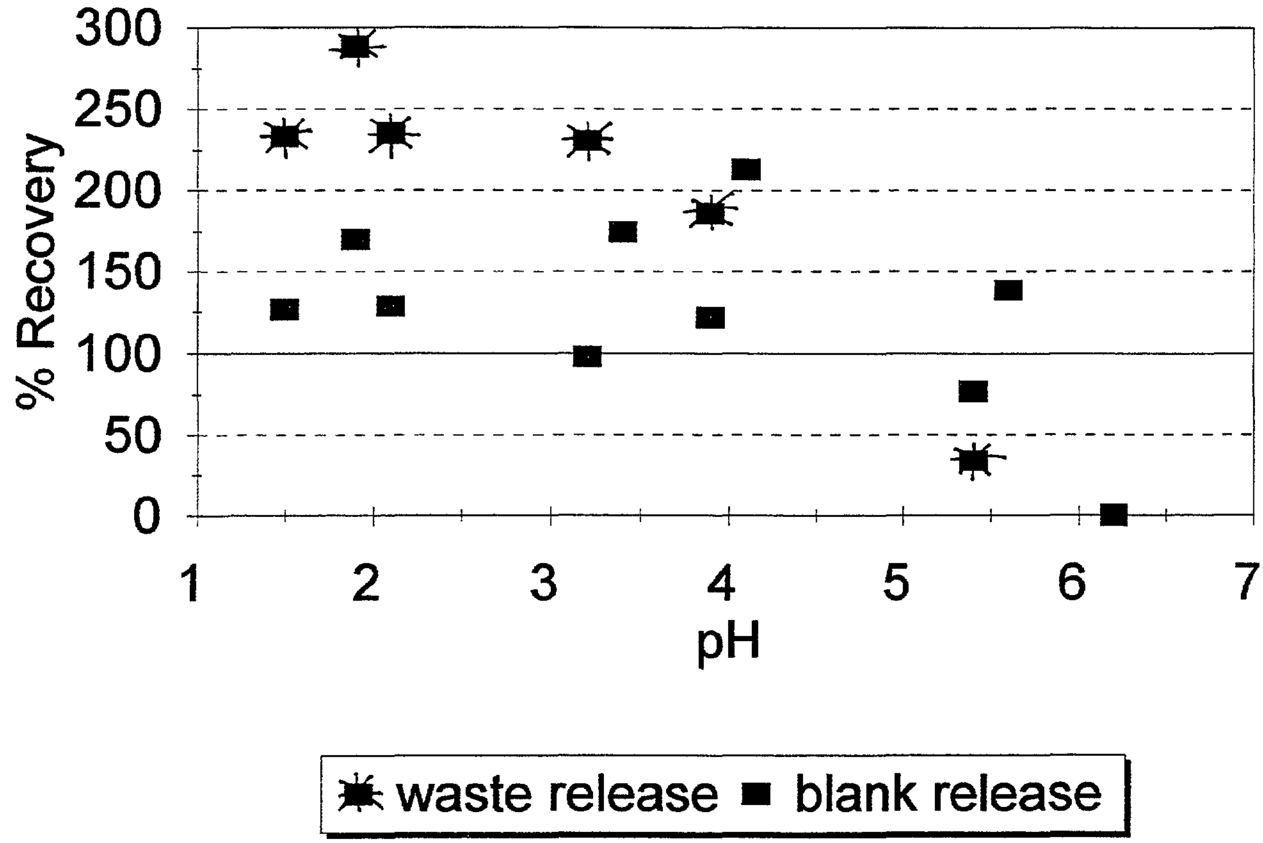
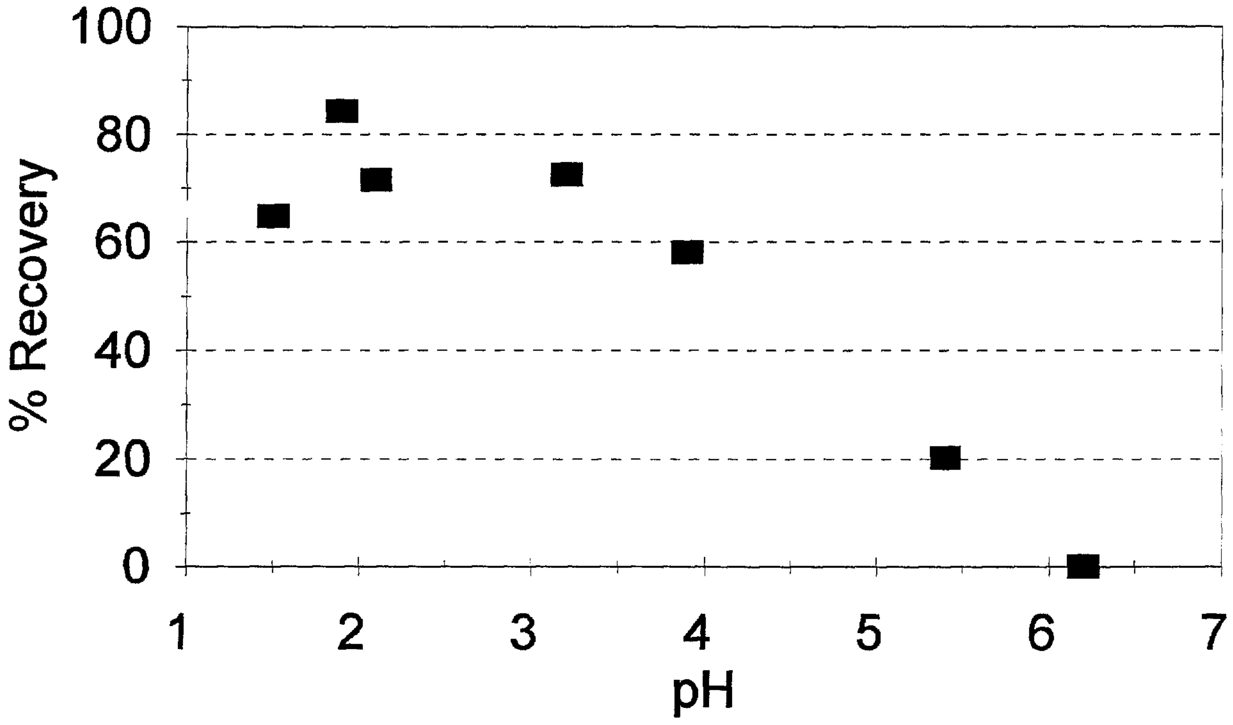


Figure 19 **Desorption of Ni from sludge**

Plant A, 4/1/96



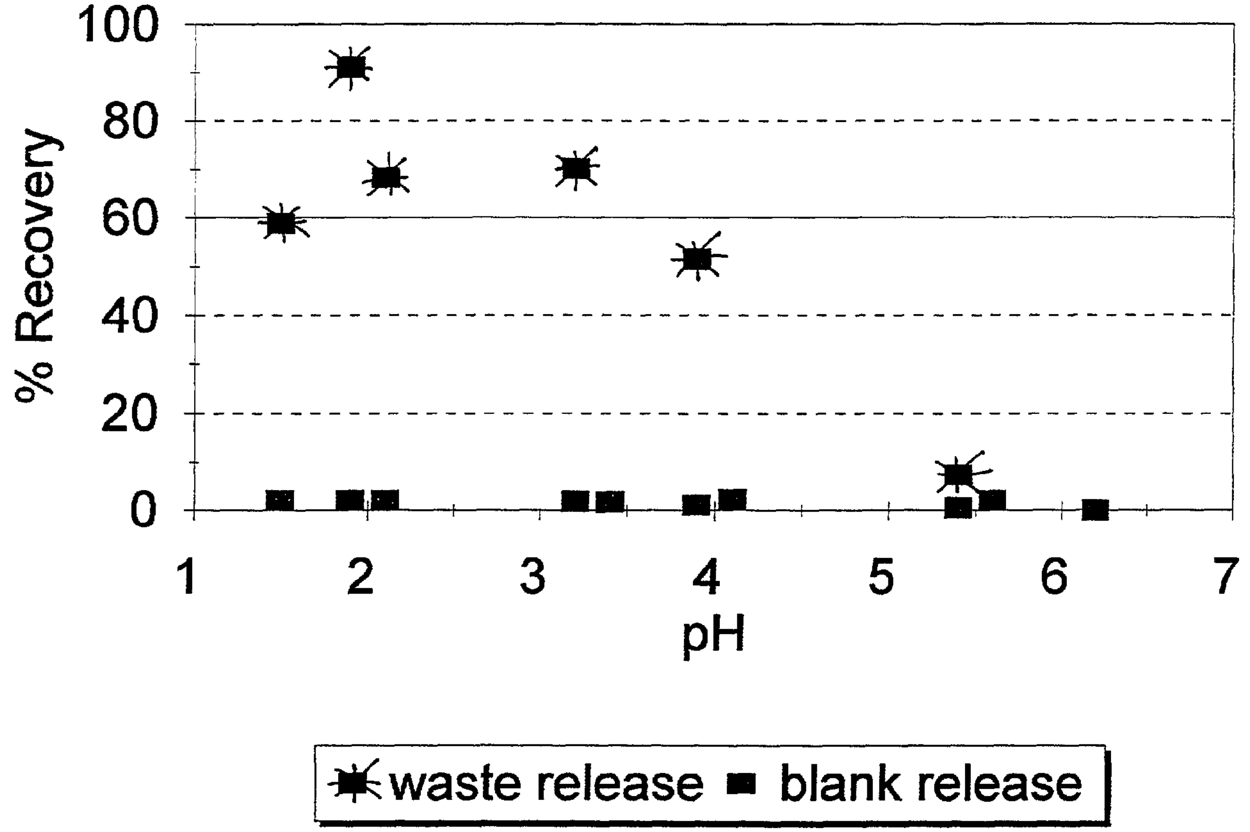


Figure 20 **Desorption of Cd from sludge**
plant A, 4/1/96

Figure 21 **Desorption of Cu from sludge**

plant A, 4/1/96

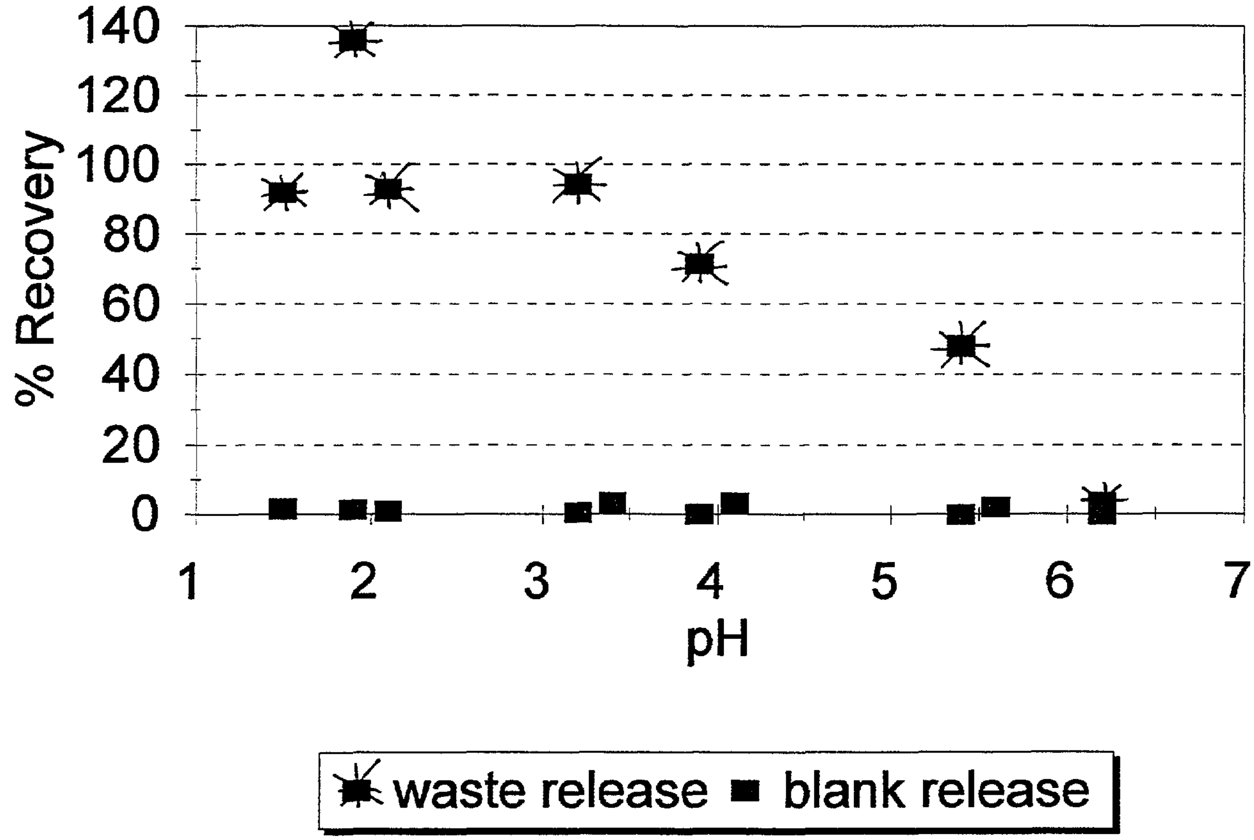
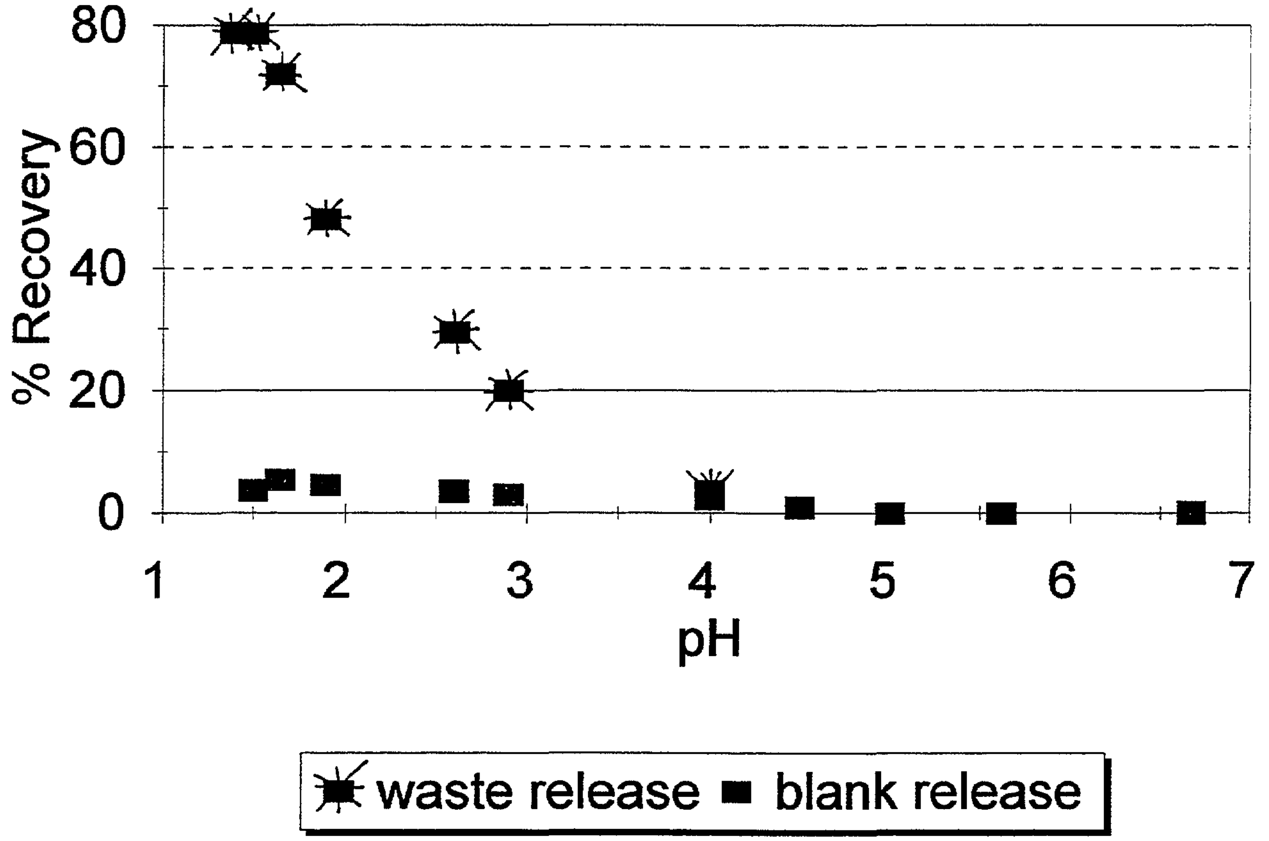


Figure 22 **Desorption of Cr from sludge**

Plant A, 17/1/96



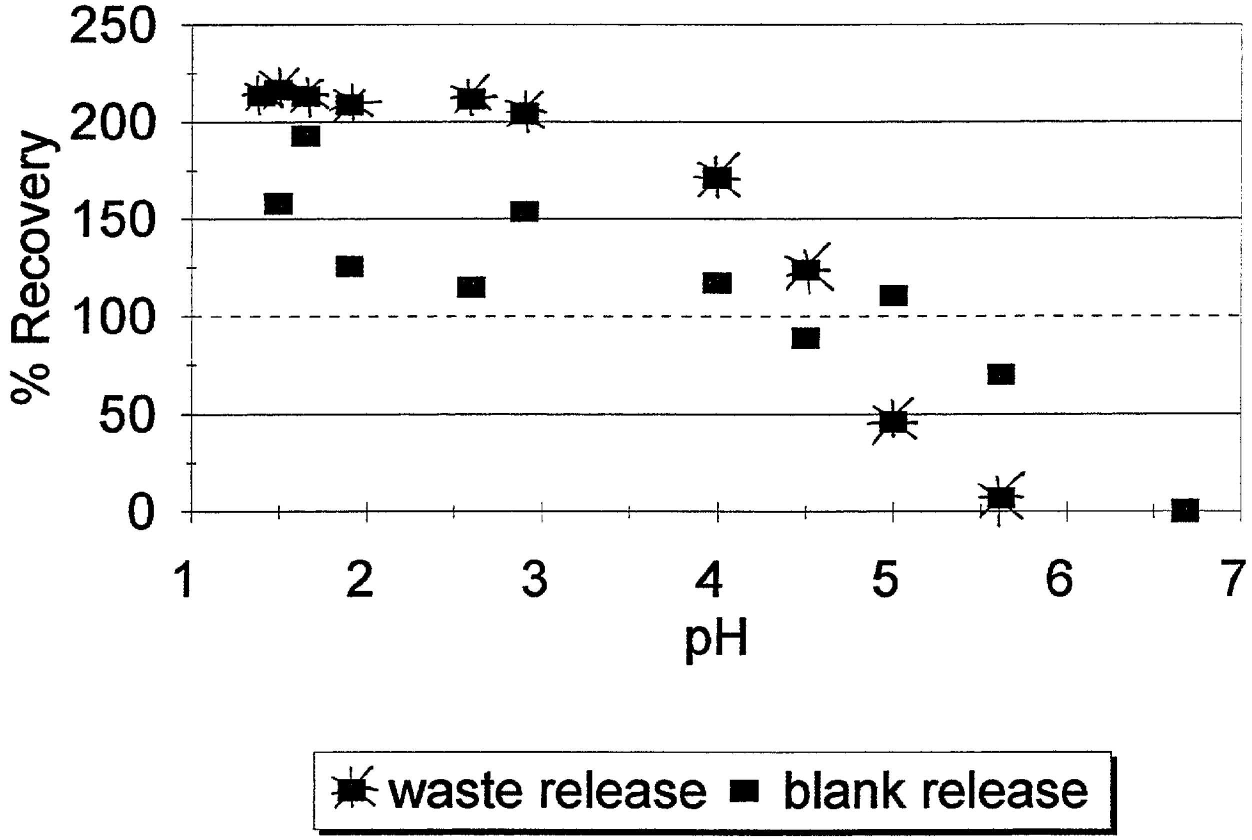


Figure 23 **Desorption of Zn from sludge**

Plant A, 17/1/96

Figure 24 **Desorption of Ni from sludge**

Plant A, 17/1/96

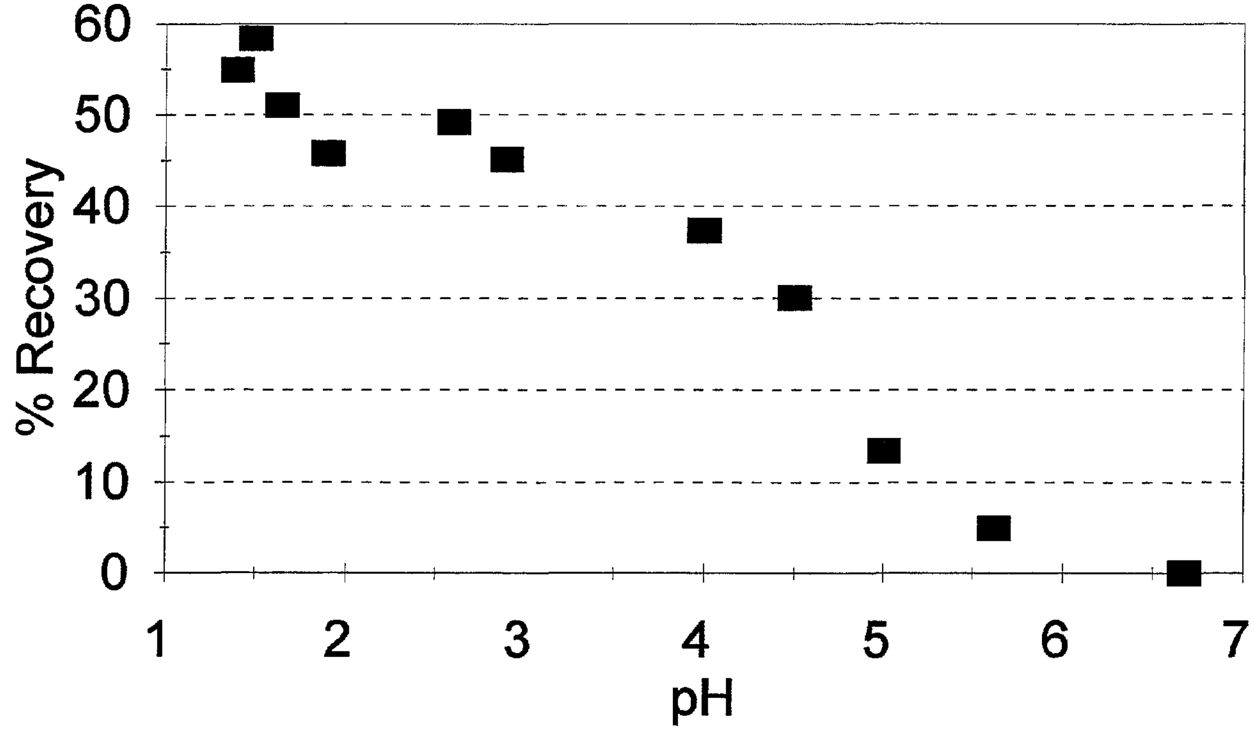


Figure 25 **Desorption of Cd from sludge**

Plant A, 17/1/96

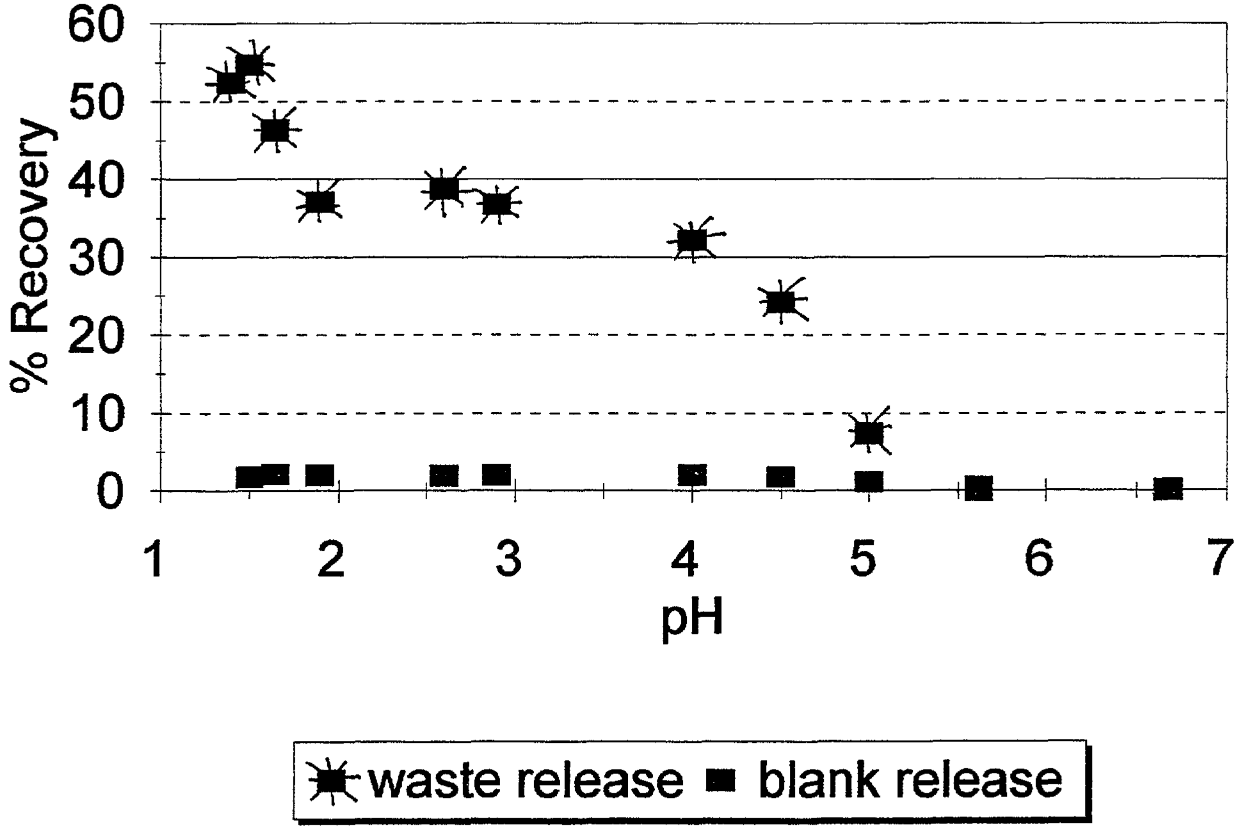
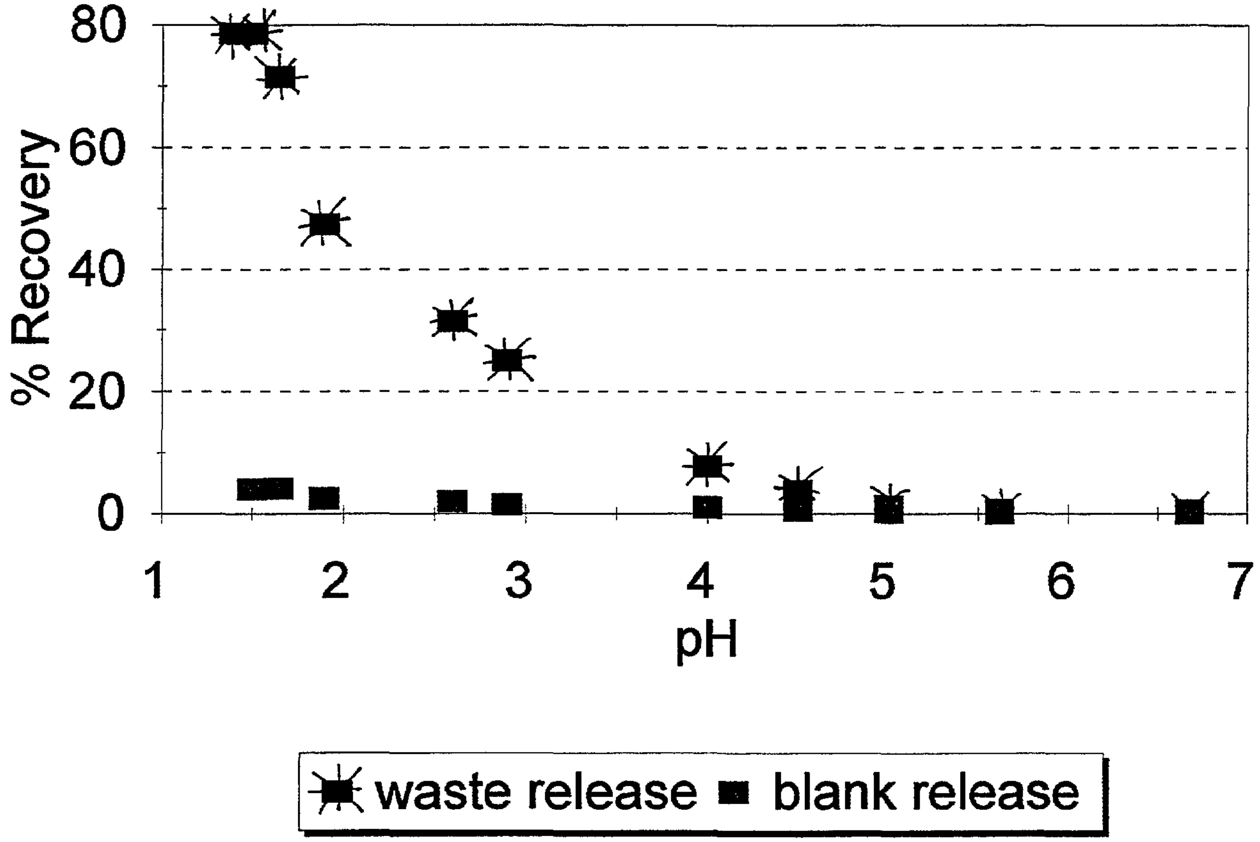


Figure 26 **Desorption of Cu from sludge**

Plant A, 17/1/96



4.2.3. Column Work

4.2.3.1. Materials

4.2.3.1 1. Chemicals

For pre-treatment of sludge and compost, acetate buffer (pH=4 5) was used
For acidification of substrate, HCl in various concentrations was used
Neutralizing of substrate was achieved by applying strong base - NaOH 5N in some cases, and in others - solid $Ca(OH)_2$
Working solutions was always waste water solution from plant A, filtered through Whatman #1

4.2 3.1 2. Adsorbents

Working Substrates, compost and sewage sludge, were prepared as described in previous chapters, by equilibrating with buffer or acid, as described in the procedure

4.2.3.2. Method

4.2.3.2.1. instruments

The instruments used for this work are the same as described in ch 2 2 2
Columns used for the adsorption process are described in appendix I
Stop watch

4.2.3.2.2. Method for adsorption of metals

250 gr of substrate, treated according to procedures, were placed into the columns
Working solution was passed through the column in a constant flow rate, and leachate was collected from the top of the column in volume fractions of 100 ml Flow rate was controlled by the valve placed in the bottom of the column, and measured with stop watch as seconds per constant volume (usually 100 ml)

After the desired volume of working solution passed through the column, pH was measured in every leachate bottle and the concentration of metals measured with ICP.
In order to determine the percent of metal adsorbed on the substrate, the concentration of stock solution was determined also in every run of the procedure.

4.2 3.3. Research results

The experiments performed are described in table no. 12. Each experiment had different conditions, as described below. The concentrations and pH values of the working solutions varied through the experiments, since the solutions came on different sampling dates. The list of solutions is given in table no. 13.
The substrate's pre-treatment is given in table no. 12 in acronym, and specified below.
The results of the experiments are shown in the figures marked in the table.

TABLE NO. 12 - LIST OF EXPERIMENTS PERFORMED

Experiment No.	Substrate	pre-treatment	Working Solution	Flow Rate (ml/sec)	Figure No.
1	sludge	WD	1	0.24	27
2	sludge	W	1	0.62	28
3	sludge	WD	1	0.56	29
4	compost	WD	3	0.47	30
5	compost	WD	3	2.15	31
6	compost	WD	3	0.78	32
7	compost	SR	3	0.16	33
8	compost	WD	3	1.07	34
9	compost	WD	4	0.4	35
10	compost	WD	9	0.42	36
11	compost	WD	8	0.8	37
12	compost	WD	8	0.58	38
13	compost	WD	9	0.49	39
14	compost	WD	5	1.68	40
15	compost	AB	6	0.53	41
16	compost	AB	7	0.47	42

pre-treatment reading (in the next page)

WD - Water washed and Drained
W - Water washed, with water inside the column
SR - Second Run on the same compost
AB - treated with Acid and then with Base

TABLE NO. 13 - WORKING SOLUTIONS USED THROUGHOUT THE EXPERIMENTS

Solution No	Date of Sampling	pH	Cr (ppm)	Cd (ppm)	Cu (ppm)	Zn (ppm)	Ni (ppm)
1	12 5 96	4 0	178 55	17 43	119 2	87 12	15 64
3	11 6 96		235 9	13 76	143 4	132 3	14 78
4	7 8 96	3 7	295 73	92 9	298 9	368 52	122 15
5	30 7 96	3 6	245 6	100 94	261 92	256 74	111 88
6	10 9 96		75 09	50 77	33 64	180 28	2 60
7	13 10 96		56 0	38 02	29 54	177 2	4 46
8	8 8 96	6 1	5 10	22 49	37 51	106 49	4 23
9	12 8 96	3 7	284 34	97 28	280 57	429 29	126 01

During the work on the columns we met with a few difficulties in the running of the columns The flow conditiond in the columns were not ideal In the sludge columns flow was so bad that we had to give up the substrate and use only compost During the refreshing process (running of acid through the column) bubling had accured, and the flow conditions became even worst By this stage we came to the conclusion that a batch operation will be more efficient, since it will not have to overcome the low hydraulic conductivity of compost and sludge

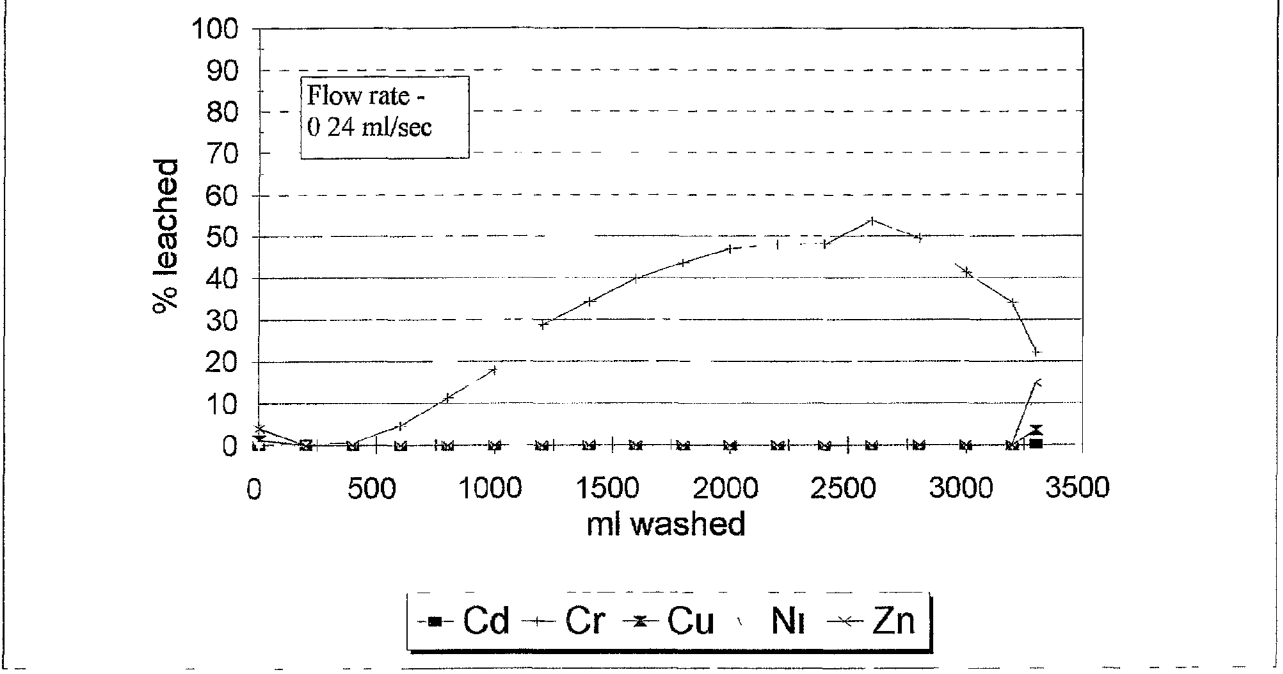
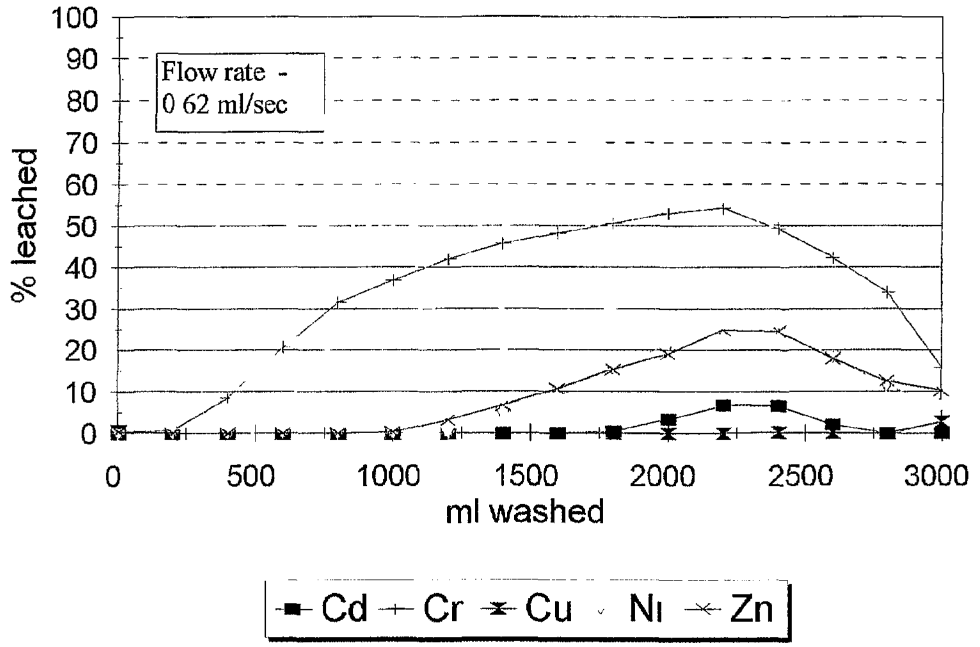


Figure 27- Adsorption in sludge column

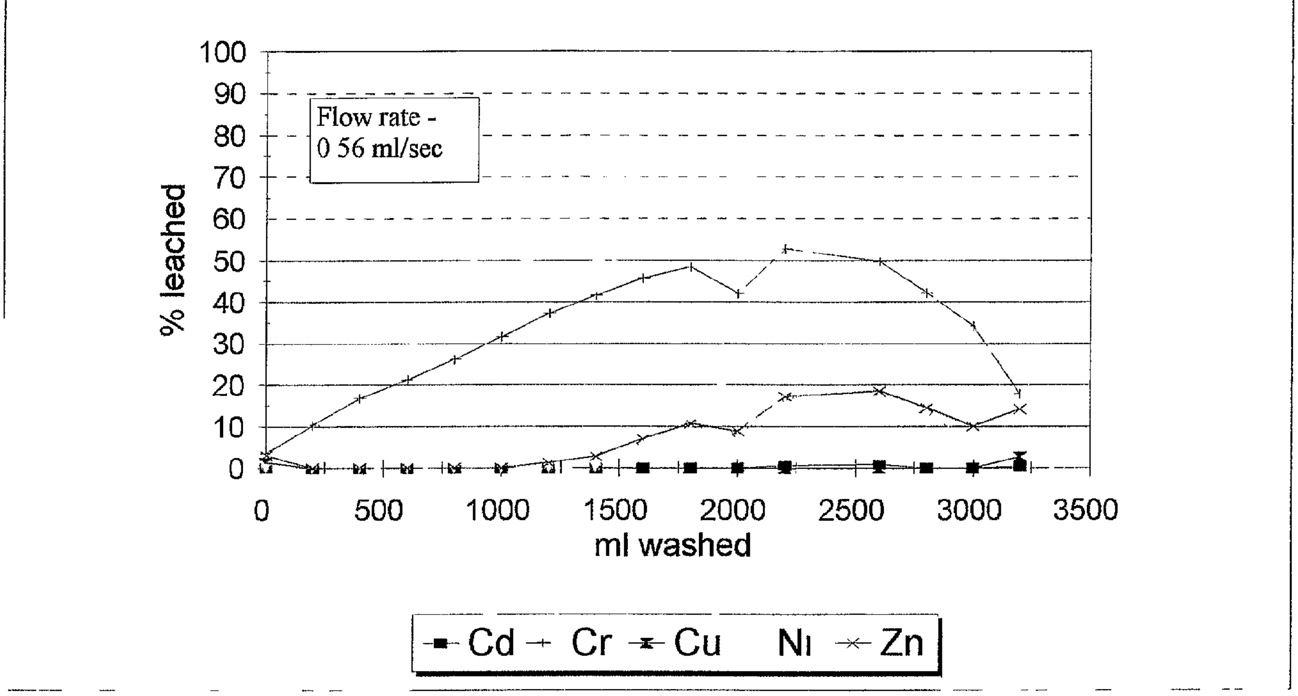
solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 28- Adsorption in sludge column



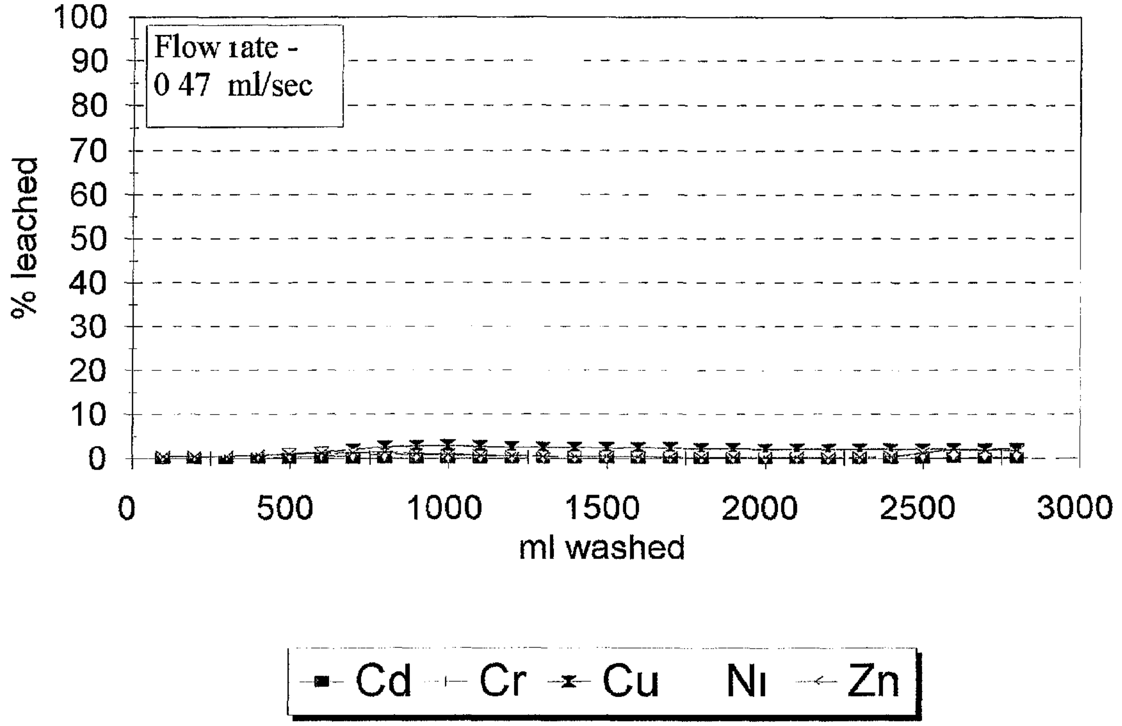
solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Nı ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 29- Adsorption in sludge column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 30-Adsorption in compost column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

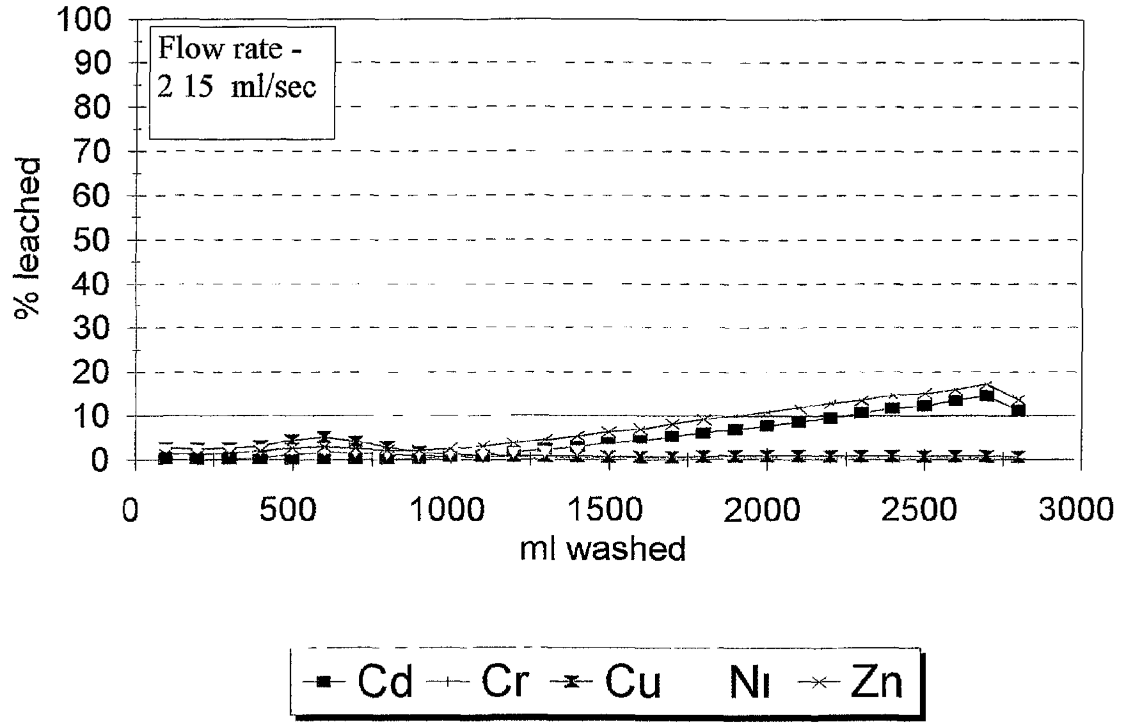


Figure 31-Adsorption in compost column

solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

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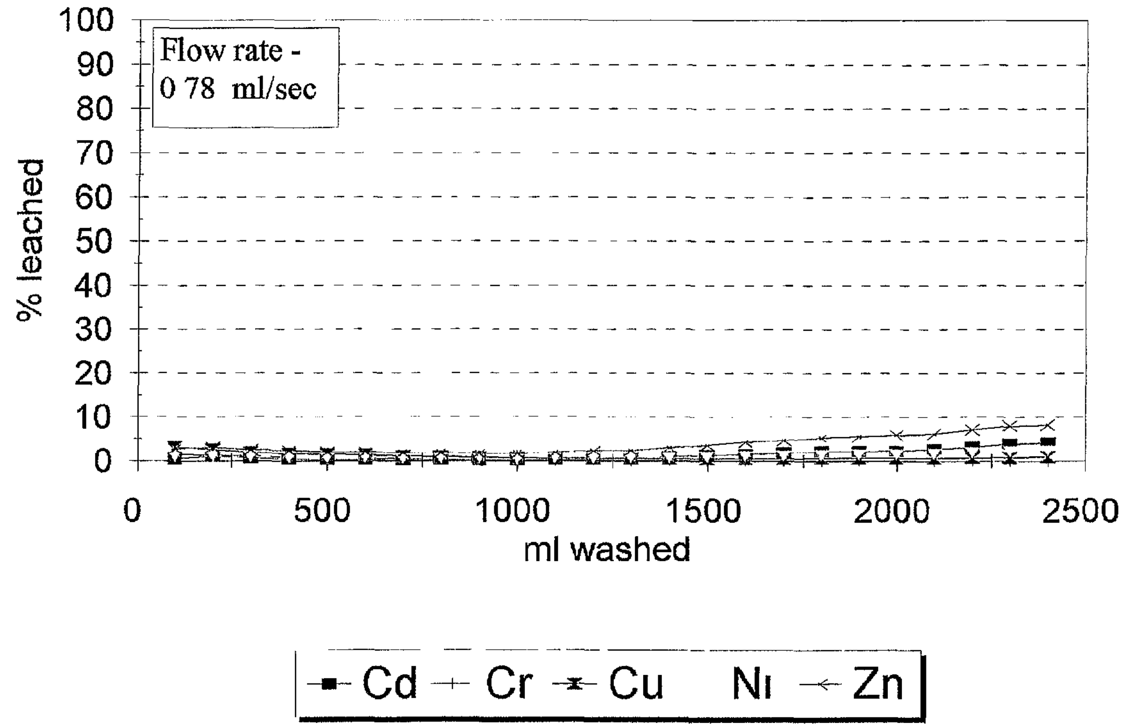
Figure 32-Adsorption in compost column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Nı ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

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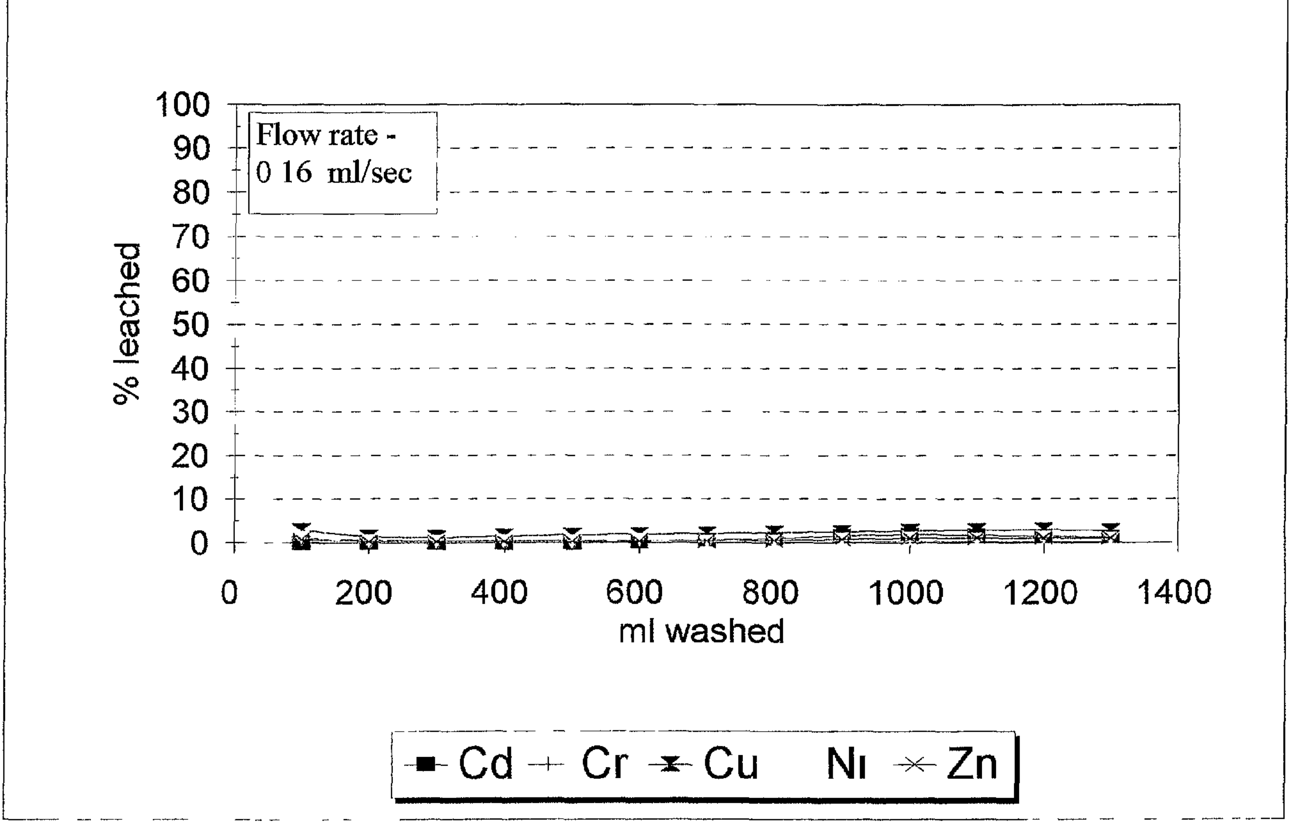
Figure 33-Adsorption in compost column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

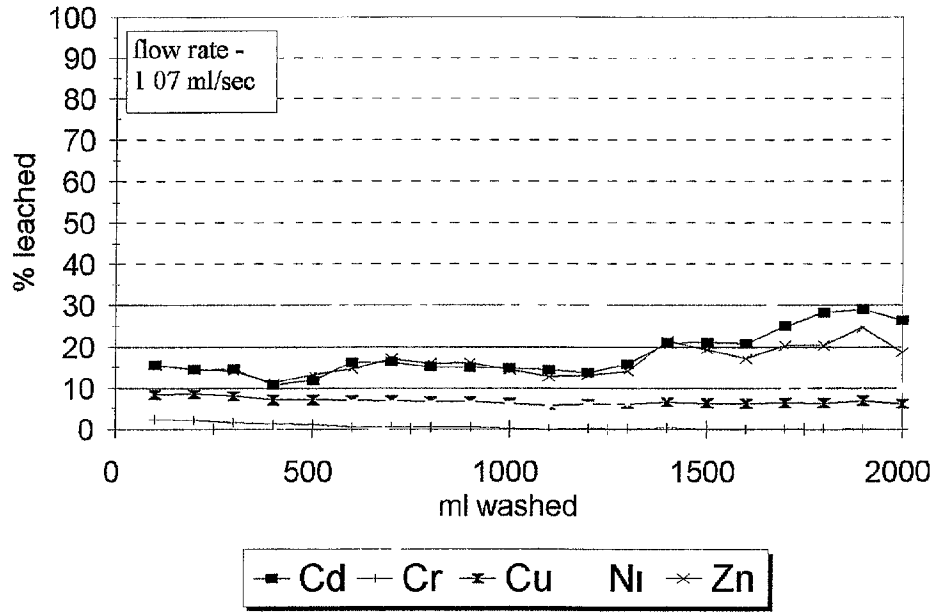


Fıgure 34-Adsorption ın compost column

solutıon No	Date of samplıng	pH	Cd ppm	Cr ppm	Cu ppm	Nı ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 9
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

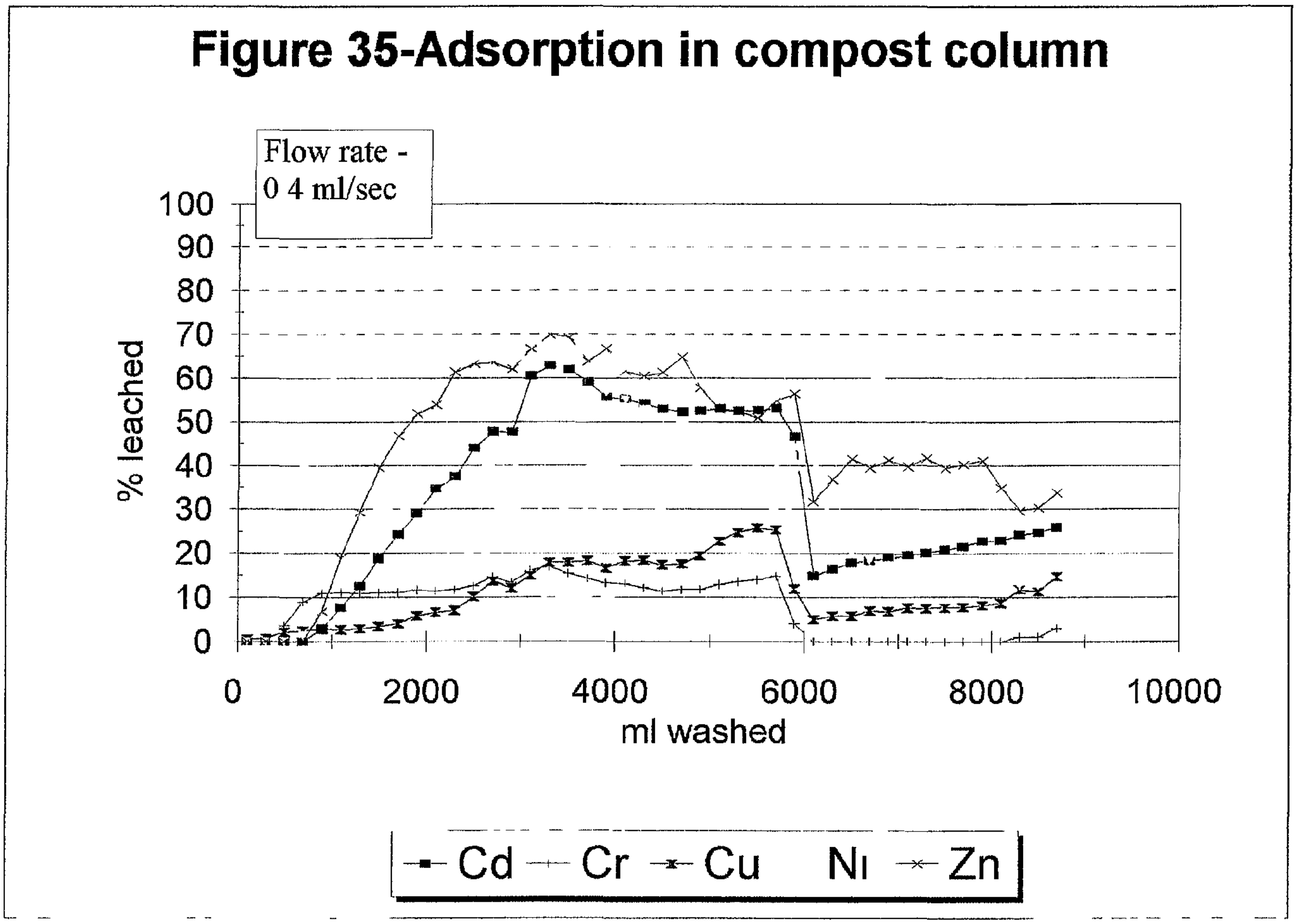
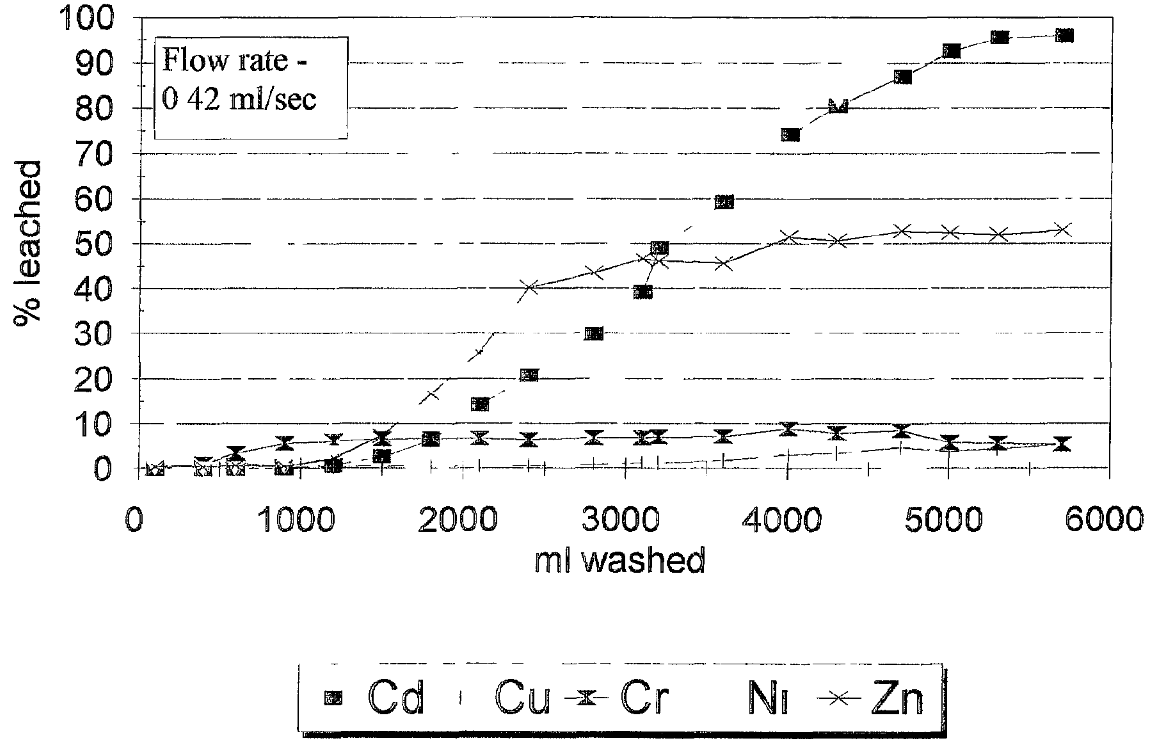


Figure 35-Adsorption in compost column

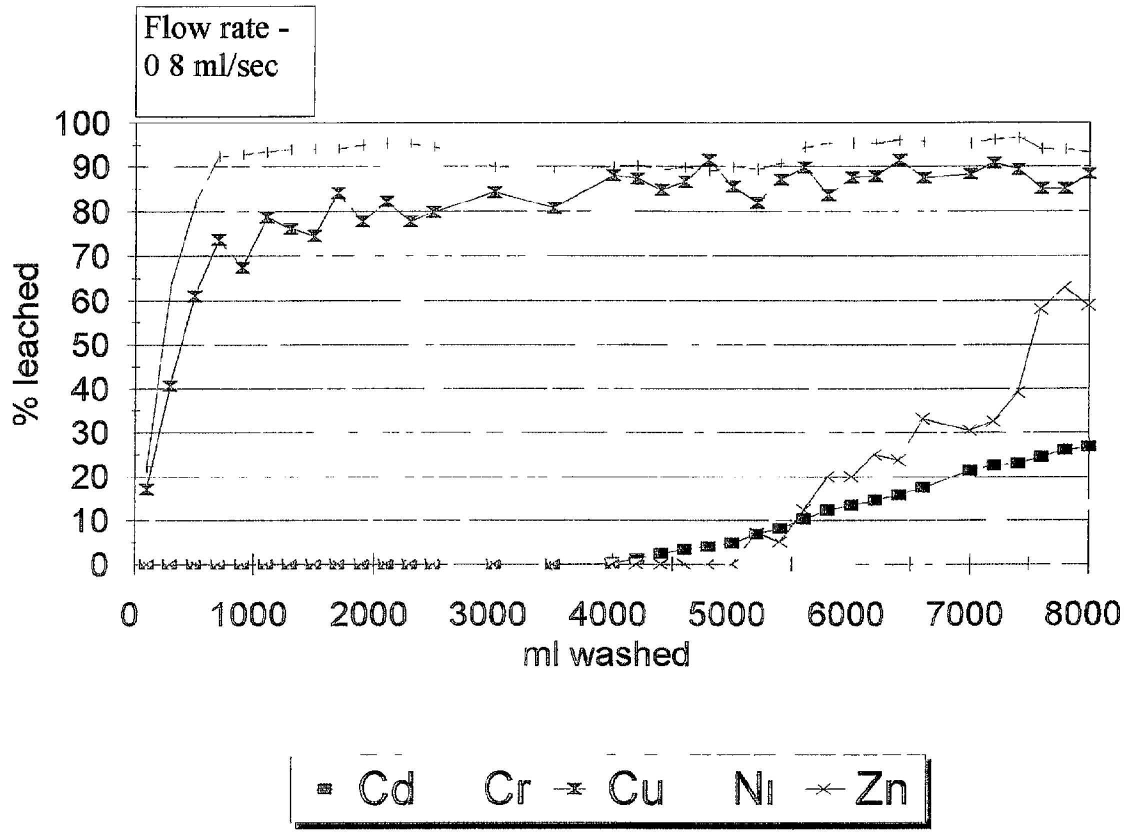
solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8.96	3.7	92 9	295 73	298 9	122.15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 36-Adsorption in compost column



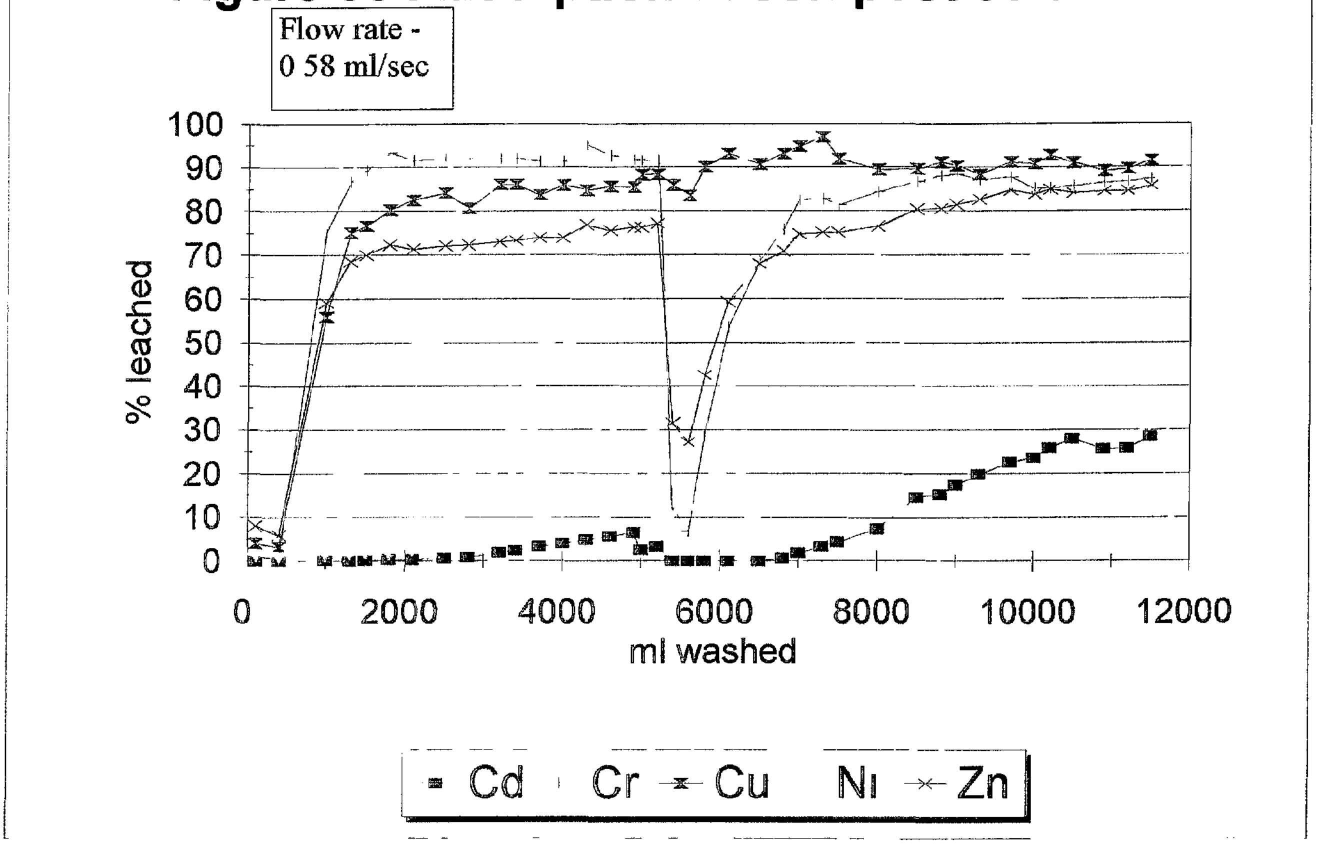
solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 37-Adsorption in compost column



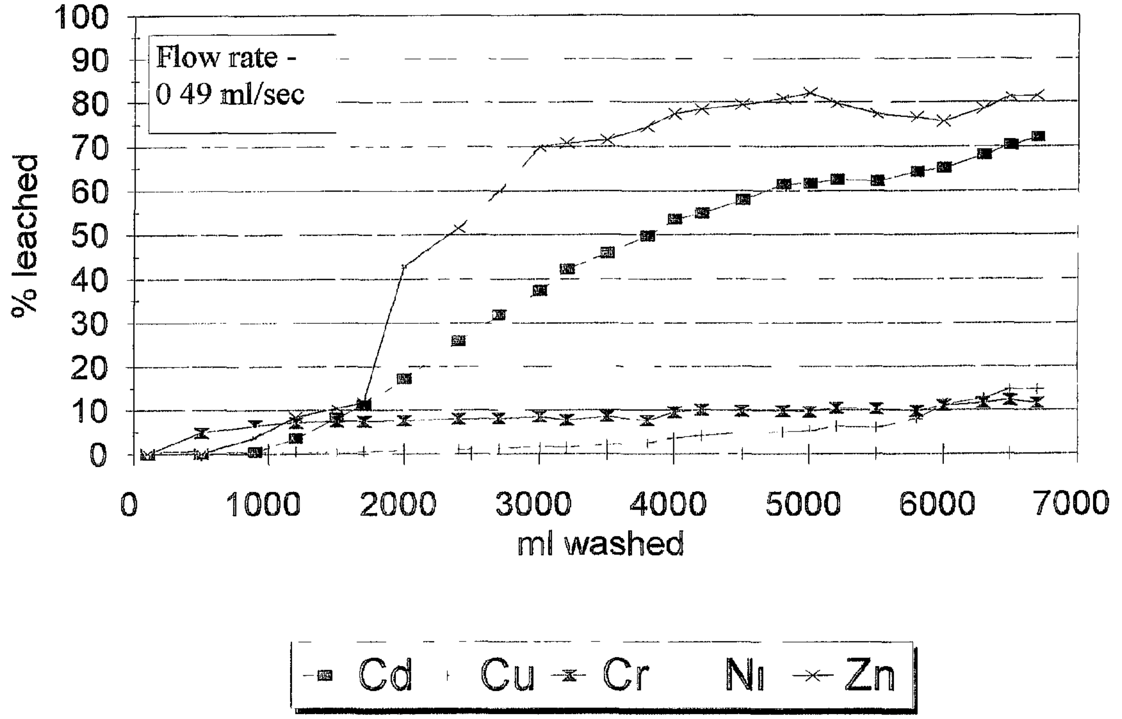
solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 38-Adsorption in compost column



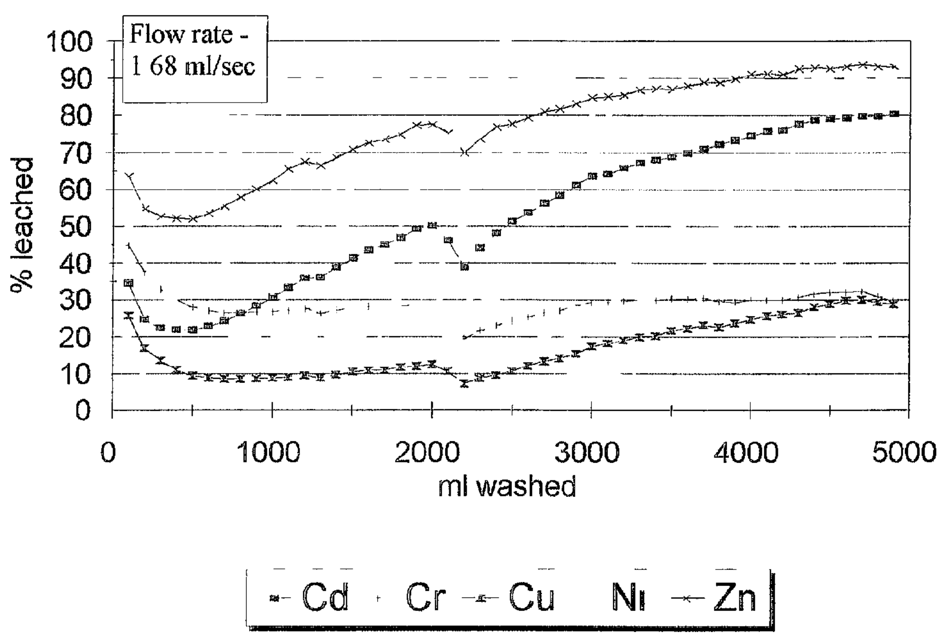
solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 39-Adsorption in compost column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 40-Adsorption in compost column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

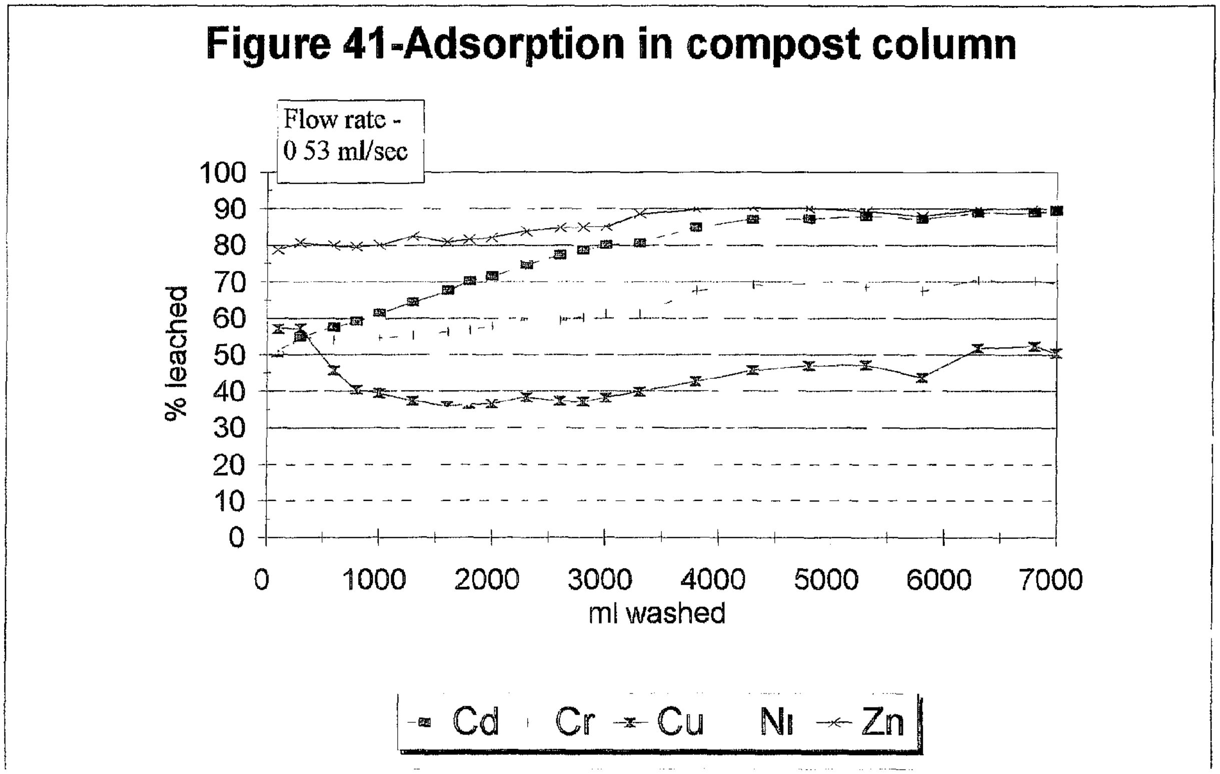
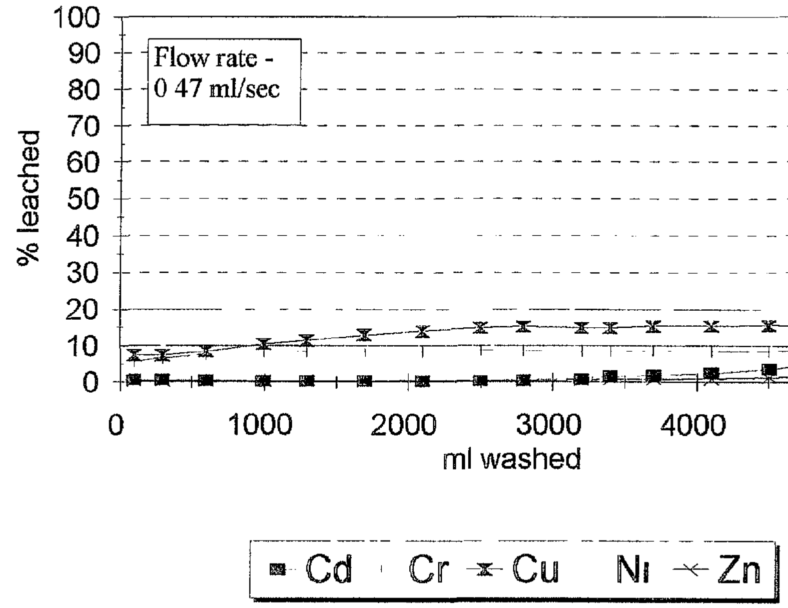


Figure 41-Adsorption in compost column

solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	76 09	33 64	2 6	180 28
7	13 10 96		38 02	56	29 54	4 46	177 2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

Figure 42-Adsorption in compost column



solution No	Date of sampling	pH	Cd ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm
1	12 5 96	4	17 43	178 55	119 2	15 64	87 12
3	11 6 96		13 76	235 9	143 4	14 78	132 3
4	7 8 96	3 7	92 9	295 73	298 9	122 15	368 52
5	30 7 96	3 6	100 94	245 6	261 9	111 88	256 74
6	10 9 96		50 77	75 09	33 64	2 6	180 28
7	13.10.96		38.02	56	29.54	4.46	177.2
8	8 8 96	6 1	22 49	5 1	37 51	4 23	106 49
9	12 8 96	3 7	97 28	284 34	280 57	126	429 29

4.2.4 Repeated batch cycles of adsorption/desorption

A cycle of batch experiments was conducted in order to check the ability of substrates to recover from exposure to different dilutions of waste water, acidification, normalization of pH and another exposure to waster water

4.2.4.1. Materials

4.2.4.1.1. Chemicals

Stock Solution, of waste water from a metal plating plant, collected and characterized as described in chapter 4 2 2 1

Working solutions were made from the stock solutions, by diluting tin different ratios with distilled H_2O

Hydrochloric acid , concentrated, and diluted to 15%

4.2.4.1.2. Adsorbents

Compost from municipal waste and commercial swage sludge were tested

4.2.4.2. Methods

4.2.4.2.1. Instruments

ICP optima 3000 DV Perkin Elmer ,pH meter "Metrohm 654", Centrifuge, Shaker and vacuum filtering device were used during the work

4.2 4.2.2. Methods of work

work was done according to the following procedure

1 Measurement of pH and metal scanning in ICP on all samples of waste water
2 9 flasks in a volume of 2 5 l were weighed
3 5 samples of 100 g compost were added to 5 flasks
4 1 lit of effluents were added in the following dilution ratios
0 1000, 250 750, 500 500, 750 250, 1000 0
5 To the other 4 flasks 100 g of sludge was added
6 1 lit of effluents were added, as in stage 4
7 All flasks were shaked for 24 hrs, and than left for 24 hrs for gravimetric separation
8 Liquid and solid were separated, and in the liquid pH was measured in a filtered sample metals were analyzed Zn, Cd, Cu, Ni, Cr)
9 All flasks were weighed again, and 10 g of substrate were taken out the small sample was dried (60° C overnight)to determine the weight of substrate left in the flask and the volume of liquid left in the solid
10 150 ml HCl 15% were added to each flask flasks were shaked for 24 hrs separation was carried out in a 250 ml centrifuge tube in small batches (5000 rpm 12 5 min)
11 pH and metals analyzed as in stage 8
12 Repeat stage 9
13 Neutralizing pH by adding 5 g $Ca(OH)_2$ in 200 ml H_2O shaking 24 hrs separating by centrifuge In this stage pH was measured and if it was still under 3 5, another 5 g of base were added
14 samples were transferred back to the flasks, weighed, checked for water content and than another two cycles of the same procedure were carried out

In the third cycle the volume of effluents was only 500 ml, since the weight of substrate was smaller

4.2.4.3. Results

a After the first shaking with waste water the liquid was very turbid and there was not a very good separation

b in the second cycle liquid was less turbid and separation was good, but still there was a small residual liquid left inside the flask

The results of this work are given in figures 43 - 47

It was found that a linear adsorption from the wastewater of Plant A continued for at least 3 consecutive cycles, using a 1 10 sludge wastewater ratio Accumulated adsorption of sewage sludge (certainly not maximal adsorption) was 10,000, 2700, 150, 1450 and 2000 µg/g, respectively

Figure 43 - Accumulation of metals - 100% waste water

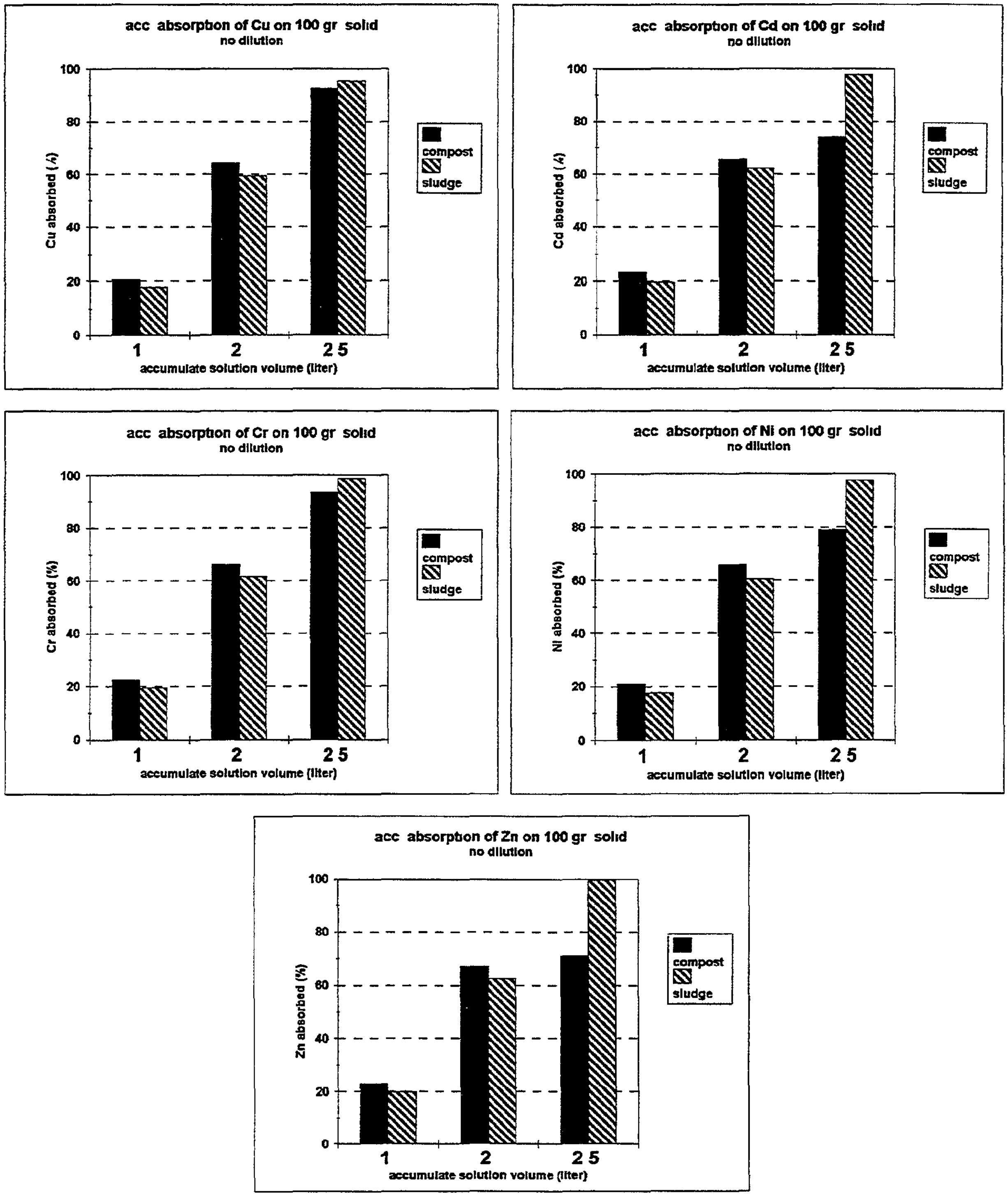


Figure 44 - Accumulation of metals - 75% waste water

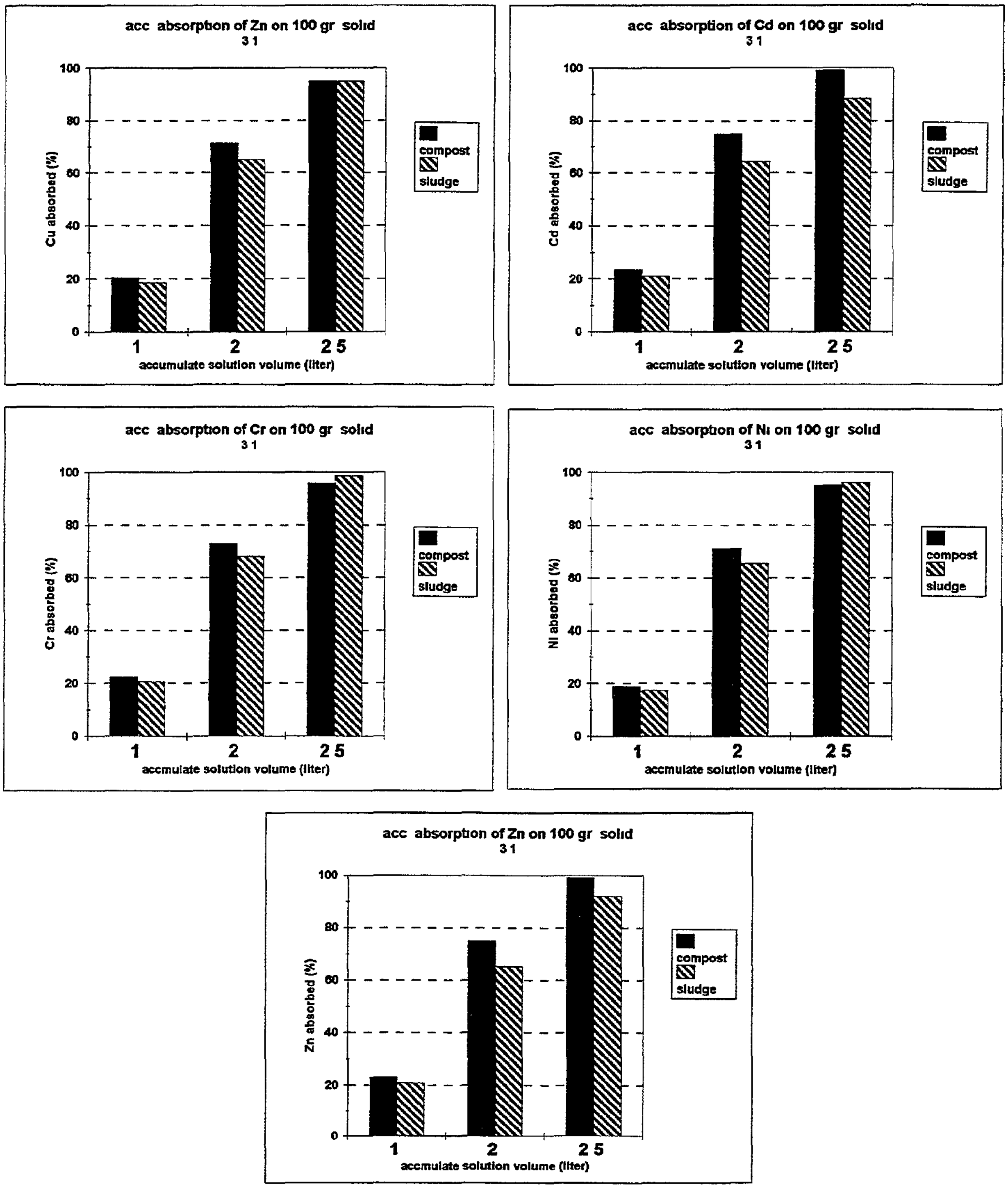


Figure 45 - Accumulation of metals - 50% waste water

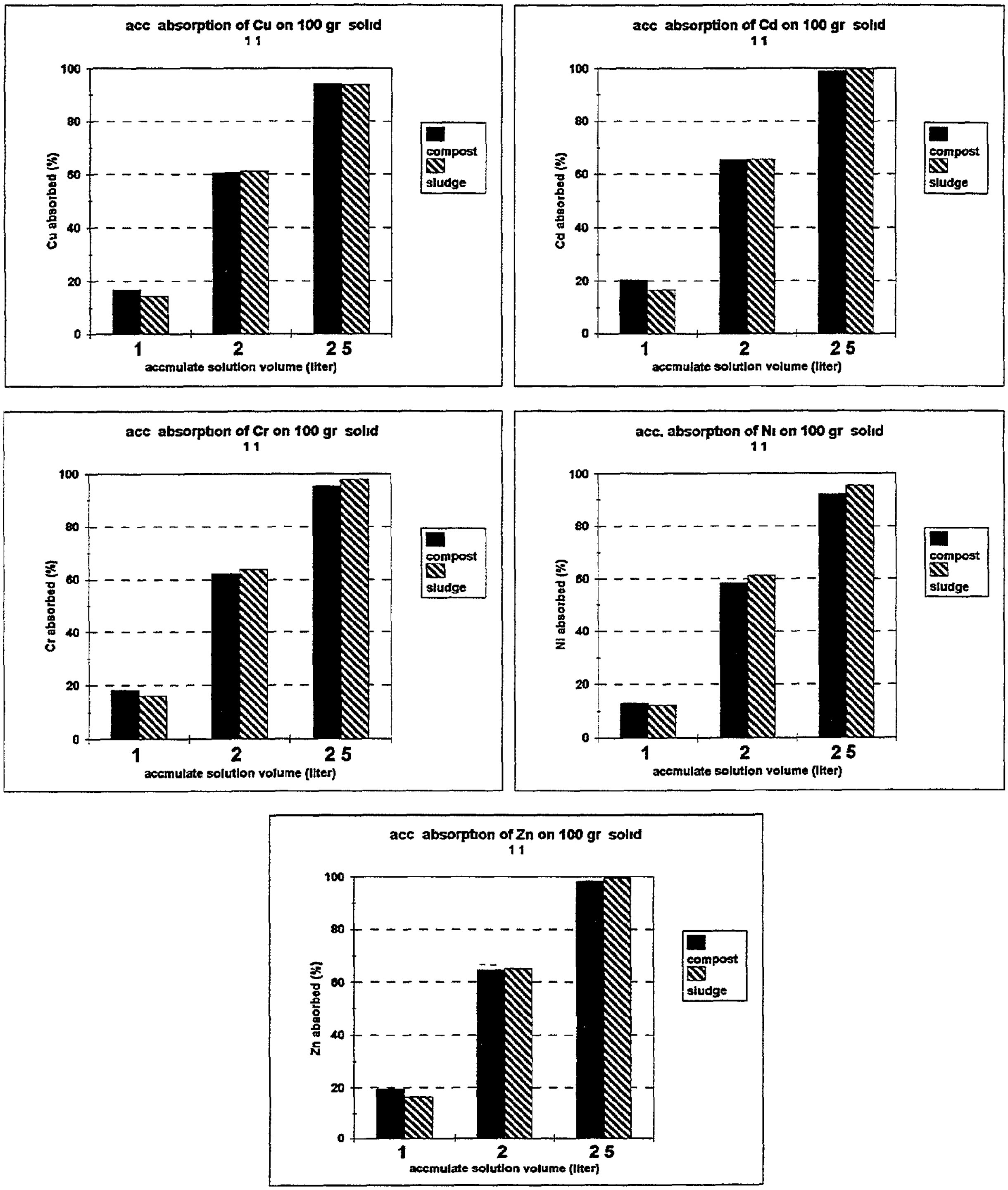


Figure 46 - Accumulation of metals - 25% waste water

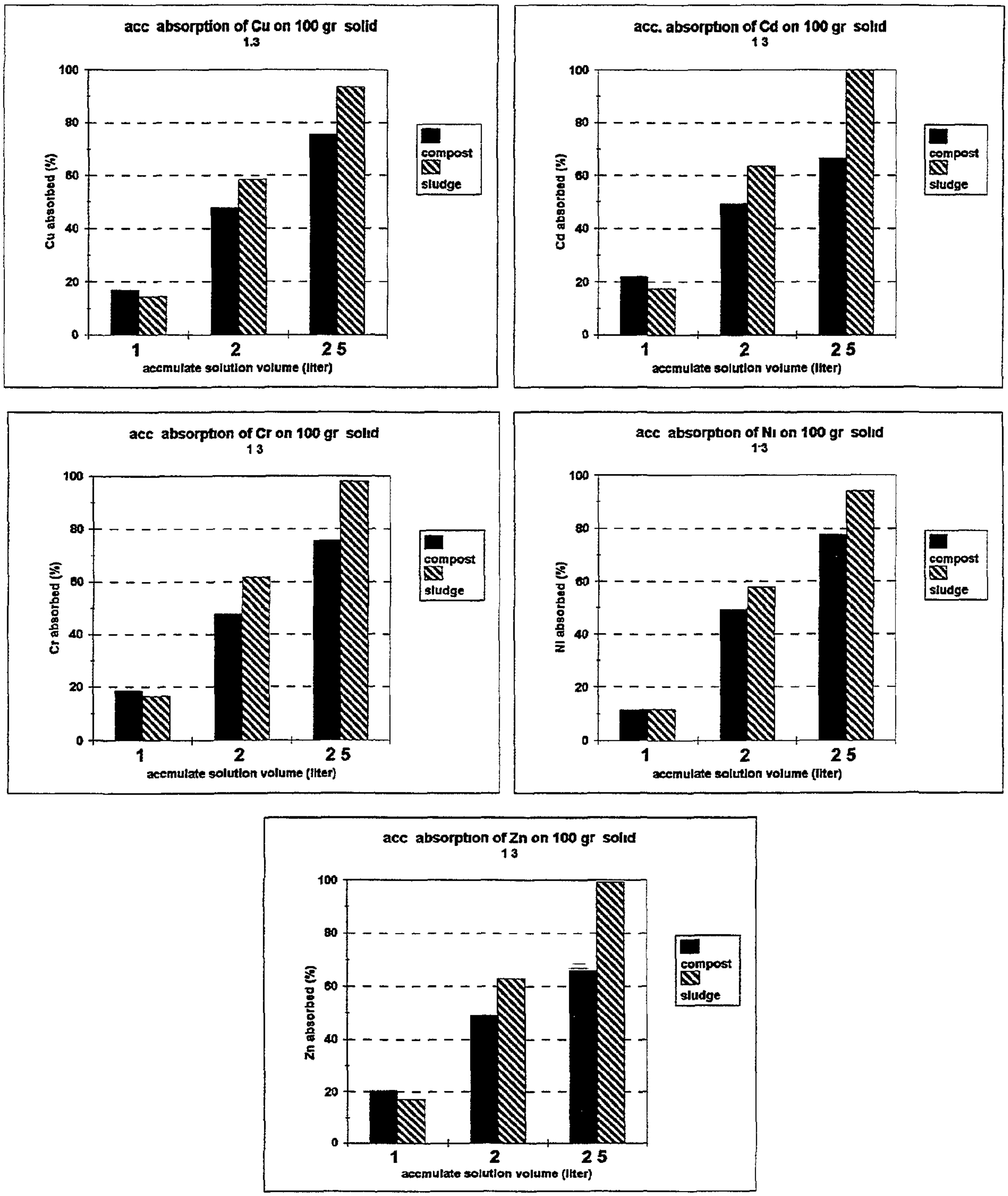
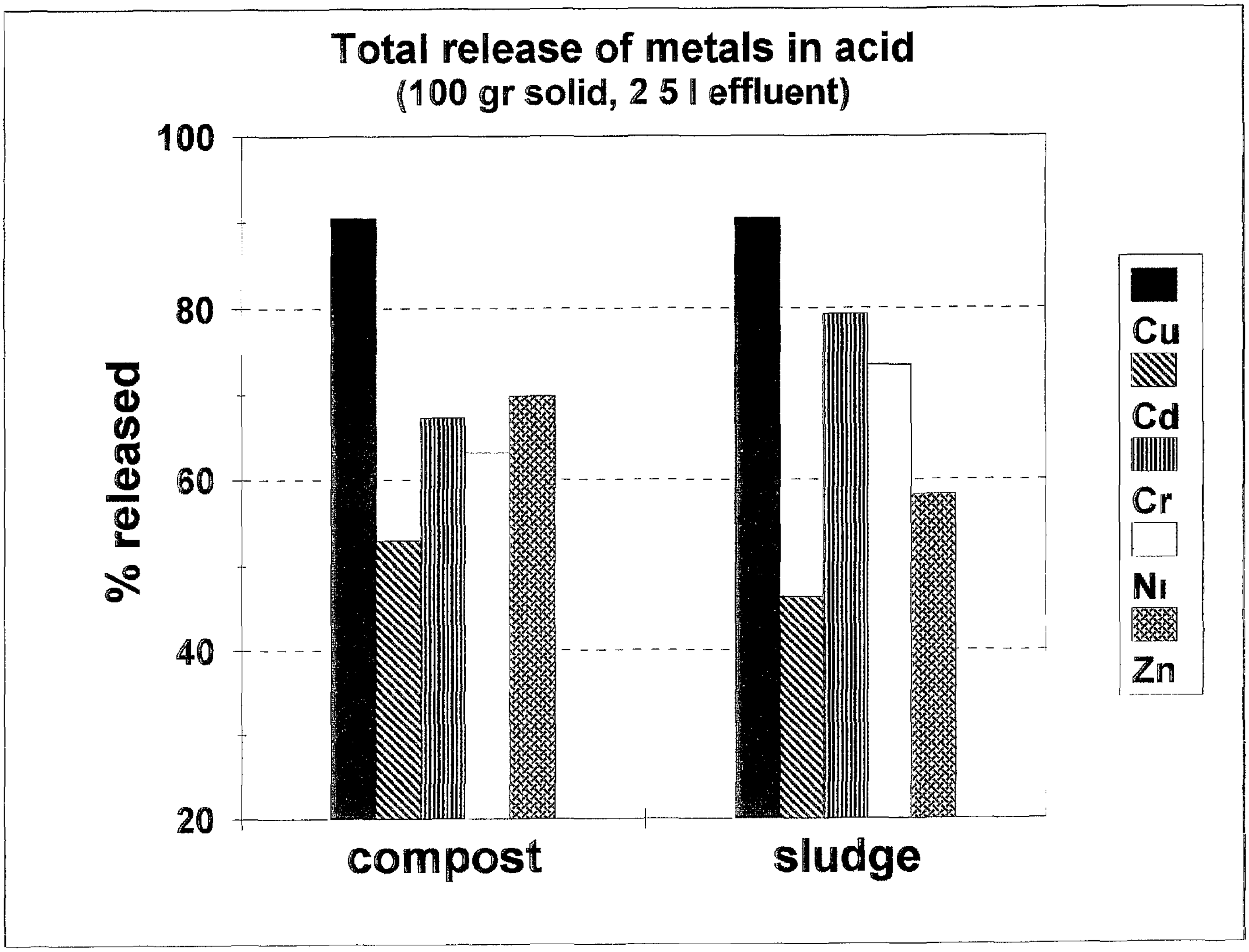


Figure 47

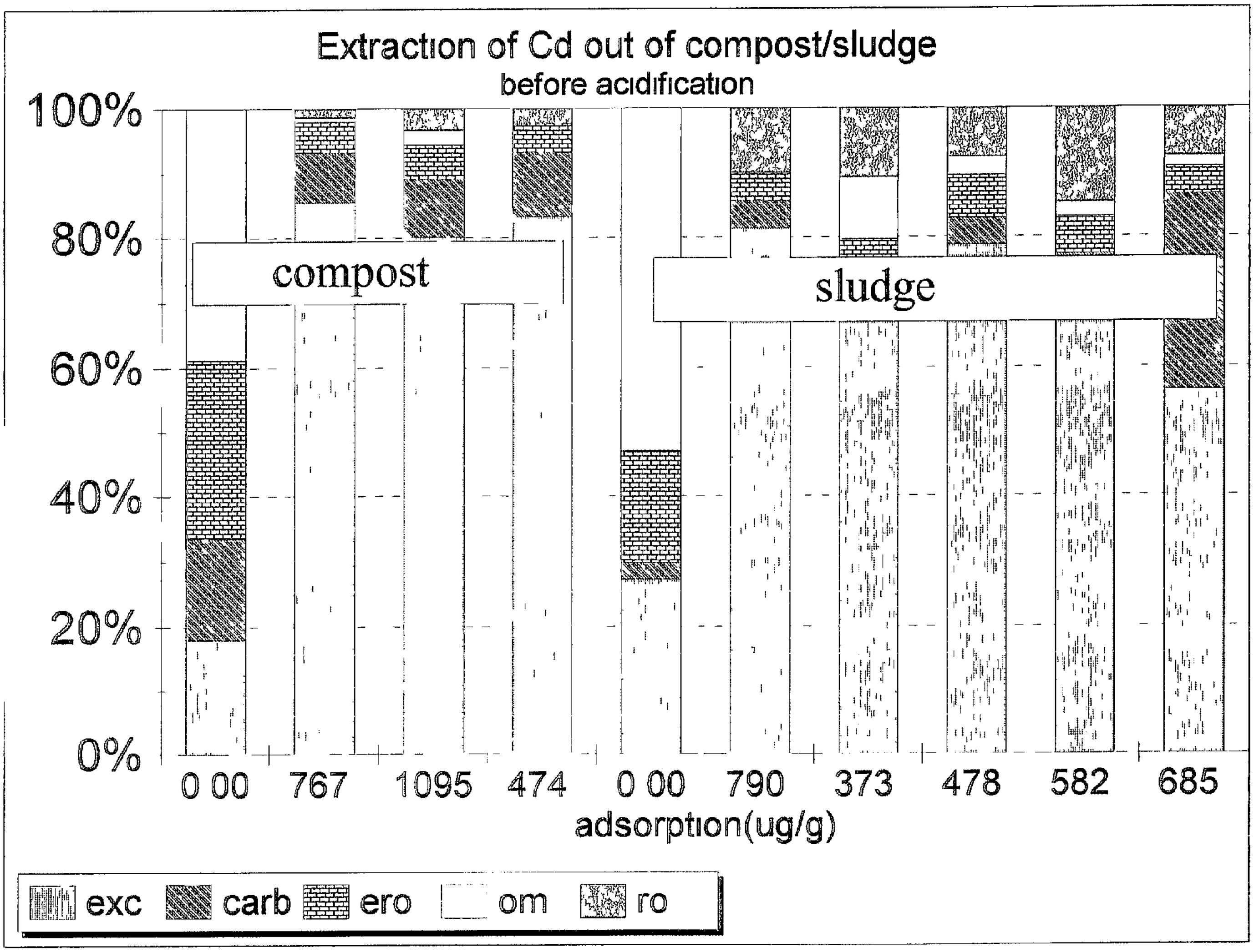

Total release of metals in acid
(100 gr solid, 2 5 l effluent)
% released
100
80
60
40
20
compost
sludge
Cu
Cd
Cr
Ni
Zn

4.2.5. Sequential Extraction in Cycle Batches

This part of our work was aimed to check the changes, if exist, in the nature of metal binding to substrate before and after acidification
metals were bound to bioadsorbent as described in the former chapters, and samples of substrate were taken after the adsorption After that the rest of adsorbent was acidified, and pH lowered to apx 1 5 The solution was analyzed and the solid sampled
The two samples of solid were analyzed according to the method described in chapter 3 1 C
All results are shown in figures 48 - 57

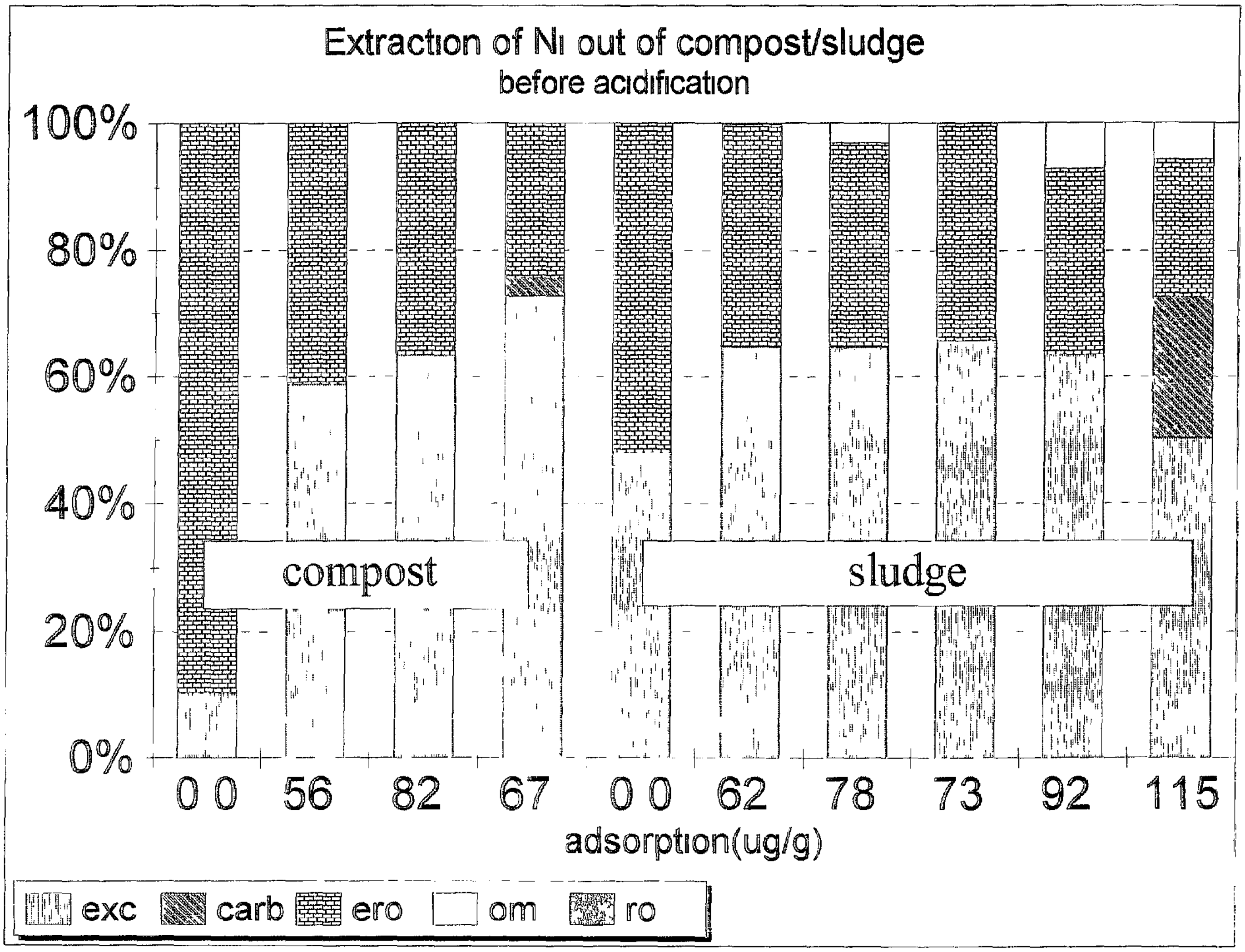
The result of the sequential extraction give some insight into the mechanism of adsorption and desorption The desorption leads, in most cases to a drastic removal of metals tied to the exchangeable sites This is the site that holds most of the adsorbed metals, yet, those are easily removed by the acidic solution In the case of Cr the desorption stage removed also a significant fraction of the carbonate and easily reduced components (previous experiments have shown that the "easily reduced" components are not necessarily oxidized species The 3d fraction may be considered a fraction less soluble in acid than the "carbonate" tied metals, that is solubilized with the additional acidic extraction)

Figure 48


Extraction of Cd out of compost/sludge
before acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0 00
767
1095
474
0 00
790
373
478
582
685
adsorption(ug/g)
exc
carb
ero
om
ro

87

Figure 49



Extraction of Ni out of compost/sludge
before acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0 0
56
82
67
0 0
62
78
73
92
115
adsorption(ug/g)
exc
carb
ero
om
ro

88

Figure 50

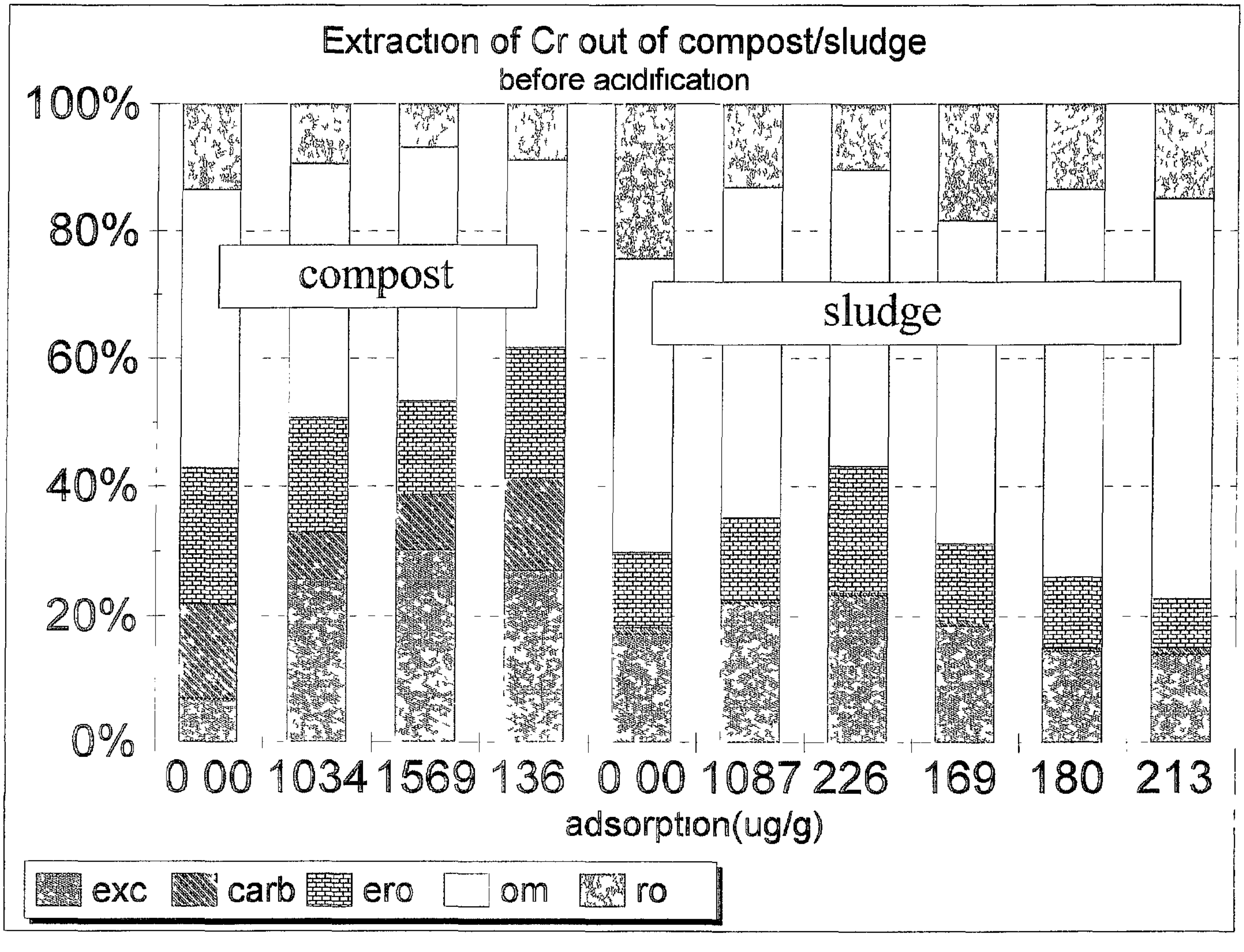

Extraction of Cr out of compost/sludge
before acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0 00
1034
1569
136
0 00
1087
226
169
180
213
adsorption(ug/g)
exc
carb
ero
om
ro

Figure 51

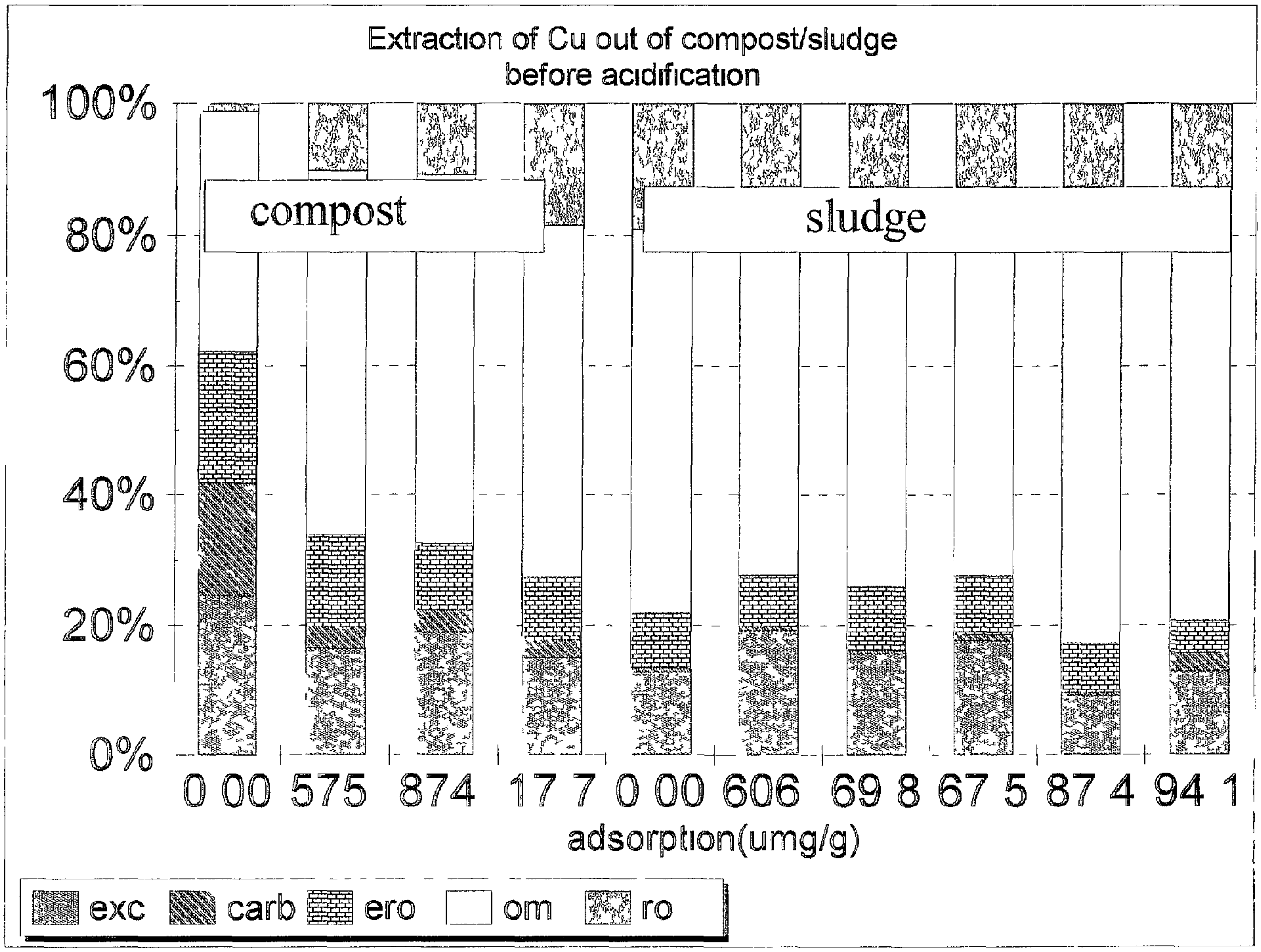

Extraction of Cu out of compost/sludge
before acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0 00
575
874
17 7
0 00
606
69 8
67 5
87 4
94 1
adsorption(umg/g)
exc
carb
ero
om
ro

Figure 52

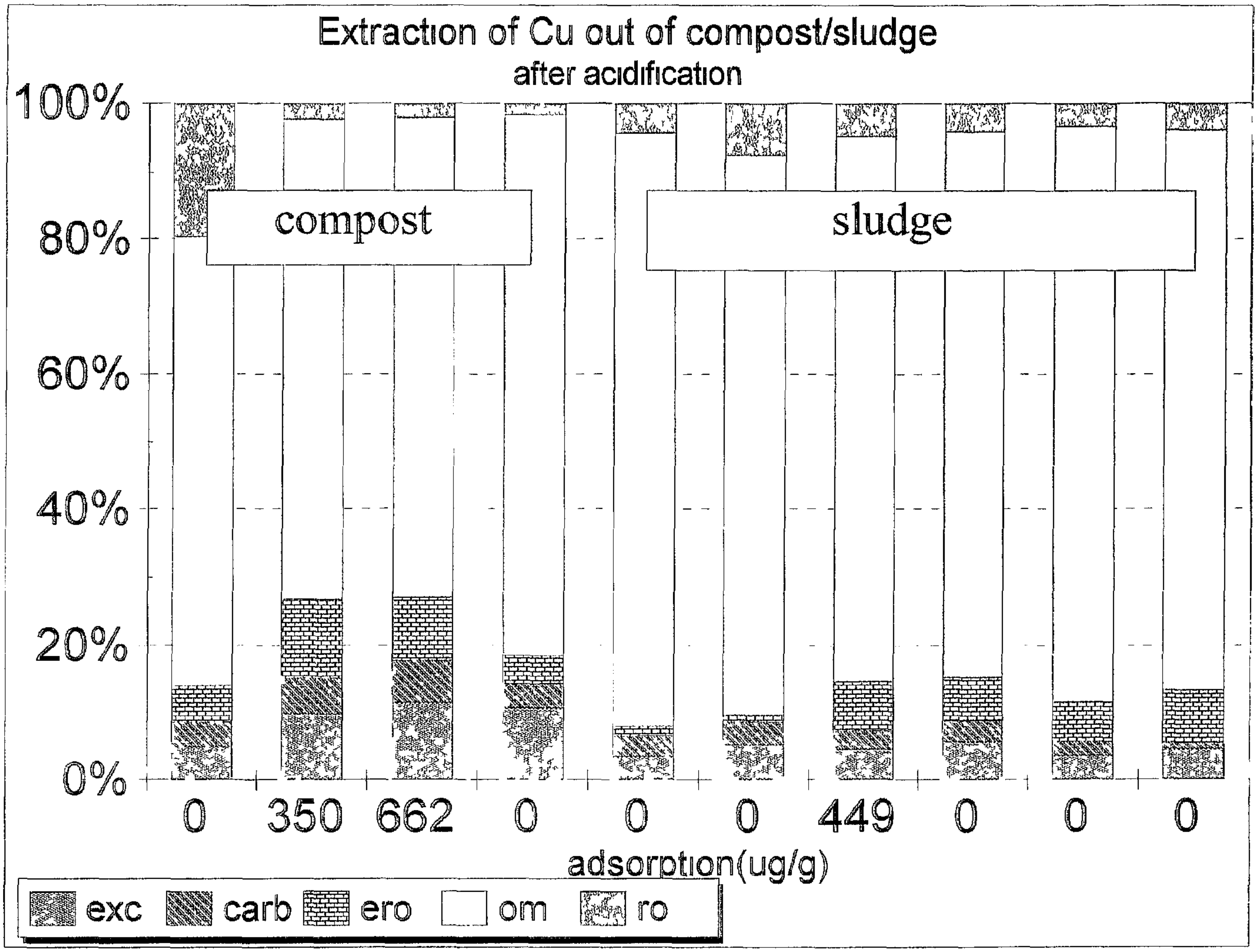
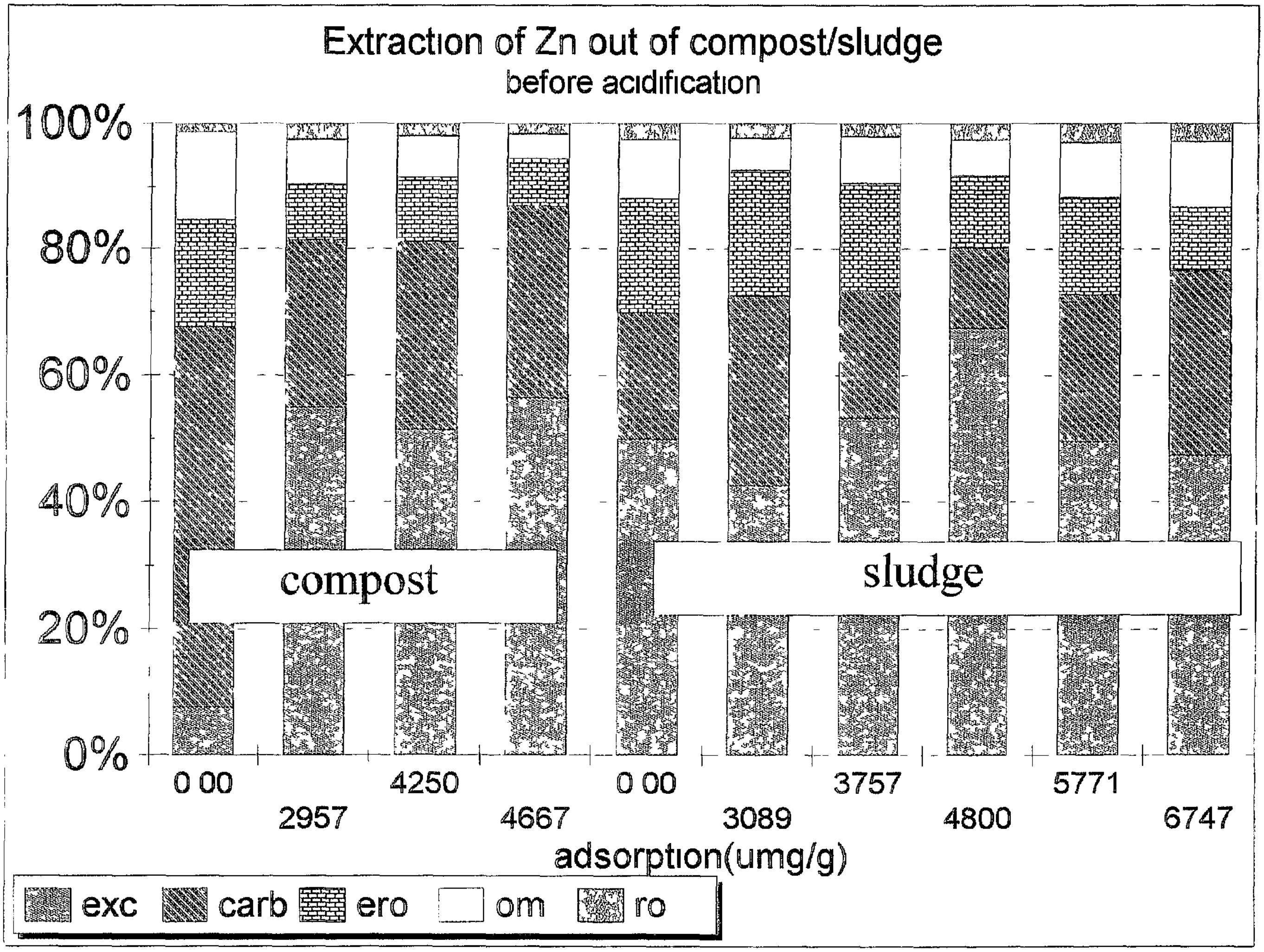
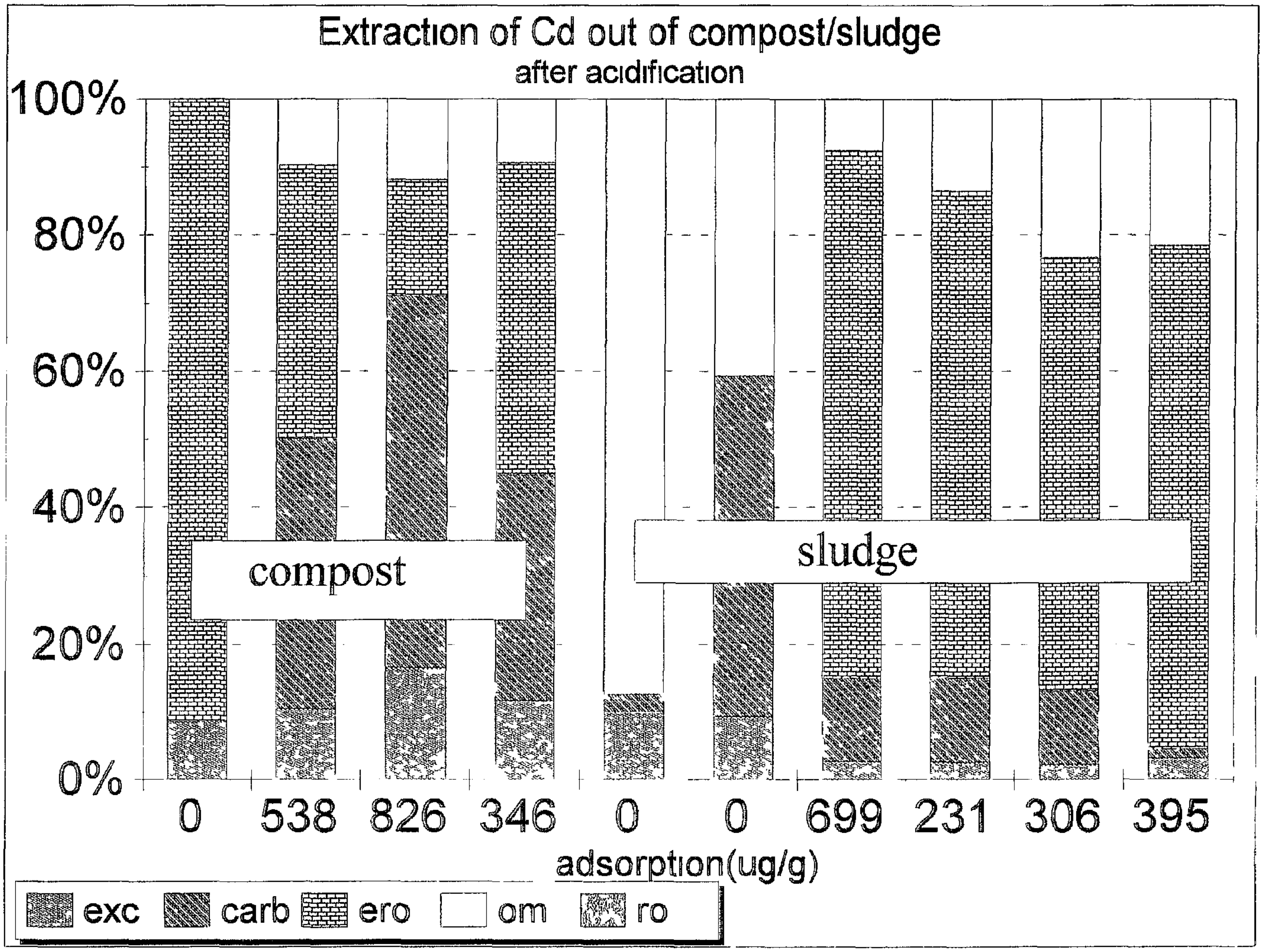

Extraction of Cu out of compost/sludge
after acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0
350
662
0
0
0
449
0
0
0
adsorption(ug/g)
exc
carb
ero
om
ro

Figure 53


Extraction of Zn out of compost/sludge
before acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0 00
2957
4250
4667
0 00
3089
3757
4800
5771
6747
adsorption(umg/g)
exc
carb
ero
om
ro

92

Figure 54



Extraction of Cd out of compost/sludge
after acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0
538
826
346
0
0
699
231
306
395
adsorption(ug/g)
exc
carb
ero
om
ro

Figure 55

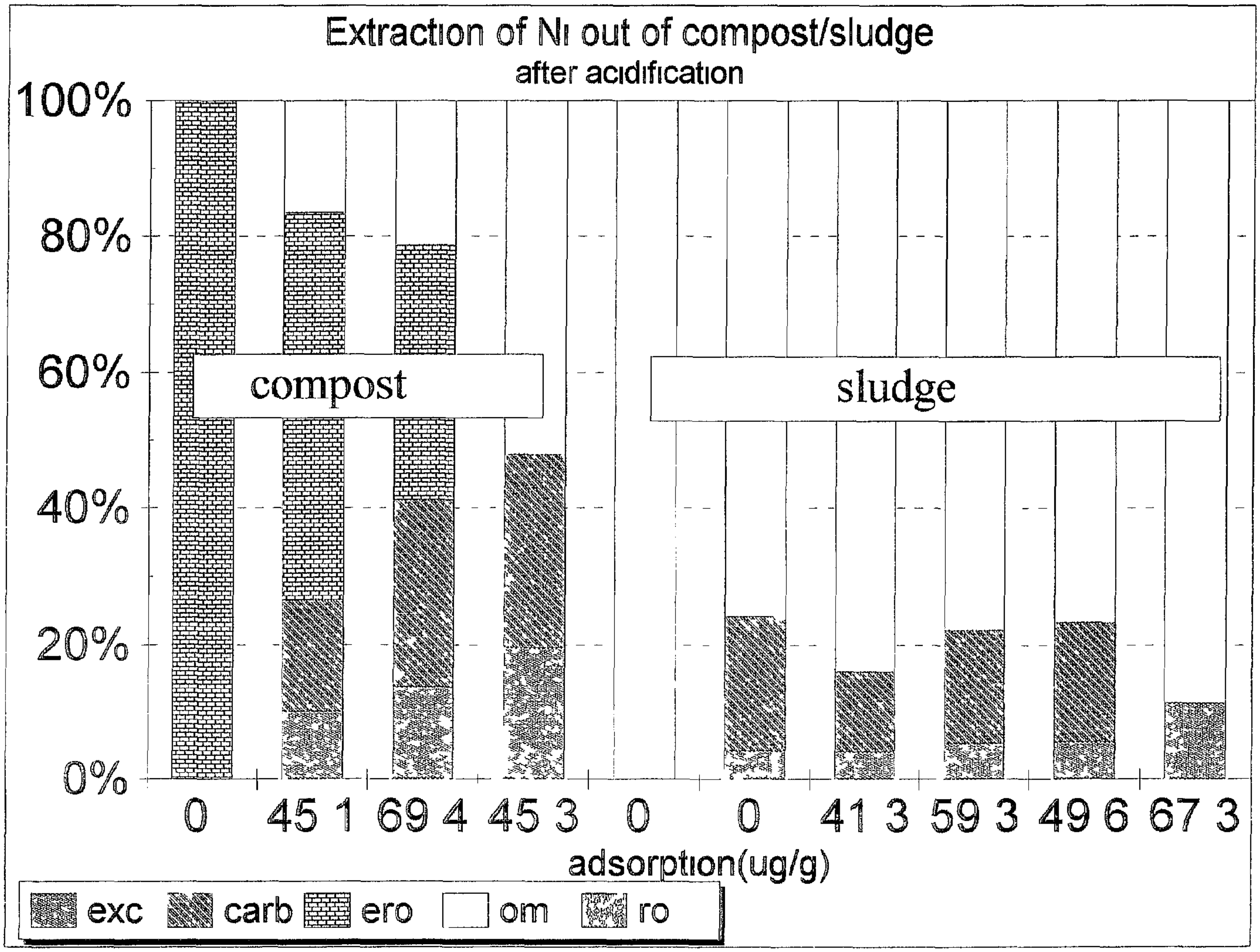
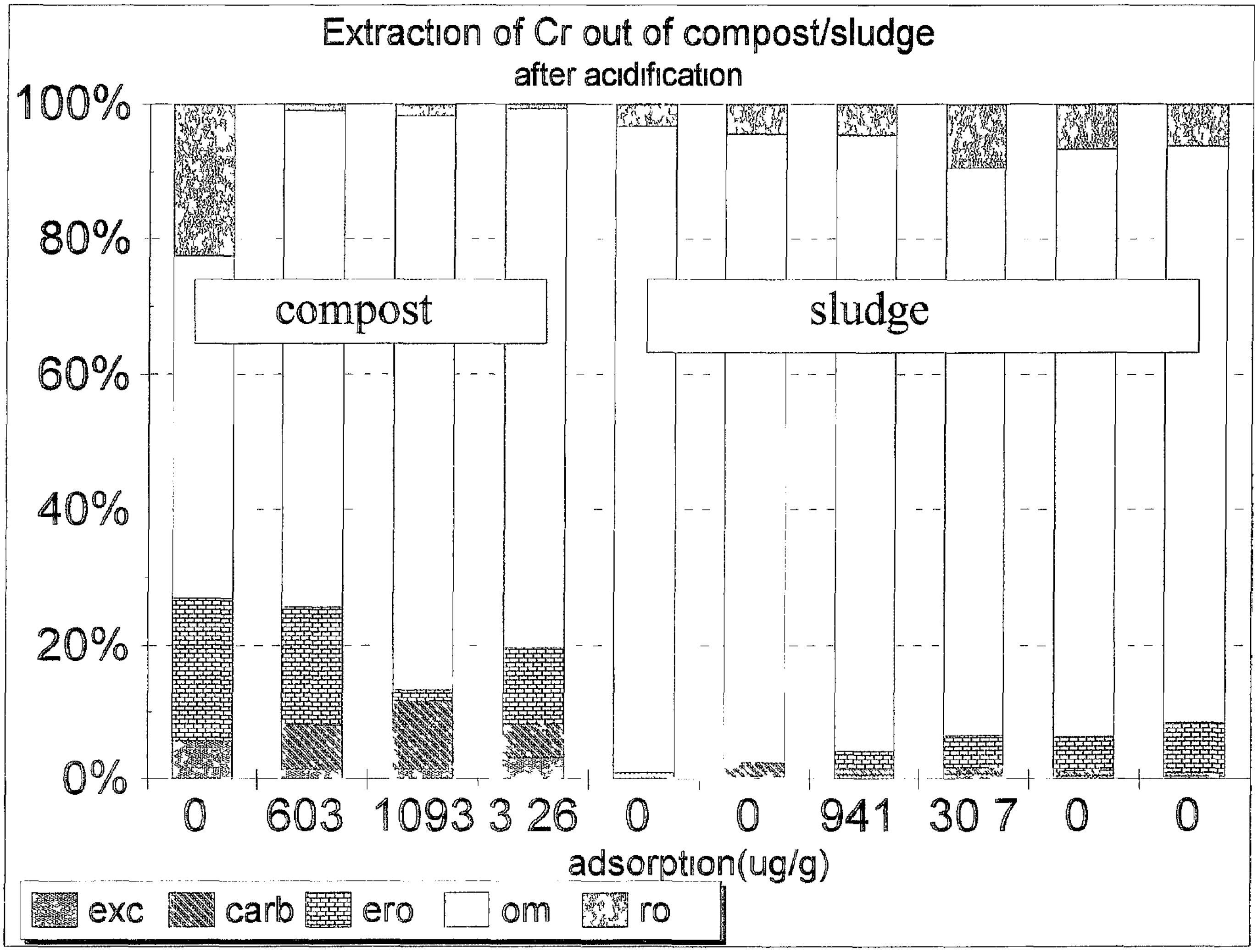

Extraction of Ni out of compost/sludge
after acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0
45 1
69 4
45 3
0
0
41 3
59 3
49 6
67 3
adsorption(ug/g)
exc
carb
ero
om
ro

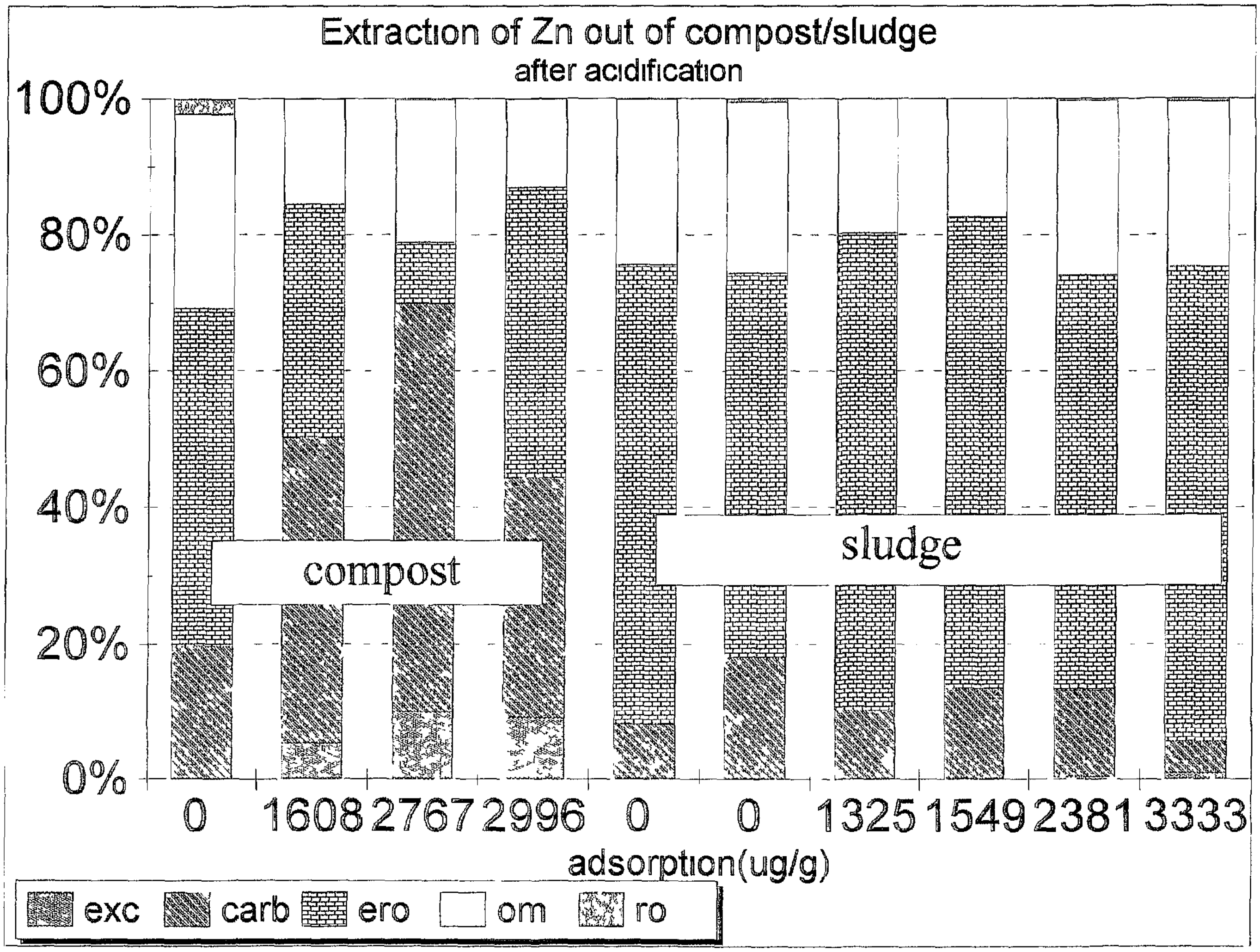
Figure 56



Extraction of Cr out of compost/sludge
after acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0
603
1093
3 26
0
0
941
30 7
0
0
adsorption(ug/g)
exc
carb
ero
om
ro

96

Figure 57


Extraction of Zn out of compost/sludge
after acidification
100%
80%
60%
40%
20%
0%
compost
sludge
0
1608
2767
2996
0
0
1325
1549
2381
3333
adsorption(ug/g)
exc
carb
ero
om
ro

4.2.6. Batch Reactor for the Adsorption of Metals from Waste Effluents

A batch reactor was built in order to allow the treatment of large volumes of water

4.2.6.1. Materials

4.2.6 1.1. Chemicals

Working solutions were waste water from a metal finishing plant collected and characterized according to the method described in chapter 4 2 2 1

4 2.6 1.2 Adsorbents

Composted sewage sludge was tested in this part of the work

4.2.6.2. Methods

4 2.6.2.1. Instruments and appliances

ICP optima 3000 DV Perkin Elmer ,pH meter "Metrohm 654" were used during the work
The experiment was carried out in reactor, which is described in figure 4 2 6
The reactor was built from a PVC barrel, to which a PVC funnel was connected, in order to allow better circulation of air and water The bottom of the barrel was connected through the funnel to the air inlet, provided by a compressor

4.2.6.2.2. Sample Preparation

Adsorbent was not pretreated as in the former experiments

4.2.6.2.3. Method of operation

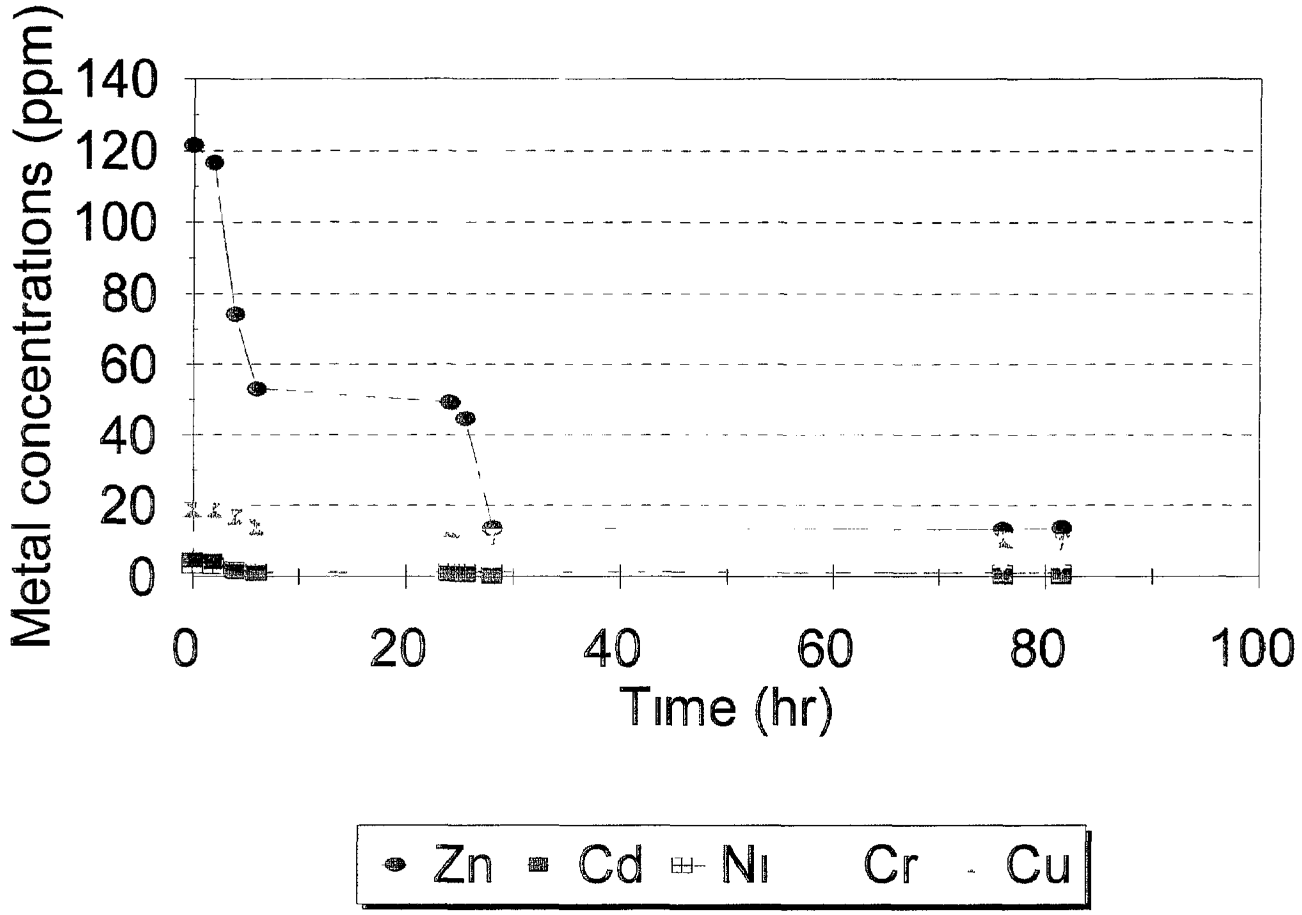
6 kg of adsorbing material was placed in the reactor, and 60 l of waste water were added to the substrate, and the air flow was activated The suspension was fluidized for up to 82 hrs, and sampled at measured time intervals the sample was then filtered through Whatman #1

Metal concentration, C_0 = metal concentration at 0 time and C_{eq} = metal concentration in equilibrium after X hrs adsorption, were determined by ICP spectrometer

4 2.6.3. The results of these experiments are given in figure 58

Figure 58

Adsorption in batch reactor



4.2.7 Pilot Reactor Trials

The final "approach" toward a practical use of our research, we constructed a pilot reactor that can be easily used in a small metal processing workshop
The basic demands from the system were
The reactor should be as simple and rigid as possible
Due to the contact with highly corrosive solutions, the reactor should be constructed with non-corrosive materials
The operation should be simple
The wastewater treatment should be cheap

4.2.7.1 The reactor - was constructed of 120 l barrel The Bottom of the barrel was cut and the barrel was cemented, using silicon glue, to a funnel (See Fig 59)

4.2.7.2. Mixing - was achieved by airflow (using a low-pressure blower as an air source) introduced into the reactor from the bottom The mixing was poor in the first runs, due to channeling of the airflow and accumulation of sludge on shoulders at the joint between the barrel and the funnel Placing a cone at the bottom of the reactor (Figure 59) solved this The cone served several purposes First, it seals the bottom of the reactor when airflow stops During operation, the air raised the cone, yet, once pressure was released, it sunk back Thus, airflow was abrupt, leading to a much better mixing and preventing any channeling, due to the irregular airflow

4.2.7.3. Operation

wastewater from plant A and sewage sludge (liquid solid ratio of 10) were introduced into the reactor Airflow was opened and the system was mixed
Samples were taken periodically for analysis
At the termination, clear solution was decanted from an outlet located above the bottom cone and the concentrated sludge drained from the bottom

4.2.7.4. Results

Results of two run are presented in Figures 60 – 63 and in Table 14
The wastewater sample taken on 19 8 97 was rather dilute Cadmium concentration was about 5 PPM and Chromium was about 10 PPM The final effluent contained only 0 3 PPM Cd and 3 6 PPM Cr, yet the relative reduction was mild
The second sample, taken on 1 12 97 was more concentrated Cadmium concentration was about 53 PPM and Cr 193 PPM Cadmium was reduced to 3 9 PPM and Cr to 9 PPM The relative reduction was very effective, as only less than 5% of metals concentrations (Zn, Cd, Ni, and Cr) were left in the solution Copper removal percentage was lower

The rate of removal was very high The reaction can be considered completed following less than 2 hours

4.2.7.5. Conclusions

We believe that we have now an effective low cost, simple and stable system to treat effluents of metal finishing workshops
The way of operation we envisage is to equip the workshops with the simple reactor and to supply the workshops with dried sewage sludge
The workshop owner will collect the wastewater in the reactor and operate the mixing for 2 hours The effluents can in most cases be released to the sewer
The sludge, drained at a volume of about 10% of the original wastewater can be treated either at the plant, or most probably at a central treatment facility
Metals can be recovered by leaching with acid and the spent sludge disposed at a landfill

TABLE NO. 14 - CONCENTRATION OF METALS IN THE WASTE WATER BEFORE AND AFTER EQUILIBRIUM

Date of sampling : 19.8.97					
	Zn	**Cd**	**Ni**	**Cr**	**Cu**
C_0 (ppm)	121 6	4 75	3 39	10 4	19
C_{eq} (ppm)	13 9	0 3	1 3	3 6	10
Date of sampling . 1.12.97					
	Zn	**Cd**	**Ni**	**Cr**	**Cu**
C_o (ppm)	163	53 4	14 9	193	172
C_{eq} (ppm)	27 1	3 86	1 92	9 02	16 8

batch Reactor

Figure 59

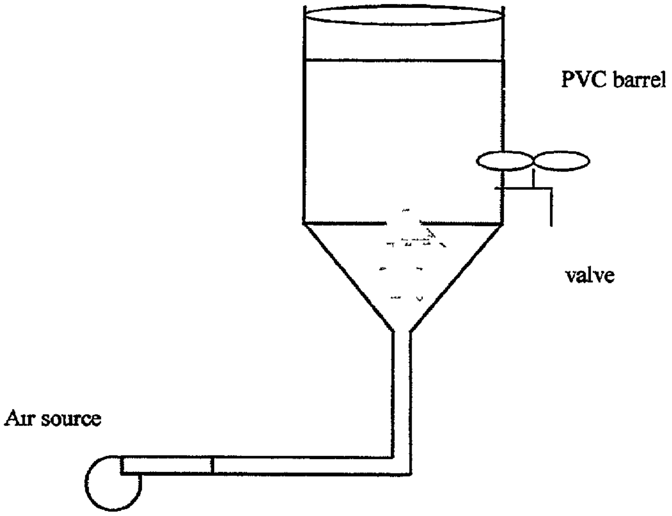


Figure 60 **Adsorption in a batch reactor**

Date of sampling : 19.8.97

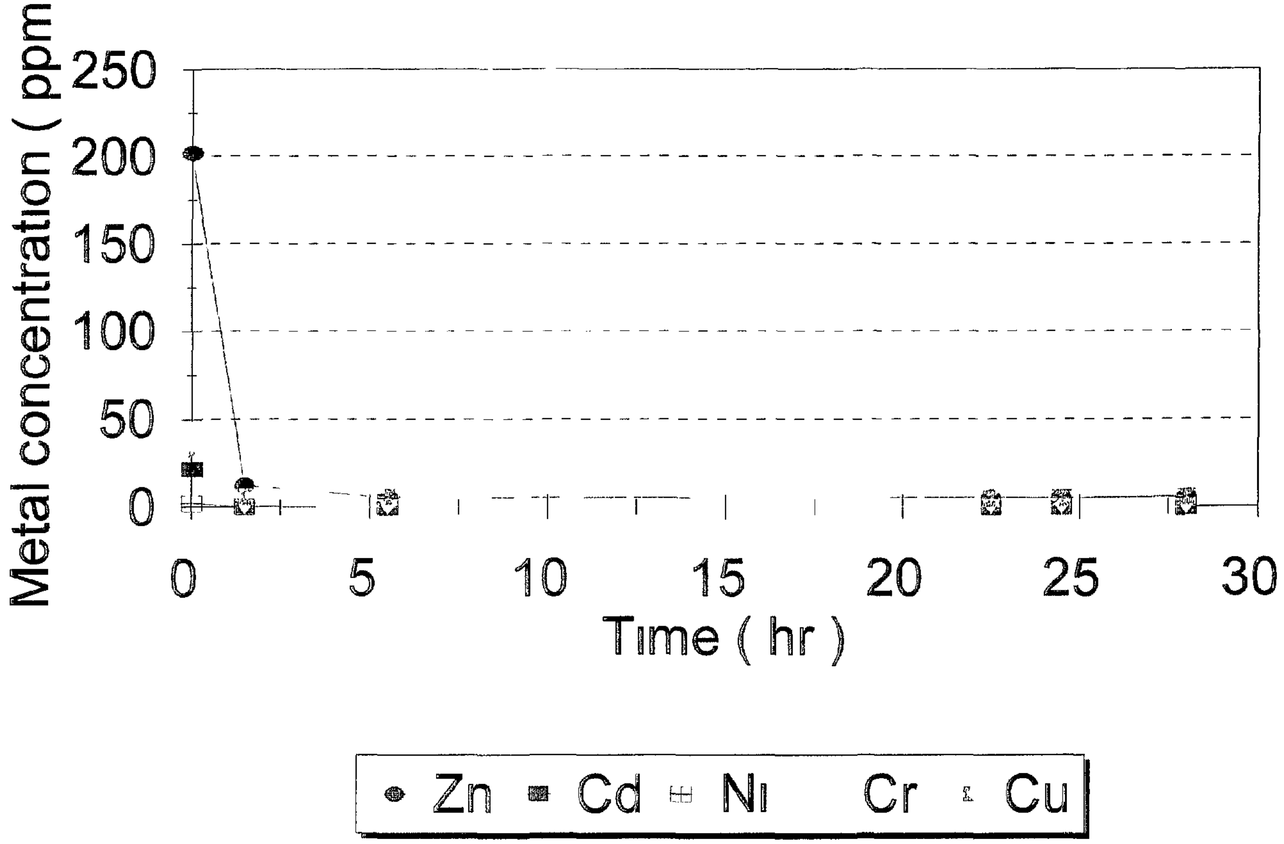


Figure 61

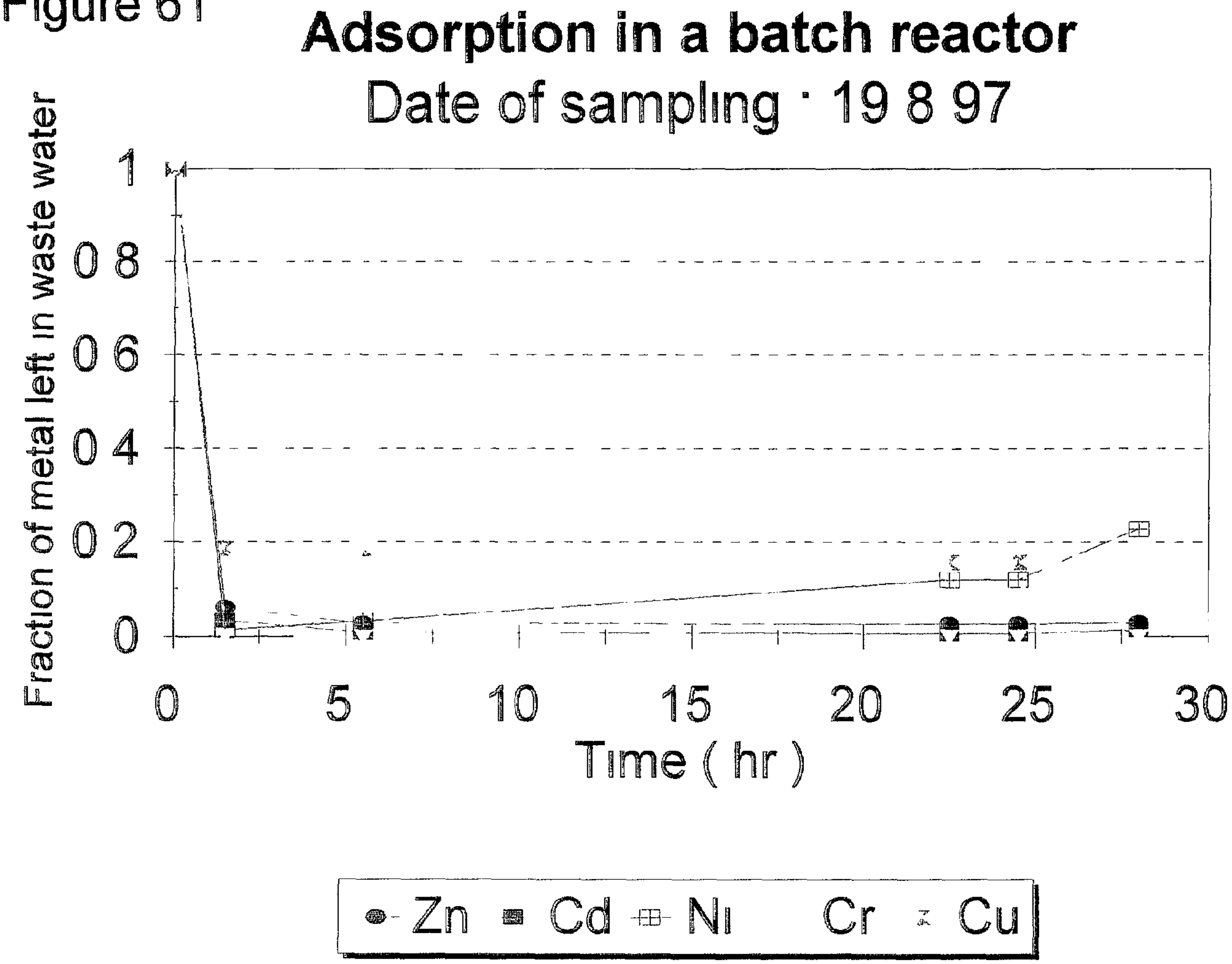

Adsorption in a batch reactor
Date of sampling · 19 8 97
Fraction of metal left in waste water
1
0 8
0 6
0 4
0 2
0
0
5
10
15
20
25
30
Time (hr)
Zn
Cd
Ni
Cr
Cu

Figure 62

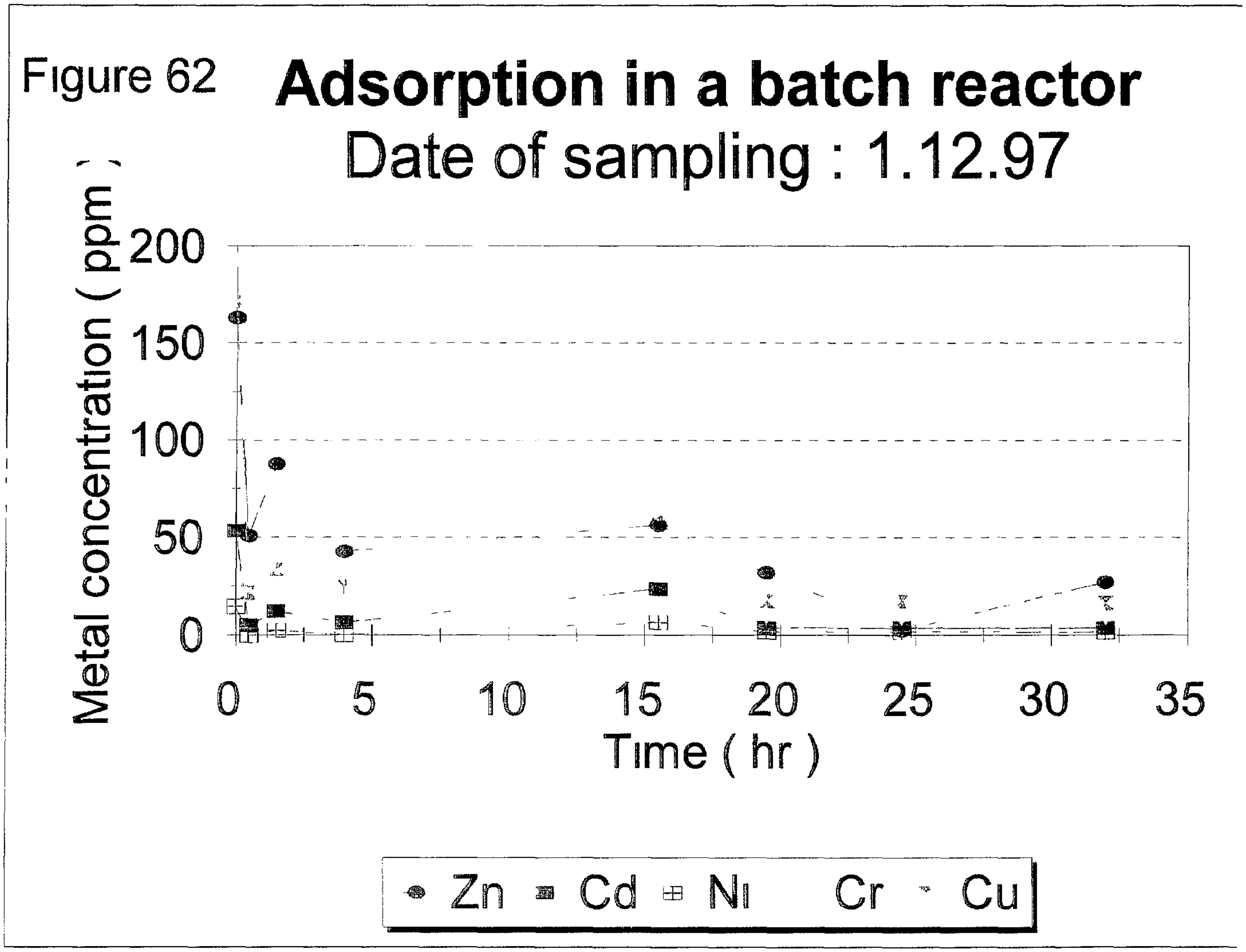
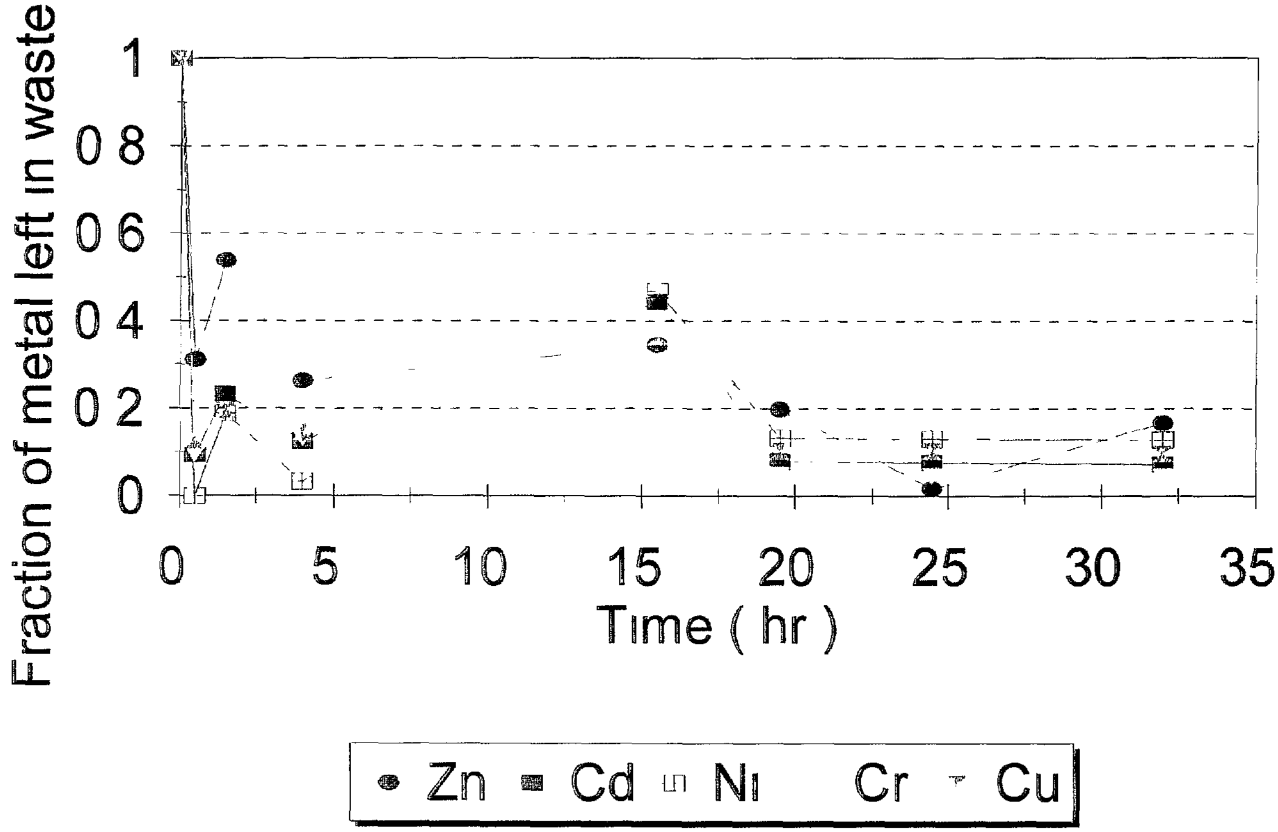

Adsorption in a batch reactor
Date of sampling : 1.12.97
Metal concentration (ppm)
200
150
100
50
0
0
5
10
15
20
25
30
35
Time (hr)
Zn
Cd
Ni
Cr
Cu

Figure 63 **Adsorption in a batch reactor**

Date of sampling : 1.12.97



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* * *

PEAT AND COMPOST FILTERS FOR THE SEPARATION OF HAZARDOUS WASTES FROM WATER

CDR Grant No TA-MOU-C12-050

FINAL REPORT

(for the period from August 10th, 1993 to December 31 10, 1997)

Project Leader

Yoram Avnimelech, Prof (Main Grantee, Israel)

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Participating Scientists (Poland)

Joanna Kyzioł, Ph D
Krystyna Janta-Koszuta, M Sc

Technical Staff and Contracted Work
6 persons

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Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L= 1 10,
Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55%), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Table 12/1-3 Equilibrium mass adsorption/desorption isotherms for Cu^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cu-Cl and binary systems (Cu+Cr)-Cl,
Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L= 1 10,
Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Table 13/1-3 Equilibrium mass adsorption/desorption isotherms for Cr^{3+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cr-Cl and binary systems (Cr+Cu)-Cl,
Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^{3}, S/L= 1 10,
Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Table 14/1-3 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-SO_4^{2-} and binary systems (Zn+Cd)-SO_4^{2},
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Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

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Batch experiments, Input solution Me-SO_4^{2}, pH 4 0, c_0 = 1 - 5000 mg Me dm^{3}, S/L= 1 10,
Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Table 16 Effect of Zn^{2+} and Cd^{2+} ion competition for sorption sites in low-moor peat (Peat Humus and Rush Reed-Sedge Peat) and pH changes of equilibrated solutions in mono-metal Zn-Cl, Cd-Cl and binary systems (Cd+Zn)-Cl,
Batch experiments, Input solution Me-Cl , pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L= 1 10 ,
Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Table 17 Effect of Zn^{2+} and Cd^{2+} ion competition for sorption sites in low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH changes of equilibrated solutions in mono-metal Zn-SO_4^{2} and binary systems (Cd+Zn)-SO_4^{2},
Batch experiments, Input solution Me-SO_4^{2}, pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10,
Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Table 18 Sequential fractionation of Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} ions sorbed from Me-Cl solution under batch conditions, at c_0 = 5000 mg Me dm^3 and pH 4 0 onto low-moor peat
Peat samples Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge)Peat (W9c),
Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

Table 19 Effect of Zn^{2+} and Cd^{2+} ion competition for sorption sites in pretreated low-moor peats (Peat Humus and Rush Reed-Sedge Peat) at fixed pH 5 5 in mono-metal Zn-SO_4^{2} and binary systems (Cd+Zn)-SO_4^{2-},
Batch experiments, Input solution Me-SO_4^{2}, pH 5 5, c_0 = 1 - 600 mg Me dm^3, S/L= 1 25,
Peat samples adjusted to pH 5 5 (1) Alder Peat Humus W1, (2) Brushwood Peat Humus W9b, (3) Rush (Reed-Sedge) Peat W9c,

Table 20 Sequential fractionation of Zn^{2+} and Cd^{2+} ions sorbed from Me-SO_4 solution in mono-metal and binary system onto pretreated low-moor peat at fixed pH 5 5,
Batch experiments, c_0 = 600 mg Me dm^3, pH 5 5, S/L=1 25,
Peat samples adjusted to pH 5 5 Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge)Peat (W9c)
Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

Table 21 Sorption of Zn^{2+} on Brushwood Peat Humus from the mono-metal Zn-SO_4 solutions under dynamic flow conditions
Column experiments, Input solution (1) c_o = 500 mg Zn dm^3 (2) c_0 = 250 mg Zn dm^3, pH 4 0, flow rate q = 0 1 cm^3 s, Adsorbent W9b, mass 90 g , water retention capacity S/L = 1 2

Table 22 Sorption of Zn^{2+} on Rush (Reed-Sedge) Peat from the mono-metal Zn-SO_4 solutions under dynamic flow conditions
Column experiments, Input solution (1) c_o = 500 mg Zn dm^3 (2) c_0 = 250 mg Zn dm^3, pH 4 0, flow rate q = 0 1 cm^3 s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1

Table 23 Sorption of Cd^{2+} on Brushwood Peat Humus from the mono-metal Cd-SO_4 solutions under dynamic flow conditions

	Column experiments, Input solution (1) c_o = 500 mg Zn dm^3 (2) c_0 = 250 mg Zn dm^3, pH 4 0, flow rate q = 0 1 cm^3 s, Adsorbent W9b, mass 90 g , water retention capacity S/L = 1 2
Table 24	Sorption of Cd^{2+} on Rush (Reed-Sedge) Peat from the mono-metal Zn-SO_4 solutions under dynamic flow conditions Column experiments, Input solution (1) c_o = 500 mg Cd dm^3 (2) c_0 = 250 mg Cd dm^3, pH 4 0, flow rate q = 0 1 cm^3 s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1
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Table 26	Sorption of Cu^{2+} on Rush (Reed-Sedge) Peat from the mono-metal Cu-SO_4 solutions under dynamic flow conditions Column experiments, Input solution (1) c_o = 500 mg Cu dm^3 (2) c_0 = 250 mg Cu dm^3, pH 4 0, flow rate q = 0 1 cm^3 s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1
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	Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual
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FIGURE CAPTIONS

Figure 1	Distribution of peatlands in Poland (after K Bitner, 1958) and location of peat-bogs selected for sampling
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Figure 3	Wetlands of the Biebrza Valley stratigraphy of peat deposits
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Figure 8/2	FTIR spectra of the representative peat samples of different kind Peat matter (IV) Calcareous Gyttia, (V) Detrituous Gyttia, Bands 1600-1630, close to 1400 and to 1040 cm^{1} - carboxylic groups of humic and fulvic acids, 3380 and 1620 cm^{1} - water, 2850 and 2920 cm^{1} - CH_2 and CH_3 groups, 1512 and 1266 cm^{1} - organic compounds containing nitrogen (amides),
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Figure 24 Sequential fractionation of Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} bound from mono-metal Me-Cl solution under batch conditions, at c_0 = 5000 mgMe dm^3 and pH 4 0 onto Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) according to the increasing binding strength Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

Figure 25 Equilibrium mass isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Peat) at fixed pH 5 5 of substrate and input solution in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl, c_0 = 1 - 600 mgMe dm^3, S/L = 1 25

Figure 26 Equilibrium mass isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Peat) at fixed pH 5 5 of substrate and input solution in mono-metal Cd-Cl and binary systems (Cd+Zn)-Cl, c_0 = 1 - 600 mgMe dm^3, S/L = 1 25

Figure 27 Sequential fractionation of Zn^{2+} and Cd^{2+} bound under batch conditions from the pre-treated mono-metal Zn-Cl and binary (Zn+Cd)-Cl solutions onto Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) according to the increasing binding strength Fixed pH 5 5 of substrate and input solution, c_0 = 600

Figure 28 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Zn^{2+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,
<u>Working parameters</u> Column φ 48 mm, H = 285 mm
Input solutions Zn-SO_4, c_0 = 500 mgZn dm^3 and 250 mgZn dm^3, pH 4 0, flow rate 0 1 cm^3/s, saturated zone flow conditions, Substrate solution ratio 1 10
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

Figure 29 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Cd^{2+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,
<u>Working parameters</u> Column φ 48 mm, H = 285 mm
Input solutions Cd-SO_4, c_0 = 500 mgCd dm^3 and 250 mgCd dm^3, pH 4 0, flow rate 0 1 cm^3/s, saturated zone flow conditions, Substrate solution ratio 1 10
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

Figure 30 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Cu^{2+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,
<u>Working parameters</u> Column φ 48 mm, H = 285 mm
Input solutions Cu-SO_4, c_0 = 500 mgCu dm^3 and 250 mgCu dm^3, pH 4 0, flow rate 0 1 cm^3/s, saturated zone flow conditions, Substrate solution ratio 1 10
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

Figure 31 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Cr^{3+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,

<u>Working parameters</u> Column φ 48 mm, H = 285 mm
Input solutions Cr-Cl, c_0 = 500 mgCr dm^3 and 250 mgCr dm^3, pH 4 0, flow rate 0 1 cm^3/s, saturated zone flow conditions, Substrate solution ratio 1 10
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

Figure 32 Sorption of Zn^{2+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Zn concentration in the input solution <u>Working parameters</u> as in Fig 28,

Figure 33 Sorption of Cd^{2+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Cd concentration in the input solution <u>Working parameters</u> as in Fig 29,

Figure 34 Sorption of Cu^{2+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Cu concentration in the input solution <u>Working parameters</u> as in Fig 30,

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Figure 36 Sequential fractionation according to the increasing binding strength of Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} bound from the mono-metal $Me-SO_4$ (Cr-Cl) solution under dynamic (saturated zone) flow conditions, at c_0 = 500 mgMe dm^3 and pH 4 0 onto Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual
Working parameters as in Fig 28-31,

Figure 37 Equilibrium mass sorption isotherms for Fe and Zn on low-moor peats (Peat Humus and Rush Peat) from liquid waste from electroplating process
Batch experiments, Liquid waste $Me-SO_4$, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Figure 38 Equilibrium mass sorption isotherms for Zn on low-moor peats (Peat Humus and Rush Peat) from liquid waste from electroplating process and pH of the equilibrated solution
Batch experiments, Liquid waste $Me-SO_4$, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Figure 39 Equilibrium mass sorption isotherms for Cd, Mn and Cr on low-moor peats (Peat Humus and Rush Peat) from liquid waste from electroplating process
Batch experiments, Liquid waste $Me-SO_4$, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Figure 40 Sequential fractionation according to the increasing binding strength of Cd, Cr, Fe, Mn and Zn bound from the electroplating liquid waste onto Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c)
Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual
Batch experiments, Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

Figure 41 Sorption of Fe and Zn from the electroplating liquid waste onto low-moor peats (Brushwood Peat Humus and Rush Peat) and pH of the effluent under dynamic flow conditions *vs* water exchange rate
Working parameters Column φ 48 mm, H = 285 mm
Flow rate 0 1 cm^{3}/s, saturated zone flow conditions,
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L=1 1 (W9c)
Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

Figure 42 Sorption of Cd and Mn from the electroplating liquid waste onto low-moor peats (Brushwood Peat Humus and Rush Peat) and pH of the effluent under dynamic flow conditions *vs* water exchange rate
Working parameters Column φ 48 mm, H = 285 mm
Flow rate 0 1 cm^{3}/s, saturated zone flow conditions,
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L=1 1 (W9c)
Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

Figure 43 Sorption of Cr from the electroplating liquid waste onto low-moor peats (Brushwood Peat Humus and Rush Peat) and pH of the effluent under dynamic flow conditions *vs* water exchange rate
Working parameters Column φ 48 mm, H = 285 mm
Flow rate 0 1 cm^{3}/s, saturated zone flow conditions,
Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L=1 1 (W9c)
Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

SUMMARY

The studies on the effects of organogenic adsorbents of a natural and anthropogenic origin on the control of metallic pollutants in the aquatic environment were undertaken as a joint research project performed in 1993/94-1997 by two research groups from TECHNION – Israel Institute of Technology in Haifa, Israel and PAS-Institute of Environmental Engineering in Zabrze, Poland under US AID-CDR grant No TA-MOU-C12-050 Of the natural matters, peat of different botanical origin as an attractive and abundant adsorbent has been selected for the studies performed within the project by the Polish research group Main objective of the research was developing an inexpensive, yet reliable filter made out of peat to adsorb and treat heavy metals from industrial effluents In order to achieve this overall goal, the studies comprised following specific objectives (i) Characterize the sorption of heavy metals on the different peat matters and at definite parameters of a sorption process in order to enable prediction of sorption capacity and strength of metal binding on peats, (ii) Evaluate potential of metal recovery from peat in order to reuse both the heavy metals and peat as adsorbent, (iii) Try high metal waste treatment

The studies on adsorption/desorption properties of peats were carried out for Zn^{2+}, Cd^{2+}, Cu^{2} and Cr^{3+}, which are the most omnipresent trace metals in the environment The potential of peat for these metals binding and release was studied as a function of the basic parameters that may affect binding capacity of matrices These parameters comprised genetic/botanical origin, decomposition rate (DR), pH of the input solution and substrate, metal input concentrations, effect of anions and competing interaction of other metal ions for sorption sites in synthetic binary and real high acid polymetallic systems (electroplating wastes) Sorption was conducted as batch and dynamic (fixed-bed) process The binding strength of selected peat matter for metal ions was evaluated by means of sequential extraction and desorption experiments Preliminary studies comprised 26 peats of different genetic/botanical origin, decomposition rate (DR) and ash content (AC) sampled from 3 peatlands of Poland Further research on metal sorption in monometallic and binary systems and on the selected representative samples of peats under batch isotherm and dynamic (fixed-bed) conditions, was focused on the effect of the parameters of a sorption process and solutions treated for metals

The low-moor peats of a different genetic origin were found to display significant binding capacity towards metal ions The kinds of peat with respect to metal sorption capacity followed the general order Wood Peat Humus $\approx$ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) $\approx$ Boggy Soil > *Sphagnum* Moss Peat (high-moor peat), while FTIR spectra for these peats showed high similarity Some peats (e g Gyttia), appeared to be highly specific and different from the general pattern of metal sorption General trends showed decrease of sorption capacity of peat matter in parallel with the decrease of pH, decomposition rate DR and ash content AC, though the correlation was not clear enough due to the diverse simultaneous effect of these parameters The binding capacities of metal ions (in mass units) onto peat in monometallic system depicted the sequence $Zn^{2+} < Cd^{2+} < Cu^{2+} < Cr^{3+}$ The decrease of pH value of the equilibrated solutions followed the same order The pattern of metal enrichment in fractions of a definite binding strength and susceptibility to desorption appeared to be highly specific for particular metal ions bound onto a wide range of peat matrices In general, the higher was sorption capacity and the extent of acidification of equilibrated solution, the stronger was metal binding and the less efficient was its removal from peat matrix Metals show predominance of different modes of binding onto peat matter the role of electrostatic binding and chelating complex formation seems to be of a comparable but diverse importance with respect to different metals It was found, that both the solubility of "soluble organic" fractions and their ability

to immobilization/release metals differ considerably This suggests the occurrence of sorption sites of different vulnerability to sorption/mobilization within each fraction The most metals enriched in fraction of the highest binding strength were assumed to be associated with "insoluble organic" residue of peat comprising humins, cellulose and lignin The competing effect of metals with each other for sorption sites onto peat was found to depend strongly on the kind of metal ions occurring in the system Weak competition between Zn and Cd ions enriching the same fractions was explained by a probable preferential metal ions affinity to the different sorption sites within the fraction of the definite binding strength The observed increase of strongly bound Zn and Cd rate in a binary system and of a total binding capacity for both metals suggested also occupying by these metals other available sorption sites of lesser affinity under stress caused by competition Opposite to equivalent and relatively weak competitive interaction of Zn^{2+} and Cd^{2+}, a very strong competition of Cu^{2+} and $Cr^{3+}$was observed, with a profound domination of Cr over Cu for the sorption sites It resulted in a displacement of Cu from the sorption sites by Cr ions, without significant increase of a total sorption capacity of a matrix The kind of anion in the input solution appeared to have strong effect on the sorption capacity for metal onto peat Chloride anion causes its evident suppression as a result of the ability of chlorides to act as complexing agents

Sorption capacity and behavior of metals bound in the dynamic process differ significantly from those in batch sorption These differences comprise both adsorption capacity and the binding strength of metals In the dynamic process, formation of a more strongly bound metal complexes in time show that the process of metal binding is more complex and comprise reactions of the different kinetics involving chemisorption of a more strong type The metal most vulnerable to time-dependent transformations appeared to be Cd and Zn These metals expand their sorption capacity mainly as a result of the high increase of enrichment in the "insoluble organic" fraction The enrichment occurs either directly, or due metal depletion in "soluble organic" fractions In the dynamic sorption metal ions react to the pH changes in a specific way For the full binding phase, pH 5 8 appears to be a firm limit equal for all the studied metals At this value, the breakthrough phase starts The pH range for a breakthrough phase differs for different metals and is the narrowest for Zn and Cd and the broadest for Cr The fixed constant pH for the full sorption and dissimilarity of the pH range for the breakthrough phase determines the rate of metals bound onto the peat matter The load of metals bound onto peat and the binding strength largely depends, besides pH, on the concentration of a metal in the input solution Sorption behavior of metals in real electroplating wastes both in batch and in the dynamic (fixed bed) process shows clearly, that the major factor controlling sorption is pH Despite occurrence in waste from electroplating process of several metals in high concentrations, with strong predominance of Fe, the binding efficiency of metals does not seem to be affected by a competing impact of their co-presence in solution Peat appears to be a good sorbent for metals from a strongly acidic liquid waste applied in batch process as undiluted solution S L=1 10 The highest sorption capacity and efficiency of removal from waste displayed metals tolerant to low pH values, in particular Cr, Fe and Cd Reduced ability of removal from the strongly acidic solution displayed Mn and Zn, particularly sensitive to pH In general, dynamic (fixed-bed) sorption at the same parameters of the input solution displays higher efficiency than a batch process The total sorption capacity for metal ions in the dynamic process is higher and metal ions are bound stronger In the fixed-bed conditions and in the systems with critical parameters (low pH, high metal competition) particularly important role appeared to play an "insoluble organic" fraction F5(OM) Metals in the conditions of a stress show high enrichment in this fraction, both due to the direct binding and as a result of the transformation of a primary fractional structure Metals can be bound from peat even from a very acidic solution Sorption potential of peat in these conditions is determined mainly by the buffering capacity of the matter in the pH range $\geq$ 5 8, the pH limit for a breakthrough phase specific for a particular metal ion, as well as by a metal concentration in the input solution The higher is metal content in the input solution, the larger is sorption potential of peat for this metal at other equal parameters The results of experiments did not confirmed statements concerning easy metal recovery and reuse with respect to low-moor kinds of peat, i e Peat Humus and Reed-Sedge Peat The acid desorption efficiency was not high enough for metals bound in batch process and appeared unsatisfactory with respect to any metal bound in dynamic (fixed bed) flow conditions For these conditions, the respective values were 57-75 % Zn, 33-57 % Cd, 28-51 % Cu and 12-13 % Cr Currently, no cost-effective and efficient metal recovery and adsorbent reuse with respect to peat is developed, and thus spent peat adsorbent should be rather disposed of by incineration

The positive results of the desorption process applied to untreated high acidic, high-metal electroplating wastes show high efficiency of peat use for industrial waste treatment, in particularly in a dynamic process Strong binding of metals onto peat matrices and low metal recovery create problems in metal recovery and reuse of the peat adsorbent This feature, though, suggests the most promising field of peat application as permanent protective liners in disposal sites of high-metal industrial wastes potentially susceptible to release metals The use of peat in constructed wetland systems is another attractive application Besides, ability of peat to act as an effective adsorbent in critical conditions of extremely low pH and high metal concentrations may be utilized in emergency cases for spill control

1 INTRODUCTION

1 1 Aims and objectives

Since environmental protection directives of many countries put forward tighter restrictions on pollutant emission to the aquatic environment, the application of inexpensive and omnipresent natural and anthropogenic adsorbents has receiving increasing attention worldwide due to high potential for removal of organic compounds, dyes and heavy metals from contaminated/waste waters Although the employment of adsorption process for contaminant removal from water has been realized for a long time, adsorption still remains one of the more novel chemical engineering processes due to the lack of adequate knowledge of adsorption mechanism and fundamental characteristics of the adsorbents This knowledge is indispensable for development of new effective adsorbents, optimization of adsorption process and application of adsorbent in specific conditions and purpose of application

To contribute to this knowledge, the studies on the effects of organogenic adsorbents of a natural and anthropogenic origin on the control of metallic pollutants in the aquatic environment were undertaken as a joint research project performed in 1993/94-1997 by two research groups from TECHNION – Israel Institute of Technology in Haifa, Israel and PAS-Institute of Environmental Engineering in Zabrze, Poland under US AID-CDR grant No TA-MOU-C12-050 Of the natural matters, peat of different botanical origin has been selected for the studies performed within the project by the Polish research group as an attractive and abundant adsorbent Main objective of the research was developing an inexpensive, yet reliable filter made out of peat to adsorb and treat heavy metals from industrial effluents In order to achieve this overall goal, the studies comprised the following specific objectives

(i) Characterize the sorption of heavy metals on the different peat matters and at definite parameters of a sorption process in order to enable prediction of sorption capacity and strength of metal binding on peats,
(ii) Evaluate potential of metal recovery from peat in order to reuse both the heavy metals and peat as adsorbent,
(iii) Try high metal waste treatment with use of peat

It is well known that this material can immobilize heavy metals by means of chemical binding and adsorption Despite relatively long-lasting interest in peats as natural sorbents, the knowledge concerning mechanism of contaminant binding in this material is extremely limited Wide practical application of peats as cost-effective and efficient adsorbents of contaminants from industrial wastes requires elucidation of sorption behavior of an adsorbent The resultant effect of a variety of parameters determines sorption capacity, binding strength, efficiency of metal sorption under the competing co-occurrence of other metals, desorption mode, possibility of multiple recycling of adsorbent and its long-term behavior under conditions of the impact of different natural and anthropogenic factors

1 2 General concept

Peat is defined as a young Quaternary, mainly Holocene, organogenic sedimentary rock in the first stage of coalification, falling in rank as one of the lowest grades of solid carbonaceous fuels

Total peat resources of the world are roughly estimated for over 1,000 billion tones (dry weight), covering about 275 10^6 ha The richest in peat deposits is the Northern Hemisphere According to incomplete list of the world resources of peat (Spedding, 1988), about 77 % of peat deposits occur in Canada and the USA, and another 7 5 % are found in Scandinavia In the Southern Hemisphere, the richest in peat deposits is regarded Indonesia (above 6 %) and some other subtropical regions of Central and South America and Africa

Over the past years peat has received increasing attention due to the potential to act as an ubiquitous effective agent either for metal ions removal from wastewater or for retrospective monitoring of their migration and accumulation in the environment (e g Wieder et al , 1990, Stack et al 1993, Allen, 1996) Potential for a recovery of valuable metals adsorbed from the metal-rich wastewater is no less attractive, taking into consideration still growing need in metals Simultaneously, huge amounts of metals are being discharged with solid or liquid wastes to the disposal sites or waters, posing threat to the environment and human health and increasing costs of disposal due to the requirement of the special protection measures For these purposes, sorption capacity and binding strength of peat with respect to different metal ions under different conditions, as well as the mechanism of binding/ release should be thoroughly known To date, this knowledge is still limited, and the understanding of the adsorption mechanism is yet to be reached (Allen, 1996) The comparison of the available data is also difficult among other because of the great variety of peat types investigated, which has a certain effect on the adsorption capacity (Brown et al , 1992) Unfortunately, most of authors have not paid much attention to the identification of a genetic origin and other basic parameters that might have influence upon the ability of peat to adsorb metals

Being a plentiful and easily accessible material, peat can find a vast application in water purification, waste treatment in natural or constructed wetlands and fixed beds, as protective liners and layers in dumping sites, for mineral beneficiacion, soil remediation and metal recovery from wastes It should be mentioned, though, that due to variable peat distribution throughout the world, as well as a fact, that wetlands are generally considered of great importance for nature protection, in many areas peat extraction is restricted Increasingly intensive agricultural practices, drainage, eutrofication and environmental pollution, infrastructural measures, changes in local management and land use pose an increasing threat to peatlands Simultaneously, the efforts focused on their preservation and conservation are growing and requirements for peat extraction have become more stringent The direct unlimited use of peat as adsorbent in many regions is therefore problematic However, the knowledge on contaminant binding onto peat is of a much wider nature and bigger importance, being applicable to all natural matrices omnipresent in the vadose zone and showing a substantial content of organic matter (e g soil humus) These materials play an important role as protective barriers against contaminants migration to ground waters through natural and anthropogenic vadose zone Besides natural adsorbents, similar properties show also a number of materials of anthropogenic origin, e g organogenic solid wastes containing humic-like substances Peat as an almost pure humic-rich organic matter creates a unique opportunity of studies of adsorption mechanism on organic matrices Research scope of the Polish research group was thus focused on peat matrices In parallel, adsorption studies were conducted by the Israeli research group on fresh humic sewage sludge and compost, i e anthropogenic waste material also rich in humic substances

In this part of the final report, the authors present results of the studies on adsorption/desorption properties of peat samples for Zn, Cd, Cu and Cr, which are the most omnipresent trace metals in the environment The potential of peat for these metals binding and release was studied as a function of the basic parameters that may affect binding capacity of matrices These parameters comprised genetic/botanical origin, decomposition rate (DR), pH of the input solution and substrate, sorption conditions (batch or fixed bed), competing effect of other ions for adsorption centers and binding strength Besides, the effects of the adsorbent/adsorbate contact conditions, as well as metal sorption from real complex solutions were investigated as priority tasks

2 MATERIAL

2 1 Site selection

2 1 1 General assumptions

Poland is rich in peat deposits of different types and genetic origin (Fig 1) In Poland, in over 50 thousand peat-bogs in total area of $1\ 3*10^6$ hectares, peat resources have been estimated for about $18*10^9$ m^3, which places it at the seventh position in the Northern Hemisphere Peat deposits are located in the area of three provinces Southern Baltic seashore province of high-moor peatlands, Northern Poland province of low-moor and high-moor forest peatlands, Polish-Northern German province of low-moor and high-moor peatlands (Frankiewicz, 1980, Lipka, 1980)

Peat-bogs for sampling were selected from the database developed by the Institute of Land Reclamation and Grassland Farming (IMUZ) in Falenty n/Warsaw, Poland (Fig 2) The inventory comprises currently 50807 peat-bogs, predominantly of low-moor type (41931 peat-bogs, which accounts for 82 5 %) Peat-bogs of high-moor and transitory type account for 8876, i e 17 4 % of the total The distribution of peat deposits in Poland is shown in Fig 2 Further development of information on peatlands in Poland was accomplished within the research "Characterization and valuation of wetlands and grasslands in Poland in the aspect of natural environment protection" coordinated by IMUZ as a bilateral Polish-Dutch project (IMUZ report, 1996) The main purpose of the project was to evaluate (i) Polish peatlands and their natural resources, (ii) impact of land use in wetland areas on hydrological changes in the natural environment, (iii) degradation of wetlands and their natural ecosystems Key research goals of the project comprised (i) elaborating 1 000 000 map of Polish wetlands and grasslands, (ii) generating 1 300,000 computer atlas of Polish wetlands, (iii) inventory of phytosociological data,(iv)identifying geomorphological and hydrographical factors governing the natural water regime,(v) validation of wetlands with respect of their uniqueness The project provided a basis for diagnosis of the wetlands condition and hazards to ecosystems, as well as defined the directions of wetland protection measures and position of Poland in the European program of wetland preservation These data, collected in the developed database, enabled to select the most characteristic and representative peat matrices

The general assumptions for site selection were as follows

- The main factors which may affect sorption properties of peat are its type, genetic and floristic origin, decomposition rate (DR), pH and ash content (AC),
- Sampling points should be placed in the known sites, of well-defined kinds of peat and their characteristics with respect to basic properties

2 1 2 Site characteristics

Taking these assumptions into consideration, three different low-moor peat-bogs sited in the north-east of Poland, in the area of Białystok region were selected for sampling the Biebrza Valley Wetlands, the Wizna peat-bog and the Zbojna peat-bog The sites are located in the distance of about 100 km from each other (Fig 1) For many years, these peatlands have been objects of investigation of the Institute of Land Reclamation and Grassland Farming (IMUZ), and hence are well characterized

Wetlands of the Biebrza Valley are the only one in Poland where the biggest part of the river valley retains in the natural state This site comprises three basins upper, middle and lower ones of the total area 116 577 hectares, of this peat deposits occupy 88 530 hectares In the upper basin lands have never been ameliorated (Okruszko, 1990, Oswit et al , 1994) Great variety of peat kinds and detrital gyttia at small depths is specific for this site Major kinds of peat deposits in the upper basin of the Biebrza Valley are presented in Fig 3 In Fig 4, location of sampling points is also shown

The Wizna peat bog (9 000 hectares) is sited in the drainage basins of the Narew and Biebrza Rivers Average thickness of peat deposits is 3 m, maximum 7 m The area was reclaimed 300 years ago and used for an intensive meadow cultivation In this site, peats of four basic kinds of low-moor type occur, i e Hypnum Moss Peats *(Brynieti)* Rush Peat *(Limno-phragmitioni)*, Sedgeous Peat *(Magnacaricioni)*, Peat Humus *(Alnioni)*, as well as different stratigraphic profiles of mixed peats (Fig 5)

The Zbojna site is located in a trough separated from the Pisa and Narew Rivers by the mineral islands Drainage water is discharged to these rivers by ditches The total area covers 1200 hectares, of that peat occupies 700 hectares, while the rest is mineral/organic soil Since 7 years the site has been reclaimed (ameliorated) and currently used as meadows and grassland for livestock Here occur deep and medium peats of a high decomposition rate (Fig 6)

According to the genetic origin, *Hypnum* Moss peat, Rush Reed-Sedge and Alder peat of different fiber content (decomposition rate) prevail in all three sites

Israel belongs to two wetland - peat-bog provinces East-Mediterranean and Highland Desert province, which covers eastern area of the country Both provinces are poor in wetlands and peat-bogs Peat deposits overgrown with halophyte and rush occur mainly close to lakes At the Dead Sea shore, papyrus peat forms a rather thin layer on marine muds In mires of the Lakes Hula and Keneret, upper layer of papyrus peat 4-6 m thick lays on limnic sediments, with another thick peat layer underneath For sampling, the Hula Valley peat bog (upper layer) was selected by the Israeli research group

In this part of the report, the researches conducted by the Polish research group are presented and discussed

2 2 Peat sampling

2 2 1 Sampling program

In total, 25 samples of low-moor peat and one sample of high-moor peat representing major genetic types of different botanical origin and the decomposition rate were collected in three sites in Poland in April, 1994

I The Biebrza Valley Wetlands (Fig, 4)

In the Biebrza Wetlands, 11 samples were taken in 9 points (B1-B9), in this in point B1 three layers of peat were sampled along the vertical profile from the depth 20 to 150 cm (B1,a,b) One sample (B9) represented high-moor peat Samples taken from the points presented in Fig 4 are specified in the list below

Sample symbol	Sampling depth, cm	Site characteristics
Profile B1		
B1	20-30 cm	cultivable meadow, *Hypnum* Moss peat
B1a	30-50 cm	Sedgeous peat
B1b	50-130 cm	Brushwood Peat Humus
B2	35-45 cm	Alder-birch forest, no fertilization
B3	below 28 cm	experimental plot of IMUZ, meadow, fertilized by PK for 35 years
B4	30-80 cm	experimental plot of IMUZ, degraded sod, not fertilized for 35 years
B5	below 80 cm	cultivable meadow
B6	45-100 cm	meadow by the river
B7	36-60 cm	meadow partially fertilized
B8	20-40 cm	meadow
B9	below 90 cm	high-moor peat, swamp

II The Wizna Peat-bog (Fig 5)

In the Wizna Peat-bog, 11 peat samples (W1-W9a,b,c) were taken in 9 points from the depth ranging from > 6 cm to > 60 cm and along a vertical profile (W9), where three subsequent layers of peat were sampled Sampling points are presented in Fig 5 and characterized in the list below

Sample symbol	Sampling depth, cm	Site characteristics
W1	below 28 cm	cultivable meadow, intensively fertilized, ground water-table below 35 cm
W2	15-50 cm	cultivable meadow, intensively fertilized
W3	below 27 cm	cultivable meadow
W4	below 20 cm	meadow formerly cultivated, now barren land
W5	17-50 cm	cultivable meadow
W6	below 35 cm	forest reservation, overgrown with birch trees
W7	below 35 cm	cultivable meadow, frequently flooded
W8	below 33 cm	cultivable meadow
Profile W9		
W9a	6-20 cm	cultivable meadow (boggy soil)
W9b	20-60 cm	Humus peat
W9c	below 60 cm	Reed-Sedge peat

III The Zbojna Site (Fig, 6)

In the Zbojna Site, 4 samples were taken in 3 points, in this in point Z2 two layers of peat were sampled along the vertical profile Sampling points are presented in Fig 5 and specified in the list below

Sample symbol	Sampling depth, cm	Site characteristics
Z1	25-100 cm	meadow fertilized for 5 years
Profile Z2		meadow fertilized for 5 years
Z2a	45-90 cm	
Z2b	100-200 cm	
Z3	50-70 cm	degraded meadow, deficiency of K, excess of N

Israeli peat from Hula valley was sampled by the Israeli research group from the upper layer of the peat deposits, at the soil surface (Surface-peat) and 120 cm below the soil surface (Bottom-peat, two samples (b) and (c)

In comparative studies, anaerobically digested (after sedimentation) sewage sludge from Haifa sewage treatment plant and compost samples from municipal waste from Afula and Naman municipal waste treatment plants (Israel) were tested as alternative easily available organic adsorbents for heavy metals

3 METHODS

3 1 Characterization of peat samples

3 1 1 Peat classification

Peat samples were classified with respect to the botanical origin and dominating species according to the Polish Standards (1976, 1985) based on the genetic division of the material, and ASTM D 2607-69 based on the genetic origin and fiber content adequate to the decomposition rate (DR, %) It should be mentioned that Polish Standards use more developed and detailed classification than ASTM D 2607-69, which specifies only five types of peat, i e Sphagnum Moss Peat *Hypnum* Moss Peat, Reed-Sedge Peat, Peat Humus and Other Peats Polish Standard PN-85/G-02500 (1985) classification comprises **3 types** of peat deposits low-moor (N), transitory (P) and high-moor (W) Within these major types, **10 kinds** of peat are differentiated according to the peat-forming groups of plants specific for a habitat Peat deposits are marked by symbols 1-5 for kinds specific for the low-moor type, by symbols 10-11 for kinds representing the transitory type, and by symbols 20-22 for kinds representing the high-moor type These basic kinds are divided in 233 species groups in accordance with dominating species/vegetation units (12 for low-moor peats, 4 for transitory types and 7 for high-moor types)

3 1 2 Physicochemical characteristics of peat samples

The methods used for peat samples characterization, have been presented elsewhere (Twardowska and Kyziol, 1996) Here, for convenience, their brief description has been given The methods not presented previously are described in a more detailed way

The samples were characterized with respect to major physical properties by standard methods used for peat characterization (Frankiewicz, 1980) These properties were described by such parameters as decomposition rate (DR), natural moisture content, porosity and ash content (AC), all in % (dry weight), as well as bulk density and specific gravity, in g cm^{3}, and pH (H_2O) Decomposition rate (DR) is a parameter specific for peat description and expressed as a percent ratio of thoroughly decomposed amorphous part of peat sample to its total volume

Further investigations and experiments were conducted using homogenized air-dried peat material, finely crushed in a beater laboratory mill and sieved through ϕ 1 mm mesh sieve

To characterize the samples, analyses of phase composition of mineral fractions and the identification of functional groups in organic fraction were carried out Preparation of samples for analysis of phase composition comprised heating of the sample for 2 h at 350^{0}C in an electric furnace separation of fraction enriched with mineral matter from water suspension after prior ultrasonic dispersion and separation of mineral matter by use of heavy liquid (*sym*-tetrabromoethane) Phase composition of mineral concentrates was analyzed by use of an X-ray diffractometer TUR with a goniometer HZG4 Radiation $Cu_{K\alpha}$ and counter rotation speed $1^0\theta$/min was applied

Functional groups in organic matter were investigated by use of FTIR- solid state spectroscopy The samples were analyzed in a form of pressed pellets of KBr, except fraction < 2 μm Sample W1 was analyzed directly and after ultrasonic separation of two fractions > 2 μm and < 2 μm Spectra were registered by use of a Fourier Spectrometer BIO-RAD FTS 165

Acid-digested (ASTM, D 5198-92) peat samples, as well as alternative organic substrates (sludge and compost Afula and Naman) were analyzed for the total initial metal content using FAAS technique by both research groups The Polish research group used AAS TJA AA-Scan 1 for metal analysis in Polish peats Israeli researchers analyzed peat from Hula valley and anthropogenic organic substrates for metals, using FAAS Varian-Spectra 300 Plus

3 2 Scope of adsorption studies

The scope of the studies on adsorption/desorption properties of peat samples for Zn^{2+}, Cd^{2+}, Cu^{2} and Cr^{3+} which are the most omnipresent trace metals in the environment, comprised

- Batch isotherm adsorption studies on metal cations binding onto peat
- (a) on untreated matrices of all 26 sampled peats from monometallic solutions Me-Cl, on the basis of these experiments, peat samples of the highest adsorption capacity were selected for further studies,
  (b} on untreated matrix in mono-metal and binary systems (Zn^{2+} - Cd^{2+}, Cu^{2+}- Cr^{3+}) equilibrating anion in input solution Cl and SO_4, pH of the input solution pH 4 0,
  (c) on pre-treated matrix at pH 5 5 adjusted to that of the input solution, systems studied monometallic Zn^{2+} and binary systems (Zn^{2+} - Cd^{2})

- Column (fixed-bed) experiments on metal cations binding onto untreated peat from synthetic monometallic solution of $MeSO_4$, at pH 4 0,

- Batch isotherm studies on metal cations binding onto untreated peat from real polymetallic liquid wastes from electroplating process, at pH 1 47

- Column (fixed-bed) experiments on metal cations binding onto untreated peat from real polymetallic liquid wastes from electroplating process, at pH 1 47

- Sequential fractionation of bound metals according to binding strength
  (a) In batch experiments,
  (b) In column experiments,

3 3 Batch isotherm studies on metal cations binding onto peat from the synthetic solution at pH 4 0

Batch experiments were conducted to evaluate the binding capacity of metal cations onto peat samples of the different genetic origin

The general procedure widely used in batch sorption studies, also on peat (e g Wieder, 1990, Allen et al , 1992), and differing only in details depending on the application target, has been applied also in this study on the sorption of the metal ions Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} onto peat matter To evaluate its binding capacity towards these cations, 2g replicate samples of homogenized, air-dried and crushed peat were placed into 125-ml Erlenmeyer flasks To each flask, 20 ml of a solution containing 1, 100, 1000, 2000, 3000, 4000, 5000 mg Me dm^3 (input concentration c_0), as Cl salts, adjusted to pH 4 0 with 0 1 Mol dm^3 HCl or 0 1 Mol dm^3 KOH, were added All flasks were shaken for 24 hours (actually, for equilibration up to 1 5 hours is required, 24 hours' period is used conventionally in similar batch experiments) After equilibration, the solution was filtered through 0 45 µm Sartorius filter paper (I of two) or centrifuged (II of two replicates) In both different methods of separation, very good conformity of results was obtained In the equilibrated filtrates, pH, conductivity and non-bound cation concentration (c_{eq}) were determined by FAAS (Perkin Elmer FAAS Mod 1100 B and TJA AA-Scan 1) An air-acetylene flame was used for all determinations Determination procedure was carried out according to standard recommendations of the manufacturer Specific amount of metal bound on peat was calculated using the mean value of 3 replicates During measurements, quality control (QC) procedures were performed as recommended, i e at least once with each analytical batch with a minimum of once per 20 samples and comprised spikes, blanks, duplicate samples and standard addition

On the basis of batch isotherm studies described above, the general conclusions concerning adsorption capacity *vs* genetic origin and other physical parameters of the investigated Polish peats were derived Among these samples, matrices of the highest adsorption capacity with respect to four individual cations (Cd^{2+}, Cu^{2+}, Cr^{3+} and Zn^{2+}) were selected for further detailed studies on untreated and pre-treated matrix

A general scope of the batch isotherm adsorption studies on the selected samples is presented above in the chapter 3 2 The studies comprised evaluating the effect on Me binding on the selected peat matter (i) of the type of anion equilibrating Me cation in the monometallic input solution (ii) the competing for adsorption centers of other metal ions in binary systems In the studies on the effect of anion, Cl and SO_4^{2} anions were used For assessment of competing effect, Zn^{2} and Cd^{2+}, as well as Cu^{2+} and Cr^{3+} as competing metals in binary systems were selected as ions displaying similar mobility in the terrestrial and aquatic environment In the studies on the effect of anion, Cl and SO_4^{2} anions have been used

Batch experiments on untreated samples of selected peats followed the pattern presented above For preparation of monometallic input solution, also SO_4^{2} salts of metals were used For studies of metal ions adsorption in binary systems Zn-Cd and Cu-Cr, input solutions of both elements in equal mass concentrations were applied This means, that equivalent concentrations of Cd^{2} in solution were 1 7 times lower than that of Zn^{2+}, and equivalent concentration of Cu^{2+} was 1 8 times lower than that of Cr^{3+} The experiments on the binary system Zn-Cd were conducted in parallel runs with input solutions of both metals as Cl and SO_4^{2} salts For binary system Cu-Cr, only Cl salts of metals were used Batch isotherm studies on representative peat samples were conducted on air-dried and crushed peats

The binding of metal ions to the selected peat samples was presented as original sorption isotherms and described also by the Langmuir and Freundlich equations As algebraic transformation of the isotherm equations can affect negatively the estimates of constants, the untransformed equations were fit to the data using nonlinear least squares regression The fitness of the isotherms was then compared on the basis of standard errors of the parameter estimates obtained from the nonlinear regressions

3 4 Batch isotherm studies on Zn^{2+} and Cd^{2+} binding onto peat with adjusted pH 5 5 from the synthetic solution at pH 5 5

The parallel set of batch isotherm experiments on selected Polish peats and on Hula Valley peat (Israel) was conducted using also substrates pre-treated prior to the experiment, to obtain uniform pH 5 5 of both substrate and input solution This part of sorption studies on the Polish peats was carried out using only Zn^{2+} in monometallic solution and Zn^{2+} - Cd^{2+} in binary system Sorption experiments were carried out on solution of SO_4^{2} salt, using pre-treatment procedure developed within this project by the Main Grantee and proposed as a standard method The concept of the pre-treatment was to measure heavy metal adsorption on organic substrates at constant major external chemical variables affecting the process first at all pH, as well as the electrolyte concentration, ionic composition and the solid/solution ratios Substrates were pre-treated with H_2O and acetate buffer At washing pre-treatment step, Whatman #1 filter paper was placed into wide Buchner funnel to which 1000 g of homogenized peat sample was added The material was slowly leached with distilled water or HCl, at water to solid ratio 5 1 Leached sample was vacuum dried and stored in refrigerator at cca 5^0C, 1000 g of washed substrate with 0 5 N HCl added in amount that yields pH 5 5, was next conditioned by shaking (100 RPM) overnight with acetate buffer added to final volume 5000 ml After checking the mixture for pH 5 5, it was filtered through 45 µm Sartorius cellulose nitrate filter paper In case of high buffering capacity of the material, which displayed most of the investigated peats, pH of the suspension was kept constant after pre-treatment entirely with HCl

Batch experiments on the Hula Valley peats, as well as on the fresh humic sludge, compost Afula and Naman, were conducted using Zn^{2+} concentration in input solution (c_0) as SO_4^{2} salt from 0 up to 600 mg/l and substrate solution ratio 1 10 Another investigated metal ion in this part of experiments carried out by Israeli research group was Cu^{2+} In the procedure applied to Polish peats the parameters used for the Israeli substrates for monometallic and binary systems, including concentration of metal ion in the input solution as well as substrate liquid ratio were considered to be followed As Polish peats displayed much higher adsorption capacity than Israeli substrates, to obtain comparable results in satisfactory range of adsorption capacity of adsorbent, either more concentrated solution, or a higher substrate solution ratio were to be applied Finally, it was decided to keep the concentrations at a higher substrate solution ratio (1 25), assuming that this parameter will affect the results to the lesser extent The other details of procedure were the same with respect to all investigated matrices

To 10 g of pre-equilibrated adsorbing material, input solutions of Zn or both Zn-Cd of required concentration c_0 were added The suspension was shaken for additional 20 hours and then filtered through 45 µm Sartorius cellulose nitrate filter paper Metals concentration, c_0 at 0 time and c_{eq} metal concentration in equilibrium after 20 hrs adsorption, was determined by flame atomic adsorption

The results of the experiments were presented the same way as described above in the chapter 3 3

3 5 Batch isotherm studies on metal cation recovery from peat with non-adjusted pH

To evaluate potential of a metal release or recovery from the peats used as adsorbents for regeneration and repeated reuse of the peat adsorbent, desorption experiments were carried out Desorption was performed by the acid treatment of the selected samples of peat with metal bound onto peats during the isotherm batch experiment The peat matter with adsorbed metal ion (as described in chapter 3 2 2) was treated by the distilled water at pH 6 0 adjusted with HCl (desorption cycle I) and by the 1% HCl (desorption cycle II) at solid liquid ratio 1 10 Desorption cycle II was conducted sequentially after the cycle I or as a single desorption cycle

The desorption procedure was carried out as follows

2g replicate samples of peat with Me ions adsorbed in monometallic and binary systems from Cl or SO_4^{2} solution as described in the chapter 3 2 2, were separated from the suspension and leached twice with distilled water in 125 ml Erlenmeyer flasks Next, to each flask, 20 ml of distilled water at pH 6 0 (desorption cycle I) or 1% HCl (desorption cycle II) were added Two replicate flasks for each solution were used All flasks were shaken for 24 hrs and, after equilibration, filtered through 0 45µm Sartorius filter paper In the equilibrated filtrates, pH, conductivity and desorbed cation concentration (c_{eq}) were determined on FAAS Perkin Elmer Mod 1100 B and TJA Scan-1 An air-acetylene flame was used for all determinations The amount of remobilized metals with respect to the unit of sample mass (D) was then calculated

3 6 Column (fixed bed) experiments

To evaluate adsorption pattern of metal ions in the dynamic conditions, column (fixed bed) experiments were carried out For the studies, open glass columns ϕ 48 mm, total height 285 mm, effective height 230 mm, packed with selected peats of mass 90 g, dry weight, were used Working parameters solution flow in saturated conditions upward from bottom to top of the column, flow rate 0 1 cm^{3} s^{1} The flow rate was determined by the stability of the peat bed during the upward flow The experiments were conducted in a full adsorption cycle, comprising thorough adsorption phase (I) and breakthrough phase (II)

The column experiments were conducted (i) on the synthetic monometallic solution and (ii) with use of real polymetallic liquid wastes from the electroplating process

The synthetic input monometallic solutions of $MeSO_4$, at pH 4 0, input Me concentrations 250 mg dm and 500 mg dm^{3}, were used For experiments on real solutions, high-acid, high-metal liquid wastes of pH 1 47, Me input concentrations $Fe^{2+} >> Zn^{2+} >> Cr^{3+} > Cd^{2+} > Mn^{2+}$ (mg dm^{3}) and Fe^{2} as a major component of the solution, were selected

The results were presented as a dimensionless function of concentrations in a liquid phase c_i/c_0 *vs* volume exchange rate and as adsorbed loads of metal ion in mg kg^{1} of peat matter (dry weight) *vs* volume exchange rate

3 7 Sequential fractionation of bound metals

For adsorbent characterization, besides adsorption capacity, also binding strength of an adsorbed metal is of particular importance It determines the metal vulnerability to remobilization from permanent protective barriers in the dumping sites due to the changing controlling factors Potential of bound metals for recovery and thus possibility of regeneration and repeated reuse of an adsorbent is also controlled by this parameter Therefore, the assessment of metal fractionation with respect to binding strength along with the elucidation of the mechanism of binding, may give the most valuable information, which would enable optimum adsorbent use, reuse, efficient metal recovery and ensure the reliability of protective barriers

To determine fractions of different binding strength where metal ions are bound, the investigated untreated and pretreated peat samples loaded with metal ion at c_0 = 5000 mg dm^{3} in batch adsorption studies in monometallic and binary systems were treated by *sequential extraction* The method, developed primary for defining chemical "forms" of metal binding, is conventionally used to differentiate between the exchangeable, carbonatic, easily reducible (hydrous Mn-oxides), moderately reducible (amorphous Fe-oxides), oxidizable (sulfides and organic phases) and residual fractions in different substrates The method is applied mostly to soil and sediments, but also to urban particulate matter and sewage sludge (Kersten and Forstner, 1988) Since 1973, more than ten sequential extraction procedures using different extractants for distinguishing from 3 to 9 extraction steps to identify chemical "forms" of metal binding have been elaborated In this study, pattern of sequential extraction by Tessier et al, 1979, modified by Kersten and Forstner, 1988, comprising 7 steps, was used This sequential leach procedure is being widely applied for the environmental studies With some modifications it is used also for geochemical applications, e g for characterizing different types of surficial geochemical anomalies, including identification of the reducible phase within the insoluble organic residue of humus (Hall et al, 1996 b, Kaszycki and Hall, 1996) A high precision of the method tested on 10 different international CRMs i e soils, marine mud, lake sediments and the till samples (Hall et al , 1996 ab) proved it to be an extremely useful and reliable tool Nevertheless, different chemical extraction sequences being in use are still subject to arguments concerning mainly the chemical "forms" of binding and redistribution of metals among phases during fractionation (e g Tessier and Campbell, 1991, Tack and Verloo, 1996) In case of humic-rich matters, the direct application of this procedure for the identification of binding mechanisms may be questionable In substrate such as peat, consisting mainly of organic matter, where the mineral fraction content usually does not exceed 10-12 % wt , the binding mechanisms can differ from the mentioned above This was already pointed out with respect to peat matter (Twardowska and Kyziol, 1996)

Many authors are focused on the use of sequential extraction procedure mainly for the identification of chemical associations of pollutants in different organic/inorganic matrices The greatest advantage of the sequential extraction is, though, a possibility to differentiate between the "pools" of metal enrichment displaying binding strength adequate to the referred fractions It enables to compare efficiency of different adsorbents apart of the possible diversity of binding mechanisms For this purpose, the method was applied in this study on peats

For reference, the abbreviated symbols of original names reflecting equivalently increasing binding strength of the consecutive fractions were retained, i e **F0** (PS) (pore solution), **F1**(EXC) (exchangeable), **F2**(CARB) (carbonatic), **F3**(ERO) (easily reducible oxides), **F4**(MRO) (moderately reducible oxides), **F5**(OM) (organic) and **F6**(R) (residue) The same symbols were used also previously (Twardowska and Kyziol, 1996) The first three steps, i e **F0** (PS), **F1**(EXC) and **F2**(CARB) Hall et al , 1996ab proposed to combine together as the most mobile fractions of the bound metal (AEC) The leach on the **F4**(MRO) step, besides amorphous Fe-oxyhydroxides, was assumed to remove significantly also soluble organics such as humic and fulvic complexes (Hall et al , 1996ab) This assumption, though, should be proved This would create a linkage between this simple operational tool and the understanding of the real binding mechanisms within each fraction

4 RESULTS AND DISCUSSION

4 1 Characteristics of the sampled material

4 1 1 Genetic origin

In all three selected sites, samples comprised 4 basic kinds of low-moor peats characteristic for the Northern Hemisphere and for Poland in particular

- Moss Peat (*Bryalo-Parvocaricioni*), belonging mainly to Sedge-Moss (*Carici-Bryaleti*) (9 samples) and moss (*Bryaleti*) (1 sample) species groups It occurred in a weakly decomposed form (DR = predominantly 18-40%), which should have considerably reduced its sorption capacity,
- Rush Peat (*Limno-Pragmitioni*) and Sedgeous Peat (*Magnocaricioni*), both classified by ASTM as Reed-Sedge Peat These peats were represented by 3 samples of reed peat (*Phragmiteti*) and 2 samples of Reed-Sedge peat (*Carici-Phragmiteti*), of a moderate decomposition rate (DR=30-65 %),
- Peat Humus (*Alnioni*) belonging to highly decomposed (DR = 55-80 %) wood peat (5 samples) originating mainly from alder (*Alneti*), osier (*Saliceti*) and mixed alder-birch (*Alno-Betuleti*) species (Alder Peat, Alder Brushwood Peat, Forest Wood Peat)

One sample of high-moor peat belonged to poorly decomposed Sphagnum Moss Peat (*Ombro-Sphagnioni*) Besides, also thoroughly decomposed Gyttia (detrituous and calcareous) typical for peat bogs (2 samples) and Mellow Boggy Soil (1 sample) was also taken

Israeli peat from Hula valley, which was sampled by the Israeli research group from the upper layer of the peat deposits, at the soil surface (Surface-peat) and 120 cm below the soil surface (Bottom-peat, two samples (b) and (c), belonged to one kind of peat specific for the area It represented highly mineralized low-moor peat, originated from moderately decomposed papyrus and according to ASTM D 2607-69 should be classified as Other Peats

For comparative studies, anaerobically digested (after sedimentation) sewage sludge from Haifa sewage treatment plant and compost samples from municipal waste from Afula and Naman municipal waste treatment plants (Israel) were tested by the Israeli research group as alternative easily available organic adsorbents for heavy metals This part of studies has been subject to discussion by the Israeli research group

4 1 2 Physicochemical characteristics of the sampled material

Classification of peat samples according to the botanical origin comprises also some characteristic properties *vs* genetic kind The numerical range of the physical parameters for the Polish and Israeli peat samples belonging to the particular genetic kind, and also for the waste organogenic substrates (Table 1, 1/1) shows general regular trends With respect to the decomposition rate (DR), besides Gyttia, which is thoroughly decomposed material of unidentified genetic origin, the investigated Polish peats followed the descending order Gyttja>Wood Peat Humus (*Alnioni*)>Rush Peat *(Limno-Phragmitioni)* > Sedgeous Peat *(Magnocaricioni)* > Hypnum Moss Peat *(Bryalo-Parvocaricioni)* > *Sphagnum* Moss Peat *(Ombro-Sphagnioni)* Generally, in the same order decreases also ash content (AC) of the investigated matrices, though as a rule in all Polish low-moor peats AC is low and ranges from 7 10 to 14 10 %

All investigated Polish peat samples of low-moor type were moderately to slightly acidic (pH 5 02-6 45), except Gyttia which showed slightly alkaline reaction (pH 7 26-7 46) High-moor *Sphagnum* Moss peat was positively acidic (pH 4 60)

Such parameters as porosity, moisture content and specific gravity does not show any regular correlation with the peat kind and DR porosity ranges from 80 73 to 90 87%, specific gravity from 1 432 to 1 627 g cm^{3} and moisture content from 61 28 to 84 92% Bulk density is generally the lowest for Rush, Sedgeous Peat (0 18-0 27 g cm^{3}) and Peat Humus (0 22-0 31 g cm^{3}), and higher for *Hypnum* Moss Peat (1 43-1 58 g cm^{3})

As it was already mentioned, Israeli low-moor peat from the Hula Valley according to ASTM D 2607-69 should be classified as Other Peats In comparison with Polish peats, it displays considerably lesser content of organic matter and natural moisture, and higher AC The peat is moderately or slightly acidic (pH 5 30-6 50), pH falling within the range typical for Polish low-moor peats

Investigated organogenic substrates exhibit lower content of organic matter and natural moisture content and higher AC, compared both to Polish and Israeli peats, while pH was close to neutral and ranged from slightly acidic to slightly alkaline values (pH 6 71-7 44) (Table 1)

The background metal concentrations in Polish and Israeli peats were low, typical for pristine areas, and reflected natural concentrations of these elements in soils (Kabata-Pendias and Pendias, 1992) Compost and sludge showed distinct enrichment with metals, particularly in sludge Zn concentrations in compost were of about an order of magnitude higher, and in sludge of almost two orders of magnitude higher than in peats Also Cd and Cu were highly enriched in compost and sludge, exceeding those detected in peat for an order of magnitude or higher

The data on metal concentrations in soils, pristine or affected by a long-range atmospheric transport, showed a consequently high correlation for the pair of elements Zn-Cd (Krosshavn et al , 1993 Steinnes et al , 1997a,b) Initial concentrations of Zn and Cd in investigated peat matrices from Poland, Israel and in European commercial peats of undefined origin (investigated by the Israeli research group) are also in line with this statement Concentrations of Cd in peat are invariably two orders of magnitude lower than Zn contents At high anthropogenic contamination of matrix or in organogenic matrices of anthropogenic origin (e g compost, sewage sludge) this relation can be less clear due to generally heavier loading by Zn, more rarely by Cd Nevertheless, the general ratio order remains unchanged (Table 1/1) Cu in natural peat matrices occurs predominantly in lesser amounts than Zn, these metals show weak correlation Concentrations of Fe, Mg and Mn are highly variable no correlation has been observed either in natural, or in anthropogenic matrices

4 1 3 Phase characteristics

X-ray structure analysis of a mineral fraction of 9 selected peat samples representing main kinds of the studied peats, pre-heated at 350^{0}C, showed occurrence of small quantities of calcite, quartz and presumably kaolinite (Fig 7) These minerals were present in amounts somewhat above the detection limits This is due to a low total content of mineral fraction in the untreated (raw) sample Only the composition of mineral fraction of Calcareous Gyttia distinctly differed from other samples showing almost 100%, dry wt , of calcite

FTIR spectra exemplified in the samples of different kinds of peat representative for studied material (Fig 8/1-8/2), are similar to each other and typical for a low-moor type of peat (except Gyttia) In general, IR spectra of peats are comparable to those of other humic substances In these spectra the following absorption bands can be distinguished

- In the area 1600-1630, close to 1400 cm^{1} and to 1040 cm^{1}, originating from carboxylic functional groups of humic and fulvic acids,
- A band with the maximum at about 3380 and 1620 cm^{1}, originating from water,

- Bands at 2850 and 2920 cm^{1} which correspond with harmonic components of CH_2 and CH_3 groups,
- Small bands at 1512 and 1266 cm^{-1} attributed to the absorption of organic compounds containing nitrogen (amides),

The FTIR spectra of the unfractionated sample W1 (Alder Peat Humus) and of fractions > 0 2 μm and < 0 2 μm (Fig 8/1) does not differ much from each other Nevertheless, the bands of a coarser fraction are more distinct and developed In the finer fraction < 0 2μm, the bands 1512 and 1266 cm^{1} attributed to amides are almost extinct, substantially lesser are the bands 1040 cm^{1} (carboxylic functional groups) and the bands 2850 and 2950 cm^{1} of CH_2 and CH_3 groups

The FTIR spectra of Gyttia (samples B5 and Z2b) display strong predominance of a band close to 1430 cm^{1}, attributed to carboxylic functional groups of humic and fulvic acids (Fig 8/2) Detrituous Gyttia shows also well developed smaller band at 1035 cm^{1} (carboxylic groups), as well as bands at 2850 and 2920 cm^{1}, specific for CH_2 and CH_3 groups In IR spectra of Calcareous Gyttia these bands are also present, though in a less developed shape Besides, in the spectra of both Gyttia matrices can be distinguished

- Sharp bands 876 and 713 cm^{1} specific for calcite,
- Weak band at 2511 cm^{1}, which may originate from the organic compounds containing sulfur (thiol)

4 2 Preliminary batch experiments on metals binding onto peat

4 2 1 Sorption capacity of Polish peats for Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} in monometallic system Me-Cl pH 4 0

4 2 1 1 General trends

The series of batch experiments on Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} binding onto 26 samples of Polish peats of different botanical origin from the monometallic solution of Me as Cl salt at pH 4 0 confirmed the substantial binding capacity of peats towards these cations (Table 2, 3, 4, 5)
With respect to sorption onto peat, the studied metals (in mass units) follow the order Zn < Cd < Cu < Cr The strong effect on binding capacity for metals appears to have the type and genetic origin of peat matter Low-moor peat shows the best sorption properties The kinds of peat with respect to Me sorption capacity may be ranged in the order Peat Humus ≈ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) and Boggy Soil > *Sphagnum* Moss Peat (high-moor peat) Metal binding capacity of thoroughly decomposed Gyttia (both Detrituous and Calcareous one), is highly specific It occupies a top of the row as an adsorbent of Cr and Cu, falling in range of 49 1-50 0 g/kg (98 1-99 9 %) and displays a similarity of an adsorption capacity for both metals At the same time, it appears to be a very weak adsorbent of Zn , adsorption capacity of Calcareous Gyttia being more than two times higher than that of Detrituous one

Alignment of the peat samples according to the sorption capacity with respect to the studied metals does not show clear correlation with pH, decomposition rate DR and ash content AC, apparently due to the simultaneous effect of these parameters This effect is additionally influenced by the diverse sorption centers in the organic fraction related to the peat kind The general trends, though, show decrease of adsorption capacity in parallel with the decrease of AC, pH and DR

The increase of input concentrations and metal loads bound onto peat resulted in the changes of pH value of the equilibrated solution Contact of the solution at pH 4 0 with low-moor peat matrices (except Gyttia) at pH 5 02-6 54 with the lowest applied Me concentrations $c_0 = 1$ mg Me m^{3} results in increasing pH value of the equilibrated solution to pH 5 80-7 99 The pH values of equilibrated solution after contact with both alkaline matrices of Gyttia and clearly acidic high-moor peat fall in the above range and account for pH 7 17-7 97 for Gyttia and for pH 5 80-7 26 for high-moor *Sphagnum* Moss Peat The increase of pH apparently is not strongly influenced by metal ions in solution and caused mainly by buffering effect of displacing ions from sorption centers in peat matrix by hydrogen ions from solution In turn, contact with the same matrices of high-metal solution at $c_0 = 5000$ mg Me dm^{3} shows effect of displacing cations, including also hydrogen ions, from sorption centers of matrices into solution The resultant pH value of equilibrated solution ranges from 2 52 to 5 22, and depends upon the two basic factors the kind of a metal ion and initial pH of peat matrix The highest resultant pH range shows equilibrated Cd-solution (pH 4 07-5 82), somewhat lower one (pH 4 01-5 22) displays Zn-solution Equilibrated solutions of Cu and Cr ions are clearly acidic and falling within the ranges pH 3 03-4 44 and pH 2 52-3 68, respectively The lowest pH of the equilibrated solutions (pH 2 52 – 4 01 and pH 2 99-3 88) is associated with the most acidic low-moor peat matrix B2 (*Hypnum* Moss Peat, pH 5 02) and high-moor peat B9 (*Sphagnum* Moss Peat, pH 4 60), respectively Resultant pH of the high-Me solution equilibrated with alkaline Gyttia (pH 7 26-7 46) ranges from pH 5 35 to 6 38, showing weak affinity to the sorbed metal ion

Adsorption isotherms in the numerical and graphical form for this series have been presented in detail in the annual report 1993-1994 (Avnimelech and Twardowska, 1995)

4 2 1 2 Sorption capacity for Zn^{2+}

Sorption capacity of peats for individual Zn ions in batch conditions was, generally, the lowest of the studied metals and comparable with binding of Cd (Table 2) It suggests a possible similarity of binding mechanisms The kinds of peat with respect to Zn sorption capacity align in the general order Peat Humus ≈ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) and Boggy Soil > *Sphagnum* Moss Peat > Gyttia Metal binding capacity of thoroughly decomposed Gyttia (both Detrituous and Calcareous one), occupies the end of the rank for Zn Adsorption capacity of Calcareous Gyttia is more than two times higher than of Detrituous one Maximum bound Zn loads for these kinds ranged, respectively 33 70-25 50 g/kg (67 4-51 0 %) > 26 90 - 15 80 g/kg (52 8 - 31 6 %) > 15 30 g/kg (30 2 %) > 8 50 - 4 0 g/kg (17 0 - 8 0 %) (Table 2) A rather wide range of bound loads within each peat kind displays a substantial diversity of binding capacity of Peat Humus, Rush Peat and *Hypnum* Moss peat, dependent upon an effect of other parameters, such as AC, DR and pH of peat matrix The sorption ranges for different peat kinds therefore partially coincide

Investigated peat rank order with regard to the maximum obtained Zn-binding capacity is Z1> B7 > W9c > B1a > W1 > B1b > W9b > B3 ≈ B6 > B4 > W5 ≈ W6 > W2 ≈ W4 ≈ W7 ≈ B1 >Z2a > Z3 > B2 > B8 > W9a > W8 > W3 > B9 > B5 > Z2b (Table 2) It should be also admitted, that despite of distinct differences in the adsorption capacity, the total range of maximum bound Zn loads is not strikingly wide for all investigated Polish peats (except Gyttia) the lowest load (15 20 g Zn kg^{1}) is only two-fold lower than the highest one (33 7 g Zn kg^{1}) Gyttia, as it has been already shown appeared to be a very poor adsorbent for Zn , compared to other kinds of peat, especially to the low-moor ones It proves that the limited range of humic acids present in Gyttia, in particular that associated with IR band close to 1430 cm^{1}does not readily bind Zn (Fig 8/2) More than double adsorption capacity of Calcareous Gyttia compared to Detritous one suggests, that this excessive loads, i e some 4 5 g/kg, may be bound onto the carbonate mineral fraction of peat

Most of equilibrium isotherms for Zn^{2+} ions showed decrease of binding with increase of input concentrations above 2000 mg $Zn^{2+}dm^{3}$, which proved a rather limited sorption capacity for Zn Several isotherms, e g for the samples of Sedge peat W4, Peat Humus (Z1, B3, B4), Rush Peat (B7) and Reed-Sedge Peat (B1a) showed still increasing trend, though close to maximum value (Avnimelech and Twardowska, 1995)

The increase of input concentrations and Zn loads bound onto peat resulted in the decrease of pH value of the equilibrated solution from pH 6 63 - 7 83 at c_0 = 1 mg $Zn^{2+}dm^{3}$ to pH 4 01-5 29 (except Gyttia) at c_0 = 5000 mg $Zn^{2+}dm^{3}$ For Gyttia, similarly to the sorption of other individual cations, much weaker acidification occurred up to pH 5 88 (B5) and pH 6 02 (Z2b) At Zn sorption onto acidic high-moor *Sphagnum* Moss peat B9, the resultant pH 3 88 was adequately lower (Table 2) In general, pH range of equilibrated solutions proved certain ability of Zn to displace hydrogen ions from the peat matrix, though much weaker than that of Cu and Cr ions

4 2 1 3 Sorption capacity for Cd^{2+}

Sorption capacity of peats for individual Cd^{2+} ions in batch conditions was similar, but distinctly higher than that of Zn^{2+} (Table 3) It suggests a possible similarity of binding mechanisms, and better affinity to sorption sites The kinds of peat with respect to Cd sorption capacity can be put in the general order Peat Humus ≈ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) and Boggy Soil ≈ Calcareous Gyttia > *Sphagnum* Moss Peat > Detritous Gyttia Metal binding capacity of thoroughly decomposed Calcareous Gyttia falls within the range displayed by *Hypnum* Moss Peat and Boggy Soil, while Detrituous one occupies the end of the rank for Cd Similarly as for Zn, adsorption capacity of Calcareous Gyttia is more than two times higher than that of Detrituous one The ranges of maximum bound Cd loads for the above peat order were, respectively 37,5-29 30 g/kg (75 0-58 6 %) > 32 2 – 20 2 g/kg (64 4 – 40 4 %) > 18 1 g/kg (36 3 %) > 11 3 g/kg (22 6 %) (Table 3) The binding capacity of different kinds of low-moor peats for Cd is variable, and no strong correlation of Cd sorption with other parameters such as the decomposition rate (DR) , ash content (AC) and pH in peat samples has been observed due to the simultaneous effect of these variable parameters Nevertheless, the general trend shows the descending order of adsorption capacity parallel to decrease of AC and pH values of substrate Investigated peat samples rank order with regard to the maximum evaluated Cd-binding capacity is W9c > B7 > B1b > Z1 > W1>B1a>W2 > W9b = B3 > W7 > B6 > W4 > W5 > B1 > B4 > B5 > W3 = W9a > B2 > Z2a >Z3 >W8>B8 > B9 > Z2b (Table 3) The range of maximum bound Cd loads is not very broad for all investigated Polish low-moor peats the lowest load (20 2 g Cd kg^{1}) is less than two-fold lower than the highest one (37 5 g Cd kg^{1}) Gyttia appeared to be better and less selective adsorbent for Cd than for Zn It suggests that humic acids present in Gyttia, in particular those associated with IR bands close to 1430 cm^{1}, bind Cd more readily than Zn Nevertheless, the last position of Detritous Gyttia in the range reflects weaker affinity of Cd to the available adsorption centers in this matrix Calcareous Gyttia displays 2 5 times higher sorption capacity compared to Detritous one Considering similarity of the IR spectra (Fig 8/2), it also suggests considerable role of carbonate mineral fraction in adsorption of Cd onto peat

Most of equilibrium isotherms for Cd^{2+} ions showed decrease of binding capacity with increase of input concentrations above 3000 mg $Cd^{2+}dm^{3}$, which also proved a rather limited sorption capacity for Cd, similarly as for Zn Several isotherms, e g for the samples of Rush (Reed) Peat W2 Reed-Sedge peat W9c and Peat Humus (B3, Z1) showed still increasing trend, close to maximum value (Avnimelech and Twardowska, 1995)

The increase of Cd loads bound to low-moor peat resulted in changes of pH value of the equilibrated solution (i) increase to pH 5 80 - 7 96 at c_0 = 1 mg $Cd^{2+}dm^{3}$ due to buffering capacity of peat matrix,, (ii) pH 4 07-5 82 at $c_0 = 5000$ mg Cd^{2+} dm^{3} For Gyttia, that shows the highest pH of matrix, pH range of the equilibrated solution changes from pH 7 82-7 97 to pH 5 35-6 38 (B5) The high-Cd solution in equilibrium with high-moor Sphagnum Moss Peat B9 became clearly acidic pH shifted from pH 5 80 to 3 64 (Table 3) Compared to the pH changes at Zn sorption, somewhat higher pH range for Cd-high solution in equilibrium with low-moor peat and Calcareous Gyttia was observed For Detritous Gyttia and high-moor peat, pH values of the equilibrated solution were lower than for Zn These distinctions may indicate also differences in the mechanism of binding

4 2 1 4 Sorption capacity for Cu^{2+}

Sorption capacity of peats for individual Cu ions in the batch conditions was clearly higher than that of Zn and Cd (Table 4) The kinds of peat with respect to Cu sorption capacity follow the order Gyttia > Peat Humus ≈ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) and Boggy Soil > *Sphagnum* Moss Peat Binding capacity of Gyttia for Cu at $c_0 = 5000$ mg Cu dm^{-3} appeared to be the highest The total added load was thoroughly bound, that suggests higher sorption capacity than the maximum one obtained in the batch experiments It is, though, difficult to attribute the sorption capacity of Gyttia for Cu to any of the functional groups of humic substance Precipitation of Cu in the form of cuprite (Cu_2O) or tenorite (CuO) within the Eh-pH stability field due to elevated pH (Brookins, 1988) may explain high binding capacity of both Gyttia matrices with respect to Cu The role of the carboxylic groups of humic acids associated with the band close to 1430 cm^{1} in Cu binding can not thus be elucidated under the conditions of a possible alternative mechanism In turn, almost no difference in Cu sorption onto Calcareous and Detritous Gyttia suggests negligible role of carbonatic mineral fraction in Cu binding This assumption should be treated as preliminary, concerning that full adsorption capacity for Cu onto Gyttia has not been yet estimated The ranges of maximum bound Cu loads for the above peat order were, respectively 49 8-49 1 g/kg (99 7-98 1%) > 47 4-37 7 g/kg (94 3 - 75 4 %) > 42 8 – 27 3 g/kg (85 6– 56 6 %) > 23 5 g/kg (47 0 %) Investigated peat samples can be ranged with regard to the maximum evaluated Cu-binding capacity as follows B5 ≈ Z2b > W9c ≈ W1 > B1b ≈ Z1 > W9b ≈ W2 ≈ B1a ≈ B7 > W5 = B3 ≈ B4 ≈ B6 > W7 ≈ B1 > W6 > W4 ≈ W9a > Z2a ≈ B8 > W3 > B2 > W8 > Z3 > B9 The range of maximum bound Cu loads is relatively as narrow as the loads of Zn and Cd bound onto investigated Polish low-moor peats the lowest load (27 3 gCu kg^{1}) is less than two-fold lower than the highest one (49 8 g Cu kg^{1}) Most of equilibrium isotherms for Cu^{2+} ions showed increase of binding capacity with increase of input concentrations in full applied range, up to 5000 mgCu dm^{3}, which also proved high sorption capacity for Cu Most of isotherms, e g for the samples of Peat Humus W1, W9b, B1b, B3, B4, Z1 Rush Peat W2, W9c, B6 B7 Sedgeous Peat B1a, *Hypnum* Moss Peat W5, Gyttia B5 and Z2b, showed still increasing trend

Binding of Cu loads onto low-moor peats resulted in changes of pH value of the equilibrated solution (i) increase to pH 6 68 - 7 99 at $c_0 = 1$ mg Cu dm^{3} due to buffering capacity of peat matrix,, (ii) acidification up to pH 3 03 - 4 44 at $c_0 = 5000$ mg Cu dm^{3} resulted from displacing hydrogen ions in functional groups by Cu For Gyttia, similarly to the sorption of other individual cations, much weaker acidification occurred up to pH 6 38 (B5) and pH 6 14(Z2b) (Table 4) In these conditions, at the border of the pH-Eh stability field, the precipitation may be the major binding mechanism This dissembles the role of the functional groups occurring in the Gyttia matrix

4 2 1 5 Sorption capacity for Cr^{3+}

Sorption capacity of peats for individual Cr^{3+} ions in batch conditions was the highest of studied metals (Table 5) The kinds of peat with respect to Cr sorption capacity follow the same order as Cu Gyttia > Peat Humus ≈ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) and Boggy Soil > *Sphagnum* Moss Peat The ranges of maximum bound Cr loads for the above peat order were, respectively 50 g/kg (100%) > 48,0-38 4 g/kg (96 0- 78 8 %) > 44 8 – 35 9 g/kg (85 6– 35 9 %) > 24 2 g/kg (48 5 %) Investigated peat samples align with regard to the maximum evaluated Cr-binding capacity as follows B5 = Z2b > W9c > W2 > B1b > W2 > B1a ≈ W9b > W1 > Z1 > B7 ≈ B4 ≈ B3 > W3 > B6 > W5 ≈ W6 > Z3 ≈ B1 ≈ W7 > B8 = W9a > W7 ≈ B2 > Z2a > W8 The range of maximum bound Cr loads is more narrow than the loads of Zn Cd and Cu bound onto investigated Polish low-moor peats the lowest load (35 9 g Cu kg^{1}) is just 1 4 times lower than the highest one (50 0 g Cr kg^{1}) Most of equilibrium isotherms for Cr^{3+} ions still showed increase of binding capacity with increase of input concentrations in full applied range up to 5000 mg Cr dm^{3} (e g the samples of Peat Humus W1, W9b, B1b, B3, B4, Z1 Rush Peat W2, W9c, B6, B7, Sedgeous Peat B1a, Hypnum Moss Peat W3, W5, W6, Gyttia B5 and Z2b)

The same observations and conclusions as for Cu binding onto Gyttia matrix can be derived for Cr (i) Binding capacity of Gyttia for Cr exceeds the maximum sorption obtained in the batch experiments, (ii) Due to pH range within the narrow stability field for Cr, the major sorption mechanism for this matrix may be precipitation Therefore, affinity to Cr binding of the functional groups occurring in Gyttia matrix, in particular of carboxylic groups of humic acids associated with the band close to 1430 cm^{1} can not be defined, (iii) The role of carbonatic mineral fraction in Cr binding is considered negligible The last assumption needs evaluating the full sorption capacity of both matrices and then analyzing the possible differences

The Cr binding onto peat matter resulted in the deepest changes of pH value of the equilibrated solution (i) increase to pH 6 11 - 7 87 at c_0 = 1 mg Cu^{2+} dm^{3} due to buffering capacity of peat matrix,(ii) deep acidification ranging from pH 2 52 to 3 68 at c_0 = 5000 mg Cu dm within this range falls also pH value of Cr solution in equilibrium with high-moor *Sphagnum* Moss Peat (pH 2 99) For Cr sorption onto Gyttia, deeper pH decrease compared to other metal ions occurred up to pH 5 95(B5) and pH 5 67 (Z2b) (Table 5) It indicates extensive hydrogen displacing by Cr from functional groups of peat organic fraction

4 3 Selection of peat matter for the sorption studies

For the further detailed studies, three samples of peat were selected As can be derived from the analysis of the metal ion sorption onto peat in batch conditions, the investigated samples exhibit considerable diversity with regard to the rank order of binding capacity for different ions in monometallic systems Probably, it results from different prevailing mechanisms of binding and occurrence of different binding phases Nevertheless, it was also shown, that the sorption capacity for metal ions of low-moor peats varies in a rather narrow range Therefore, among the ten samples showing the best sorption properties were selected the three ones, all from Wizna peat-bog With regard to sorption capacity for Zn^{2+}, Cd^{2+}, Cu^{2+}and Cr^{3+}in the batch conditions, the samples occupy the following places in a ranking list

- Rush (Reed-Sedge) Peat W9c	(2-2-3-1)
- Peat Humus (Alder Peat) W1	(5-2'-3-6)
- Peat Humus (Brushwood) Peat W9b	(5"-5-5-5)

All three selected peat samples W9c, W1 and W9b represent low-moor type (Table 1) Among them, the highest degree of transformation of the original plant material (DR 70 %, AC 12 55%) shows sample W1 belonging to Peat Humus according to ASTM and to Alder Peat (*Alnioni* kind, *Alneti* class) according to Polish Standards The dominating peat forming plants are strongly decomposed Alder (*Alnus glutinosa*), but also minor amount of reed (*Phragmites communis*) and sedge (*Carex)* Other two samples of the lower decomposition rate (DR 55 %) and ash content (AC 9 5 % and 10 4 %, respectively) represent Rush Peat (*Limno-Phragmitioni* kind) belonging to Reed-Sedgeous (*Phragmiteti-Carici*) class (sample W9c) and to Brushwood Humus Peat, *Alnioni* kind *Saliceti* class (sample W9b) In the sample W9c the dominating peat-forming plants are reed (*Phragmites communis*) and in lesser amount sedge (*Carex*), in the sample W9b peat-forming species are willow (*Salix cinerea*) and birch (*Betula humilia*) with admixture of reed (*Phragmites communis*) and sedge (*Carex)*

pH value of all three samples is similar and ranges from pH 6 21 (W9c) to pH 6 45 (W1) This suggests also similarity of buffering properties, which was confirmed by measurements of buffering capacity

The pattern of FTIR spectrum is also similar, in particular of W9b and W9c samples (Fig 8/1), FTIR spectrum of W1 sample displays some differences in the size of peaks (Fig 8/1) In comparison with the spectra of W9b and W9c, the area close to 1040 cm^{1} issued from carboxylic groups of fulvic acids, as well as bands 2850 and 2920 cm^{1} corresponding with harmonic components of CH_2 and CH_3 groups are much smaller Small bands at 1512^{1} are not present, band 1266 cm^{1} is distinctly smaller - both bands reflect absorption of organic compounds containing nitrogen (amides) Some differences in peak size display fractionated particles (< 2 μm and > 2 μm) of the same material (Fig 8/1) More detailed analysis of these differences is given in the chapter 4 1 3

These differences were not reflected in the metal binding capacity of these peats evaluated in batch isotherm studies The sorption capacities of the peats W9c, W1 and W9b for Zn^{2+} in monometallic system Zn-Cl, at pH 4 0 were estimated for 32700, 32500 and 32050 mg Zn kg^{1}, respectively For Cd^{2+}, the respective values were 37520, 35100 and 33200 mg Cd kg^{1} For Cu^{2+} 47390 47150 and 45540 mg Cu kg^{1} For Cr^{3+} 49380, 47370 and 47620 mg Cr kg^{1}(Tab 2-5) Therefore, these matrices seem to be similar regarding metal binding potential evaluated in batch isotherm studies, while W9c shows the highest sorption capacity for all four investigated metals

The selection of matters showing similar potential to metal sorption in the batch experiments despite belonging to two different genetic types and kinds was intended to identify eventual dissimilarities in sorption behavior of these matters in different systems and conditions It would also prove the reliability of batch isotherm studies for evaluating actual sorption capacity of the systems working mostly in the dynamic (fixed bed) operational conditions

Adsorption experiments on these samples were carried out in parallel with Israeli samples of Hula peat and anthropogenic humic substrates (sludge and composts Afula and Naman) conducted by Israeli group

4 4 Evaluation of sorption /desorption potential of selected peat matters for metals *vs* different parameters in batch conditions

Among the factors that might have significant effect on the metal binding capacity, the botanical origin of a peat matter, a kind of anion equilibrating metal cation in the input solution, as well as possible competition of other metal cations for adsorption sites onto peat were considered For sorption/desorption batch experiments, two different anions, Cl and SO_4^{2} in monometallic systems with Zn^{2} , Cd^{2+} and in binary systems with (Zn^{2+}- Cd^{2+}) were selected Due to the comparably high lability of both metals in the environment, the affinity of both metals to the same sorption sites and therefore strong competitive interaction was anticipated

Other series of batch sorption/desorption experiments was carried out on selected peats using monometallic systems Cu^{2+} - Cl , Cr^{3+}- Cl^{-} and the binary system (Cu^{2+}-Cr^{3+})-Cl in equal mass concentrations applied as Cl solution, at pH 4 0

4 4 1 Effect of the botanical origin of peat matrix and a kind of metal ion

The results of experiments carried out in order to elucidate qualitatively and quantitatively the studied metal binding on the selected peats are presented in Tables 6,7 and 8 and in Fig 9,10,11 and 12 as equilibrium adsorption/desorption mass isotherms for Zn^{2+}, Cd^{2+}, Cu^{2+}and Cr^{3+}, along with pH of an equilibrated solution The analysis of isotherms shows high similarity, both of a pattern and the numerical results of each metal sorption/desorption onto all three studied peat matters This suggests a rather limited effect on the metal binding of such factors as the peat-forming species of high-moor peats, in particular in wood, reed and sedge peats There is a probability of the bigger diversity of metal binding mechanisms between the above matters and peats originated from mosses, which is suggested by considerably lower sorption capacity of mosses (Table 2-5) This assumption, though, is not supported by the data from FTIR studies IR spectra of Moss Peat (e g Moss Peat W8) does not differ from the spectra of peat originated from wood, reed and sedge, including the selected peats (Fig 8/1) The role of humic acids, and mechanisms of metal ion reaction with the specific functional groups of humic acids are still far from being clear and subject to controversy There is an evidence, that the surface area of organic substance may also play an important part in metal sorption, both as a separate process, and due to facilitating access of metal ions to functional groups of humic acids (Ong and Swanson, 1966) Stack et al , 1993 came to the conclusion that the controlling factor for most metal ions sorption onto different peat types is fiber content According to their observations, the more fibrous peats adsorbed most metals (except Cu^{2+}) better than the less fibrous ones The coarser peat fractions appeared to display lesser adsorption potential than the finer grained samples This also suggests an important role of the specific surface in metal sorption At the same time, the same authors observed that the degree of decomposition of peat (DR) might not always be the controlling factor in its sorption abilities Similarly as in these studies, they observed that peats of the same DR exhibited greatly different sorption potential that might be attributed to the different botanical physical and chemical composition These observations, though, are of the more general character and do not explain any mechanisms of the sorption process There is, therefore, a strong need for elucidation of the diversity of the sorption/desorption behavior of metals bound onto organic matter

This study has been focused on the identification of specificity of the studied metals sorption under different conditions Similarity of binding and mobilization of metals onto the three different kinds of peat matter is a proof, that the sorption behavior is specific for the metal ion within a wide range of organic matrices of high-moor peat matter In the further studies, the selection of matrices showing clear differences with respect to properties, such as occurrence of functional groups reflected in the adequate differences in sorption behavior of metals (e g Peat Humus and Gyttia), may be helpful in the identification of binding mechanisms

The equilibrium isotherms for different single metal ions onto investigated peat samples depict the general order of the binding capacities (in mass units) Zn^{2+}< Cd^{2+}<Cu^{2+}< Cr^{3+} The decrease of pH value of the equilibrated solutions follows the same order the highest displacing of hydrogen ions into solution occurs at Cr^{3+} sorption The order of the binding capacities expressed in equivalent units is somewhat different Cd^{2+}< Zn^{2+}<Cu^{2+}< Cr^{3+} This series is in good agreement with a known order of increasing binding to soil organic matter of monovalent alkali cations<H_3O^+< alkaline earth cations< transitional group monovalent cations < transitional group divalent cations (among them Cu^{2+} and Zn^{2+}) < trivalent cations (Cr^{3+}) (Talibudeen, 1981) Other results obtained by Wieder, 1990, confirm this conclusion, too

Desorption experiments displayed different susceptibility of metals to release from peat, clearly reflecting different mechanisms of binding Identically with adsorption pattern, also desorption isotherms for single metals showed high similarity of binding strength on all three matrices Distilled water at pH 3 0 applied to all metal-loaded matrices gave negligible effect Application of 1% HCl resulted in pH <1 of equilibrated solution and the removal of maximum sorbed metal loads from peat matter, which ranged from 86 9 –92 8 % of bound load of Cd, 73 3-86 2 % of Zn, 59 5-61 4 % of Cu and only 6 11-6 38 % of Cr The different susceptibility to release from peat matrices appears therefore to be highly specific for particular metal ions bound onto a wide range of peat matrices In general, the higher is sorption capacity and the extent of acidification of equilibrated solution, the less efficient is metal removal from peat matrix (Tab 6-8, Fig 9-12) This conclusion appears to be valid also with respect to other stripping processes from matters of high organic fraction, e g to desorption of metals from soils with chelating agents such as silage effluents (Fischer et al , 1993) The extraction rates reported for the soil bound metals at self-regulating pH values (final pH 4 4-4 9) were Cd 74 7%, Zn 55 7 %, Cu 53 5 % and Cr 12 7 % These values well correspond with the aforementioned desorption rates obtained for peat treated with 1%HCl

Some rough idea about the mechanism of metal binding might be given by the fitting the actual values to the Langmuir or Freundlich isotherms Langmuir isotherms are based on the assumption that the sorbed layer is one molecule thick and all sorption sites have equal affinities for molecules of adsorbate The empirical Freundlich model assumes that the adsorbent has a heterogeneous surface composed of different kinds of adsorption sites It was found that Langmuir isotherms showed better fitness to the obtained results than the Freundlich equation (Table 9, Fig 13) This conclusion is in agreement with that of Bencheikh-Lelocine (1989) who found the Langmuir model was a better fit to the experimental data than the Freundlich model for peat metal ion systems In turn Bhattacharya (1983) studying Cd removal from solution by sorption on crushed coal noted that sorption data could be also described by Freundlich isotherm According to the results of these studies, apart from a better fitness of the Langmuir model, neither this model, nor Freundlich isotherm does describe sorption data for peat-metal ion systems correctly enough It should be pointed out that the binding capacity for Zn^{2+} $Cd^{2+}$and Cu^{2+} evaluated experimentally is roughly by 35 % higher than calculated by the Langmuir isotherm Therefore, the standard error is too high to consider these models satisfactory for the description of the metal binding onto peats

4 4 2 Competitive effect of metal ion interaction in binary systems

The results of comparative studies on metal binding onto peat matrices in single component and binary systems showed that the presence of the competing ion in the input solution had distinct, but variable effect on the sorption capacity for each metal The sorption capacity for Zn in monometallic system Zn-Cl was evaluated experimentally for 32050-32700 mg kg^{-1}, which accounted for 64 1 to 65 4 % of the maximum load applied (for all three studied peats) The sorption capacity for Cd^{2+} in Cd-Cl system ranged from 33200 to 37250 mg kg^{-1}, i e 66 4 to 75 0% of the load applied Competitive effect of Cd^{2+} ions present in input solution in equal mass concentration with Zn^{2+} also resulted in decrease of Zn^{2+} sorption capacity, which in (Zn-Cd)-Cl system for the studied peats ranged from 11 to 22 % (Table 10, Fig 14) The effect of Zn on Cd binding was similar in the presence of Zn, sorption capacity for Cd decreases in the range from 8 to

20 % (Table 11, Fig 15) The total sorption capacity for two co-occurring metals in the binary system was, though, significantly higher (for 55-73 %) than for a single Zn ion in the monometallic Zn-Cl system, and for 36-66 % higher than for a single ion in the monometallic Cd-Cl system Also a deeper decrease of pH of the equilibrated solution was observed To summarize, the competitive effect of these two metal ions on binding of each other is almost equal and is much weaker than could have been anticipated Significantly higher total sorption capacity of both ions in the binary system indicates lack of competition in a substantial part of binding centers and possible occurrence of spare capacity in the centers jointly occupied by both metals Very characteristic for Zn and Cd binding in the binary system is a distinct increase of the both metals load strongly bound to the matrix and resistant to stripping by acid For Zn, desorption rate in the binary (Zn-Cd)-Cl system decreased from 73 3-86 2 % to 53,1-64 4 % of the adsorbed load The Zn load strongly bound on peat increased from 4500-8550 mg kg^{1} in the monometallic solution to 9318-13312 mg kg^{1} in the conditions of competing with Cd An increase of the Zn load strongly bound onto matrix in the binary system for the investigated peats ranged from 1318 to 6334 mg kg^{1}

For Cd^{2+}, desorption rate in the binary system (Zn-Cd)-Cl decreased from 92 8-86 9 % to 74 7-62 9 % of the adsorbed load (Tab 11, Fig 15) The Cd load strongly bound onto peat increased from 2400-4600 mg/kg in the monometallic Cd-Cl system to 8916-9466 mg kg^{1} under the conditions of competing with Zn^{2+} The increase of the Cd load tightly bound onto matrix in the binary system for the particular investigated peats ranged from 1548 to 6516 mg kg^{-1} The decrease of pH of equilibrated solution in binary (Zn-Cd)-Cl system during sorption and increase of strongly bound Zn and Cd loads may suggest an occurrence of the spare sorption capacity for these ions in the phases of the matrix, which display high binding strength These phases are probably more resistant to sorption of Zn^{2+} and Cd^{2+} ions and bind these metals under the stress caused by competition

Opposite to equivalent and relatively weak competitive interaction of Zn^{2+} and Cd^{2+}, in the binary system (Cu-Cr)-Cl a very strong competition between Cu^{2+} and Cr^{3+} was observed, with a profound domination of Cr over Cu for the sorption centers (Tab 12, 13, Fig 16, 17) This competitive behavior of Cr confirms the known increasing order of cations with respect to binding onto organic matter of soil According to this order, the trivalent cations, among them Cr^{3+}are placed at the top of the rank (Talibudeen, 1981)

The sorption of Cu^{2+} in the monometallic system Cu-Cl was evaluated experimentally for 47390-45540 mg kg^{1}, which accounted for 94 8 to 94 1 % of the maximum load applied (for all three studied peats) The sorption for Cr^{3+} in Cr-Cl system ranged from 49380 to 47620 mg kg^{1}, i e from 98 8 to 95 2% of the load applied Almost full binding of both metal ions indicates that sorption capacity of peat for these ions is higher than the maximum loads evaluated from the experiments Competitive effect of Cr^{3+} ions present in input solution in equal mass concentrations with Cu^{2-} resulted in the dramatic decrease of Cu sorption capacity, up to 48 8 - 52 9 % of the load applied This means, that the decrease of Cu sorption in (Cu-Cr)-Cl system for the studied peats ranged from 38 to 46 %, i e sorption capacity was reduced almost in half (Table 12, Fig 16) The effect of Cu^{2+} on Cr^{3+} binding was much weaker in the presence of Cu, sorption capacity for Cr decreased in the range from 16 0 to 19 8 % (Table 13, Fig 17) Therefore, suppressing effect of Cu on Cr binding is some three times lower than that of Cr on Cu, and comparable with the decrease of Zn and Cd ions in the binary system Zn-Cd

The total sorption capacity of the studied peat matters for two co-occurring metals in binary system (Cu-Cr)–Cl was only for 12-14 % higher than for a single Cu ion in a monometallic Cu-Cl system It was also 10-12 % higher than for a single ion in a monometallic Cr-Cl system, while a decrease of pH of the equilibrated solution was also observed To summarize, the competitive effect of these two metal ions on binding each other is very strong, with the high domination of Cr over Cu Opposite to Zn-Cd interaction, the total sorption capacity of both ions in a binary system proves strong suppression of Cu by Cr in binding sites and an extremely limited spare capacity in the centers jointly occupied by both metals This results in occupying sorption sites mainly by Cr, and in a lower extent also by Cu The character of these metals binding onto peat seems to controvert the assumption of sequential adsorption of metals in accordance with ionic potential expressed by Ong and Swanson (1966) There is much higher probability of the simultaneous occupying the free sites available on the organic matter and partial displacing the weaker ions by stronger ones in joint binding sites Also differences in the affinity of the competing metals to binding sites should be considered The selectivity of metals with respect to such sites gives also the weaker metals an opportunity of a partially non-competitive sorption This conclusion confirms also desorption behavior of Cu and Cr in a binary system (Tab 12,13) Unlike Zn and Cd, no changes in the desorption rate of both metals, either in a mono-, or in a binary system have been observed The desorption rate for Cu in both systems invariably ranged in a narrow limits of 57 4-61 4 % of the initial load This means the decrease of the bound load of Cu of a strong type from 18290 –18440 mg/kg to 7578-8990 mg/kg, i e more than two-fold (for 9450-10712 mg/kg, i e 51 2-58 6%) (Tab 12, Fig 16)

The similar desorption pattern shows also Cr^{3+} (Tab 13, Fig 17) The desorption rate for both systems is very low and ranges from 6 08 to 6 45 %, the major amount of Cr is strongly bound onto the peat matrix The bound load of Cr in binary system shows lesser extent of reduction, from 44382-46230 mg kg^{1} to 30052-32962 mg kg^{1}, i e for 13268 to 14657mg kg,^{1} that is for 28 7-32 8%) Due to the lesser strongly bound loads of both metals in the binary system, an increase of pH of equilibrated solution from pH<1 in monometallic system to pH>1 in binary system after desorption was observed It should be also mentioned that in binary system, also total strongly bound load of Cu + Cr decreases for 12 3-12 7 % in comparison with the respective load of Cr in a monometallic system For all three studied peat matters, the adsorption-desorption behavior of Cr and Cu in monometallic and binary systems is remarkably similar, along with the numerical values This suggests high stability of binding-mobilization mechanism and properties with respect to sorption sites of high binding strength

4 4 3   Effect of the kind of anion

The kind of anion in the input solution appeared to have strong effect on the sorption capacity for metal ion onto peat Chloride anion causes its evident suppression, most probably as a result of the ability of chlorides to act as complexing agents The sorption capacity for Zn in monometallic system Zn-Cl was evaluated experimentally for 32050-32700 mg kg^{1}, that is 64 1 to 65 4 % of the total input load (for all three studied peats) In the system Zn-SO_4 at the same working parameters estimated experimentally maximum adsorbed load ranged from 36370 to 37208 mg Zn/kg, was still far below the adsorption capacity and comprised from 82 5 to 84 7 % of the input Zn load Pattern of Cd ion binding onto peat also shows an increase of sorption capacity from 33200-37520 mg Cd kg^{1} (66 4-75 %) in Cd-Cl solution to 45029-46285 mg Cd kg^{1} (93 1-95 7 %) in Cd-SO_4 solution (Tab 14, 15, 16, 17, Fig 18, 19) Chaney and Heendemann (1979) observed the influence of anions on the metal sorption also They noted, that chloride, residual cyanide, or other strong complexing agents might reduce the efficiency of Cd removal from peat columns Janta-Koszuta and Twardowska (1994,1996) reported significant suppressing effect of Cl anion on metal sorption also on inorganic matrices

In case of the monometallic Zn-SO_4 and binary (Zn-Cd)-SO_4 system in sulfate solution, the patterns of equilibrium mass isotherms also show reduction of Zn sorption due to competitive effect of Cd (Table 14, 17, Fig 20) For (Zn+Cd)-SO_4 binary system maximum adsorbed loads of Zn evaluated experimentally, were distinctly higher than Zn loads bound from chloride solution (Fig 22), but still below the adsorption capacity for Zn on the studied peats (Fig 20) The extent of decrease was not though very high, and generally did not exceed some 10 % of the input load (Table 16, 17) The total maximum bound load for both metals was about two times higher than for a single Zn ion, while no significant decrease of pH values of equilibrated solution was observed A comparison of equilibrium mass isotherms for Zn in binary systems (Zn-Cd)-Cl and (Zn-Cd)-SO_4 (Table 16, 17, Fig 22), displays their similarity for all three studied high-moor peats, and reflects suppressing effect of both factors (i e kind of anion and competitive effect of Cd) on the adsorption capacity For these systems, characteristic is almost identical resultant pH values of equilibrated solutions, changing in the range from pH 6 50 to 4 69 at Me concentration range in input solution 1-5000 mg dm^{3} at pH 4 0 Cd sorption onto peats from monometallic and binary (Cd+Zn) sulfate solution follows the same pattern as Zn binding in the similar systems (Tab 15, 17, Fig 19, 21, 23) The suppressing effect of both metals on sorption capacity onto peats for each other, and the simultaneous substantial increase of the total sorption capacity of these substrates for both metals in the presence of SO_4 ions, confirms competition of both these metals for the same sorption centers of limited capacity On the other hand, relatively low decrease of Zn and Cd sorption indicates non-competitive binding of both metals onto peat matrices by different mechanisms, or in centers with undersaturated binding capacity, capable to bound both metals within the applied concentration range In turn, similarity of pH values of equilibrated solution in (Zn-Cd)-Cl and (Zn-Cd)-SO_4 systems suggests saturation of adsorption capacity of peats for both ions caused by displacement of H^+ in adsorption sites available for these ions (Fig 22,23)

4 4 4 Sequential fractionation of metal ions bound onto peat

In the background of the attempts of identifying sorption mechanisms and chemical "forms" of binding lays the need of correct prediction of adsorbent - adsorbed metal interactions in actual changeable conditions and systems In the situation, when the nature of metal binding is still subject to arguments, selective extraction scheme appears to be an extremely useful tool It may be used for distinguishing the "pools" of metal enrichment in the matrix where the metal ions are bound in the fractions of an identified, sequentially increasing binding strength and decreasing susceptibility to release Such fractionation enables also identification of probable competition of metals in multimetallic systems for different adsorption centers and characterizes the properties of organic substrate (such as peat) as adsorbent

The distribution of metals bound in batch experiments onto selected kinds of low-moor peat matters representing Rush Reed-Sedge Peat (W9c), as well as two kinds of Peat Humus of different botanical origin Alder Peat (W1) and Brushwood Peat (W9b), exhibits high similarity of fractions enrichment in all three matrices (Table 18, Fig 24) At the same time, it shows the diversity of prevailing fractions of the different bonding strength for the metal ions studied

With respect to species distribution (in % of mass units) in the studied peat matters according to the binding strength, Zn and Cd generally show affinity to the same fractions These metals are similarly bound in the most labile forms F1(EXC) (40 3 – 52 0 %) and F2(CARB) (19 4-33 5 %), This well explains the susceptibility of these metals to mobilization due to changes of the chemical environment The pattern of pH changes of equilibrated solution indicates replacement by these ions, besides H_3O^+, of exchangeable alkaline earth cations and probably also monovalent basic cations (mainly Na^{+}) Other fractions were poorly enriched by Zn and Cd In the stable F5(OM) fraction these metals also occurred in the similar range (3 7-10 2 %), showing some variability in the studied peat within these limits Zn was somewhat more enriched in the moderately reducible F4(MRO) fraction (10 4-16 2 %), while Cd was bound there in lesser amounts (3 4-6 6 %) Some amounts of Zn and Cd ions were retained also in pore solution F(0),

(2 9-8 2 %)

The fractionation of Cu did not show high affinity to the particular fraction this metal was rather uniformly distributed in fractions displaying both high lability and high binding strength In two peat matrices W9c (Rush Peat) and W9b (Brushwood Peat Humus) Cu was highly enriched in the the most stable F5(OM) (30 3-34 4 %), moderately reducible F4(MRO) (21 7-27 5 %), as well as the most labile F1(EXC) (27 2-28 9 %) and F2(CARB) (12 7-12 7 %) fractions In one peat matter (Alder Peat Humus W1), bound Cu load appeared to be more diversely distributed between four fractions of different mobility moderately reducible F4 (MRO) (37 1 %) as well as the most labile F1(EXC) (26 5 %), strongly bound F5(OM) (17 9 %) and F2(CARB) (16 2 %) fractions In other fractions, including pore solution, just 2 4-3 4 % of Cu was bound The equal affinity of Cu to the fractions of different susceptibility to mobilization explains desorption behavior of this metal which is released from peat matrix in about half of the total bound load

Cr was firmly bound predominantly in F5 (OM) fraction (54 7-69 5 %) forming presumably stable organic complexes Lower amounts of Cr occupied moderately reducible phase F4(MRO) (15 2-28 3 %) Minor loads of Cr were bound in the labile F1(EXC) (8 4-10 7%) and F2(CARB) (4 0-5 4 %) Some 0 4-3 4 % were distributed mainly in easily reducible F3(ERO) phase, while the amounts retained in pore solutions were negligible Compared to other metals, chromium ions were positively dominating in F5 (OM) fraction This form of enrichment appears to be specific for Cr, which was observed in sorption studies involving other heterogeneous substrates (Twardowska and Jarosinska, 1991,1992) Cr thus shows high affinity to the "insoluble organic" fraction, which comprise more stable forms of organic compounds such as humin, cellulose and lignin Probably Cr preferentially forms chelating complexes with the carboxylic groups of humic acids, which are particularly selective towards multivalent cations It has long been recognized (Talibudeen, 1981), that carboxylic sites show a higher selectivity towards multivalent cations, when they are attached to adjacent carbon atoms in a ring structure as if they are widely spaced The nature of binding sites for Cr should be confirmed by additional studies Strong acidification of the equilibrated solution at individual Cr^{3+}ions sorption experiments (Tab 13, Fig 12) indicates extensive displacement of H_3O into solution by Cr ions from the carboxylic sites The nature of Cr binding suggests that no strong competition from other studied metals can be expected, unless some other multivalent cations are also present in the input solutions The results of sorption/desorption behavior of Cr in a binary system (Cr-Cu) –Cl (Tab 13, Fig 17) confirms this assumption

With respect to the extent of metal ion enrichment, fractions of different binding strength followed the order (in mass units, mg kg^{1})

Zn	F1(EXC) > F2(CARB) > F4(MRO) > F5(OM) ≈ F0(PS) > F3(ERO)
Cd	F1(EXC) > F2(CARB) >> F5(OM)>< F4(MRO) ≈ F0(PS) ≈ F3(ERO)
Cu	F5(OM) > F4(MRO) >< F1(EXC) > F2(CARB)>> F3(ERO)≈F0(PS)
Cr	F5(OM) > F4(MRO) >>F1(EXC)> F2(CARB) > F3(ERO) >>F0(PS)

In case of Alder Peat Humus W1, the fraction order for Cu was different Cu was highly enriched in the stable F4(MRO) and the highly labile F1(EXC) fractions, In the most stable F5(OM) and labile F2(CARB)fractions almost equal loads of Cu were bound The affinity of the studied metal ions bound onto peat matrices to the fractions of a different binding strength (rates in %) followed the order (Table 18, Fig 24)

Fraction	**%**	**% range**
F0(PS)	Zn≈Cd > Cu >> Cr	0 04 - 8 80
F1(EXC)	Cd≈Zn > Cu >> Cr	8 40 - 52 04
F2(CARB)	Cd>Zn > Cu >> Cr	4 00 - 29 17

F3(ERO)	Cd> Zn >Cr > Cu	0 40 - 6 21
F4(MRO)	Cu≥ Cr >> Zn > Cd	3 40 - 37 10
F5 (OM)	Cr > Cu >> Cd>< Zn	3 70 - 59 50
F6(0)	0	0

Of these fractions, the easily reducible F3(ERO) fraction played a negligible role The metal retention capacity of pore solution F0(PS) was also low, in particular with respect to Cr cations showing narrow pH-Eh stability field in a liquid phase In the residual fraction F6(0) metals did not occur in detectable amounts mainly due to high predominance of organic matter in the substrates The highest metal enrichment occurred in fractions F1(EXC), F2(CARB), F4(MRO) and F5(OM) The metal enrichment in the fractions F1(EXC) and F2(CARB) of a weak binding strength was particularly high for Zn and Cd and appeared significant also for Cu The moderately reducible F4(MRO) fraction and F5(OM) phase of the strongest binding strength showed high affinity to Cr and Cu cations, while for Cd and Zn they were of a minor importance

Comparing rates of metals enrichment in the "soluble organic" phases F1(EXC)-F4(MRO) and "insoluble organic" F5(OM) fractions with their desorption rates, it can be noticed that metals vulnerable to remobilization are enriched mostly in F1(EXC) fraction This fraction release bound Zn^{2+}, Cd^{2+} and Cu^{2+} ions thoroughly, but only in 57-75 % sorbed load of Cr^{3+} From F1(EXC) originate the highest rates of desorbed metal loads 51-66 % of Zn^{2+}, 46-60 % of Cd^{2+}, 43-49 % of Cu^{2+} and ≥ 99% of Cr^{2+} Another fraction that contribute to the desorption rate of Cd, Zn and Cu thoroughly and significantly (from 21 % to 37 % of the total desorbed loads) is F2(CARB) From the fraction F4(MRO), only Cu^{2+} has been released in higher quantities (26-31 % of the total desorbed load, and 57-72 % of the total bound load of this ion) Cr^{3+} appears to be strongly complexed on peat and even from the most labile F1(EXC) fraction can not be removed completely

To utilize the sequential extraction not entirely as operational tool, the actual mechanisms of metal sorption adequate to the fractions of different binding strength should be known, though current state of knowledge with this respect is far from being satisfactory The character of binding sites and affinity of particular metal ions to these sites within each fraction of equal binding strength can be diverse Therefore, despite similar structure of metals enrichment in the fractions, the interaction between the metals may be weak This observation is well exemplified in Zn and Cd sorption in a binary system These metals appeared to be weak competitors for sorption sites with respect to each other, in spite of a highly similar structure of fraction enrichment (Tab 18)
According to the sequential extraction procedure (Tessier et al , 1979, Kersten and Forstner, 1989, Hall et al , 1996), developed by Hall et al , 1996, exchangeable metals, which are held through electrostatic attraction on exchange sites on the surface and interface of negatively charged complexes of matrices, are enriched in the most labile F1(EXC) fraction Hall et al , 1966 a,b, in their modification of sequential extraction methodology for surficial geochemical applications in order to facilitate phase selectivity, considered the water-soluble fraction F0(PS) as usually negligible

F2(CARB) fraction is generally considered as metals co-precipitated with carbonates In peats this fraction probably reflects to some extent the actual binding of metals by carbonates present in the mineral and organic matter of peat The rate of the mineral matter in investigated peats ranges from 7 10 to 14 10 % In the selected peat samples, it accounts for 12 55 % (W1), 10 40 % (W9b) and 9 50 % (W9c), while pH values account for pH 6 45, pH 6 32 and pH 6 21, respectively As a rule, CaO contents in low-moor peats are no less than 1 5 % in general 3 – 6 % In calcareous peats it can be as high as up to 30 % CaO There is an evidence, that CaO in peats occurs mainly in organic matter, bound to humic substances (Frankiewicz, 1980) Comparing relatively high rate of Zn and Cd binding in F2(CARB) fraction and lesser Cr and Cu enrichment in this fraction in selected peats (Table 18, Fig 24) with the sorption capacity of Ca-rich calcareous Gyttia B5 for these metals (Tab 2-5), the co-precipitation with carbonates does not seem to be a sole mechanism of metals enrichment in F2(CARB) phase This question should be thus cleared up in detailed studies

Hall et al , 1966 a,b suggested to group exchangeable and adsorbed metals with those co-precipitated with carbonates into one fraction labeled as AEC (Adsorbed, Exchangeable, Carbonate–bound metals) referring to small proportion of F1(EXC) The easily and moderately reducible fractions F3(ERO) + F4(MRO) are reported by Hall et al ,1996 a, b, as the ones comprising metals scavenged besides the secondary amorphous oxides of Mn and Fe also by significant part of humic and fulvic acids as complexes These fractions are described as the ones containing "soluble organics", i e humic and fulvic acid complexes with metals In case of peats, which are predominantly organic matter, the division on AEC and "soluble organic" fractions seems to be somewhat artificial The "soluble organic" fraction appears to comprise all four fractions from F1(EXC) to F4(MRO), displaying variety of sorption sites and binding mechanisms Of these, metal ions bound electrostatically and forming chelating complexes seem to enrich different functional groups of the same "soluble organic" compounds

The most metals enriched in F5 (OM) fraction of the highest binding strength is probably associated with "insoluble organic" residue of peat comprising humins that are estimated for 10 5-38 9 % of organic matter, as well as with cellulose and lignin (Frankiwicz, 1980) These data give rough idea about the possible mode and forms of metal binding onto organic matter such as peat associated with pools of a different binding strength Mechanisms, interaction, dynamics of metal binding still remain unclear that creates well known difficulties both in controlling metals in the organogenic matters and in proper use of organic sorbents

Analysis of sequential fractionation of metals bound onto peat in batch experiments (Table 18 Fig 24), displays clear affinity of metals to the definite fractions and therefore predominance of different modes of binding Assuming that enrichment in F1(EXC) fraction reflects the rates of metals bound electrostatically and in F4(MRO) fraction due to chelating complex formation, the role of both mechanisms in metal binding onto peat matter seems to be of a comparable but diverse importance with respect to different metals The diverse affinity of metals to the "soluble organic " fraction seems to be also indisputable Fractionation of Zn bound in the batch experiments (Table 18 Fig 24), shows that specific for this ion is enrichment in two separate major "pools" of the definitely different binding strength dominating labile fraction F0(PS)+F1(EXC)+F2(CARB), adequate to AEC (Hall et al , 1996 a,b), and a minor, moderately reducible F4(MRO) and strongly bound F5(OM) fractions comprising humic acids complexes ("soluble organic") and humins ("insoluble organic") reported to be an important sink for metals in organogenic materials (Hall et al,, 1996 a,b, Kaszycki and Hall 1996, Allen, 1996) There was no fluent linkage of these two pools by the "transitional" fraction F3(ERO) adequate with respect to binding strength to Mn-oxides (Kersten and Forstner, 1988) No definite binding mechanism specific for organic matter is attributed to this fraction

The fractionation of Cd appeared to be similar to Zn, with even higher predominance of the labile AEC fraction, and a minor role of a more stable bound complexes Cu was uniformly distributed in three fractions of the weakest (AEC), moderate F4(MRO) and the highest F5(OM) binding strength For Cr characteristic is a predominant enrichment in the most strongly bound F5(OM) phase ("insoluble organic") Moderately reducible F4(MRO) phase attributed to the formation of HA chelating complexes ("soluble organic") was also of a considerable significance

It should be stressed, that batch experiments show a very high reproducibility, but does not reflect the effect of different fractions of organic matter on the dynamics of metals in a real surficial geochemistry Kaszycki and Hall (1996), using own modification of sequential extraction techniques by Tessier et al , 1979 and Kersten and Forstner, 1989, (Hall et al , 1996a,b) tried to identify the residence sites of metals in a variety of surficial materials, including humus, in the Chisel Lake area They explained the observed vertical re-distribution of trace metals (Zn, Cu, Fe and Mn) by their mobilizing by organic complexes in humus, transport within organic compounds into underlying soil horizons, and cation exchange from metal-enriched soil solutions in contact with exchange sites in the B horizon Also other authors suggest the controlling role of humic and fulvic acids in metal mobility in the near-surface environment (Baker, 1986, Curtin and King, 1986) They assume that depletion of Cu, Mn and other metals in the B-horizon of soils has been attributed to organic complexing and transport of metals through the soil system The role of humic and fulvic acids in these processes, though, was not clearly defined and therefore concurrent biogeochemical studies were suggested to augment discussion of the role of biological cycling of metals through the soil profile

4 4 5 Metal sorption onto peat in buffered systems at pH 5 6

It is well known that for metal binding processes, pH value is a major controlling factor Frankiewicz (1980) noted that adsorption capacity of alkaline or neutral low-moor peats is considerably higher than of acidic high-moor ones Allen, 1996, has summarized the conclusions of several authors discussing the subject of cation sorption onto peat as follows (i) the optimum range of pH for metal sorption onto peat has been estimated for pH 3 5-6 5, (ii) the pH values, at which adsorption on peat occurs, ranges from 3 0 to 8 5, (iii) the upper limit of pH value for peat adsorbents is dictated by matrix instability at pH >8 5 This last statement was confirmed also by own experiments with low-moor peat

Equilibrium isotherms for studied metals sorption/desorption on low-moor peat matrix at pH 6 35-6 42 and at pH 4 0 of input zinc solution exhibit substantial changes of pH of the equilibrated solution in both directions These changes resulted from buffering by peat matrix and displacement of H^+ ions into solution by bound metals (Tab 10-13, Fig 14-17) To exclude the effect of the initial pH of a matrix, experiments on Zn^{2+} and Cd^{2+} sorption in monometallic $Zn\text{-}SO_4$, $Cd\text{-}SO_4$ and binary systems $Zn\text{-}Cd\text{-}SO_4$ at adjusted pH 5 5 of both peat and input solution were conducted (The method of samples pretreatment and parameters of the experiment are described in the chapter 3 4) The results of these experiments are presented in Tables 19, 20 and in Fig 25, 26 and 27

From the equilibrium isotherms for Zn^{2+} and Cd^{2+} sorption on the pre-treated peats can be assumed that in the applied range of input concentrations and loads, sorption capacity for these metals in monometallic systems $Zn\text{-}SO_4$ and $Cd\text{-}SO_4$ has not been yet exhausted It was, though, already close to be filled, in particular with respect to Cd^{2+} (Tab 19, Fig 25, 26) Maximum bound loads of Zn evaluated experimentally for pretreated samples appeared to be similar for all three peats (12485-13560 mg Zn/kg, 85 to 89 % of the input load) and some 2 7-2 8 times lower than the adequate values for untreated samples The sorption behavior of Cd has been very much the same Maximum bound loads of Cd for studied pretreated peats ranged from 13800 to 13970 mg kg^{1} (93-94 % of the input load) and also displayed similar extent of decrease as Zn (3 2-3 3 times lower compared to the untreated peat matter) Such significant reduction of adsorption capacity is due to the deep interference during pre-treatment into the original sorption complex of peat

In the binary system $(Zn\text{-}Cd)\text{-}SO_4$, rather small decrease of both Zn^{2+} and Cd^{2+} sorption onto Alder and Brushwood Peat Humus samples (W1 and W9b) has been observed compared to mono-metal system This is an evidence of a rather weak competition of Zn and Cd for adsorption sites in these systems observed also in Zn and Cd binding onto untreated peat Bound mass loads of Cd were close to those of Zn Total binding capacity for both metals in the binary $Zn\text{-}Cd\text{-}SO_4$

systems for pre-treated Peat Humus was roughly two times higher than that for Zn or Cd only, but about three times lower than that for untreated peat Suppressing effect on binding capacity of pretreated matters besides pre-treatment may have also lower maximum concentration of both studied metals in input solution The effect of adsorbent adsorbate ratio should be elucidated in separate studies

Adsorption of Zn and Cd in binary system (Zn-Cd)-SO_4 onto Rush (Reed-Sedge) Peat W9c after the equilibrating adjustment to pH 5 5 appeared to be more sensitive to competing effect of both metals Maximum bound load of Zn evaluated experimentally was about 50 % lower than that in monometallic system and more than 4 times lower than the maximum bound load in untreated system Sorption of Cd in this matrix decreased to about the same extent (~ 40 %) Also total Zn+Cd load bound onto Reed-Sedge Peat W9c was lower than that on the Peat Humus W1 and W9b In adjusted system, pH values were practically the same during the sorption

Sequential fractionation of Zn and Cd in the samples of Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush Peat (W9c) with pH values non-adjusted and adjusted to pH 5 5, confirms both similarity and diversity of prevailing binding fractions for the studied metal ions The comparison of these systems displayed the fractions, where the effect of pre-treatment and competition is the strongest (Table 20 *vs* 18, Fig 27 *vs* Fig 24)

The fractional structure of Zn and Cd binding in monometallic Zn-SO_4 and Cd-SO_4 system is almost identical for all three peats adjusted to pH 5 5 (Table 20, Fig 27) As the pre-treatment procedure to the great extent was similar to the partial F1(EXC) leach, a significant reduction of this most labile fraction occurred, so that the rate of more strongly bound F2(CARB) in the labile AEC phase (Hall et al, 1966 a,b) associated with "soluble organic" fraction increased Pretreatment caused reduction of mass loads of Zn bound practically in all fractions, but to the different extent Comparison of sequential fractionation of Zn enrichment in untreated and pre-treated peats exhibits particular role of F4(MRO) phase of the "soluble organic" fraction in Zn binding under changing external impact (Fig 27 *vs* 24) While the proportion of F1(EXC) was reduced and rate of other fractions was practically at the same level, the proportion of F4(MRO) substantially increased (from 10 4-16 22% to 30 68-37 61 %), and its numerical values showed the lowest decrease For Zn sorption in mono-metal system, the binding fractions in pre-treated peats followed the descending order

Zn F4(MRO) ≥ F2(CARB) > F1(EXC) >> F5 (OM) > F3(ERO) >> F0(PW)

Therefore, in the structure of fractions controlling the sorption capacity and binding strength of Zn in the pretreated matter, the moderately reducible fraction became dominating Hence, Zn in such matter will be more strongly bound and less susceptible to release than in the original untreated matter, where the sequential fractionation is as follows

Zn F1(EXC) > F2(CARB) > F4(MRO) > F5(OM) ≈ F0(PS) > F3(ERO)

Changes in sequential fractionation of Cd due to pretreatment, resulted in the similar to Zn reduction of the loads enriched in the most labile F1(EXC) and F2(CARB) fractions At the same time, no changes or increase of the Cd enrichment in the fraction F5(OM) of the highest binding strength, and parallel reduction of loads bound in other stable fraction F4(MRO) resulted in significant difference of fractionation of Cd and Zn With respect to Cd adsorbed in mono-metal system, the fraction structure followed the order

Cd F2(CARB)≥F1(EXC)>F5(OM)>> F4(MRO)>F3(ERO)>F0(PS)

In the structure of fractions controlling the sorption capacity and binding strength of Cd, significantly increased thus the role of F5(OM) fraction of the highest binding strength compared to the untreated matter, where the fraction structure was as follows

Cd F1(EXC) > F2(CARB) >> F5(OM)>< F4(MRO) ≈ F0(PS) ≈ F3(ERO)

Zn and Cd enrichment in binary system (Zn+Cd)-SO_4 compared to mono-metal systems does not show any changes (Table 20, Fig 27, which confirms weak competition of Cd ions for sorption sites in the applied range of metal loading Fractionation of Cd co-occurring in solution showed its similar enrichment in fractions of the labile ACE phase, while in the more stable and "insoluble organic" phases the highest Cd enrichment occurred in F5(OM) and low in F4(MRO) phase This well explains weak competition of these two metals in the studied system, at metal concentration range and loads applied In case of higher applied metal loads, when the sorption capacity in fractions of ACE phase is limited, a stronger competitive impact of Cd is anticipated Also in equimolar concentrations of these two metals the competition of Cd for the sorption sites available may be stronger According to Ong and Swanson (1966), Cd as a metal having greater ionic potential than Zn should be bound first, and next Zn would be sorbed in sequence The presented results for a system with undersaturated sorption capacity suggest rather parallel binding and next re-displacing part of weaker ions by stronger ones

4 5 Column (fixed bed) experiments on metal binding onto peat from the synthetic solution

4 5 1 Sorption pattern

The conditions of metal binding in the fixed bed (column) differ significantly from those in batch sorption In batch conditions the amount of solution is in great excess compared to the mass of an adsorbent In the batch experiments presented above, the S/L (solid to liquid) ratio applied was 1 10 for the studies on the untreated peat and 1 25 for pre-treated peat with adjusted pH 5 5 In columns, the S/L ratio determined by the water retention capacity of peat in the saturated conditions was much lower For Brushwood Peat Humus (W9b) S/L ratio accounted for 1 2, and for Rush (Reed-Sedge) Peat W9c it was 1 1

The total amount of solution applied to the sample during the full sorption cycle in a column is, though, a multiplication of the water retention capacity The sorption cycle comprises two basic phases (i) phase of full binding, when the metal load in a treated solution has been thoroughly retained in the peat matter, (ii) breakthrough phase, when the metal is being only partially bound onto the sorption sites and appears in effluent in the gradually increasing concentrations until the equation with the input concentration The total water exchange rate for a column packed with adsorbent is determined by the full break-through of the bound metals The single exchange of water retention capacity of the Brushwood Peat Humus (W9b) lasted for 30 min The single exchange time for Rush (Reed-Sedge) Peat W9c was two times shorter, i e 15 min The total contact time of substrate with exchangeable volumes of metal-containing solution during the sorption cycle is determined as total water exchange rate multiplied by the duration of a single exchange cycle

The results of Zn, Cd, Cu and Cr sorption from a mono-metal solution Me-SO$_4$ and Cr from Cr-Cl solution onto Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c under the dynamic conditions are presented in tables 21-28 The metal concentrations in the input solution were 500 mg Me dm^{-3} and 250 mg Me dm^{-3}, at pH 4 0 In Figures 28-31 the sorption cycles for each metal are shown as dimensionless liquid phase concentrations vs summary exchange rate of solution in peat volume The total loads of metal bound onto peat in a full adsorption cycle are given in Figs 32-35 A comparison of sorption efficiency under batch and dynamic conditions in the full binding phase and as total sorption capacity for the studied concentrations is shown in Table 29 Desorption rates are presented in Table 30 Table 31 and Fig 35 illustrate sequential fractionation of bound metal according to binding strength

In general, sorption capacity for metals onto studied peat matter under dynamic conditions differed considerably from that evaluated in the batch experiments (Table 29) Under batch conditions, equilibrium isotherms and the numerical values of the sorption capacity for each metal on Peat Humus and Rush Reed-Sedge Peat were similar for Zn and Cd For Cu and Cr, Reed-Sedge Peat showed better potential as adsorbent of Cu and Cr than Peat Humus The capacity of these matrices to bind metals (in mass units) followed the descending order Cr>Cu>Cd>Zn The difference between the highest (S$_{Cr}$) and the lowest value of adsorption capacity (S$_{Zn}$) was not strikingly high for Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c, the ratio S$_{Cr}$ S$_{Zn}$ was 1 31 and 1 36, respectively

In column experiments, the sorption behavior showed much bigger diversity dependent upon the botanical origin and the concentration of the solution applied It also differed substantially from the results obtained in batch experiments Brushwood Peat Humus appeared to be considerably better adsorbent for all the studied metals than Rush (Reed-Sedge) Peat Total sorption capacity of the Brushwood Peat Humus ranged from 50506 mg Cu kg^{1} to 72514 mgCd kg^{1} at c$_o$=500 mMe dm^{3} and from 40924 mgCu kg^{1} to 53122 mgCd kg^{1} at c$_0$=250 mgMe dm^{3} Therefore, two-fold decrease of input concentration resulted in 20 0 % reduction of sorbed Cu^{2+} and 26 7 % lower sorption of Cd^{2+}

The range of the sorption capacities of Rush (Reed-Sedge) Peat was from 38399 mgCr kg^{1} to 63958 mgCd kg^{-1} and from 33297mgCr kg^{1} to 45032 mgCd kg^{1}, respectively For this peat matter, two-fold decrease of the input concentrations caused rather weak effect on Cu and Cr sorption (6 6 % Cu and 13 3 % Cr) Simultaneously, sorption capacity for Cd decreased for almost 30 % This comparison displays different sensitivity of metals to the changes of the operational parameters and also the diverse reaction of metal ions to these parameters

With respect to the total binding capacity onto peats, metals (in mass units) in both applied concentrations followed an order (Table 29) Cd > Zn > Cr > Cu (for Brushwood Peat Humus W9b) and Cd > Zn > Cu > Cr (for Rush Reed-Sedge Peat W9c) The order was the same for both metal ions input concentrations, but different from that obtained in batch experiments and differed also for the studied peat matters Under the dynamic conditions, the highest total sorption capacity onto peats displayed thus Cd and Zn The same metals occupy the end of the sorption capacity order under batch conditions The differences of sorption capacity for Cu and Cr are not so explicit Under the dynamic conditions, Cr and Cu binding on the Rush (Reed-Sedge) Peat were significantly lower than batch sorption The batch sorption capacity of Brushwood Peat Humus for these metals was somewhat higher in column experiments (13 and 11 %, respectively)

Under dynamic conditions, the relative range of numerical values between the highest and the lowest total sorption capacity was higher for c$_0$= 500 mgMe dm^{3} and comparable to that from batch experiments for c$_0$=250 mgMe dm^{3} For Brushwood Peat Humus, the ratio S$_{Cd}$ S$_{Cu}$ was 1,44 at c$_0$=500 mgMe dm^{3} and 1 30 at c$_0$=250 mgMe dm^{3} For Rush Reed-Sedge Peat, the respective values of S$_{Cd}$ S$_{Cr}$ were 1 66 and 1 35

The disparity between the sorption pattern of metals onto Peat Humus and Rush Peat is particularly high with respect to the value and the rate of the full binding phase compared to the total sorption capacity for the given metal Sorption pattern for metals on Rush (Reed-Sedge) Peat against the summary solution exchange rate has a longer full sorption phase than the Brushwood Peat Humus For the both matrices, full adsorption phase lasts longer also for the input solutions of a lesser metal concentration The sorption pattern of the Rush (Reed-Sedge) Peat displays a steeper breakthrough phase than the Brushwood Peat Humus, therefore the filling of both full binding phase and the total sorption capacity lasts shorter and requires less metal solution to be applied (Table 29, Fig 28-32) The metal loads thoroughly bound onto both studied peat matter in the full binding phase fell little short of the respective values for each matrice For Brushwood Peat Humus, they ranged from 24556 mgCr kg^{1} to 51975 mgCd kg^{1} at c_0=500 mgMe dm^{3} and from 13293 mgZn kg^{1} to 34687 mgCd kg^{1} at c_0=250 mgMe dm^{-3} For Rush (Reed-Sedge) Peat, the respective ranges were from 18800 mgCr kg^{1} to 51810 mgCd kg^{1} at c_0=500 mgMe dm^{3} and from 18730 mgZn kg^{1} to 36707 mgCd kg^{1} at c_0=250 mgMe dm^{3} At the same time, no regularity in the order of metals with respect to the value of the load thoroughly bound in the full sorption phase has been observed Only Cd invariably occupied the first position, while the other metals showed quite high variability, in particular for different concentrations of input solutions For Brushwood Peat Humus, the full binding capacity for metals followed an order Cd>Zn>Cu>Cr at c_0=500 mgMe dm^{3} and Cd>Cr>Cu>Zn at c_0=250 mgMe dm^{3}

For these metals, the full binding phase comprised 71 7%, 71 3%, 67% and 45 8% of the total sorption capacity at c_0=500 mgMe dm^{3} and 65 3%, 73 4%, 49 0% and 28 1% at 250 mgMe dm^{-3} For Rush (Reed-Sedge) Peat, the respective ranges were Cd>Zn>Cu>Cr at c_0=500 mgMe dm^{3} and Cd>Cu>Cr>Zn at c_0=250 mgMe dm^{3} For these metals, the full binding phase comprised 81 0%, 83 6%, 68 5% and 49,0% of the total sorption capacity at c_0=500 mgMe dm^{3} and 65 3%, 73 4%, 49 0% and 28 1% at 250 mgMe dm^{3} Therefore, in general, the higher is the metal sorption in the full binding phase, the lower is the load bound in the breakthrough phase

It was found that the critical parameter for the sorption of all the studied metals is the pH value of the effluent For the full binding phase, pH 5 8 appears to be firm limit equal for all the studied metals At this level, the breakthrough phase starts The pH range for the breakthrough phase is different for different metals and is the narrowest for Cd and Zn and the broadest for Cr The removal of Cd from the solution ceases at pH 4 5-4 6 Sorption of Zn ceases at pH 4 6-4 8 The limit of Cu sorption is pH 3 5-3 8, while Cr is bound from the solution up to the pH 2 2-2 5 of the effluent (Fig 29-36) The fixed constant pH of the full sorption and dissimilarity of the pH range for the breakthrough phase for the metals determines the rate of metals bound onto the matrix The load of metals bound onto the peat matter and the binding phase largely depends on the pH and the concentration of a metal in the input solution Of all the studied metals, Zn appears to be most sensitive to these parameters, while Cr is the most stable with respect to sorption potential onto the peat matter

4 5 2 Recovery of metals bound onto peat

The experiments on recovery metals bound onto the Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c under the dynamic conditions of adsorbent (peat) contact with adsorbate (mono-metallic Me solution, c_0=500 mgMe dm^{3}, pH 4 0) are presented in Table 30 The desorption by 1% HCl carried out in the same procedure as in batch experiments, showed that susceptibility to desorption of metals bound under the dynamic conditions displays dissimilarity of the both matrices compared to each other and to the results of batch experiments In general, for both peats the relative susceptibility of bound metals to release (in % of the sorbed loads) follows the order

Zn > Cd > Cu > Cr

The differences between the results of batch and dynamic sorption experiments consist in a definitely lower desorption capacity of Brushwood Peat Humus and somewhat lower desorption capacity of the Rush (Reed-Sedge) Peat loaded with metals under dynamic conditions The least receptive to changes of the released absolute loads appeared to be Zn (Tab 30 *vs* Tab 14/2,3) The relative efficiency of stripping metals from Rush (Reed-Sedge) Peat accounted roughly for 75 % Zn, 57 % Cd, 51 % Cu and only 2 3 % Cr (the respective values from batch experiments accounted for 70 % Zn, 64 % Cd, 61 % Cu and 6 4 % Cr) Therefore, only Zn shows the satisfactory removal For Cd and Cu, somewhat more than half recovery was attained, while the desorption capacity of Cr was negligible

Desorption efficiency from the Brushwood Peat Humus loaded by metals in the dynamic conditions was unsatisfactory with respect to any metal It accounted for 57 % Zn, 33 % Cd, 28 % Cu and just 1 % Cr (the respective values for batch experiments were 77 % Zn, 81 % Cd, 60 % Cu and 6 % Cr) This suggests an adequate increase of binding strength of these metals onto peat matter compared to the batch conditions, besides of the observed remarkable enrichment of these metals in sorption sites The pH of the equilibrated solution after desorption appeared to be higher than for batch experiments and ranged for both matters from pH 1 23 to 1 46

The probable explanation of the stronger binding properties of the Brushwood Peat Humus lays in a two times longer contact of the single portion of solution with the adsorbent and 1 2-1 6 times longer total effective contact time than with the Rush (Reed-Sedge) Peat (effective sorption cycle for Zn lasted 11 h, Cd 8 h, Cu 4 h and Cr 15 h longer)

4 5 3 Sequential fractionation of sorbed metals according to the binding strength

The sequential fractionation of metals bound onto peat matter under dynamic conditions of contact with the mono-metal solution at pH 4 0 and c_0=500 mgMe dm^{3} compared to the adequate batch experiments confirmed these assumptions (Table 31, Fig 36 *vs* Table 18, Fig 24) The most significant for the sorption under the dynamic conditions is high metals enrichment mainly in the most strongly bound F5(OM) fraction This resulted in the increase of the total sorption capacity of the metals and decrease of their relative susceptibility to desorption The most significant changes were observed in the Brushwood Peat Humus, while Rush (Reed-Sedge) Peat reacted to the dynamic conditions of sorption in a somewhat different way

Fraction structure of the Brushwood Peat Humus W9b loaded with Cd in the dynamic total sorption cycle shows profound enrichment in the most strongly bound F5(OM) phase (from 1262 mg kg^{1} in the batch sorption to 45504 mg kg^{1} in the dynamic conditions) In all other fractions Cd was enriched similarly to the batch sorption This resulted in the adequate increase of the total sorbed load of Cd and change in the fraction structure for F5(OM) > F1(EXC) > F2(CARB) >> F0(PS) > 3(ERO) > F4(MRO) compared to F1(EXC) > F2(CARB) >> F4(MRO) > F3(ERO) > F5(OM) > F0(PS) The desorption rate suggests release of metals bound mainly in the most labile phases F1(EXC) and F2(CARB)

Fractionation of Zn bound under the dynamic conditions displays Zn enrichment in two fractions in the most labile F1(EXC) fraction (from 13759 mg kg^{1} in the batch sorption to 24507 mg kg^{1} under the dynamic conditions) and in the strongly bound F5(OM) fraction (from 3040 mg kg^{1} to 19383 mg kg^{1}, respectively) Simultaneously, Zn binding in the moderately reducible F4(MRO) fraction significantly decreased The fraction structure for Zn sorbed under the dynamic conditions became therefore F1(EXC) > F5(OM) > F2(CARB) >> F0(PS) > F3(ERO) > F4(MRO) compared to F1(EXC) > F2(CARB) > F4(MRO) > F5(OM) > F0(PS) > F3(ERO) in batch sorption

Fraction structure of Cu binding onto the Brushwood Peat Humus W9b under the dynamic conditions compared to the batch sorption resulted in the almost two-fold decrease of the Cu load bound in the most labile F1(EXC) fraction (from 13153 mg kg^{1} to 6156 mg kg^{1}) along with the increase of Cu load in the most stable F5(OM) fraction (from 15656 mg kg^{1} to 24768 mg kg^{1}) The fraction structure for Cu bound under the dynamic conditions is F5(OM) > F4(MRO) > F1(EXC) > F2(CARB) >> F3(ERO) > F0(PS) compared to F5(OM) > F1(EXC) > F4(MRO) > F2(CARB) >>> F0(PS) > F3(ERO) in the batch sorption cycle In the desorption cycle this change of Cu enrichment reflected by the decrease of the released load due to the reduced load of Cu in the F1(EXC) fraction

Changes in fraction structure of Cr binding under the dynamic conditions are the most extensive and comprised, besides a very high enrichment of Cr in the strongly bound F5(OM) fraction which became the predominant one (87 2 %), the parallel deep decrease of the Cr bound in F1(EXC), F2(CARB) and F4(MRO) fractions Due to it, Cr sorption displayed relatively low increase of the total binding capacity at the simultaneous very significant change of the fraction structure on F5(OM) >> F4(MRO) > F2(CARB) >> F1(EXC) > F0(PS) compared to F5(OM) > F4(MRO) > F1(EXC) >> F2(CARB) > F3(ERO) >> F0(PS) The predominance of the most strongly bound fraction F5(OM) and reduction of the most labile fractions to 3 04 % in total caused that the susceptibility of this metal to desorption practically ceased

Therefore, in the transformations of the fraction structure of the metals bound onto the Brushwood Peat Humus under the dynamic conditions mainly three fractions are involved the most strongly bound F5(OM) fraction, which invariably increases, and moderately reducible F4(MRO) fraction, which shows decrease of Zn, Cd and Cr enrichment The most labile F1(EXC) fraction, displays an increase of Zn , decrease of Cu and Cr and practically stable level of Cd enrichment The most stable fractions are F2(CARB) that undergo substantial changes only in Cr enrichment and F3(ERO) fraction, that plays in the fraction structure only a marginal role

Rush (Reed-Sedge) Peat, as it was reported, does not show the same unidirectional changes of sorption properties under the dynamic conditions of contact with Me-solution as Brushwood Peat Humus, where an increase of sorption capacity with respect to all studied metals was observed, though in a different extent Here, only sorption capacity for Cd increased comparably high Zn binding remained practically at the same level, while Cu and Cr sorption decreased It was found that both Cd and Zn under dynamic conditions exhibits decrease of F4(MRO) and F2(CARB) fractions and high enrichment in the strongly bound F5(OM) and labile F2(EXC) fractions, The fraction structure for Zn bound in dynamic conditions onto both peat matters was identical For Cd, due to the parallel enrichment in two fractions of the diverse binding strength, the fraction structure appeared to be more balanced than for the Brushwood Peat Humus This was reflected in the higher susceptibility of Cd to desorption from the matrix, evaluated for 57 3 % of the sorbed load (Table 30) This load is adequate to Cd bound in the most labile fractions F0(PS), F1(EXC) and F2(CARB) that accounted for 58 8 % in total

Fraction structure of Cu binding on the Rush (Reed-Sedge) Peat under the dynamic conditions remained almost unchanged compared to the batch sorption cycle The decrease of the bound load was due to the relatively uniformly lower Cu enrichment in every fraction except F4(MRO) This fraction showed the highest, over 2-fold extent of Cu reduction

Similar extensive decrease of loads bound in all the fractions except F5(OM) occurred in the Cr sorption cycle under the dynamic conditions In the F4(MRO)fraction, the reduction of Cr enrichment was also the highest Simultaneously, an increase of F5(OM) fraction occurred This determined dominance of the strongly bound F5(OM) fraction in the structure of Cr sorption A very low rate of the labile fractions (9 63 % in total) resulted in the negligible susceptibility of Cr to desorption also from this matrix

To summarize, chemical partitioning of peat samples loaded with metals under dynamic conditions shows virtual difference with respect to batch systems (Table 31, Fig 36 *vs* Table 18, Fig 24) consisting mainly in metal enrichment in the "insoluble organic" fraction Metal sorption under dynamic conditions mostly exhibits depletion of F4(MRO) fraction and shifting the major load into more strongly bound F5(OM) fraction This phenomenon specific to the dynamic conditions of metal sorption occurred in both studied low-moor peats, i e Brushwood Peat Humus W9b and Rush Reed-Sedge Peat, therefore the casualness of it should be excluded The comparison of fraction structure in batch and column experiments leads to the assumption, that chemical forms of F4(MRO) phase comprising Me complexes with humic and fulvic acids in "soluble organic" fraction are not stable and tend to transformation with time into stronger bound compounds in "insoluble organic" fraction This assumption, though, disagrees with the changes occurring in the fraction structure of Cr and Cu in the dynamic sorption onto Rush (Reed-Sedge) Peat compared to the batch cycle Significant reduction of the Cu and Cr loads in the F4(MRO) fraction did not result there in the adequate Cu and Cr enrichment in the F5(OM) fraction It, therefore, suggests also parallel mechanisms and different kinetics of metal binding onto sorption sites, which results in dissimilarity of sorption capacity and fraction structure of metals with respect to the binding strength The diversity between batch and dynamic sorption at different exchange rates of Me-containing solution is clearly illustrated in Fig 24 and 36

4 5 4 Concluding remarks derived from the column experiments

In general, there is an evidence from many sources, derived from batch experiments (Ong , 1966, Lee and Low, 1989, Stack et al , 1993, Allen, 1996) that the rate of adsorption is rapid, and maximum adsorption can be achieved within 20 min to 1 hour of contact between the peat and dissolved contact solute It is generally agreed that for batch process, a 1-hour residence time is necessary for completing the process Stack et al , 1993, tested the batch kinetic data for adsorption of Zn, Cr, Cu and Cd for a first order reaction They indicated that different peat types have distinct adsorption characteristics and concluded that peats responded similarly only to copper (within the aforementioned time of contact) Some authors reported much more rapid kinetics of metal ion binding on peat, than the data quoted by the most researchers Ahmad and Qureshi, 1989, Bunzl, 1974, and Bunzl et al , 1976, cited also by Allen, 1996, found that the time required to reach adsorption equilibrium between the solid and liquid phases was 10 s to 2 min

The reported comparison between batch and column experiments undermines these statements The observed transformations of metal ions fractionation, directed to formation of more strongly bound complexes in time show that the process of metal binding is more complex and comprise reactions of the different kinetics involving chemisorption of a more strong type that occurs in course of a longer time Hence, the observed significant differences between the long-term column experiments and batch process These differences comprise both adsorption capacity and the binding strength of metals The metal most susceptible to time-dependent contact conditions of adsorbent adsorbate system appeared Cd, and to a lesser extent Zn These metals show ability to expand their sorption capacity mainly due to a high increase of enrichment in the "insoluble organic" F5(OM) fraction This well explains lack of competitive effect of these metals in batch sorption process The "insoluble organic" F5(OM) fraction shows invariably high enrichment of all studied metal ions in dynamic sorption conditions The mechanism of the enrichment seems to be diverse, dependent on the metal ion It occurs either independently, which results in high increase of the sorption capacity (Cd, Zn) or simultaneously with the decrease of a metal enrichment in "soluble organic" fractions In particular, decreasing moderately reducible F4(MRO) fraction associated with chelating complex formation with HA and FA, or F1(EXC) fraction, which supposed to indicate electrostatically bound metal ions suggests the transformations of binding mechanisms from the weaker to the stronger binding ones (e g Zn, Cd, Cr)

Batch process seems to be much less sensitive to such factors as peat type, kind or decomposition rate, than the long-term process in the dynamic flow conditions In batch conditions, sorption potential of the Brushwood Peat Humus and Rush (Reed-Sedge) Peat appears to be almost identical, whereas in the dynamic sorption these two substrates differ significantly both with respect to sorption capacity and fraction structure of metal binding strength

The critical factor controlling sorption abilities of peat is pH value In general, this is a long recognized statement, and all authors studying the subject agree with it (Ong and Swanson, 1966, Chaney and Heendemann, 1979, Gossett et al , 1986, Wieder, 1990, Allen, 1996) Surprisingly enough, up to now there is still lack of more precise data on the threshold pH values Probably, this is due to focusing the most authors on the batch experiments, which give only rough estimation Gossett et al (1986) noted that the pH operational range for the metal sorption process varies within pH 4 0 to 5 0 units Lee and Low (1989) evaluated optimum adsorption range for pH 3 5 to 6 5 on the basis of batch sorption experiments of Cu onto peat Ong and Swanson (1966), Coupal and Lalancette (1976) and Lee and Low (1989) estimated also the threshold pH range According to these authors, for metal sorption on peats, pH should be no lower than pH 3 0-3 5 and no higher than pH 8 0-8,5 Below pH 3 0-3 5 the metal sorption ceases due to the stripping from the peat by hydrogen ions At pH above 8 5 peat itself is unstable Bencheikh-Lehocine (1989) reported enhancing effect of high pH on Zn adsorption

The dynamic experiments reported here showed that metal ions react to the pH changes in a specific way that was not noted by the aforementioned authors It was found that for the full binding phase, pH 5 8 appears to be firm limit equal for all the studied metals At this level, the breakthrough phase starts In turn the pH range for the breakthrough phase is different for different metals and is the narrowest for Cd and Zn and the broadest for Cr The removal of Cd from the solution ceases at pH 4 5-4 6 Sorption of Zn ceases at pH 4 6-4 8 The limit of Cu sorption is pH 3 5-3 8, while Cr is bound from the solution up to the pH 2 2-2 5 of the effluent The fixed constant pH of the full sorption and dissimilarity of the pH range for the breakthrough phase for the metals determines the rate of metals bound onto the matrix The load of metals bound onto the peat matter and the binding phase largely depends on the pH and the concentration of a metal in the input solution Of all the studied metals, Zn appears to be most sensitive to these parameters, while Cr is the most stable with respect to sorption potential onto the peat matter

Gossett et al (1986) and Allen (1996) after Gossett et al suggested that metals may be easily removed from peat during an acid treatment According to these authors, except for Ni, that gives only 50 % of attainment of desorption at pH 1 2 to 2 0 due to strong complexation on peat, other metals may be easily removed from peat during an acid treatment The cations adsorbed were reported to be easily released with a small volume of acid and the peat repeatedly used as an adsorbent The stripping effect was reported to be significant at pH<3 The results of our experiments have not confirmed these statements with respect to the investigated kinds of peat, i e Peat Humus and Reed-Sedge Peat The hard acid desorption efficiency (by 1%HCl, output pH<1 0) was not high enough for metals bound in batch process It accounted for 70-77% Zn, 64-81% Cd, 60-61 % Cu and only 6-6 4 % Cr and appeared unsatisfactory with respect to any metal bound in dynamic (fixed bed) flow conditions For these conditions, the respective values were 57-75 % Zn, 33-57 % Cd, 28-51 % Cu and 1-2 3 % Cr Moreover, already peat pretreatment, which was reported in the chapter 4 4 5 caused reduction up to 70 % of the peat matter adsorption capacity Hence, it is rather unlikely that after acid desorption metal binding potential can be easily restored to the level acceptable for the repeated reuse This problem has, though, to be proved, as in the reported experiments the repeated desorption was not studied Nevertheless, the experiments with organic extractants showed the metal stripping efficiency from soils and peat to be very similar to the data reported here These data are also in a good conformity with the experiments on desorption of heavy metals from soil and peat with organic chelating agents (Fisher et al , 1992, 1993, 1994) The remobilization rate from peat by glycine followed the sequence Cd < Pb < Zn < Ni < Cu and accounted from 40-60 % for Cu to 7 7 % for Cd For other chelating agents (silage effluents) the extraction rates from peat followed the sequence Cd 74 7 % > Zn 55 7 % > Cu 53 5 % > Ni 38 9 % > Cr 12 7 % > Pb 8 9 % For food engineering residues as extractant, maximum desorption rate yielded Cu 50 3 % > Ni 38 7 % Hence, currently no cost-effective metal recovery and adsorbent reuse with respect to peat is developed, and thus spent peat adsorbent should be rather disposed of by incineration

4 6 Metal binding onto peat from liquid wastes from electroplating process in batch conditions

4 6 1 Characteristics of wastes

Liquid wastes used for experiments were typical for the technological process of electroplating and contained several metals (Fe, Zn, Cr, Cd, Mn) in various concentrations, in strongly acid (pH 1 47) sulfate solution. The concentrations of metals followed descending order 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{-3} > 171 mgCd dm^{3} > 122 mgMn dm^{3} The sequence shows therefore a profound domination of Fe over other metals present in the solution The concentration of Zn is an order of magnitude lower than that of Fe The next in a rank Cr is in the same relation to Zn, while Cd and Mn occur in amounts comparable to Cr concentration

Experiments on the metal sorption were carried out under batch and dynamic conditions (as fixed bed column studies)

4 6 2 Batch experiments on metal sorption from electroplating liquid wastes

Results of the dynamic experiments on metal sorption onto peat from synthetic solutions showed, that within the range of pH 4 8-2 2 under dynamic conditions the sorption of Zn, Cd, Cu and Cr terminates The pH limits, at which sorption ceased, were estimated as follows (chapter 4 5 1)

I	Phase of a full binding	pH 5 8
II	Breakthrough phase	
	Zn	pH 4 6-4 8
	Cd	pH 4 5-4 6
	Cu	pH 3 5-3 8
	Cr	pH 2 2-2 5

Raw wastes from the electroplating process have much lower pH than the tolerable limits for metal sorption It was though assumed, that peat matter itself has satisfactory buffering capacity to rise pH to the level required for metal sorption to occur

The equilibrium mass adsorption isotherms for metals occurring in the solution (Cd, Cr, Fe, Mn and Zn) for the studied peat matters W1, W9b and W9c and pH of equilibrated solutions are presented in Tables 32-34 and Fig 37-39 The input solutions obtained from the subsequent dilution of electroplating waste with distilled water in the range from 1 10 to 1 1 had pH ranging from 2 30 to 1 47 and pH of equilibrated solution from 4 40 to 1 67 The sorption conditions were thus mostly below the tolerable limits for Zn and Cd, and below the limit for full sorption phase for all the studied metals Therefore, sorption conditions were extremely inappropriate

4 6 2 1 Fe sorption

The equilibrium mass isotherms for Fe from electroplating acid wastes on studied Alder Peat Humus W1, Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c under batch conditions showed maximum sorption capacity ranging in very narrow limits from 101090 to 107330 mg kg^{-1} (Fig 37) That accounted for 67 5-71 6% of the input load, at pH of the equilibrated solution 1 67-1 68 Full sorption (99 6-99 8 %) accounted for 29851-29928 mgFe kg^{1}, at pH 2 47-3 13 of equilibrated solution Under batch conditions almost instant strong acidification of equilibrated solution occurred Fe was bound at relatively high rates even at pH < 2 Decrease of pH of equilibrated solution from 4 41 to 1 67 caused decrease of Fe sorption rate from 99 9% to 67 5-71 6 % All three matrices show high similarity of Fe sorption behavior and may be considered as effective adsorbents of Fe from acidic Fe-rich wastes

4 6 2 2 Zn sorption

The equilibrium mass isotherms for Zn from acid raw electroplating wastes on studied peats W1, W9b and W9c in batch conditions showed sorption capacity ranging in a narrow limits from 2258 to 4093 mg kg^{1} (Fig 38) at a very low pH and increasing acidity of equilibrated solution Under batch conditions almost instant strong acidification of equilibrated solution occurred Zn was observed to be bound even at pH < 2, but in a very low rates Decrease of pH of equilibrated solution from 4 41 to 1 67 caused reduction of Zn sorption rate from 80 4-91 3 % to 11 9 –12 7 % This shows high sensitivity of Zn sorption to pH values Of the studied matrices, Alder Peat Humus W1 appears to have somewhat better sorption potential for Zn from highly acidic electroplating wastes Correction of pH of the input solution would probably highly enhance the sorption process At the studied parameters of input solution, Zn sorption in batch conditions onto studied peats is a low-efficient process

4 6 2 3 Cd sorption

The efficiency of Cd sorption in batch conditions from the same wastes appeared to be relatively higher than that of Zn due to the somewhat lower pH limit for this metal (Table 32-34, Fig 39) Almost full sorption occurs at pH 4 4 For this pH value, sorption capacity accounted for 166 0-169 3 mgCd kg^{1} (96 2-98 4 % of the load applied) The pH decrease to 1 67-1 68 caused reduction of sorption efficiency to 61 3-63,3 % The sorption efficiency within the range 65 8-61 3 % was adequate to pH range of equilibrated solution 2 01-1 67 that covered most of the applied input concentrations at pH 1 88-1 47 The maximum sorption capacity for Cd onto studied peats from undiluted waste 1 10 was 1053-2064 mgCd kg^{-1} with the efficiency 61 3-63 3 % As a sorbent of cadmium from waste, peat thus appears to be a promising material

4 6 2 4 Cr sorption

The equilibrium mass isotherms for Cr from electroplating acid wastes on studied Alder Peat Humus W1, Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c under batch conditions showed maximum sorption capacity ranging from 1982 to 2038 mgCr kg^{1} for undiluted waste 1 10 (Fig 39) That accounted for 84 3-86 7 % of the input load, at pH of the equilibrated solution 1 67-1 68 Full sorption (99 1-99 4 %) accounted for 466-700 mgCr kg^{-1}, at pH 2 43-2 47 of the equilibrated solution As in batch conditions almost instant strong acidification of equilibrated solution occurred, high tolerance of Cr to low pH values is of particular importance Cr was bound at high rates even at pH $<$ 2 Decrease of pH of equilibrated solution from 4 41 to 1 67 caused reduction of Cr sorption rate from 99 8% to 84 3-86 7% All three matrices show similarity of Cr sorption behavior and may be considered as efficient adsorbents of Cr from acidic metal-rich wastes Somewhat higher sorption properties for Cr displayed Alder Peat Humus W1

4 6 2 5 Mn sorption

The efficiency of Mn sorption in batch conditions from the same wastes appeared to be uniformly low (Table 32-34, Fig 39) The highest sorption rate occurring at pH 4 4 did not exceeds 59 2-66 7 % of the input load For this pH value, sorption capacity accounted only for 72 3-81 3 mgMn kg^{1} The pH decrease to 1 67-1 68 caused reduction of sorption efficiency to 27 7-30 4 % The sorption efficiency within the range 24 4-32 2 % was adequate to pH range of equilibrated solution 2 05-1 67 that covered most of the applied input concentrations at pH 1 88-1 47 The maximum sorption capacity for Mn onto studied peats from undiluted waste 1 10 was 338-371 mgMn kg^{-1} with the efficiency 27 7-30 4 % Therefore, besides the major heavy metals, a partial reduction of Mn in wastes treated by peat in batch conditions may be expected

4 6 2 6 Concluding remarks

Tu summarize, peat appears to be a good sorbent for metals from a strongly acid liquid waste applied in batch conditions as undiluted solution 1 10 Despite occurrence in waste from electroplating process of several metals in high concentrations, with strong predominance of Fe, the binding efficiency of metals does not seem to be affected by a competing impact of their co-presence in solution The factor strongly controlling the efficiency of sorption is pH The highest sorption capacity and efficiency of removal from waste displayed metals tolerant to low pH values, in particular Cr, Fe and Cd Reduced ability of removal from the strongly acidic solution displayed Mn and Zn, particularly sensitive to pH

4 6 3 Metal recovery

Adsorbed loads of metals were partially recoverable by 1% HCl treatment, within the pH range of equilibrated solution pH 1 49-2 60 (Tab 32-34) Desorption was conducted as II-step process In the first step, the metal-loaded peat matter was washed with distilled water pH 6 0 The second step was desorption by means of 1% HCl treatment After washing with distilled water, pH of the equilibrated solution increased within the range from pH 3 64-3 80 to pH 2 86-2 88 for peat loaded with the maximum sorbed loads Acid treatment resulted in the renewed decrease of pH of the equilibrated solution from pH 2 55-2 60 to pH 1 38-1 49 The differences between pH values of equilibrated solution at sorption and acid desorption cycles ranged from 1 8 to 0 18 units, that shows still high buffering capacity of the system The susceptibility of the studied matrices to metal release was similar

In these conditions, the highest desorption potential showed Zn, Mn and Fe For these metals, up to more than half of the maximum sorbed load was recovered (49 6-81 5 % of Zn, of this 40,6-62 0 % was recovered during the acid treatment) Mn recovery accounted uniformly for

58 0-58 9 %, by acid treatment for 47 7-50 7 %, respectively Maximum sorbed load of Fe was stripped in 47 5-63 9 %, by acid treatment for 39 4-49,0 % The recovery of Cd accounted for 20 0-23 7 % in total, in acid stripping only 6 7-7 4 % at pH close to that of sorption Cr showed the weakest susceptibility to release, from 11 4 to 12 7 %, mainly in acid leach step (8 0-8 8 %) Rush Reed-Segde Peat exhibited the highest susceptibility to Zn desorption (81 5 % of the sorption capacity) This suggested higher rate of zinc enrichment in the labile fractions This assumption is being confirmed by a relatively high rate of Zn release in the first step (washing with distilled water at pH 6 0) Similarly high proportion of metal release in this step displayed also Cd, where the desorption appeared to be higher in the first step and very low in the acid leach Comparable proportions of desorption during the washing with distilled water showed also Mn and Fe For Cr, washing out was negligible (3-4 %) In general, the results confirm the strong binding of metals onto peat matter and generally low desorption rates

4 6 4 Sequential fractionation of metals sorbed from electroplating wastes in a batch process

Sequential fractionation of metals bound onto peat matter from the polymetallic electroplating wastes in a batch process displays a pattern in many aspects similar to the sequential fractionation of Zn, Cu, Cd and Cr bound in the dynamic conditions from a monometallic solution (Table 34, Fig 40) This confirm the assumption, that under the stress caused by the competition, the transformation of metal enrichment in binding sites occurs, As a result, some more flexible metal ions displaced from their preferred binding sites enter to the sites not readily occupied by them in a less stressed conditions

The studied system (polymetallic electroplating wastes) exhibits two critical parameters creating conditions of a stress (i) low pH 1 47 of input solution, much below the optimum and threshold ranges required for a sorption process to occur, (ii) overwhelming domination of one ion (Fe^{2+}), occurring in the solution in concentration 1-2 orders of magnitude higher than other 4 ions ($Zn^{2+} > Cr^{3+} > Cd^{2+} > Mn^{2+}$) Analysis of sorption behavior of metals both in batch (Tab 32 33, Fig, 37-39) and in the dynamic (fixed bed) process (Tab 35,36, Fig 41-43) shows clearly, that the factor controlling sorption is pH The competing effect of Fe under the circumstances is of a minor importance Hence, the loads bound onto the peat matter were determined by the buffering capacity of peat and the concentration of a metal in the input solution The bound loads of Zn, Cd and Cr are therefore some one order of magnitude lower than those sorbed from the synthetic monometallic solution at pH 4 0 either in batch or in dynamic process

In this system, most of metals were highly enriched and stably bound in the "insoluble organic" F5(OM) fraction The rate of metal ion enrichment in this fraction ranges from 10 0 - 21 7 % (Zn) to 93 5-93 6 % (Cr) The highest depletion from metals, in particular Cd, Cr and Mn, shows moderately reducible fraction F4(MRO) supposed to be attributed to the formation of humic acid complexes with metals and Fe oxyhydroxides (Hall et al 1996a,b) For this system, F4(MRO) appeared to be solely enriched by Fe ions (39 8-44 9 %) Zn retains specific for this metal enrichment of this fraction at the level of 9-10 % Another fraction showing deep depletion of the bound metals is a labile F2(CARB), which binds negligible amounts of Cd, Cr, Fe and Mn Zn enriches this fraction in several percent, (12-14 %), The significant amounts of Cd and Zn are bound in the most labile F1(EXC) fraction High enrichment compared to other studied systems showed pore solution F0(PS), from which metals can be easily released The most abundant in this fraction is Mn, occurring in amounts > 50 % Therefore, in this system the major binding fraction is "insoluble organic" F5(OM) phase Ths well explains low desorption potential of metals bound on peat" In the different studied systems, the most conservative appears to be Zn, displaying the lowest transformation of the binding phases depending on the applied system The lowest Zn enrichment in the F5(OM) phase for Rush (Reed-Sedge)Peat (9 7 %) corresponds with the relatively high desorption potential of this ion sorbed in the analyzed process (81 5 %) In general, metal binding fractionation pattern for studied peat matters appears to be similar Rush (Reed-Sedge) Peat shows some differences in metal fraction structure compared to Wood Peat Humus, similar to those observed in the dynamic process The differences are attributed mainly to lower proportions of Zn and Cd bound in stable fraction F5(OM) and higher enrichment inF0(PS), and hence higher desorption potential of these ions

Regarding the sorption capacity of the metal ions from high-acidic polymetallic wastes onto the peat matters W1, W9b and W9c representing Wood Peat Humus and Rush (Reed-Sedge) Peat, the binding fractions followed the sequence (Tab 34, Fig 40)

F0(PS)	**Mn** >> Zn ≈ Cd ≈ Fe >> Cr
F1(EXC)	**Cd > Zn** > Mn >> Fe > Cr
F2(CARB)	Zn >> Mn > Fe > Cd > Cr
F3(ERO)	Zn >< Fe >> Mn > Cd >Cr
F4(MRO)	**Fe** >> Zn >> Mn > Cr > Cd
F5(OM)	**Cr > Cd >< Fe > Mn > Zn**

The fraction structure of metal ion binding onto peat matters in the studied system is as follows

Fe	**F4(MRO) > F5(OM)** >> F0(PS) >< F3(ERO) > F2(CARB) > F1(EXC)
Zn	**F1(EXC) > F5 (OM)** >> F0(PS) ≈ F2(CARB) > F4(MRO) ≈F3(ERO)
Cr	**F5(OM)** >>>> F0(PS) > F4(MRO) > F2(CARB) > F3(ERO) > F1(EXC)
Cd	**F5(OM) >< F1(EXC)** > F0(PS) >> F2(CARB) > F3(ERO) > F4(MRO)
Mn	**F0(PS) > F5(OM)** >> F1(EXC) > F2(CARB) > F4(MRO) > F3 (ERO)

From this sequence can be easily defined the predominant role of strongly bound "insoluble organic" F5(OM) and labile F1(EXC)fractions The role of F4(MRO) fraction has become marginal This illustrates the directions of transformations of metal binding mechanisms in the actual conditions It also shows the limited reliability of the batch monometallic systems for characterization of real systems

4 7 Metal binding onto peat from liquid wastes from electroplating process in dynamic (fixed bed) conditions

4 7 1 Sorption pattern

Sorption potential of peat matter for metals from the high-acid polymetallic wastes in the dynamic (fixed bed) conditions appeared to be considerably higher than in batch process Due to the low solution substrate of subsequent portion of wastes (Tab 35, 36, Fig 41-43), the attaining by the system of the critical pH values lasts longer than in batch process In the conditions of a low pH of input solution, metal sorption onto peat is determined by three major factors (i) buffering capacity of a peat matter, (ii) critical pH values for the sorbed metal, (iii) concentration of a bound metal in the input solution In case of the applied waste containing a wide array of metal concentrations, within the range of two orders of magnitude, and a fast decreasing pH value of the system, the sorption efficiency of the matter with respect to metals differs substantially

The pH threshold values for the full binding and the breakthrough phases for the studied metals evaluated from the dynamic experiments on the monometallic synthetic wastes (chapter

4 5 1) appeared to be valid also for the reported case of polymetallic real waste For both studied peat matters, i e Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c full sorption cycle was very short and accounted for ER (exchange rate) = 3 and 4, respectively After the attaining pH 5 8 by the system, the breakthrough phase started Its duration was different for each metal and was the shortest for Mn and the longest for Cr, in accordance to the sensitivity of a particular metal to pH changes Specific for the threshold phase was high instability of pH values of leachates, probably caused by the irregularity of the displacement of buffering ions in the peat matrix by H_3O due to the different availability of the exchange sites in the peat matrix in the extremal conditions It should be mentioned, that while the threshold pH value for a full sorption phase remained unchanged (pH 5 8), the threshold limiting pH values for a breakthrough phase for this system appeared to be lower Hence, the pH limits, at which sorption ceased, were re-estimated for this complex system as follows

I	Phase of a full binding	pH 5 8
II	Breakthrough phase	
	Mn	pH 4 9
	Fe	pH 4 2-4 3
	Zn	pH 4 2-4 3
	Cd	pH 2 2-2 4
	Cr	pH 1 75-1 8

The reasons for the clearly lower threshold pH values for the breakthrough phase for this system lay in the instability of pH in this phase Also a lack of the sharp border between the minimum sorption at the end of the phase and a complete termination of binding (Tab 35, 36, Fig 41-43) results in the extending the borders of a breakthrough phase The threshold values evaluated in the stable process (chapter 4 5 1) and listed in the chapter 4 6 2 seem to be the most reliable (Tab 22-29, Fig 28-35) Nevertheless, the pH changes during the dynamic sorption process reflect the real conditions occurring in the breakthrough phase at extremal parameters of metal stripping onto peat from high-acid solutions

4 7 2 Fe sorption

Also for Fe, threshold pH value for full binding phase onto both peat matters appeared to be the same as for the studied four metals (pH 5 8) The sorption capacity for this phase accounted for about 90 and 60 % of that obtained in batch process (89649 mg Fe kg^{1} for Brushwood Peat Humus W9b and 59939 mg Fe kg^{1} for Rush Peat W9c) For both substrates sorption cycle was very short and comprised ER = 3 and 4 (S L = 1 6 and 1 4) for full binding phase and ER = 5 and 8 (S L = 1 10 and 1 8) for the total sorption cycle including breakthrough phase The total sorption capacity for Fe in the dynamic conditions was very close to the value estimated for batch process (125877 mgFe kg^{1}, i e 125 % for W9b and 90288 mg Fe kg^{1}, i e 84 % for W9c) In both processes, therefore, iron was a dominating sorbed metal

4 7 3 Zn sorption

Sorption of Zn from the polymetallic liquid wastes under dynamic condition exhibits much higher efficiency due to the low solution substrate ratio of subsequent portions of wastes (Fig 41-43) In full binding phase, from 11200 to 14000 mgZn kg^{1} were bound at pH range 6 33-5,81, while total Zn load bound onto peat comprising break-through phase ranged from 19000 to 24000 mgZn kg^{1} (lower values pertain to binding capacity of Rush Peat) In comparison with the batch process, the sorption capacity in dynamic conditions is thus >3-4 times higher in full binding phase and 7-6 times higher in both phases The difference in the binding pattern for both matrices (Brushwood Peat Humus W9c and Rush Peat W9c) consists mainly in a higher sorption capacity of Brushwood Peat Humus in the breakthrough phase, while in a full binding phase the sorption capacity is very close to each other Zn binding in these systems definitely ceased at pH 4 07 Identically as for Fe, for both substrates sorption cycle was very short and comprised ER = 3 and 4 (S L = 1 6 and 1 4) for full binding phase and ER = 5 and 8 (S L = 1 10 and 1 8) for the total sorption cycle including breakthrough phase It can be thus concluded that pH is the major controlling factor in Zn binding under dynamic conditions, while other factors e g competition of other ions is of a minor effect in this system The pH limit values for Zn appeared to be rather high pH ≥ 5 8-6 0 for full binding phase and pH ≥ 4 2 for full sorption cycle comprising break-through phase Therefore, the sorption capacity of peat for Zn can be highly enhanced in less acidic systems

4 7 4 Cd sorption

Sorption of Cd from the polymetallic liquid wastes under dynamic condition appeared to be much lower than that of Zn, mainly due to the low concentrations of this ion in the input solution, more than an order of magnitude lower than that of Zn (Tab 35,36, Fig 41-43) In the full sorption phase (ER=3-6, L S = 6, pH range 6 82-5 85 and 6 33-4 90) sorption capacity of both peats for Cd was almost identical with that in batch process and accounted for 1026 mg Cd kg^{1} Total sorption capacity for Cd reached the value approximately two times as high as for full binding phase, at ER =9 and 14, S L =1 18 and 1 14) For these two matrices, total sorption capacity for Cd accounted for 2167 and 2031 mg kg^{1} The pH limit values for Cd were comparatively low and reached pH 2 19 - 2 4 The sorption behavior of Cd in the conditions of high stress caused by a low pH and a competition of other metals occurring in much higher concentrations in the input solution, displays high flexibility of this metal, in particular in a break-through phase For the studied system pH values are in this phase highly unstable and range from 3 8-4 3 Within these values, Cdis still bound, though with decreasing efficiency The residual concentrations of Cd in effluent below 10 % of the input content occur up to pH 4 2-4 25 In further portions of effluent, efficiency of Cd binding falls down from < 90 % up to 0 % For the operational requirements, pH 4 3 should be considered as a critical threshold value for an effective Cd removal

4 7 5 Cr sorption

Sorption cycle for Cr from the polymetallic liquid wastes under the dynamic conditions displays a wery short phase of a full binding, limited by pH 5 8, and a long break-through phase, up to the threshold value pH 1 85 At this value, Cr sorption definitely ceased The respective solution exchange rates were

- for full binding phase ER=3 and 4, i e S L = 1 6 and 1 4
- for both phases ER = 44 and 66, i e S L = 1 88 and 1 66

Compared to the batch process, in the dynamic conditions full binding capacity of peat for Cr was lower but the total one was roughly 6- 9 times higher For a longer part of the process, within pH range between pH 2 5-1 85 the residual concentrations of Cr in the leachate exceeded 10 % of the input values, and therefore the efficiency of Cr removal was below 90 % For the operational requirements, therefore, the threshold value of pH 2 2-2 5 that has been estimated for a stable process (chapter 4 6 2) seems to be the most acceptable

4 7 6 Mn sorption

Mn appeared to be most sensitive for pH The sorption process definitely ceased at pH 4 90 The breakthrough phase was therefore extremely short and did not exceed 2 exchange rates after full sorption At limit value pH 5 8 for full sorption phase, first effluent appeared containing <5% of the initial concentration of Mn in effluent, The next portion showed still efficiency ≥ 90 %, while the subsequent portion was close to the extinction of a sorption capacity (efficiency < 30%) The full binding phase for Mn onto Brushwood Peat Humus W9b in this system accounted for 482 mg Mn kg^{1} (136 % of binding capacity in a batch process) and a total sorption capacity was as high as 783 mg Mn kg^{1} i e 2 2-fold higher than in a batch process The same values for Rush (Reed-Sedge) Peat W9c were 483 and 627 mg Mn kg^{1}, i e 130 % and 170 % of the sorption capacity in a batch process These data confirm high sensitivity of Mn sorption to pH value and a low flexibility of this ion in the conditions of a high stress

4 7 7 Concluding remarks

The results of the experiments on metal binding from high-acid polymetallic liquid wastes showing high domination (1-2 orders of magnitude) of Fe content over other four metals (Zn, Cr, Cd, Mn) occurring in different concentrations, prove generally high efficiency of peat as an adsorbent also in extremal conditions For each metal the controlling factor, which determined a full binding phase was pH 5 8 With respect to the input loads of metals in wastes, the full binding capacity for Brushwood Peat Humus accounted for 6-fold for Fe, 4-fold for Zn, 6-fold for Cd, 6-fold for Cr and 4-fold for Mn In numerical values, full sorption capacity was as high as 89649 mg Fe kg^{1}, 11223 mg Zn kg^{1}, 1026 mg Cd kg^{1}, 1410 mg Cr kg^{1}, and 482 mg Mn kg^{-1} The total binding capacity for Brushwood Peat Humus accounted for 8-fold for Fe, 8 5-fold for Zn, 12 6-fold for Cd, 74-fold for Cr and 6 4-fold for Mn In numerical values, the total sorption capacity was as high as 125877 mg Fe kg^{1}, 23889 mg Zn kg^{1}, 2167 mg Cd kg^{1}, 17430 mg Cr kg^{1}, and 783 mg Mn kg^{1}

The full binding capacity for Rush (Reed-Sedge) Peat accounted for 4-fold for Fe, 5-fold for Zn, 8-fold for Cd, 5-fold for Cr and 4-fold for Mn In numerical values, full sorption capacity was as high as 59939 mg Fe kg^{1}, 14035 mg Zn kg^{1}, 1368 mg Cd kg^{1}, 1174 mg Cr kg^{1}, and 483 mg Mn kg^{1} The total binding capacity for Rush (Reed-Sedge) Peat accounted for 6-fold for Fe, 7-fold for Zn, 12-fold for Cd, 53 5-fold for Cr and 5-fold for Mn In numerical values, the total sorption capacity was as high as 90388 mg Fe kg^{1}, 19006 mg Zn kg^{1}, 2031 mg Cd kg^{1}, 12566 mg Cr kg^{1}, and 625 mg Mn kg^{1} Considering the controlling role of pH and a constant pH value limiting the full sorption phase, the sorption capacity for metals from the polymetallic solution of about pH 1 5 will be determined, in general, by the concentration of metal in the input solution multiplied by the exchange rate required for attainment of the threshold value pH 5 8 at a wide range of the input concentrations It should be, though, considered, that the metals having high potential for displacing hydrogen ions from the matrix into solution (Cu, Cr) would enhance acidification of matrix and therefore the significantly high concentration of these metals in the input solution would cause the decrease of the exchange rate At the undersaturated sorption capacity, pH will be the only controlling factor In case of the metal concentrations close to the sorption capacity of a metal at a given pH of the input solution, the competitive effect similar to that observed in the binary systems on the synthetic solutions should be anticipated also The kind of a dominating anion can have an effect on the sorption capacity as well It is, though, most unlikely in the real wastes, that the metals there occur all in the same maximum concentrations The real system most often resembles the liquid waste investigated within this project

To illustrate the diversity of the sorption parameters and their influence on the binding capacity of metals, in Table 37/1,2,3 the sorption capacities of the studied peat matter (W1, W9b and W9c) are presented for different systems

In general, the dynamic (fixed-bed) sorption at the same parameters of the input solution displayed higher efficiency than a batch process The total sorbed loads of metal were higher and metal ions were bound stronger than in a batch process In the fixed-bed conditions, particularly important role appeared to have an "insoluble organic" fraction F5(OM) Metals in this fraction show high enrichment, both due to the direct binding and as a result of the transformation of a primary fractional structure

Metals can be bound from peat even from a very acidic solution Sorption potential of peat in these conditions is determined mainly by the buffering capacity of the matter in the pH range ≥ 5 8, the pH limit for a breakthrough phase specific for a particular metal and its concentration in the input solution The higher is metal content in the input solution, the larger is sorption potential of peat for this metal at other equal parameters

Of the studied metals, the most sensitive to the conditions of sorption process is Cd, displaying high variability depending on the parameters of the system

The positive results of the desorption process applied to untreated high acidic, high-metal electroplating wastes show high efficiency of peat use for industrial waste treatment, in particularly in a dynamic process Strong binding of metals onto peat matrices and low metal recovery create problems in metal recovery and reuse of the peat adsorbent This feature, though, suggests the most promising field of peat application as permanent protective liners in disposal sites of high-metal industrial wastes potentially susceptible to release metals The use of peat in constructed wetland systems is another attractive application Besides, ability of peat to act as an effective adsorbent in critical conditions of extremely low pH and high metal concentrations may be utilized in emergency cases for spill control

5 CONCLUSIONS

From the presented series of batch and dynamic studies on Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} sorption onto peat matter carried out within the reported project, the following general conclusions can be derived

1 Peat appears to be an attractive adsorbent due to its high potential to bond metals from wastewater and leachates to be used in the variety of applications in batch or fixed bed systems

2 The low-moor peats of different botanical origin display significant binding capacity for metal ions

3 The binding capacities of peat for metal ions (in mass units) in batch monometallic system depict the general order $Zn^{2+} < Cd^{2+} < Cu^{2+} < Cr^{3+}$ The decrease of pH value of the equilibrated solutions follows the same order The binding capacities expressed in equivalent units are somewhat different $Cd^{2+} < Zn^{2+} < Cu^{2+} < Cr^{3+}$ In the dynamic process and in polymetallic systems the sorption capacity and binding strength of metals undergoes deep transformations, which results in changes of the sequence

3 The type and genetic origin of peat matter influence the binding capacity for metals Low-moor peat shows the highest sorption properties The kinds of peat with respect to metal sorption capacity followed the general order Wood Peat Humus ≈ Rush Peat (Reed/Sedge Peat) > *Hypnum* Moss Peat (Sedge-Moss Peat) ≈ Boggy Soil > *Sphagnum* Moss Peat (high-moor peat), while FTIR spectra for these peats show high similarity

4 Metal binding capacity of thoroughly decomposed Gyttia appeared to be highly specific and different from the general metal sorption It displayed the highest sorption capacity for Cr and Cu, and a very weak ability of binding Zn and Cd FTIR spectra also differ distinctly from the rather uniform pattern of FTIR spectra of other peat matters

5 The general trends are the decrease of sorption capacity of peat matter in parallel with the decrease of pH, decomposition rate DR and ash content AC, though the correlation is not clear enough due to the diverse simultaneous effect of these parameters

6 The increase of input concentrations and metal loads bound onto peat in batch isotherm conditions resulted in changes of pH value of the equilibrated solution Contact of the solution at pH 4 0 with originally slightly acidic low-moor peat matrices (except Gyttia) (pH 5 0-6 5) resulted in increasing pH value of the equilibrated solution to pH 5 8-8 0 at low metal concentrations Next, decrease of pH values in parallel with the increase of metal concentrations in the input solution up to pH 2 5-5 2, depending on the sorbed metal ion and initial pH value of the peat matrix occurred

7 The initial increase of pH is not strongly influenced by metal ions in solution and caused mainly by buffering effect of displacing ions from sorption sites in peat matrix by hydrogen ions from solution In turn, contact with the same matrices of high-metal solution showed effect of displacing cations by metals, including also hydrogen ions, from sorption sites of matrices into solution

8 The highest resultant pH range in a batch process showed equilibrated Cd-solution (pH 4 1-5 8), somewhat lower values (pH 4 0-5 2) displays Zn-solution Equilibrated solutions of Cu and Cr ions were clearly acidic and falling within the ranges pH 3 0-4 4 and pH 2 5-3 7, respectively The lowest pH of the equilibrated solutions (pH 2 5 – 4 0 and pH 3 0-3 9) is associated with the most acidic moss peat matrices low-moor peat B2 (*Hypnum* Moss Peat, pH 5 0) and high-moor peat B9 (*Sphagnum* Moss Peat, pH 4 6), respectively

9 The pH values of equilibrated low-metal solution after contact with both alkaline matrices of Gyttia and acidic high-moor peat fell in the common range pH 5 8-8 0, accounting for pH 7 2-8 0 for Gyttia and for pH 5 8-7 3 for high-moor *Sphagnum* Moss Peat Resultant pH of the high-metal solution equilibrated with alkaline Gyttia (pH 7 3-7 5) ranged from pH 5 3 to 6 4, showing weak affinity to the sorbed metal ion

10 Deeper pH decrease of equilibrated solution compared to other metal ions indicates extensive hydrogen displacing by Cu^{2+} and Cr^{3+} from carboxylic functional groups of peat organic matter

11 For the further detailed studies, three low-moor peat kinds showing the best sorption properties were selected Alder Peat Humus W1, Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c The material is different with respect to botanical origin, but shows high similarity of FTIR spectra, pH values (pH 6 21-6 45), pattern of equilibria isotherms and binding capacity for metals evaluated in batch studies The selection of matters showing similar potential to metal sorption in the batch experiments despite belonging to two different genetic types and kinds was intended to identify eventual dissimilarities in sorption behavior of these matters in different systems and conditions It would also show the reliability of batch isotherm studies for evaluating actual sorption capacity of the systems working mostly in the dynamic (fixed-bed) operational conditions

12 The study has been focused on the identification of specificity of the studied metals sorption under different conditions Similarity of binding and mobilization pattern of metals onto the different kinds of peat matter (Alder Peat Humus, Brushwood Peat Humus and Rush Reed-Sedge Peat) has been a proof, that the sorption behavior is specific for the metal ion within a wide range of organic matrices of high-moor peat matter

13 There is a probability of the bigger diversity of metal binding mechanisms between the above matters and highly decomposed Gyttia, showing strong differences in metal binding and also in a pattern of FTIR spectra Significant differences in binding mechanisms may occur also in peats originated from mosses, which is suggested by considerably lower sorption capacity of these peat matters This assumption, though, is not supported by the data from FTIR studies IR spectra of Moss Peat do not differ from the spectra of peat originated from wood, read and sedge

14 Neither the Langmuir model, nor Freundlich isotherm describes sorption data for peat-metal ion systems correctly enough The standard error is too high to consider these models satisfactory for the description of the metal binding onto peats

15 Sequential extraction scheme appears to be an extremely useful operational tool for distinguishing the fractions of metal enrichment in the matrix of an identified, sequentially increasing binding strength and decreasing susceptibility to releasing metals Such fractionation may enable also identification of probable competition of metals in multi-metallic systems for different adsorption sites and characterizes the properties of organic substrate (such as peat) as adsorbent To utilize this tool thoroughly, the actual mechanisms of metal sorption adequate to the fractions of

different binding strength should be identified

16 The pattern of metal enrichment in fractions of a definite binding strength and susceptibility to desorption appears to be highly specific for particular metal ions bound onto a wide range of peat matrices In general, the higher is sorption capacity and the extent of acidification of equilibrated solution, the stronger is metal binding and the less efficient is its removal from peat matrix

17 Analysis of sequential fractionation of metals bound onto peat in batch process reflects clear affinity of metals to the definite fractions and therefore predominance of different modes of binding Assuming that enrichment in F1(EXC) fraction reflects the rates of metals bound electrostatically and in F4(MRO) fraction due to chelating complex formation, respectively, the role of both mechanisms in metal binding onto peat matter seems to be of a comparable but diverse importance with respect to different metals

18 The highest metal enrichment in batch process occurred in fractions F1(EXC), F2(CARB), F4(MRO) and F5(OM) The metal enrichment in the fractions F1(EXC) and F2(CARB) of a weak binding strength was particularly high for Zn^{2+} and Cd^{2+} and appeared significant also for Cu^{2+} The moderately reducible F4(MRO) fraction and F5(OM) phase of the strongest binding strength showed high affinity to Cr^{2+} and Cu^{2+} cations, while for Cd^{2+} and Zn^{2+} they were of a minor importance

19 The most metals enriched in F5 (OM) fraction of the highest binding strength are probably associated with "insoluble organic" residue of peat comprising humins, cellulose and lignin The mode and mechanism of metal binding onto this fraction requires elucidation

20 The fraction array from F1(EXC) to F4(MRO) with respect to predominantly organic matter such as peat can be defined as a "soluble organic" one as a whole, though both the solubility of these fractions and ability of immobilization/release metals differ considerably This suggests the occurrence of diverse sorption sites of different vulnerability to sorption/mobilization within each fraction

21 The mechanism of binding on the labile F2(CARB) fraction of peat is unclear and also requires elucidation

22 Metal ions vulnerable to remobilization are enriched mostly in F1(EXC) fraction Another fraction that contribute to the desorption rate of Cd, Zn and Cu thoroughly and significantly (from 21 % to 37 % of the total desorbed loads) is F2(CARB) From the fraction F4(MRO), only Cu^{2+} has been released in higher quantities (26-31 % of the total desorbed load) Cr^{3+} appears to be strongly complexed on peat and even from the most labile F1(EXC) fraction can not be removed completely

23 The competing effect of metals with each other for sorption sites onto peat strongly depends on the metal ions occurring in the system

24 The competitive effect of Zn^{2+} and Cd^{2} on binding onto peat in a binary systems (Zn-Cd)-Cl and (Zn-Cd)-SO_4 appeared to be almost equivalent (decrease of sorption capacity for each of both metals in the range from 8 to 22 %) It was much weaker than could have been anticipated from the affinity of both metals to the same sorption centers Significantly higher total sorption capacity of

both ions in the binary system indicates lack of competition in a substantial part of binding sites and an occurrence of a spare capacity in the sites jointly occupied by both metals

25 Very characteristic for Zn and Cd binding in the binary system is a distinct increase of the both metals load strongly bound to the matrix and resistant to stripping by acid It suggests an occurrence of the spare sorption capacity for these ions in the phases of the matrix, which display high binding strength

26 Preferential metal complexation with particular functional groups may differentiate the metal ion affinity to the different sorption sites within the same fraction of the definite binding strength This may explain the weak competition between metal ions enriching the same fraction within their full sorption capacity The observed increase of strongly bound Zn and Cd rate in a binary system suggests also occupying by these metals other available sorption sites of lesser affinity under stress caused by competition

27 Opposite to equivalent and relatively weak competitive interaction of Zn^{2+} and Cd^{2+}, in the binary system (Cu-Cr)-Cl a very strong competition between Cu^{2+} and Cr^{3+} was observed, with a profound domination of Cr over Cu for the sorption sites The low increase of a total sorption capacity of both ions in a binary system (for 10-14 % higher than in a single metal system) proves a limited spare capacity in the sites jointly occupied by both metals

28 Unlike Zn^{2+} and Cd^{2+}, no changes in the desorption rate of both metals in a binary system compared to the monometallic ones have been observed The desorption rate for Cu^{2+} in both systems invariably ranged in a narrow limits of 57-61 % of the initial load Cr^{3+} The desorption rate for both systems for Cr^{3+} is very low and ranges from 6 0 to 6 5 %, the major amount of Cr being strongly bound onto the peat matrix

29 For all three studied peat matters, the adsorption-desorption behavior of metals in monometallic and binary systems was remarkably similar, along with the numerical values This suggests high stability of binding-mobilization mechanism and properties with respect to sorption sites of high binding strength

30 The kind of anion in the input solution appeared to have strong effect on the sorption capacity for metal ion onto peat Chloride anion causes its evident suppression, most probably as a result of the ability of chlorides to act as complexing agents

31 Experiments with Zn^{2+} and Cd^{2+} binding onto pre-treated peat with pH 5 6 adjusted to that of input solution showed dramatic reduction (roughly 3–fold for each metal) of adsorption capacity compared to the untreated matter due to the deep interference during pre-treatment into the original sorption complex of peat It consisted in the reduction of a binding capacity practically in all fractions, but to the greatest extent in the most labile one F1(EXC) In the fraction structure of Zn and Cd enrichment in pre-treated peats the less labile fractions become dominating Zn became enriched mostly in F4 (MRO) and F2(CARB) fractions while Cd showed the highest affinity to F2(CARB)fraction

32 Different enrichment in the F4(MRO) fraction may explain a weak competition of Zn and Cd metal ions in the binary system (Zn-Cd)-SO_4

33 Significant differences between the long-term dynamic and batch processes were observed These differences comprise both adsorption capacity and the binding strength of metals

34 The metals most susceptible to time-dependent transformations of the binding capacity and fraction structure resulted from a different mode of a contact of adsorbent adsorbate in a dynamic process appeared to be Cd, and to a lesser extent Zn These metals show ability to expand their sorption capacity mainly due to a high increase of enrichment in the “insoluble organic” F5(OM) fraction This well explains lack of competitive effect of these metals in batch sorption process

35 The observed transformations of metal ions fractionation, directed to formation of more strongly bound complexes in time show that the process of metal binding is more complex and comprise reactions of the different kinetics involving chemisorption of a more strong type that occurs in course of a longer time This sorption behavior undermines the opinion about the rapid kinetics of the process

36 The “insoluble organic” F5(OM) fraction shows invariably high enrichment of all studied metal ions in dynamic process The mechanism of the enrichment seems to be diverse, dependent on the metal ion It occurs either independently, which results in high increase of the sorption capacity (Cd, Zn) or simultaneously with the decrease of a metal enrichment in "soluble organic” fractions In particular, decreasing moderately reducible F4(MRO) fraction associated with chelating complex formation with humic and fulvic acids or F1(EXC) fraction, which supposed to indicate electrostatically bound metal ions suggests the transformations of binding mechanisms from the weaker to the stronger binding ones (e g Zn, Cd, Cr)

37 Batch process seems to be much less sensitive to such factors as peat type, kind or decomposition rate, than the long-term process in the dynamic flow conditions In batch conditions, sorption potential of the Brushwood Peat Humus and Rush (Reed-Sedge) Peat appears to be almost identical, whereas in the dynamic sorption these two substrates differ significantly both with respect to sorption capacity and fraction structure of metal binding strength

38 The critical factor controlling sorption abilities of peat is pH value The dynamic process reported here showed that metal ions react to the pH changes in a specific way It was found that for the full binding phase, pH 5 8 appears to be firm limit equal for all the studied metals At this level, the breakthrough phase starts In turn the pH range for the breakthrough phase is different for different metals and is the narrowest for Cd and Zn and the broadest for Cr The removal of Cd from the solution ceases at pH 4 5-4 6 Sorption of Zn ceases at pH 4 6-4 8 The limit of Cu sorption is pH 3 5-3 8, while Cr is bound from the solution up to the pH 2 2-2 5 of the effluent

39 The fixed constant pH of the full sorption and dissimilarity of the pH range for the breakthrough phase for the metals determines the rate of metals bound onto the matrix The load of metals bound onto the peat matter and the binding phase largely depends on the pH and the concentration of a metal in the input solution Of all the studied metals, Zn appears to be most sensitive to these parameters, while Cr is the most stable with respect to sorption potential onto the peat matter

40 In the dynamic conditions, the bigger dissimilarities of sorption capacity and binding pattern occur between the peats of a different kind, e g between Brushwood Peat Humus and Rush (Reed-Sedge) Peat In the bath process, a sorption behavior of these two matters is almost identical

41 The results of our experiments have not confirmed statements concerning easy metal recovery and reuse of the investigated kinds of peat, i e Peat Humus and Reed-Sedge Peat The acid desorption efficiency (with 1%HCl, output pH<1 0) was not high enough for metals bound in batch process It accounted for 70-77% Zn, 64-81% Cd, 60-61 % Cu and only 6-6 4 % Cr and appeared unsatisfactory with respect to any metal bound in dynamic (fixed bed) flow conditions For these conditions, the respective values were 57-75 % Zn, 33-57 % Cd, 28-51 % Cu and 1-2 3 % Cr

42 Peat pretreatment to fixed pH 5 6 caused reduction up to 70 % of the peat matter adsorption capacity Hence, it is unlikely that after acid desorption metal binding potential can be easily restored to the level acceptable for the repeated reuse This problem has, though, to be proved Currently, no cost-effective and efficient metal recovery and adsorbent reuse with respect to peat is developed, and thus spent peat adsorbent should be rather disposed of by incineration

43 Polymetallic electroplating wastes exhibit two critical parameters creating conditions of a stress (i) low pH<2 of input solution, much below the optimum and threshold ranges required for a sorption process to occur, (ii) overwhelming domination of one ion (Fe^{2+}), occurring in the solution in concentration 1-2 orders of magnitude higher than other ions ($Zn^{2+} > Cr^{3+} > Cd^{2+} > Mn^{2+}$)

44 Sorption behavior of metals in electroplating wastes both in batch and in the dynamic (fixed bed) process shows clearly, that the factor controlling sorption is pH Despite occurrence in waste from electroplating process of several metals in high concentrations, with strong predominance of Fe, the binding efficiency of metals does not seem to be affected by a competing impact of their co-presence in solution

45 The loads bound onto the peat matter were determined by the buffering capacity of peat and the concentration of metals in the input waste The bound loads of Zn, Cd and Cr are therefore some one order of magnitude lower than those sorbed from the synthetic monometallic solution at pH 4 0 either in batch or in dynamic process

46 In batch process, pH value of equilibrated solutions for high-acidic electroplating wastes due to a high L S ratio are mostly below the tolerable limits for Zn and Cd, and below the limit for full sorption phase for all the metals occurring in wastes in different concentrations Therefore, sorption conditions are extremely inappropriate It was found, though, that peat matter itself has satisfactory buffering capacity to rise pH to the level required for metal sorption to occur

47 Peat appears to be a good sorbent for metals from a strongly acidic liquid waste applied in batch conditions as undiluted solution S L=1 10 The highest sorption capacity and efficiency of removal from waste displayed metals tolerant to low pH values, in particular Cr, Fe and Cd Reduced ability of removal from the strongly acidic solution displayed Mn and Zn, particularly sensitive to pH

48 The maximum sorption capacity of peat matters in a batch process from undiluted waste at S L = 1 10 and pH < 2 accounted for 12-13 % for Zn, 24-32 % for Mn, 61 – 63 % for Cd, 68-72 % for Fe and 84-87 % for Cr Correction of pH of the input solution would highly enhance the sorption process for Mn and Zn

49 Metal recovery from the peat matter used for high acidic electroplating waste treatment in a batch process confirmed the strong binding of metals and generally low desorption rates Desorption conducted as a II-step process (I step – washing with distilled water, II step – 1% HCl

treatment) showed the highest desorption potential of Zn, Mn and Fe For these metals, up to more than half of the maximum sorbed load was recovered (mostly within the range from 50 to 64 %), predominantly in the acid treatment step The recovery of Cd and Cr was very low (20-24 % and 11-13 %, respectively)

50 Rush Reed-Sedge Peat exhibited the highest susceptibility to Zn desorption (81 5 % of the sorption capacity) This was an effect of a higher rate of zinc enrichment in the labile fractions A relatively high rate of Zn release in the first step (washing with distilled water at pH 6 0) and a sequential fractionation of sorbed metals confirmed this assumption

51 Sequential fractionation of metals bound onto peat matter from the polymetallic electroplating wastes in a batch process displays a pattern in many aspects similar to the sequential fractionation of Zn, Cu, Cd and Cr bound in the dynamic conditions from a monometallic solution This confirms the assumption that the stress caused by the competition of hydrogen ions or other metals effects in the transformation of metal enrichment in binding sites As a result, some more flexible metal ions displaced from their preferred binding sites enter to the sites not readily occupied by them in a less stressed conditions

52 The polymetallic high acidic system shows the fraction structure of metal binding onto peat matter, which differs considerably from that obtained in the batch process for the monometallic solution In this system the predominant modes of metal binding are strongly bound "insoluble organic" F5(OM) and labile F1(EXC)fractions The role of F4(MRO) fraction has become marginal This illustrates the directions of transformations of metal binding mechanisms in the actual conditions It also shows the limited reliability of the batch monometallic systems for characterization of real systems

53 The dominance of "insoluble organic" F5(OM) phase in metal binding from high acid polymetallic solutions well explains low desorption potential of metals bound on peat In the different studied systems, the most conservative appears to be Zn, displaying the lowest transformation of the binding phases depending on the applied system

54 In general, metal fractionation pattern for binding onto studied peat matters appears to be similar Rush (Reed-Sedge) Peat shows some differences in metal fraction structure compared to Wood Peat Humus, similar to those observed in the dynamic process The differences are attributed mainly to lower proportions of Zn and Cd bound in stable fraction F5(OM) and higher enrichment in F0(PS), The lowest Zn enrichment in the F5(OM) phase for Rush (Reed-Sedge)Peat (9 7 %) corresponds with the relatively high desorption potential of this ion sorbed in the analyzed process (81 5 %)

55 Metal binding from high-acid polymetallic liquid wastes in a dynamic process, proves considerably higher efficiency of peat as an adsorbent than in a batch process For each metal the controlling factor, which determined a full binding phase was pH 5 8, that seems to be a constant threshold value for this phase

56 Due to a constant threshold pH value limiting the full sorption phase, the full sorption capacity for metals from the high acidic polymetallic solution will be adequate, in general, to the relative concentration of metal in the input solution multiplied by the threshold exchange rate It should be, though, considered, that at high input concentrations the metals having high potential for displacing hydrogen ions from the matrix into solution (Cu, Cr) would enhance

acidification of matrix Therefore, the significantly higher concentration of these metals in the input solution would cause the decrease of the threshold exchange rate

57 Considering the variable pH limit in a breakthrough phase for different metals, the total sorption capacity may be much higher than the full sorption, up to more than an order of magnitude for Cr tolerant to low pH

58 In general, dynamic (fixed-bed) sorption at the same parameters of the input solution displays higher efficiency than a batch process The total sorption capacity for metal ions in the dynamic process is higher and metal ions are bound stronger In the fixed-bed conditions and in the systems with critical parameters (low pH, high metal competition) particularly important role appeared to have an “insoluble organic” fraction F5(OM) Metals in the conditions of a stress show high enrichment in this fraction, both due to the direct binding and as a result of the transformation of a primary fractional structure

59 Metals can be bound from peat even from a very acidic solution Sorption potential of peat in these conditions is determined mainly by the buffering capacity of the matter in the pH range ≥ 5 8, the pH limit for a breakthrough phase specific for a particular metal ion, as well as by a metal concentration in the input solution The higher is metal content in the input solution, the larger is sorption potential of peat for this metal at other equal parameters

60 Of the studied metals, the most sensitive to the sorption conditions is Cd, which shows high variability of binding mode and sorption capacity depending on the parameters of the system

61 Peat can be successfully used as an effective filter for heavy metal stripping from high metal, high acidic wastes, though its potential for metal recovery and repeated reuse is low Currently, no cost-effective and efficient metal recovery and adsorbent reuse with respect to peat has been developed, and thus spent peat adsorbent should be rather disposed of by incineration

GENERAL CONCLUSION

The positive results of the desorption process applied to untreated high acidic, high-metal electroplating wastes show high efficiency of peat use for industrial waste treatment, in particularly in a dynamic process Strong binding of metals onto peat matrices and low metal recovery create problems in metal recovery and reuse of the peat adsorbent This feature, though, suggests the most promising field of peat application as permanent protective liners in disposal sites of high-metal industrial wastes potentially susceptible to release metals The use of peat in constructed wetland systems is another attractive application Besides, ability of peat to act as an effective adsorbent in critical conditions of extremely low pH and high metal concentrations may be utilized in emergency cases for spill control

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TABLES

Table 1
Physiochemical properties of investigated peats

Nr	Peat		Decomposition Rate (DR), (%)	pH (H_2O)	Natural moisture content (%)	Bulk density (g/cm^3)	Specific gravity (g/cm^3)	Porosity (%)	Ask content (AC), (%)
	Type	Kind							
	WIZNA SITE								
W1	Peat Humus	Alder Peat	70	6 45	73 60	0 310	1 609	80 73	12 55
W2	Rush Peat	Reed Peat	55	6 28	84 92	0 217	1 609	86 51	12 60
W3	Hypnum Moss Peat	Sedge-Moss Peat	35	6 03	81 27	0 182	1 576	88 45	9 80
W4	Sedgeous Peat	Sedge Peat	30	5 81	78 45	0 195	1 587	87 11	9 10
W5	Hypnum Moss Peat	Sedge-Moss Peat	25	6 08	83 51	0 157	1 557	89 92	8 20
W6	Hypnum Moss Peat	Sedge-Moss Peat	40	6 09	78 50	0 149	1 432	90 87	8 80
W7	Hypnum Moss Peat	Sedge-Moss Peat	30	6 19	76 27	0 188	1 552	87 89	7 80
W8	Hypnum Moss Peat	Moss Peat	18	5 76	92 80	0 156	1 551	89 94	7 20
W9a	Mellow Boggy Soil			6 11	73 31				
W9b	Peat Humus	Brushwood	55	6 32	79 67	0 295	1 587	81 88	10 40
W9c	Rush Peat	Reed-Sedge Peat	55	6 21	75 11	0 247	1 597	85 54	9 50
	BIEBRZA SITE								
B1	Hypnum Moss	Sedge-Moss Peat	60	6 21	68 81	0 281	1 541	81 84	7 40
B1a	Sedgeous Peat	Reed-Sedge Peat	60	6 54	74 11	0 278	1 554	82 11	8 00
B1b	Peat Humus	Brushwood Peat	65	6 18	75 21	0 232	1 598	83 12	10 20
B2	Hypnum Moss Peat	Sedge-Moss Peat	40	5 02	73 68	0 198	1 565	87 35	8 90
B3	Peat Humus	Forest Wood	80	5 81	70 00	0 248	1 599	84 49	11 70

Nr	Peat		Decomposition Rate (DR), (%)	pH (H_2O)	Natural moisture content (%)	Bulk density (g/cm^3)	Specific gravity (g/cm^3)	Porosity (%)	Ask content (AC), (%)
	Type	Kind							
B4	Peat Humus	Forest Wood	60	5 52	78 95	0 257	1 585	83 78	10 55
B5	Gyttja	Calcareous		7 46	61 28				
B6	Rush Peat	Reed Peat	50	6 46	83 45	0 189	1 569	87 95	9 25
B7	Rush Peat	Reed Peat	65	6 24	84 90	0 187	1 587	88 22	10 70
B8	Hypnum Moss Peat	Sedge-Moss Peat	40	6 05	69 32	0 151	1 468	80 12	7 10
B9	Highmoor Peat	Sphagnum Moss Peat	15	4 60	78 91				
	ZBOJNA SITE								
Z1	Peat Humus	Alder Peat	60	6 42	83 10	0 228	1 627	85 99	14 10
Z2a	Hypnum Moss Peat	Sedge Moss Peat	40	6 30	69 60	0 137	1 549	91 16	7 55
Z2b	Gyttja	Detrituous		7 26	72 69	0 263			
Z3	Hypnum Moss Peat	Sedge-Moss Peat	65	5 82	80 10	0 146	1 582	92 12	7 90

Table 1/1 Physicochemical properties of investigated peat and organogenic substrates

Peat		Decompo-sition rate (DR), (%)	pH (H_2O)	Natural moisture content (%)	Bulk dencity (g/cm^3)	Specific gravity (g/cm^3)	Porosity (%)	Ash content (AC), (%)
Type	Number of samples							
Low-moor peats								
Peat humus	6	55- 80	5 52-6 45	70 00-83 10	0 22-0 31	1 58-1 62	80 73-85 99	10 20-14 10
Rush peat	4	50- 65	6 21-6 46	75 11-84 92	0 18-0 24	1 56-1 60	85 54-88 22	9 25-12 60
Sedgeous peat	2	30- 60	5 81-6 54	74 11-78 45	0 19-0 27	1 55-1 58	82 11-87 11	8 00- 9 10
Hypnum moss peat	10	18- 60	5 02-6 30	68 81-92 80	1 13-1 28	1 43-1 58	80 12-92 12	7 10- 9 80
Gytja	2	90-100	7 26-7 46	61 28-72 69	n d	n d	n d	n d
High-moor peat	1	15	4 60	78 91	n d	n d	n d	n d

Selected substrates	Dry matter DR (%)	Ash content (AC), (%)	pH (H_2O)	Initial metal concentration				
				Cu	Zn	Cd	Mn	Fe
Alder peat humus - W1	22 40	12 55	6 45	5 02	20 83	0 243	186 9	5125
Brushwood peat humus – W9b	20 33	10 40	6 32	4 95	24 22	0 291	173 9	5324
Rush (Reed-Sedge) peat - W9c	24 99	9 50	6 21	3 70	59 45	0 370	153 9	2670 5
Peat Hula								
Up peat		48 9	5 30	13 7	36 8	0 25	69 1	23146
Bottom peat		41 9	6 50	10 5	27 5	0 36	86 0	15834
Bottom peat	68 8	38 6						
Sludge	88 2	52 6	6 71	306 5	1943 5	10 70	200 7	17562
Compost Afula								
0-5 mm	74 9	54 7	6 78	362 4	490 9	2 48	774 5	9568
0-8 mm	71 8	72 0	7 44	364 3	628 7	2 42	192 7	10402
8-18 mm	75 9	67 7	7 18	336 4	469 1	13 03	216 2	15456
Compost Naman								
A		56 1	7 10	132 0	646 3	9 10	126 9	5797
B	69 2	40 3	7 37					

Table 2 Binding capacity of Polish peats for Zn^{2+} in mono-metal system Zn-Cl, pH 4 0, evaluated from batch experiments,

Peat		Decomposition Rate (DR) (%)	pH H_2O	pH	Ash content (AC),(%)	Sorption of Zn S (mg/kg)
Peat Humus						
Alder Peat	Z1	60	6 42	7 03-4 80	14 10	33700 (67 4%)
Alder Peat	W1	70	6 45	7 50-5 15	12 55	32500 (65 0%)
Brushwood Peat	W9b	55	6 32	7 55-5 15	10 40	32050 (64 1%)
Brushwood Peat	B1b	65	6 18	7 15-4 87	10 20	31400 (62 8%)
Forest Wood Peat	B3	80	5 81	7 13-4 59	11 70	28500 (57 0%)
Forest Wood Peat	B4	60	5 52	7 15-4 37	10 55	27300 (54 6%)
Rush Peat						
Reed Peat	B7	65	6 24	7 11-5 24	10 70	33200 (66 4%)
Reed Sedge Peat	W9c	55	6 21	7 72-5 16	9 50	32700 (65 4%)
Reed Peat	B6	50	6 46	6 96-5 29	9 25	28300 (56 6%)
Reed Peat	W2	55	6 28	7 22-5 22	12 60	25800 (51 6%)
Sedgeous Peat						
Reed Sedge Peat	B1a	60	6 54	7 36-5 04	8 00	32600 (65 2%)
Sedge Peat	W4	30	5 81	7 83-4 62	9 10	25500 (51 0%)
Hypnum Moss Peat						
Sedge Moss Peat	W5	25	6 08	6 90-4 55	8 20	26900 (53 8%)
Sedge-Moss Peat	W6	40	6 09	7 15-4 54	8 80	26400 (52 8%)
Sedge-Moss Peat	W7	30	6 19	7 16-4 52	7 80	25100 (50 2%)
Sedge-Moss Peat	B1	60	6 21	7 49 5 06	7 40	24800 (49 6%)
Sedge-Moss Peat	Z2a	40	6 30	7 06-4 34	7 55	23250 (46 5%)
Sedge-Moss Peat	Z3	65	5 82	6 95-4 40	7 90	20250 (40 5%)
Sedge-Moss Peat	B2	40	5 02	6 63-4 01	8 90	18200 (36 4%)
Sedge-Moss Peat	B8	40	6 05	7 70-5 09	7 10	17850 (35 7%)
Moss Peat	W8	18	5 76	7 24-4 41	7 20	16600 (33 2%)
Sedge-Moss Peat	W3	35	6 03	7 26-4 64	9 80	15800 (31 6%)
Mellow Boggy Soil						
Mellow Boggy Soil	W9a		6 11	7 27-4 62		17400 (34 8%)
High-moor Peat						
Sphagnum Moss Peat	B9	15	4 60	6 06 3 88		15200 (30 2%)
Gyttja						
Calcareous	B5		7 46	7 17-5 88		8500 (17 0%)
Detrituous	Z2b		7 26	7 63-6 02		4000 (8 0%)

Table 3 Binding capacity of Polish peats for Cd^{2+} in mono-metal system Cd-Cl, pH 4 0, evaluated from batch experiments,

Peat		Decomposition Rate (DR) (%)	pH H_2O	pH	Ash content (AC),(%)	Sorption of Cd S (mg/kg)
			Peat Humus			
Brushwood Peat	B1b	65	6 18	6 90-5 65	10 20	37160 (74 3%)
Alder Peat	Z1	60	6 42	7 41-5 10	14 10	36800 (73 6%)
Alder Peat	W1	70	6 45	7 95-6 01	12 55	35100 (70 2%)
Brushwood Peat	W9b	55	6 32	7 96-5 01	10 40	33200 (66 4%)
Forest Wood Peat	B3	80	5 81	7 44-5 10	11 70	33200 (66 4%)
Forest Wood Peat	B4	60	5 52	6 87-4 40	10 55	29300 (58 6%)
			Rush Peat			
Reed-Sedge Peat	W9c	55	6 21	7 42-5 30	9 50	37520 (75 0%)
Reed Peat	B7	65	6 24	7 67-5 46	10 70	37200 (74 4%)
Reed Peat	W2	55	6 28	7 10-5 05	12 60	33400 (66 8%)
Reed Peat	B6	50	6 46	7 18-4 95	9 25	31500 (63 0%)
			Sedgeous Peat			
Reed-Sedge Peat	B1a	60	6 54	7 76-5 32	8 00	34000 (68 0%)
Sedge Peat	W4	30	5 81	7 45-4 83	9 10	29800 (59 6%)
			Hypnum Moss Peat			
Sedge-Moss Peat	W7	30	6 19	7 24-4 50	7 80	32200 (64 4%)
Sedge Moss Peat	W5	25	6 08	6 85-4 87	8 20	30800 (61 6%)
Sedge Moss Peat	B1	60	6 21	7 89-5 82	7 40	30160 (60 3%)
Sedge-Moss Peat	W6	40	6 09	7 20-4 16	8 80	27800 (55 6%)
Sedge Moss Peat	W3	35	6 03	6 60-4 88	9 80	27600 (55 2%)
Sedge-Moss Peat	B2	40	5 02	5 80-4 07	8 90	25200 (50 4%)
Sedge-Moss Peat	Z2a	40	6 30	6 88-4 40	7 55	24500 (49 0%)
Sedge-Moss Peat	Z3	65	5 82	6 60-4 59	7 90	22000 (44 0%)
Moss Peat	W8	18	5 76	6 55-4 83	7 20	21900 (43 8%)
Sedge-Moss Peat	B8	40	6 05	7 69-5 72	7 10	20200 (40 4%)
			Mellow Boggy Soil			
Mellow Boggy Soil	W9a		6 11	7 40-4 80		27600 (55 2%)
			Highmoor Peat			
Sphagnum Moss Peat	B9	15	4 60	5 80-3 64		18150 (36 3%)
			Gyttja			
Calcareous	B5		7 46	7 82-6 38		28000 (56 0%)
Detrituous	Z2b		7 26	7 97 5 35		11300 (22 6%)

Table 4 Binding capacity of Polish peats for Cu^{2+} in mono-metal system Cu-Cl, pH 4 0, evaluated from batch experiments,

Peat		Decomposition Rate (DR) (%)	pH H_2O	pH	Ash content (AC) (%)	Sorption of Cu S (mg/kg)
Peat Humus						
Alder Peat	W1	70	6 45	7 78-4 11	12 55	47150 (94 3%)
Brushwood Peat	B1b	65	6 18	7 64-3 87	10 20	46690 (93 4%)
Alder Peat	Z1	60	6 42	7 07-4 06	14 10	46100 (92 2%)
Brushwood Peat	W9b	55	6 32	7 60 3 77	10 40	45540 (91 1%)
Forest Wood Peat	B3	80	5 81	7 26-3 52	11 70	42780 (85 6%)
Forest Wood Peat	B4	60	5 52	7 51-3 48	10 55	42560 (85 1%)
Rush Peat						
Reed-Sedge Peat	W9c	55	6 21	7 54-4 44	9 50	47390 (94 8%)
Reed Peat	W2	55	6 28	7 26-3 80	12 60	45300 (90 6%)
Reed Peat	B7	65	6 24	7 43-3 66	10 70	45000 (90 0%)
Reed Peat	B6	50	6 46	7 33-3 67	9 25	42260 (84 5%)
Sedgeous Peat						
Reed-Sedge Peat	B1a	60	6 54	7 59-3 81	8 00	45260 (90 5%)
Sedge Peat	W4	30	5 81	7 75-3 78	9 10	37700 (75 4%)
Hypnum Moss Peat						
Sedge Moss Peat	W5	25	6 08	7 99-3 55	8 20	42800 (85 6%)
Sedge-Moss Peat	W7	30	6 19	6 97-3 53	7 80	40800 (81 6%)
Sedge-Moss Peat	B1	60	6 21	7 67-3 80	7 40	40700 (81 4%)
Sedge Moss Peat	W6	40	6 09	7 44-3 50	8 80	39540 (79 1%)
Sedge Moss Peat	Z2a	40	6 30	6 68 3 41	7 55	34800 (69 6%)
Sedge-Moss Peat	B8	40	6 05	7 87-3 57	7 10	34700 (69 4%)
Sedge-Moss Peat	W3	35	6 03	7 47-3 48	9 80	33400 (66 8%)
Sedge Moss Peat	B2	40	5 02	6 88-3 03	8 90	30100 (60 2%)
Moss Peat	W8	18	5 76	6 85 3 36	7 20	28700 (57 4%)
Sedge-Moss Peat	Z3	65	5 82	6 78 3 47	7 90	27300 (54 6%)
Mellow Boggy Soil						
Mellow Boggy Soil	W9a		6 11	7 36-3 85		37400 (74 8%)
High-moor Peat						
Sphagnum Moss Peat	B9	15	4 60	7 15-3 50		23500 (47 0%)
Gyttja						
Calcareous	B5		7 46	7 69 6 38		49845 (99 7%)
Detrituous	Z2b		7 26	7 85-6 14		49100 (98 1%)

Table 5 Binding capacity of Polish peats for Cr^{3+} in mono-metal system Cr-Cl, pH 4 0, evaluated from batch experiments,

Peat		Decomposition Rate (DR) (%)	pH H_2O	pH	Ash content (AC), (%)	Sorption of Cr S (mg/kg)
Peat Humus						
Brushwood Peat	B1b	65	6 18	7 59-3 02	10 20	48010 (96 0%)
Brushwood Peat	W9b	55	6 32	7 87-3 18	10 40	47620 (95 2%)
Alder Peat	W1	70	6 45	6 95-3 11	12 55	47370 (94 7%)
Alder Peat	Z1	60	6 42	6 65-3 10	14 10	46850 (93 7%)
Forest Wood Peat	B4	60	5 52	7 13-2 72	10 55	45230 (90 3%)
Forest Wood Peat	B3	80	5 81	7 26-2 87	11 70	45130 (90 3%)
Rush Peat						
Reed-Sedge Peat	W9c	55	6 21	7 65-3 22	9 50	49380 (98 8%)
Reed Peat	W2	55	6 28	7 07-3 43	12 60	48900 (97 8%)
Reed Peat	B7	65	6 24	7 34-2 87	10 70	45530 (91 1%)
Reed Peat	B6	50	6 46	7 33-3 68	9 25	43890 (87 8%)
Sedgeous Peat						
Reed-Sedge Peat	B1a	60	6 54	7 63-3 00	8 00	47890 (95 8%)
Sedge Peat	W4	30	5 81	7 56-2 98	9 10	38420 (78 8%)
Hypnum Moss Peat						
Sedge-Moss Peat	W3	35	6 03	7 46-3 06	9 80	44750 (89 5%)
Sedge-Moss Peat	W5	25	6 08	7 28-2 79	8 20	43680 (87 4%)
Sedge-Moss Peat	W6	40	6 09	7 11 2 83	8 80	43640 (87 3%)
Sedge-Moss Peat	Z3	65	5 82	7 31-2 85	7 90	43060 (86 1%)
Sedge-Moss Peat	B1	60	6 21	7 64-2 81	7 40	43040 (86 1%)
Sedge-Moss Peat	W7	30	6 19	7 21-2 72	7 80	42960 (85 9%)
Sedge-Moss Peat	B8	40	6 05	7 35-2 73	7 10	39460 (78 9%)
Sedge-Moss Peat	B2	40	5 02	6 98-2 52	8 90	39200 (78 4%)
Sedge-Moss Peat	Z2a	40	6 30	6 91-2 69	7 55	37500 (75 0%)
Moss Peat	W8	18	5 76	7 12-2 76	7 20	35920 (71 8%)
Mellow Boggy Soil						
Mellow Boggy Soil	W9a		6 11	7 45-2 93		39450 (78 9%)
Highmoor Peat						
Sphagnum Moss Peat	B9	15	4 60	7 26-2 99		24250 (48 5%)
Gyttja						
Detrituous	Z2b		7 26	7 54-5 67		49999 (99 9%)
Calcareous	B5		7 46	7 47 5 95		49998 (99 9%)

Table 6 Equilibrium mass adsorption-desorption isotherms for heavy metals (Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+}) bound on low-moor Alder Peat Humus and pH of equilibrated solutions in mono-metal systems Me-Cl ,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L = 1 10
Peat sample W1 (pH 6 45, DR 70 %)

Sample	Peat Humus (Alder Peat) - W1 (DR 70%) pH 6 45												
	Sorption				Desorption by distilled water, pH 6			Desorption by distilled water adjusted to pH 3			Desorption by 1% HCl		
C_o	pH	EC	C_{eq}	S	pH	EC	D	pH	EC	D	pH	EC	D
Zn													
1	7 50	301	0 03	9 7 (97 0)	7 02	211	0 00 (0 00)	6 70	287	0 00 (0 00)	0 99	41700	5 55 (57 22)
100	7 63	611	1 49	985 (98 5)	6 87	326	6 5 ((0 66)	6 45	312	1 01 (0 10)	0 94	43700	680 5 (69 09)
1000	6 78	3680	110	9100 (91 0)	6 31	1048	38 0 (0 43)	6 17	496	28 2 (0 31)	0 89	49400	5918 (65 03)
2000	6 25	5320	404	17760 (88 8)	6 11	1811	388 0 (2 18)	5 94	628	146 8 (0 83)	0 89	49600	13622 (76 70)
3000	5 69	8250	730	25260 (84 2)	5 71	2370	1290 (5 11)	5 13	809	188 (0 74)	0 88	49300	18217 (72 12)
4000	5 59	10400	1210	28900 (72 2)	5 47	3360	2545 (8 81)	5 11	1219	788 (2 72)	0 84	49800	23300 (80 62)
5000	5 15	11300	1750	32500 (65 0)	5 04	3810	2855 (8 78)	5 03	1430	957 (2 94)	0 84	53400	24500 (75 38)
Cd													
1	7 95	180	0 00	10 0 (100)	7 22	177	0 12 (1 2)	6 75	337	0 06 (0 6)	0 98	53100	9 68 (96 80)
100	7 61	340	0 61	994 (99 4)	7 28	223	1 35 (0 14)	6 50	333	2 51 (0 25)	0 94	53100	866 8 (87 20)
1000	6 55	1250	11 4	9886 (98 7)	6 77	704	36 9 (0 37)	6 19	352	19 62 (0 20)	0 92	49800	8581 (86 80)
2000	6 16	2860	96 0	19040 (95 2)	6 12	1440	105 1 (0 55)	5 58	523	79 25 (0 42)	0 91	47600	17612 (92 50)
3000	6 72	6010	338	26620 (88 7)	5 61	1288	395 1 (1 48)	5 56	524	132 3 (0 50)	0 95	51500	23379 (87 82)
4000	6 11	7120	679	33210 (83 0)	5 68	1780	1028 1 (3 09)	5 11	621	192 0 (0 58)	0 94	55100	28360 (85 39)
5000	6 01	7940	1490	35100 (70 2)	5 55	2110	2271 0 (6 47)	5 16	750	454 (1 29)	0 93	57600	30500 (86 89)

Sample	Peat Humus (Alder Peat) - W1, (DR 70%) pH 6 45												
	Sorption				Desorption by distilled water, pH 6			Desorption by distilled water adjusted to pH 3			Desorption by 1% HCl		
C_o	pH	EC	C_{eq}	S	pH	EC	D	pH	EC	D	pH	EC	D
Cu													
1	7 78	316	0 00	10 (100)	7 20	238	0 00 (0 00)	6 25	243	0 2 (2 00)	0 96	51000	1 83 (18 30)
100	7 29	650	0 26	997 (99 7)	6 89	352	2 30 (0 23)	6 10	392	1 5 (0 15)	0 90	55400	391 6 (39 28)
1000	6 05	4330	1 78	9982 (99 8)	6 45	1107	6 30 (0 06)	5 68	498	7 7 (0 08)	0 88	55300	6848 (68 60)
2000	5 05	6740	9 15	19908 (99 5)	5 85	1750	11 4 (0 06)	5 31	590	15 6 (0 08)	0 87	51600	13660 (68 62)
3000	5 42	8540	39 0	29610 (98 7)	5 58	2090	27 0 (0 09)	5 23	710	29 8 (0 10)	0 84	55500	19067 5 (64 39)
4000	4 76	10670	92 0	39080 (97 7)	5 15	2650	111 (0 28)	5 15	720	49 2 (0 13)	0 83	50200	24630 (63 02)
5000	4 11	13360	285	47150 (94 3)	5 11	3430	452 (0 96)	5 02	820	126 7 (0 27)	0 83	65000	28750 (60 96)
Cr													
1	6 95	211	0 00	10 (100)	7 43	137	0 00 (0 00)	6 97	316	0 1 (1 00)	0 98	47300	4 65 (46 50)
100	7 57	705	0 06	999 (99 9)	6 78	333	0 2 (0 02)	6 32	371	0 5 (0 05)	0 95	48000	89 04 (8 91)
1000	7 34	4630	0 22	9998 (99 9)	6 19	1447	0 5 (0 005)	5 92	757	0 8 (0 008)	0 93	54000	798 9 (8 00)
2000	6 24	7990	0 47	19995 (99 9)	5 52	2148	0 9 (0 004)	5 11	896	0 9 (0 004)	0 86	56200	1421 5 (7 11)
3000	4 78	10550	1 16	29988 (99 9)	5 01	3310	1 6 (0 005)	4 25	1193	2 7 (0 009)	0 85	61600	2049 3 (6 83)
4000	3 91	12930	5 32	39947 (99 9)	4 67	4340	2 9 (0 007)	3 68	1370	4 1 (0 01)	0 94	64300	2450 0 (6 13)
5000	3 11	16030	260	47370 (94 7)	4 20	5950	17 6 (0 04)	3 31	1530	7 4 (0 02)	0 93	65800	2988 0 (6 31)

Table 7 Equilibrium mass adsorption-desorption isotherms for heavy metals (Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+}) bound on low-moor Brushwood Peat Humus and pH of equilibrated solutions in mono-metal systems Me-Cl ,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L = 1 10
Peat sample W9b (pH 6 32, DR 55 %)

Sample	Peat Humus (Brushwood) - W9b (DR 55%) pH 6 32												
	Sorption				Desorption distilled water pH 6			Desorption distilled water pH 3 (adjusted)			Desorption 1% HCl		
C_0	pH	EC	C_{eq}	S	pH	EC	D	pH	EC	D	pH	EC	D
Zn													
1	7 55	292	0 03	9 7 (97 0)	6 34	160	0 00 (0 00)	6 18	361	0 1 (1 00)	0 93	46100	8 80 (90 72)
100	7 50	536	0 52	995 (99 5)	6 34	265	11 2 (1 13)	6 12	393	2 4 (0 24)	0 91	48600	578 5 (58 14)
1000	6 42	3590	10 17	9898 (98 9)	6 22	851	75 0 (0 76)	6 06	457	64 2 (0 65)	0 88	54800	6095 (61 58)
2000	6 52	5500	248	17520 (87 6)	5 91	1415	597 5 (3 41)	5 47	630	216 4 (1 23)	0 87	55500	12771 (72 89)
3000	5 35	8330	680	23200 (77 3)	6 23	2380	1570 (6 77)	5 32	811	354 (1 53)	0 85	57200	16908 (72 88)
4000	5 58	10850	1105	28950 (72 4)	5 42	3510	2740 (9 46)	5 08	1110	1008 (3 48)	0 84	56000	22360 (77 24)
5000	5 15	12230	1795	32050 (64 1)	5 47	3750	2631 (8 21)	5 08	1185	1302 (4 06)	0 83	57900	23500 (73 32)
Cd													
1	7 96	280	0 00	10 (100)	6 72	124	0 14 (1 4)	6 26	310	0 37 (3 7)	0 92	53800	9 01 (90 20)
100	7 24	395	0 60	994 (99 4)	6 27	194	1 67 (0 17)	5 99	466	1 89 (0 19)	0 91	64000	650 8 (65 47)
1000	6 80	1462	10 6	9894 (98 9)	5 90	739	38 91 (0 39)	5 77	432	22 45 (0 23)	0 90	42100	8518 (86 09)
2000	6 53	2880	106	18940 (94 7)	5 72	1319	249 0 (1 31)	5 34	494	78 90 (0 42)	0 88	54800	17027 (89 90)
3000	6 50	5790	457	25430 (84 8)	5 47	1740	858 8 (3 38)	5 31	535	167 2 (0 66)	0 86	57000	22362 (87 94)
4000	5 66	6480	900	31000 (77 5)	5 22	2240	783 (2 53)	5 02	1000	286 8 (0 93)	0 84	53800	28450 (91 77)
5000	5 01	7820	1680	33200 (66 4)	5 01	2260	954 (2 87)	4 88	1149	540 0 (1 63)	0 84	54750	30800 (92 77)

Sample	Peat Humus (Brushwood) - W9b, (DR 55%) pH 6 32													
	Sorption				Desorption distilled water pH 6			Desorption distilled water pH 3 (adjusted)			Desorption 1% HCl			
C_o	pH	EC	C_{eq}	S	pH	EC	D	pH	EC	D	pH	EC	D	
Cu														
1	7 60	294	0 00	10 (100)	6 83	186	0 1 (1 00)	6 04	216	0 1 (1 00)	0 92	60200	7 82 (78 20)	
100	7 16	620	0 42	996 (99 6)	6 54	273	1 7 (0 17)	6 02	262	3 1 (0 31)	0 90	62200	625 5 (62 80)	
1000	4 96	3810	2 73	9973 (99 7)	5 45	1108	9 4 (0 09)	5 25	455	11 2 (0 11)	0 89	56800	7081 (71 00)	
2000	4 87	6690	16 6	19833 (99 2)	5 08	1660	23 4 (0 12)	4 98	690	15 6 (0 08)	0 88	67500	11226 (56 60)	
3000	4 66	9000	58 0	29420 (98 1)	4 79	2450	84 3 (0 29)	4 29	720	34 2 (0 12)	0 75	56900	20123 (68 40)	
4000	4 74	10620	166	38340 (95 8)	4 51	2600	172 5 (0 45)	4 40	760	68 5 (0 18)	0 74	60300	23997 (62 59)	
5000	3 77	13510	446	45540 (91 1)	4 23	3410	657 0 (1 44)	4 11	1130	138 (0 30)	0 72	61200	27100 (59 51)	
Cr														
1	7 87	264	0 00	10 (100)	6 63	146	0 00 (0 00)	6 53	310	0 00 (0 00)	0 94	50800	5 09 (50 90)	
100	7 76	604	0 16	998 (99 8)	6 53	296	1 1 (0 11)	6 18	479	0 6 (0 06)	0 92	51400	165 2 (16 55)	
1000	6 53	4450	0 36	9996 (99 9)	5 46	1572	1 4 (0 014)	5 42	863	1 3 (0 013)	0 78	52600	1037 (10 37)	
2000	5 92	7810	0 72	19993 (99 9)	5 15	2620	1 7 (0 008)	4 84	1054	1 9 (0 009)	0 76	57100	1749 (8 75)	
3000	5 47	10450	1 07	29990 (99 9)	4 40	2820	2 1 (0 007)	4 29	930	3 4 (0 011)	0 85	58700	2041 (6 81)	
4000	4 43	12870	6 40	39936 (99 8)	4 15	4320	8 9 (0 022)	3 50	1440	3 8 (0 009)	0 84	63000	2417 (6 05)	
5000	3 18	13400	238	47620 (95 2)	4 12	5420	33 0 (0 06)	3 41	2250	10 6 (0 022)	0 83	65400	2911 (6 11)	

Table 8 Equilibrium mass adsorption-desorption isotherms for heavy metals ((Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+}) bound on low-moor Rush (Reed-Sedge) Peat and pH of equilibrated solutions in mono-metal systems Me-Cl

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L = 1 10
Peat sample W9c (pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) - W9c, (DR 55%), pH 6 21												
	Sorption				Desorption by distilled water pH 6			Desorption by distilled water adjusted to pH 3			Desorption by 1% HCl		
C_o	pH	EC	C_{eq}	S	pH	EC	D	pH	EC	D	pH	EC	D
Zn													
1	7 72	289	0 00	10 (100)	7 20	226	0 00 (0 00)	6 60	370	0 00 (0 00)	0 86	44700	5 29 (52 90)
100	7 42	551	0 30	997 (99 7)	6 78	420	4 6 (0 46)	6 45	420	1 1 (0 11)	0 92	46500	555 (55 67)
1000	6 43	3650	56	9440 (94 4)	6 12	1020	41 5 (0 44)	5 42	520	28 2 (0 30)	0 90	43600	5013 (53 10)
2000	6 20	5490	178	18220 (91 1)	5 56	1555	292 0 (1 60)	5 47	658	149 1 (0 82)	0 88	43400	13240 (72 67)
3000	5 32	8330	360	26400 (88 0)	5 41	2400	884 0 (3 35)	5 40	1149	350 (1 32)	0 85	50900	19275 (73 01)
4000	5 65	10610	1040	29600 (74 0)	5 46	3710	1088 (3 68)	5 22	1283	822 (2 78)	0 83	54200	23464 (79 27)
5000	5 16	11900	1730	32700 (65 4)	5 27	4360	1360 (4 16)	5 09	1561	1294 (3 96)	0 82	55100	28200 (86 24)
Cd													
1	7 42	195	0 00	10 (100)	6 71	123	0 05 (0 5)	6 25	291	0 07 (0 70)	0 92	54200	9 11 (91 10)
100	6 10	365	0 25	997 (99 7)	6 93	260	1 20 (0 12)	6 16	344	1 28 (0 13)	0 91	64000	690 2 (69 23)
1000	5 94	1510	12 6	9874 (98 4)	6 09	736	33 76 (0 34)	5 99	365	20 92 (0 21)	0 88	49900	8746 (88 58)
2000	5 98	2870	107	18925 (94 6)	6 54	1284	212 3 (1 12)	5 78	566	72 50 (0 38)	0 87	55400	15278 (80 73)
3000	5 67	5640	301	26990 (90 0)	5 12	1670	546 6 (2 02)	5 09	694	169 1 (0 62)	0 85	54600	24780 (91 81)
4000	5 35	6790	696	33040 (82 6)	5 06	2100	1512 5 (4 58)	4 99	731	249 0 (0 75)	0 84	53900	26230 (79 39)
5000	5 30	7960	1248	37520 (75 0)	5 06	2520	1904 (5 07)	4 80	1025	632 0 (1 68)	0 92	61000	33200 (88 49)

Sample	Rush Peat (Reed-Sedge Peat) - W9c, (DR 55%), pH 6 21											
	Sorption				Desorption by distilled water, pH 6			Desorption by distilled water adjusted to pH 3			Desorption by 1% HCl		
C_0	pH	EC	C_{eq}	S	pH	EC	D	pH	EC	D	pH	EC	D
Cu													
1	7 54	290	0 00	10 (100)	7 10	222	0 1 (1 00)	5 91	266	0 1 (1 00)	0 88	52000	7 82 (78 20)
100	7 29	665	0 28	997 (99 7)	6 61	382	0 8 (0 08)	5 71	460	1 1 (0 11)	0 86	49200	606 4 (60 82)
1000	6 30	4060	2 80	9972 (99 7)	5 48	1094	3 9 (0 04)	5 37	565	5 5 (0 06)	0 92	53300	7063 (70 83)
2000	4 94	6620	9 28	19907 (99 5)	4 68	2221	17 1 (0 09)	4 53	740	22 0 (0 11)	0 89	51900	13990 (70 28)
3000	4 84	9070	32 0	29984 (99 9)	4 57	2760	52 8 (0 18)	4 34	920	24 5 (0 08)	0 86	52700	21077 (70 29)
4000	4 67	10340	81 0	39190 (97 9)	4 44	3040	120 (0 31)	4 41	1150	42 5 (0 11)	0 85	53900	23760 (60 63)
5000	4 44	13300	261	47390 (94 8)	4 35	4320	480 (1 01)	4 24	1310	116 (0 25)	0 84	60400	29100 (61 41)
Cr													
1	7 65	365	0 00	10 (100)	6 77	174	0 00 (0 00)	6 63	271	0 00 (0 00)	0 91	48600	3 45 (34 50)
100	7 53	706	0 08	999 (99 9)	6 64	316	0 2 (0 02)	6 30	329	0 2 (0 02)	0 89	50900	109 4 (10 95)
1000	6 54	4620	0 29	9997 (99 9)	5 65	1850	0 7 (0 007)	5 43	740	0 7 (0 007)	0 87	52000	638 8 (6 39)
2000	6 00	7840	0 41	19996 (99 9)	5 39	2730	0 8 (0 004)	4 83	1091	1 0 (0 005)	0 85	55100	1362 (6 81)
3000	4 98	10560	0 80	29992 (99 9)	4 67	3280	1 7 (0 006)	4 52	1111	2 5 (0 008)	0 84	62000	1851 (6 17)
4000	4 56	12750	3 21	39968 (99 9)	4 11	4500	2 4 (0 006)	3 69	1540	4 5 (0 011)	0 83	64500	2417 (6 05)
5000	3 22	13640	62 0	49380 (98 8)	3 45	6300	26 0 (0 05)	3 40	2080	13 7 (0 03)	0 83	65400	3150 (6 38)

Table 9 Maximum bound metal loads evaluated experimentally and parameters of Langmuir and Freundlich equilibrium isotherms for Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} sorption onto Alder Peat

	$S_{(max)}$ (exp)	Langmuir equilibrium isotherm $S = bK_Lc_{eq}/(1+K_LC_{eq})$			Freundlich equilibrium isotherm $S = K_Fc_{eq}^{1/n}$		
		b	K_L	R	K_F	n	R
	mg/kg (%)	mg/kg	dm^3/mg		dm^3/mg		
Zn	32500 (65.0%)	22899	0.018	0.985	1574	2.542	0.984
Cd	35100 (70.2%)	25889	0.152	0.963	5304	3.716	0.970
Cu	47150[a] (94.3%)	39946	0.159	0.991	9507	3.405	0.972
Cr	47370[a] (94.7%)	61253	0.426	0.961	20817	6.035	0.768

S - bound quantity of metal per unit of adsorbent c_{eq} - equilibrium concentration of metal in solution, $S_{(max)}$ - maximum bound metal loads evaluated experimentally (in mass units or in percent of mass applied), b - constant corresponding to the surface concentration and monolayer coverage and representing the maximum adsorption, K_L - constant related to the energy of adsorption, K_F - constant related primarily to the capacity of adsorbent R - regression coefficient

[a] - Below the adsorption capacity

Table 10/1 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10 ,
Peat sample Alder Peat Humus W1 (pH 6 45, DR 70%),

Sample	Peat Humus (Alder Peat) - W1 (DR 70%) pH 6 45								
	Sorption			Desorption by distilled water, pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
Zn									
1	7 50	0 03	9 7 (97 0)	7 02	0 00 (0 00)	6 70	0 00 (0 00)	0 99	5 55 (57 22)
100	7 63	1 49	985 (98 5)	6 87	6 5 (0 66)	6 45	1 01 (0 10)	0 94	680 5 (69 09)
1000	6 78	110	9100 (91 0)	6 31	38 0 (0 43)	6 17	28 2 (0 31)	0 89	5918 (65 03)
2000	6 25	404	17760 (88 8)	6 11	388 0 (2 18)	5 94	146 8 (0 83)	0 89	13622 (76 70)
3000	5 69	730	25260 (84 2)	5 71	1290 (5 11)	5 13	188 (0 74)	0 88	18217 (72 12)
4000	5 59	1210	28900 (72 2)	5 47	2545 (8 81)	5 11	788 (2 72)	0 84	23300 (80 62)
5000	5 15	1750	32500 (65 0)	5 04	2855 (8 78)	5 03	957 (2 94)	0 84	24500 (75 38)
Zn in presence of Cd									
1	6 15	0 025	9 75 (97 5)	6 40	0 00 (0 00)			1 02	7 11 (72 92)
99 5	6 36	0 99	985 1 (99 0)	6 35	2 70 (0 27)			0 98	485 6 (49 29)
435	6 00	16 75	4182 (96 2)	5 62	24 11 (0 58)			0 95	2687 2 (65 03)
1005	5 70	109 87	8951 (89 1)	5 59	92 62 (1 03)			0 93	5469 (61 09)
2970 5	5 16	5800	23905 (80 5)	5 19	297 9 (1 34)			0 92	12770 (53 42)
4620	4 75	1998 6	26214 (56 7)	4 89	371 9 (1 42)			0 90	16896 (64 45)

Table 10/2 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10 ,
Peat samples Brushwood Peat Humus W9b (pH 6,32, DR 55 %)

Sample	Peat Humus (Brushwood) - W9b (DR 55%), pH 6 32								
	Sorption			Desorption by distilled water, pH 6		Desorption distilled water adjusted to pH 3		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D	pH	D
Zn									
1	7 55	0 03	9 7 (97 0)	6 34	0 00 (0 00)	6 18	0 1 (1 00)	0 93	8 80 (90 72)
100	7 50	0 52	995 (99 5)	6 34	11 2 (1 13)	6 12	2 4 (0 24)	0 91	578 5 (58 14)
1000	6 42	10 17	9898 (98 9)	6 22	75 0 (0 76)	6 06	64 2 (0 65)	0 88	6095 (61 58)
2000	6 52	248	17520 (87 6)	5 91	597 5 (3 41)	5 47	216 4 (1 23)	0 87	12771 (72 89)
3000	5 35	680	23200 (77 3)	6 23	1570 (6 77)	5 32	354 (1 53)	0 85	16908 (72 88)
4000	5 58	1105	28950 (72 4)	5 42	2740 (9 46)	5 08	1008 (3 48)	0 84	22360 (77 24)
5000	5 15	1795	32050 (64 1)	5 47	2631 (8 21)	5 08	1302 (4 06)	0 83	23500 (73 32)
Zn in presence of Cd									
1	6 50	0 033	9 67 (96 7)	6 58	0 00 (0 00)			1 09	8 33 (86 14)
99 5	6 28	0 96	985 4 (99 0)	6 55	1 70 (0 17)			0 96	539 1 (54 71)
435	6 00	14 78	4202 (96 6)	5 64	32 51 (0 77)			0 94	2692 (64 06)
1005	5 68	92 16	9128 4 (90 8)	5 60	121 1 (1 33)			0 93	5201 (56 98)
2970 5	5 15	586 8	23837 (83 6)	5 11	338 1 (1 42)			0 92	11692 (49 04)
4620	4 75	1781	28390 (61 4)	4 90	476 2 (1 68)			0 85	15078 (53 11)

Table 10/3 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10 ,
Peat sample Rush (Reed-Sedge)Peat W9c,(pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) - W9c (DR 55%) pH 6 21								
	Sorption			Desorption by distilled water pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
Zn									
1	7 72	0 00	10 (100)	7 20	0 00 (0 00)	6 60	0 00 (0 00)	0 86	5 29 (52 90)
100	7 42	0 30	997 (99 7)	6 78	4 6 (0 46)	6 45	1 1 (0 11)	0 92	555 (55 67)
1000	6 43	56	9440 (94 4)	6 12	41 5 (0 44)	5 42	28 2 (0 30)	0 90	5013 (53 10)
2000	6 20	178	18220 (91 1)	5 56	292 0 (1 60)	5 47	149 1 (0 82)	0 88	13240 (72 67)
3000	5 32	360	26400 (88 0)	5 41	884 0 (3 35)	5 40	350 (1 32)	0 85	19275 (73 01)
4000	5 65	1040	29600 (74 0)	5 46	1088 (3 68)	5 22	822 (2 78)	0 83	23464 (79 27)
5000	5 16	1730	32700 (65 4)	5 27	1360 (4 16)	5 09	1294 (3 96)	0 82	28200 (86 24)
Zn in presence of Cd									
1	5 46	0 037	9 63 (96 3)	6 16	0 00 (0 00)			0 90	7 57 (78 61)
99 5	5 70	0 83	986 7 (99 2)	5 84	2 02 (0 21)			0 90	507 7 (51 45)
435	5 67	18 48	4165 2 (95 7)	5 36	34 09 (0 82)			0 88	2416 (58 02)
1005	5 47	123 77	8812 3 (87 7)	5 51	141 04 (1 50)			0 87	4356 (49 43)
2970 5	4 95	583 6	23869 (80 3)	5 00	338 1 (1 34)			0 88	10054 (42 12)
4620	4 69	2072	25480 (55 15	4 64	580 3 (2 28)			0 85	14646 (57 48)

Table 11/1 Equilibrium mass adsorption/desorption isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cd-Cl and binary systems (Cd+Zn)-Cl,

Batch experiments, Input solution pH 4 0, c$_0$ = 1 - 5000 mgMe dm^{3}, S/L= 1 10 ,
Peat sample Alder Peat Humus W1 (pH 6 45, DR 70%),

Sample	Peat Humus (Alder Peat) - W1, (DR 70%) pH 6 45								
	Sorption			Desorption by distilled water pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C$_0$	pH	C$_{eq}$	S	pH	D	pH	D	pH	D
Cd									
1	7 95	0 00	10 0 (100)	7 22	0 12 (1 2)	6 75	0 06 (0 6)	0 98	9 68 (96 80)
100	7 61	0 61	994 (99 4)	7 28	1 35 (0 14)	6 50	2 51 (0 25)	0 94	866 8 (87 20)
1000	6 55	11 4	9886 (98 7)	6 77	36 9 (0 37)	6 19	19 62 (0 20)	0 92	8581 (86 80)
2000	6 16	96 0	19040 (95 2)	6 12	105 1 (0 55)	5 58	79 25 (0 42)	0 91	17612 (92 50)
3000	6 72	338	26620 (88 7)	5 61	395 1 (1 48)	5 56	132 3 (0 50)	0 95	23379 (87 82)
4000	6 11	679	33210 (83 0)	5 68	1028 1 (3 09)	5 11	192 0 (0 58)	0 94	28360 (85 39)
5000	6 01	1490	35100 (70 2)	5 55	2271 0 (6 47)	5 16	454 (1 29)	0 93	30500 (86 89)
Cd in presence of Zn									
1 00	6 15	0 024	9 76 (97 6)	6 40	0 00 (0 00)			1 02	8 03 (82 27)
100	6 36	0 32	996 8 (99 7)	6 35	1 51 (0 15)			0 98	664 2 (66 63)
463 1	6 00	5 52	4576 (98 8)	5 62	16 32 (0 36)			0 95	3626 (79 24)
1242 5	5 70	170 2	10723 (86 3)	5 59	72 20 (0 67)			0 93	6948 (64 79)
2860	5 16	644 4	22156 (77 5)	5 19	748 8 (3 28)			0 92	15004 (67 72)
4644	4 75	2210	24340 (52 4)	4 89	1411 5 (5 80)			0 90	18192 (74 74)

Table 11/2 Equilibrium mass adsorption/desorption isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cd-Cl and binary systems (Cd+Zn)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10 ,
Peat sample Brushwood Peat Humus W9b (pH 6,32, DR 55%),

Sample	Peat Humus (Brushwood) - W9b, (DR 55%), pH 6,32								
	Sorption			Desorption by distilled water, pH 6		Desorption distilled water adjusted to pH 3		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cd									
1	7 96	0 00	10 (100)	6 72	0 14 (1 4)	6 26	0 37 (3 7)	0 92	9 01 (90 20)
100	7 24	0 60	994 (99 4)	6 27	1 67 (0 17)	5 99	1 89 (0 19)	0 91	650 8 (65 47)
1000	6 80	10 6	9894 (98 9)	5 90	38 91 (0 39)	5 77	22 45 (0 23)	0 90	8518 (86 09)
2000	6 53	106	18940 (94 7)	5 72	249 0 (1 31)	5 34	78 90 (0 42)	0 88	17027 (89 90)
3000	6 50	457	25430 (84 8)	5 47	858 8 (3 38)	5 31	167 2 (0 66)	0 86	22362 (87 94)
4000	5 66	900	31000 (77 5)	5 22	783 (2 53)	5 02	286 8 (0 93)	0 84	28450 (91 77)
5000	5 01	1680	33200 (66 4)	5 01	954 (2 87)	4 88	540 0 (1 63)	0 84	30800 (92 77)
Cd in presence of Zn									
1 00	6 50	0 0	9 98 (99 8)	6 58	0 00 (0 00)			1 09	6 90 (69 14)
100	6 28	0 33	996 7 (99 7)	6 55	1 60 (0 16)			0 96	720 2 (72 26)
463 1	6 00	7 46	4556 4 (98 4)	5 64	23 01 (0 51)			0 94	3248 (71 23)
1242 5	5 68	47 46	10950 (96 2)	5 60	132 6 (1 11)			0 93	6222 (52 07)
2860	5 15	637 4	22226 (77 7)	5 11	294 6 (1 33)			0 92	14228 (64 02)
4644	4 75	1943 6	27004 (58 2)	4 90	575 36 (2 31)			0 89	18088 (66 98)

Table 11/3 Equilibrium mass adsorption/desorption isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cd-Cl and binary systems (Cd+Zn)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10 ,
Peat sample Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) W9c (DR 55%), pH 6 21								
	Sorption			Desorption by distilled water pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cd									
1	7 42	0 00	10 (100)	6 71	0 05 (0 5)	6 25	0 07 (0 70)	0 92	9 11 (91 10)
100	6 10	0 25	997 (99 7)	6 93	1 20 (0 12)	6 16	1 28 (0 13)	0 91	690 2 (69 23)
1000	5 94	12 6	9874 (98 4)	6 09	33 76 (0 34)	5 99	20 92 (0 21)	0 88	8746 (88 58)
2000	5 98	107	18925 (94 6)	6 54	212 3 (1 12)	5 78	72 50 (0 38)	0 87	15278 (80 73)
3000	5 67	301	26990 (90 0)	5 12	546 6 (2 02)	5 09	169 1 (0 62)	0 85	24780 (91 81)
4000	5 35	696	33040 (82 6)	5 06	1512 5 (4 58)	4 99	249 0 (0 75)	0 84	26230 (79 39)
5000	5 30	1248	37520 (75 0)	5 06	1904 (5 07)	4 80	632 0 (1 68)	0 92	33200 (88 49)
Cd in presence of Zn									
1	5 46	0 016	9 84 (98 4)	6 16	0 00 (0 00)			0 90	5 99 (60 87)
100	5 70	0 2533	997 5 (99 7)	5 84	1 89 (0 19)			0 90	680 2 (68 19)
463 1	5 67	54 16	4576 (98 8)	5 36	24 04 (0 53)			0 88	3226 (70 49)
1242 5	5 47	615 7	11883 (95 64	5 51	123 1 (1 04)			0 87	5874 (49 43)
2860	4 95	2093 6	22443 (78 47	5 00	375 7 (1 67)			0 88	13024 (58 03)
4644	4 69	1943 6	25504 (54 9)	4 64	770 6 (3 02)			0 85	16038 (62 88)

Table 12/1 Equilibrium mass adsorption/desorption isotherms for Cu^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cu-Cl and binary systems (Cu+Cr)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10,
Peat sample Alder Peat Humus W1 (pH 6 45, DR 70%),

Sample	Peat Humus (Alder Peat) - W1 (DR 70%) pH 6 45								
	Sorption			Desorption by distilled water, pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cu									
1	7 78	0 00	10 (100)	7 20	0 00 (0 00)	6 25	0 2 (2 00)	0 96	1 83 (18 30)
100	7 29	0 26	997 (99 7)	6 89	2 30 (0 23)	6 10	1 5 (0 15)	0 90	391 6 (39 28)
1000	6 05	1 78	9982 (99 8)	6 45	6 30 (0 06)	5 68	7 7 (0 08)	0 88	6848 (68 60)
2000	5 05	9 15	19908 (99 5)	5 85	11 4 (0 06)	5 31	15 6 (0 08)	0 87	13660 (68 62)
3000	5 42	39 0	29610 (98 7)	5 58	27 0 (0 09)	5 23	29 8 (0 10)	0 84	19067 5 (64 39)
4000	4 76	92 0	39080 (97 7)	5 15	111 (0 28)	5 15	49 2 (0 13)	0 83	24630 (63 02)
5000	4 11	285	47150 (94 3)	5 11	452 (0 96)	5 02	126 7 (0 27)	0 83	28750 (60 96)
Cu in presence of Cr									
0 82	7 60	0 065	7 55 (92 1)	7 12	0 07 (1 15)			1 30	0 57 (7 56)
66 5	7 19	0 37	661 1 (99 4)	6 80	2 50 (0 38)			1 25	355 5 (53 78)
450 3	6 70	0 58	4497 (99 9)	6 66	4 35 (0 09)			1 21	2412 6 (53 64)
738 9	6 01	1 45	7375 (99 8)	6 20	5 95 (0 08)			1 20	4433 (60 11)
1920	3 56	153 1	17665 (92 0)	3 73	443 7 (2 51)			1 11	10556 (59 76)
3991	2 66	1888	21030 (52 7)	2 99	497 6 (2 37)			1 06	12764 (60 69)

Table 12/2 Equilibrium mass adsorption/desorption isotherms for Cu^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cu-Cl and binary systems (Cu+Cr)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10,
Peat sample Brushwood Peat Humus W9b (pH 6,32, DR 55 %),

Sample	Peat Humus (Brushwood) - W9b (DR 55%), pH 6 32								
	Sorption			Desorption by distilled water pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cu									
1	7 60	0 00	10 (100)	6 83	0 1 (1 00)	6 04	0 1 (1 00)	0 92	7 82 (78 2)
100	7 16	0 42	996 (99 6)	6 54	1 7 (0 17)	6 02	3 1 (0 31)	0 90	625 5 (62 80)
1000	4 96	2 73	9973 (99 7)	5 45	9 4 (0 09)	5 25	11 2 (0 11)	0 89	7081 (71 00)
2000	4 87	16 6	19833 (99 2)	5 08	23 4 (0 12)	4 98	15 6 (0 08)	0 88	11226 (56 60)
3000	4 66	58 0	29420 (98 1)	4 79	84 3 (0 29)	4 29	34 2 (0 12)	0 75	20123 (68 40)
4000	4 74	166	38340 (95 8)	4 51	172 5 (0 45)	4 40	68 5 (0 18)	0 74	23997 (62 59)
5000	3 77	446	45540 (91 1)	4 23	657 0 (1 44)	4 11	138 (0 30)	0 72	27100 (59 51)
Cu in presence of Cr									
0 82	7 63	0 096	7 23 (88 2)	7 35	0 062 (0 86)			1 32	0 81 (11 1)
66 5	7 18	0 23	662 6 (99 6)	7 10	1 91 (0 29)			1 22	167 5 (25 26)
450 3	6 65	0 39	4499 (99 9)	6 71	3 74 (0 08)			1 19	1569 2 (34 88)
738 9	5 14	2 25	7366 (99 7)	6 20	9 19 (0 13)			1 15	3888 5 (52 79)
1920	3 36	271 4	16482 (85 7)	3 53	378 8 (2 30)			1 09	11108 (67 39)
3991	2 54	1878	21122 (52 9)	2 74	505 2 (2 39)			1 05	12132 (57 44)

Table 12/3 Equilibrium mass adsorption/desorption isotherms for Cu^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cu-Cl and binary systems (Cu+Cr)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L= 1 10,
Peat sample Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) - W9c (DR 55%) pH 6 21								
	Sorption			Desorption by distilled water, pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cu									
1	7 54	0 00	10 (100)	7 10	0 1 (1 00)	5 91	0 1 (1 00)	0 88	7 82 (78 20)
100	7 29	0 28	997 (99 7)	6 61	0 8 (0 08)	5 71	1 1 (0 11)	0 86	606 4 (60 82)
1000	6 30	2 80	9972 (99 7)	5 48	3 9 (0 04)	5 37	5 5 (0 06)	0 92	7063 (70 83)
2000	4 94	9 28	19907 (99 5)	4 68	17 1 (0 09)	4 53	22 0 (0 11)	0 89	13990 (70 28)
3000	4 84	32 0	29984 (99 9)	4 57	52 8 (0 18)	4 34	24 5 (0 08)	0 86	21077 (70 29)
4000	4 67	81 0	39190 (97 9)	4 44	120 (0 31)	4 41	42 5 (0 11)	0 85	23760 (60 63)
5000	4 44	261	47390 (94 8)	4 35	480 (1 01)	4 24	116 (0 25)	0 84	29100 (61 41)
Cu in presence of Cr									
0 82	6 68	0 027	7 93 (96 7)	7 45	0 013 (0 16)			1 24	0 46 (5 83)
66 5	6 56	0 24	662 4 (99 6)	7 20	2 21 (0 33)			1 22	130 89 (19 76)
450 3	6 21	0 53	4498 (99 9)	6 90	3 02 (0 07)			1 18	1257 2 (27 95)
738 9	5 10	2 07	7368 (99 7)	6 27	8 92 (0 12)			1 14	3168 8 (43 00)
1920	3 22	178 8	17408 (90 7)	3 70	685 2 (3 94)			1 10	9264 (53 22)
3991	2 52	2042	19486 (48 8)	2 94	588 4 (3 02)			1 08	11908 (61 11)

Table 13/1 Equilibrium mass adsorption/desorption isotherms for Cr^{3+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cr-Cl and binary systems (Cr+Cu)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^3, S/L= 1 10,
Peat sample Alder Peat Humus W1 (pH 6 45, DR 70%),

Sample	Peat Humus (Alder Peat) - W1 (DR 70%) pH 6 45								
	Sorption			Desorption by distilled water, pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cr									
1	6 95	0 00	10 (100)	7 43	0 00 (0 00)	6 97	0 1 (1 00)	0 98	4 65 (46 50)
100	7 57	0 06	999 (99 9)	6 78	0 2 (0 02)	6 32	0 5 (0 05)	0 95	89 04 (8 91)
1000	7 34	0 22	9998 (99 9)	6 19	0 5 (0 005)	5 92	0 8 (0 008)	0 93	798 9 (8 00)
2000	6 24	0 47	19995 (99 9)	5 52	0 9 (0 004)	5 11	0 9 (0 004)	0 86	1421 5 (7 11)
3000	4 78	1 16	29988 (99 9)	5 01	1 6 (0 005)	4 25	2 7 (0 009)	0 85	2049 3 (6 83)
4000	3 91	5 32	39947 (99 9)	4 67	2 9 (0 007)	3 68	4 1 (0 01)	0 94	2450 0 (6 13)
5000	3 11	260	47370 (94 7)	4 20	17 6 (0 04)	3 31	7 4 (0 02)	0 93	2988 0 (6 31)
Cr in presence Cu									
0 73	7 60	0 072	6 58 (90 1)	7 12	0 005 (0 04)			1 30	0 43 (6 47)
75 25	7 19	0 107	751 4 (99 9)	6 80	0 703 (0 09)			1 25	49 33 (6 56)
392	6 70	0 301	3916 (99 9)	6 66	7 67 (0 19)			1 21	237 1 (6 05)
760	6 01	0 474	7592 (99 9)	6 20	50 48 (0 66)			1 20	404 2 (5 32)
1978	3 56	12 54	19659 (99 4)	3 73	80 75 (0 41)			1 11	1032 (5 25)
4253	2 66	987 4	32660 (76 8)	2 99	144 1 (0 44)			1 06	2002 (6 07)

Table 13/2 Equilibrium mass adsorption/desorption isotherms for Cr^{3+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cr-Cl and binary systems (Cr+Cu)-Cl,
Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^3, S/L= 1 10,
Peat sample Brushwood Peat Humus W9b (pH 6,32, DR 55 %),

Sample	Peat Humus (Brushwood) - W9b (DR 55%) pH 6 32								
	Sorption			Desorption by distilled water, pH 6		Desorption distilled water pH 3 (adjusted)		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D	pH	D
				Cr					
1	7 87	0 00	10 (100)	6 63	0 00 (0 00)	6 53	0 00 (0 00)	0 94	5 09 (50 90)
100	7 76	0 16	998 (99 8)	6 53	1 1 (0 11)	6 18	0 6 (0 06)	0 92	165 2 (16 55)
1000	6 53	0 36	9996 (99 9)	5 46	1 4 (0 014)	5 42	1 3 (0 013)	0 78	1037 (10 37)
2000	5 92	0 72	19993 (99 9)	5 15	1 7 (0 008)	4 84	1 9 (0 009)	0 76	1749 (8 75)
3000	5 47	1 07	29990 (99 9)	4 40	2 1 (0 007)	4 29	3 4 (0 011)	0 85	2041 (6 81)
4000	4 43	6 40	39936 (99 8)	4 15	8 9 (0 022)	3 50	3 8 (0 009)	0 84	2417 (6 05)
5000	3 18	238	47620 (95 2)	4 12	33 0 (0 06)	3 41	10 6 (0 022)	0 83	2911 (6 11)
				Cr in presence of Cu					
0 73	7 63	0 035	6 95 (95 2)	7 35	0 027 (0 39)			1 32	0 51 (7 34)
75 25	7 18	0 095	751 6 (99 9)	7 10	1 78 (0 24)			1 22	72 84 (9 69)
392	6 65	0 306	3916 (99 9)	6 71	4 22 (0 11)			1 19	223 5 (5 71)
760	5 14	0 457	7592 (99 9)	6 20	13 13 (0 17)			1 15	404 8 (5 33)
1978	3 36	23 86	19545 (98 8)	3 53	44 22 (0 23)			1 09	1051 (5 37)
4253	2 54	1047 6	32058 (75 4)	2 74	55 34 (0 17)			1 05	2006 (6 88)

Table 13/3 Equilibrium mass adsorption/desorption isotherms for Cr^{3+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cr-Cl and binary systems (Cr+Cu)-Cl,

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^3, S/L= 1 10,
Peat sample Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) - W9c, (DR 55%), pH 6 21								
	Sorption			Desorption by distilled water, pH 6		Desorption by distilled water adjusted to pH 3		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D	pH	D
Cr									
1	7 65	0 00	10 (100)	6 77	0 00 (0 00)	6 63	0 00 (0 00)	0 91	3 45 (34 50)
100	7 53	0 08	999 (99 9)	6 64	0 2 (0 02)	6 30	0 2 (0 02)	0 89	109 4 (10 95)
1000	6 54	0 29	9997 (99 9)	5 65	0 7 (0 007)	5 43	0 7 (0 007)	0 87	638 8 (6 39)
2000	6 00	0 41	19996 (99 9)	5 39	0 8 (0 004)	4 83	1 0 (0 005)	0 85	1362 (6 81)
3000	4 98	0 80	29992 (99 9)	4 67	1 7 (0 006)	4 52	2 5 (0 008)	0 84	1851 (6 17)
4000	4 56	3 21	39968 (99 9)	4 11	2 4 (0 006)	3 69	4 5 (0 011)	0 83	2417 (6 05)
5000	3 22	62 0	49380 (98 8)	3 45	26 0 (0 05)	3 40	13 7 (0 03)	0 83	3150 (6 38)
Cr in presence of Cu									
0 73	6 68	0 010	7 20 (98 6)	7 45	0 039 (0 55)			1 24	0 42 (5 90)
75 25	6 56	0 163	750 9 (99 8)	7 20	1 10 (0 15)			1 22	44 89 (5 97)
392	6 21	0 417	3915 (99 9)	6 90	2 27 (0 06)			1 18	187 3 (4 78)
760	5 10	0 628	7591 (99 9)	6 27	4 12 (0 05)			1 14	315 6 (4 16)
1978	3 22	15 58	19628 (99 2)	3 70	38 84 (0 20)			1 10	776 8 (3 96)
4253	2 52	730	35234 (82 8)	2 94	186 4 (0 53)			1 08	2272 (6 45)

Table 14/1 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-SO_4^{2-} and binary systems (Zn+Cd)-SO_4^{2},

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^{3}, S/L= 1 10,
Peat samples Alder Peat Humus W1 (pH 6 45, DR 70%),

Sample	Peat Humus (Alder Peat) - W1, (DR 70%) pH 6 45						
	Sorption			Desorption by distilled water pH 6		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D
			Zn				
1	5 60	0 034	9 66 (96 6)	6 51	0 066 (0 68)	0 98	8 51 (88 09)
106 2	5 73	0 96	1052 6 (99 1)	6 49	4 91 (0 47)	0 95	676 3 (64 25)
492 8	5 96	4 49	4883 (99 1)	5 99	25 01 (0 51)	0 98	3181 (65 14)
997 4	5 85	26 82	9705 8 (97 3)	5 50	78 90 (0 81)	0 96	6810 (70 16)
2800	5 50	242 8	25572 (91 3)	5 55	816 2 (3 19)	0 93	15380 (60 14)
4394	5 21	673 2	37208 (84 7)	5 30	1397 6 (3 76)	0 98	32752 (88 02)
			Zn in presence by Cd				
1	6 26	0 06	9 40 (94 0)	6 18	0 00 (0 00)	1 04	8 49 (90 32)
99 5	5 79	0 49	989 7 (98 9)	6 34	2 54 (0 26)	1 03	518 8 (52 42)
497 7	5 69	8 67	4890 3 (98 2)	5 90	31 79 (0 65)	0 95	3175 2 (64 93)
1053	5 70	46 54	10065 (95 6)	5 52	166 1 (1 65)	1 00	6293 (62 53)
2650	5 54	389 9	22601 (85 3)	5 29	277 6 (1 23)	1 00	16030 (70 93)
5138	5 00	1588	35500 (69 1)	5 10	622 9 (1 75)	0 98	25848 (72 81)

Table 14/2 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-SO_4^{2-} and binary systems $(Zn+Cd)$-SO_4^{2},

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^3, S/L= 1 10,
Peat sample Brushwood Peat Humus W9b (pH 6,32, DR 55 %),

Sample	Peat Humus (Brushwood) - W9b, (DR 55%), pH 6 32						
	Sorption			Desorption by distilled water, pH 6		Desorption by 1% HCl	
Zn							
1	5 70	0 025	9 75 (97 5)	6 78	0 068 (0 69)	0 90	6 91 (70 87)
106 2	6 58	0 39	1058 8 (99 6)	6 55	6 78 (0 64)	0 92	652 2 (61 59)
492 8	5 36	5 38	4874 2 (98 9)	5 99	24 16 (0 49)	0 89	3039 5 (62 36)
997 4	5 87	27 85	9695 5 (97 2)	5 59	114 48 (1 18)	0 90	6588 (67 95)
2800	5 47	295 8	25041 (89 4)	5 58	894 2 (3 37)	0 81	14264 (56 96)
4394	5 18	757 0	36370 (82 8)	5 30	1706 4 (4 69)	0 80	28176 (77 47)
Zn in presence of Cd							
1	6 38	0 046	9 50 (95 0)	6 69	0 00 (0 00)	1 04	8 16 (85 89)
99 5	6 14	0 62	988 4 (99 4)	6 40	2 17 (0 22)	0 99	669 5 (67 74)
497 7	5 81	10 11	4875 9 (97 9)	5 68	40 19 (0 82)	1 00	3142 (64 44)
1053	5 70	51 65	10014 (95 1)	5 35	202 6 (2 02)	0 95	6897 (68 88)
2650	5 20	322 85	23272 (87 8)	5 30	1227 2 (5 27)	0 91	14238 (61 18)
5138	4 91	1589	35484 (69 1)	5 04	2702 32 (7 61)	0 88	26608 (74 98)

Table 14/3 Equilibrium mass adsorption/desorption isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Zn-SO_4^{2-} and binary systems (Zn+Cd)-SO_4^{2},

Batch experiments, Input solution pH 4 0, c_0 = 1 - 5000 mg Me dm^{3}, S/L= 1 10,
Peat sample Rush (Reed-Sedge)Peat W9c,(pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) - W9c, (DR 55%), pH 6 21						
	Sorption			Desorption by distilled water pH 6		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D
Zn							
1	5 98	0 067	9 33 (93 3)	6 16	0 00 (0 00)	0 88	5 87 (62 91)
106 2	5 70	1 004	1052 2 (99 1)	6 15	5 12 (0 49)	0 94	586 9 (55 78)
492 8	6 004	5 28	4875 2 (98 9)	5 40	20 44 (0 42)	0 90	2956 5 (60 64)
997 4	5 70	31 54	9658 6 (96 8)	5 18	121 11 (1 16)	0 88	5524 (57 19)
2800	5 25	341 65	24584 (87 8)	5 40	504 4 (2 05)	0 90	14194 (57 74)
4394	5 10	767 6	36264 (82 5)	5 17	1414 (3 89)	0 86	25096 (69 20)
Zn in presence of Cd							
1	5 96	0 052	9 48 (94 8)	6 56	0 00 (0 00)	1 00	5 12 (54 01)
99 5	5 84	0 54	989 2 (99 5)	5 90	2 93 (0 29)	0 98	415 9 (42 04)
497 7	5 72	10 05	4876 5 (97 9)	5 34	38 60 (0 79)	0 97	2785 2 (57 11)
1053	5 63	64 2	9888 (93 9)	5 10	236 6 (2 39)	0 95	5118 (51 76)
2650	5 19	399 2	22508 (84 9)	5 16	718 5 (3 19)	1 00	13062 (58 03)
5138	4 80	1460	36776 (71 6)	4 92	963 4 (2 62)	0 94	21456 (58 34)

Table 15/1 Equilibrium mass adsorption/desorption isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cd-SO_4^2 and binary systems (Cd+Zn)-SO_4^2,

Batch experiments, Input solution Me-SO_4^2, pH 4 0, c_0 = 1 - 5000 mg Me dm^3, S/L= 1 10, Peat sample Alder Peat Humus W1 (pH 6 45, DR 70%),

Sample	Peat Humus (Alder Peat) - W1 (DR 70%) pH 6 45						
	Sorption			Desorption by distilled water pH 6		Desorption by 1% HCl	
C_0	pH	C_{eq}	S	pH	D	pH	D
Cd							
1	6 31	0 07	9 30 (93 0)	6 46	0 09 (0 96)	0 98	8 61 (92 47)
90 2	6 23	0 39	898 1 (99 6)	6 12	1 21 (0 13)	0 95	756 6 (84 24)
462 4	6 18	1 66	4607 4 (99 6)	6 10	10 9 (0 24)	0 98	3844 (83 43)
1075	6 17	5 99	10690 (99 4)	5 69	26 17 (0 25)	0 94	7282 (68 12)
2546 5	6 00	61 89	24846 (97 6)	5 90	156 0 (0 68)	0 93	18612 (74 91)
4835 5	5 70	207	46285 (95 7)	5 60	1366 4 (2 95)	0 90	33126 (71 56)
Cd in presence of Zn							
1 00	6 18	0 04	9 60 (96 0)	6 18	0 09 (0 94)	1 04	8 93 (03 02)
102	6 34	0 44	1015 6 (99 6)	6 34	2 23 (0 22)	1 03	695 1 (68 44)
500 2	5 90	4 41	4957 9 (99 1)	5 90	15 12 (0 31)	0 95	3333 (67 23)
1088	5 52	26 1	10619 (97 6)	5 52	78 97 (0 74)	1 00	7964 (74 99)
2256	5 29	111 2	21443 (95 05	5 29	692 5 (3 23)	1 00	16944 (79 02)
4645	5 10	808 5	38365 (82 6)	5 10	2424 (6 32)	0 98	30588 (79 73)

Table 15/2 Equilibrium mass adsorption/desorption isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cd-SO_4^{2} and binary systems (Cd+Zn)-SO_4^{2-},

Batch experiments, Input solution Me-SO_4^{2}, pH 4 0, c_0 = 1 - 5000 mg Me dm^3, S/L= 1 10,
Peat samples Brushwood Peat Humus W9b (pH 6,32, DR 55 %),

Sample	Peat Humus (Brushwood) - W9b, (DR 55%), pH 6 32						
	Sorption			Desorption by distilled water, pH 6		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D
Cd							
1	6 98	0 03	9 70 (97 0)	6 70	0 081 (0 85)	0 98	7 17 (73 92)
90 2	6 30	0 29	899 1 (99 7)	6 61	1 67 (0 18)	0 97	689 8 (76 72)
462 4	6 41	2 62	4597 8 (99 4)	5 83	8 81 (0 19)	0 95	3589 (78 06)
1075	6 25	7 49	10675 (99 3)	5 73	26 66 (0 25)	0 93	8008 (75 02)
2546 5	6 00	85 36	24611 (96 6)	5 55	201 1 (0 82)	0 88	16232 (65 95)
4835 5	5 57	332 6	45029 (93 1)	5 25	1794 6 (3 98)	0 81	36408 (80 85)
Cd in presence of Zn							
1 00	6 38	0 026	9 74 (97 4)	6 69	0 051 (0 52)	1 04	9 02 (92 61)
102	6 14	0 63	1013 7 (99 4)	6 40	2 14 (0 21)	0 99	708 0 (69 84)
500 2	5 81	4 00	4962 0 (99 2)	5 68	21 32 (0 43)	1 00	3355 (67 61)
1088	5 70	25 6	10624 (97 6)	5 35	110 9 (1 04)	0 95	8470 (79 73)
2256	5 20	142 7	21133 (93 7)	5 30	428 1 (2 02)	0 91	18792 (88 92)
4645	4 91	1175	34700 (74 7)	5 04	1706 4 (4 92)	0 88	26668 (76 85)

Table 15/3 Equilibrium mass adsorption/desorption isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH of equilibrated solutions in mono-metal Cd-SO_4^{2} and binary systems (Cd+Zn)-SO_4^{2},

Batch experiments, Input solution Me-SO_4^{2}, pH 4 0, c_0 = 1 - 5000 mg Me dm^{3}, S/L= 1 10, Peat sample Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

Sample	Rush Peat (Reed-Sedge Peat) - W9c, (DR 55%)						
	Sorption			Desorption by distilled water pH 6		Desorption by 1% HCl	
C_o	pH	C_{eq}	S	pH	D	pH	D
Cd							
1	6 70	0 017	9 83 (98 3)	6 45	0 084 (0 85)	0 90	7 50 (76 29)
90 2	6 44	0 27	899 3 (99 7)	5 60	1 11 (0 12)	0 97	524 6 (58 33)
462 4	6 30	1 69	4607 1 (99 6)	5 24	10 94 (0 24)	0 95	3239 5 (70 31)
1075	6 14	6 02	10405 (99 4)	5 20	36 62 (0 35)	0 88	6658 (63 99)
2546 5	5 83	79 56	24669 (96 9)	5 80	249 3 (1 01)	0 94	15480 (62 75)
4835 5	5 38	246 6	45889 (94 9)	5 40	1856 (4 04)	0 83	29352 (63 96)
Cd in presence of Zn							
1 00	5 96	0 02	9 80 (98 0)	6 56	0 06 (0 63)	1 00	6 44 (65 71)
102	5 84	0 34	1016 6 (99 7)	5 90	1 96 (0 19)	0 98	632 1 (62 18)
500 2	5 72	4 75	4955 (99 1)	5 34	21 39 (0 23)	0 99	2794 (56 38)
1088	5 63	25 12	10629 (97 7)	5 10	129 41 (1 22)	0 96	7220 (67 93)
2256	5 19	105 7	21503 (95 3)	5 16	322 58 (1 50)	0 91	20104 (93 49)
4645	4 80	718 9	39261 (84 5)	4 92	672 6 (1 71)	0 87	29892 (76 14)

Table 16 Effect of Zn^{2+} and Cd^{2+} ion competition for sorption sites in low-moor peat (Peat Humus and Rush Reed-Sedge Peat) and pH changes of equilibrated solutions in mono-metal Zn-Cl , Cd-Cl and binary systems (Cd+Zn)-Cl,

Batch experiments, Input solution Me-Cl , pH 4 0, c_0 = 1 - 5000 mgMe dm^3, S/L= 1 10 ,

Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

No	Substrat	pH	Zn Added ppm	Cd Added ppm	Zn Adsorbed $\mu g/g$ (%)	Cd Adsorbed $\mu g/g$ (%)
1	Alder Peat Humus	6 15	1 00	1 00	9 75 (97 5)	9 76 (97 6)
2	Alder Peat Humus	6 36	99 50	100	985 1 (99 0)	996 8 (99 7)
3	Alder Peat Humus	6 00	435 0	463 1	4182 (96 2)	4576 (98 8)
4	Alder Peat Humus	5 70	1005	1242 5	8951 (89 1)	10723 (86 3)
5	Alder Peat Humus	5 16	2971	2860	23905 (80 5)	22156 (77 5)
6	Alder Peat Humus	4 75	4620	4644	26214 (56 7)	24340 (52 4)
7	Alder Peat Humus	7 50	1	0	9 70 (97 0)	
8	Alder Peat Humus	7 63	100	0	985 0 (98 5)	
9	Alder Peat Humus	6 78	1000	0	8900 (89 0)	
10	Alder Peat Humus	6 25	2000	0	15960 (79 8)	
11	Alder Peat Humus	5 69	3000	0	22700 (75 7)	
12	Alder Peat Humus	5 59	4000	0	27900 (69 7)	
13	Alder Peat Humus	5 15	5000	0	32500 (65 0)	
14	Alder Peat Humus	7 95	0	1		10 0 (100)
15	Alder Peat Humus	7 61	0	100		994 (99 4)
16	Alder Peat Humus	6 55	0	1000		9886 (98 7)
17	Alder Peat Humus	6 16	0	2000		19040 (95 2)
18	Alder Peat Humus	6 72	0	3000		26620 (88 7)
19	Alder Peat Humus	6 11	0	4000		33210 (83 0)
20	Alder Peat Humus	6 01	0	5000		35100 (70 2)
1	Brushwood Peat Humus	6 50	1 00	1 00	9 67 (96 7)	9 98 (99 8)
2	Brushwood Peat Humus	6 28	99 50	100 0	985 4 (99 0)	996 7 (99 7)
3	Brushwood Peat Humus	6 00	435 0	463 1	4202 (96 6)	4556 (98 4)
4	Brushwood Peat Humus	5 68	1005	1242 5	9128 (90 8)	11950 (96 2)
5	Brushwood Peat Humus	5 15	2971	2860	23837 (83 6)	22226 (77 7)
6	Brushwood Peat Humus	4 75	4620	4644	28390 (61 4)	27004 (58 2)
7	Brushwood Peat Humus	7 55	1	0	9 70 (97 0)	
8	Brushwood Peat Humus	7 50	100	0	995 (99 5)	
9	Brushwood Peat Humus	6 42	1000	0	9898 (98 9)	
10	Brushwood Peat Humus	6 52	2000	0	17520 (87 6)	
11	Brushwood Peat Humus	5 35	3000	0	23200 (77 3)	
12	Brushwood Peat Humus	5 58	4000	0	28950 (72 4)	
13	Brushwood Peat Humus	5 15	5000	0	32050 (64 1)	

No	Substrat	pH	Zn Added ppm	Cd Added ppm	Zn Adsorbed μg/g (%)	Cd Adsorbed μg/g (%)
14	Brushwood Peat Humus	7 96	0	1		10 0 (100)
15	Brushwood Peat Humus	7 24	0	100		994 (99 4)
16	Brushwood Peat Humus	6 80	0	1000		9894 (98 9)
17	Brushwood Peat Humus	6 53	0	2000		18940 (94 7)
18	Brushwood Peat Humus	6 50	0	3000		25430 (84 8)
19	Brushwood Peat Humus	5 66	0	4000		31000 (77 5)
20	Brushwood Peat Humus	5 01	0	5000		33200 (66 4)
1	Rush (Reed-Sedge) Peat	5 46	1 00	1 00	9 63 (96 3)	9 84 (98 4)
2	Rush (Reed-Sedge) Peat	5 70	99 50	100 0	986 7 (99 2)	997 5 (99 8)
3	Rush (Reed-Sedge) Peat	5 67	435 0	463 1	4165 2 (95 7)	4576 (98 8)
4	Rush (Reed-Sedge) Peat	5 47	1005	1242 5	8812 (87 7)	11883 (95 6)
5	Rush (Reed-Sedge) Peat	4 95	2971	2860	23869 (80 3)	22443 (78 5)
6	Rush (Reed-Sedge) Peat	4 69	4620	4644	25480 (55 2)	25504 (54 9)
7	Rush (Reed-Sedge) Peat	7 72	1	0	10 0 (100)	
8	Rush (Reed-Sedge) Peat	7 42	100	0	997 (99 7)	
9	Rush (Reed-Sedge) Peat	6 43	1000	0	9440 (94 4)	
10	Rush (Reed-Sedge) Peat	6 20	2000	0	18220 (91 1)	
11	Rush (Reed-Sedge) Peat	5 32	3000	0	26400 (88 0)	
12	Rush (Reed-Sedge) Peat	5 65	4000	0	29600 (74 0)	
13	Rush (Reed-Sedge) Peat	5 16	5000	0	32700 (65 4)	
14	Rush (Reed-Sedge) Peat	7 42	0	1		10 0 (100)
15	Rush (Reed-Sedge) Peat	6 10	0	100		997 (99 7)
16	Rush (Reed-Sedge) Peat	5 94	0	1000		9874 (98 4)
17	Rush (Reed-Sedge) Peat	5 98	0	2000		18925 (94 6)
18	Rush (Reed-Sedge) Peat	5 67	0	3000		26990 (90 0)
19	Rush (Reed-Sedge) Peat	5 35	0	4000		33040 (82 6)
20	Rush (Reed-Sedge) Peat	5 30	0	5000		37520 (75 0)

Table 17 Effect of Zn^{2+} and Cd^{2+} ion competition for sorption sites in low-moor peats (Peat Humus and Rush Reed-Sedge Peat) and pH changes of equilibrated solutions in mono-metal Zn-SO_4^{2} and binary systems (Cd+Zn)-SO_4^{2} ,

Batch experiments, Input solution Me-SO_4^{2-}, pH 4 0, c_0 = 1 - 5000 mgMe dm^{3}, S/L= 1 10, Peat samples (1) Alder Peat Humus W1 (pH 6 45, DR 70%), (2) Brushwood Peat Humus W9b (pH 6,32, DR 55 %), (3) Rush (Reed-Sedge) Peat W9c,(pH 6 21, DR 55 %)

No	Substrate	pH	Added Zn ppm	Added Cd ppm	Adsorbed Zn μg/g (%)	Adsorbed Cd μg/g (%)
1	Alder Peat Humus	6 26	1 00	1 00	9 40 (94 0)	9 60 (96 0)
2	Alder Peat Humus	5 79	99 46	102	989 7 (98 9)	1016 (99 6)
3	Alder Peat Humus	5 69	497 7	500 2	4890 (98 2)	4958 (99 1)
4	Alder Peat Humus	5 70	1053	1088	10065 (95 6)	10619 (97 6)
5	Alder Peat Humus	5 54	2650	2256	22601 (85 3)	21443 (95 1)
6	Alder Peat Humus	5 00	5138	4645	35500 (69 1)	38365 (82 6)
7	Alder Peat Humus	5 78	1 00	0	9 66 (96 6)	
8	Alder Peat Humus	5 88	106 2	0	1053 (99 1)	
9	Alder Peat Humus	5 96	492 8	0	4883 (99 1)	
10	Alder Peat Humus	5 85	997 4	0	9706 (97 3)	
11	Alder Peat Humus	5 50	2800	0	25572 (91 3)	
12	Alder Peat Humus	5 21	4394	0	37208 (84 7)	
13	Alder Peat Humus	6 31	0	1 00		9 30 (93 0)
14	Alder Peat Humus	6 23	0	90 2		898 (99 6)
15	Alder Peat Humus	6 18	0	462 4		4607 (99 6)
16	Alder Peat Humus	6 17	0	1075		10690 (99 4)
17	Alder Peat Humus	6 00	0	2547		24846 (97 6)
18	Alder Peat Humus	5 70	0	4836		46285 (95 7)
1	Brushwood Peat Humus	6 38	1 00	1 00	9 50 (95 0)	9 74 (97 4)
2	Brushwood Peat Humus	6 14	99 46	102	988 4 (99 4)	1014 (99 4)
3	Brushwood Peat Humus	5 81	497 7	500 2	4876 (97 9)	4962 (99 2)
4	Brushwood Peat Humus	5 70	1053	1088	10014 (95 1)	10624 (97 6)
5	Brushwood Peat Humus	5 20	2650	2256	23272 (87 9)	21133 (93 7)
6	Brushwood Peat Humus	4 91	5138	4645	35484 (69 1)	34700 (74 7)
7	Brushwood Peat HumusÑ	6 70	1 00	0	9 75 (97 5)	
8	Brushwood Peat Humus	6 58	106 2	0	1059 (99 6)	
9	Brushwood Peat Humus	5 96	492 8	0	4874 (98 9)	
10	Brushwood Peat Humus	5 87	997 4	0	9696 (97 2)	
11	Brushwood Peat Humus	5 47	2800	0	25041 (89 4)	
12	Brushwood Peat Humus	5 18	4394	0	36370 (82 8)	
13	Brushwood Peat Humus	6 98	0	1 00		9 70 (97 0)
14	Brushwood Peat Humus	6 30	0	90 2		899 1 (99 7)
15	Brushwood Peat Humus	6 41	0	462 4		4598 (99 4)
16	Brushwood Peat Humus	6 25	0	1075		10675 (99 3)
17	Brushwood Peat Humus	6 00	0	2546 5		24611 (96 6)
18	Brushwood Peat Humus	5 57	0	4835 5		45029 (93 1)

No	Substrate	pH	Added Zn ppm	Added Cd ppm	Adsorbed Zn μg/g (%)	Adsorbed Cd μg/g (%)
1	Rush (Reed-Sedge) Peat	5 96	1 00	1 00	9 48 (94 8)	9 80 (98 0)
2	Rush (Reed-Sedge) Peat	5 84	99 46	102 0	989 2 (99 5)	101 7 (99 7)
3	Rush (Reed-Sedge) Peat	5 72	497 7	500 2	4876 5 (97 9)	4954 5 (99 1)
4	Rush (Reed-Sedge) Peat	5 63	1053	1088	9888 (93 9)	10629 (97 7)
5	Rush (Reed-Sedge) Peat	5 19	2650	2256	22508 (84 9)	21503 (95 3)
6	Rush (Reed-Sedge) Peat	4 80	5138	4645	36776 (71 6)	39261 (84 5)
7	Rush (Reed-Sedge) Peat	5 98	1 00	0	9 33 (93 3)	
8	Rush (Reed-Sedge) Peat	5 91	106 2	0	1052 (99 1)	
9	Rush (Reed-Sedge) Peat	6 04	492 8	0	4845 (98 9)	
10	Rush (Reed-Sedge) Peat	5 70	997 4	0	9659 (96 3)	
11	Rush (Reed-Sedge) Peat	5 25	2800	0	24583 (87 8)	
12	Rush (Reed-Sedge) Peat	5 10	4394	0	36264 (82 5)	
13	Rush (Reed-Sedge) Peat	5 99	0	1 00		9 83 (98 3)
14	Rush (Reed-Sedge) Peat	6 44	0	90 2		899 3 (99 7)
15	Rush (Reed-Sedge) Peat	6 30	0	462 4		4607 (99 6)
16	Rush (Reed-Sedge) Peat	6 14	0	1046 5		10405 (99 4)
17	Rush (Reed-Sedge) Peat	5 83	0	2546 5		24669 (96 9)
18	Rush (Reed-Sedge) Peat	5 38	0	4835 5		45889 (94 9)

Table 18 Sequential fractionation of Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} ions sorbed from Me-Cl solution under batch conditions, at c_0 = 5000 mg Me dm^3 and pH 4 0 onto low-moor peat

Peat samples Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge)Peat (W9c),
Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

SAMPLE Alder Peat Humus W1 (DR 70%), INPUT CONCENTRATION c_o = 5000 mg/dm^3					
		Cr	Cu	Cd	Zn
SORPTION mg/kg		47370	47150	35100	32500
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	17 6 (0 04)	452 (0 96)	2271 (6 5)	2855 (8 8)
Most labile	F1 (EXC)	4943 (10 4)	20498 (43 5)	18265 (52 04)	16280 (50 1)
Labile	F2 (CARB)	1900 (4 0)	7640 (16 2)	9100 (25 9)	7120 (21 9)
Easily reducible	F3 (ERO)	171 (0 4)	580 (1 2)	700 (2 0)	410 (1 3)
Moderately reducible	F4 (MRO)	7200 (15 2)	17500 (37 1)	1200 (3 4)	3390 (10 4)
Strongly bound	F5 (OM)	28200 (59 5)	480 (1 0)	3564 (10 2)	2445 (7 52
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)
SAMPLE Brushwood Peat Humus W9b (DR 55%), INPUT CONCENTRATION c_o = 5000 mg/dm^3					
		Cr	Cu	Cd	Zn
SORPTION mg/kg		47620	45540	33200	32050
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	33 0 (0 07)	657 (1 44)	954 (2 87)	2631 (8 21)
Most labile	F1 (EXC)	5083 (10 67)	13153 (28 88)	16796 (50 59)	13759 (42 93)
Labile	F2 (CARB)	2268 (4 77)	5770 (12 67)	10200 (30 72)	6208 (19 37)
Easily reducible	F3 (ERO)	157 2 (3 30)	440 (0 97)	1808 (5 45)	1212 (3 78)
Moderately reducible	F4 (MRO)	11025 (23 15)	9864 (21 66)	2180 (6 57)	5200 (16 22)
Strongly bound	F5 (OM)	27636 (58 03)	15656 (34 38)	1262 (3 80)	3040 (9 49)
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)

SAMPLE Rush (Reed-Sedge) Peat W9c (DR 55%), INPUT CONCENTRATION c_o = 5000 mg/dm^3					
		Cr	Cu	Cd	Zn
SORPTION mg/kg		49380	47390	37520	32700
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	26 0 (0 05)	480 (1 01)	1904 (5 07)	1360 (4 16)
Most labile	F1 (EXC)	4150 (8 40)	12868 (27 15)	15116 (40 3)	14460 (44 20)
Labile	F2 (CARB)	2680 (5 43)	6012 (12 69)	12580 (33 53)	9538 (29 17)
Easily reducible	F3 (ERO)	1540 (3 12)	660 (1 39)	2328 (6 21)	1812 (5 54)
Moderately reducible	F4 (MRO)	13980 (28 31)	13020 (27 47)	2450 (6 53)	4320 (13 21)
Strongly bound	F5 (OM)	27004 (54 69)	14350 (30 28)	3142 (8 37)	1210 (3 70)
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)

Table 19 Effect of Zn^{2+} and Cd^{2+} ion competition for sorption sites in pretreated low-moor peats (Peat Humus and Rush Reed-Sedge Peat) at fixed pH 5 5 in mono-metal Zn-SO_4^2 and binary systems (Cd+Zn)-SO_4^2,

Batch experiments, Input solution Me-SO_4^2, pH 5 5, c_0 = 1 - 600 mg Me dm^3, S/L= 1 25, Peat samples adjusted to pH 5 5 (1) Alder Peat Humus W1, (2) Brushwood Peat Humus W9b, (3) Rush (Reed-Sedge) Peat W9c,

No	Substrat	pH	Added Zn ppm	Added Cd ppm	Adsorbed Zn µg/g (%)	Adsorbed Cd µg/g (%)
1	Alder Peat Humus	5 55	95 2	102 2	2292 5 (96 3)	2437 5 (95 4)
2	Alder Peat Humus	5 45	211 5	208	5005 (94 6)	5026 (96 2)
3	Alder Peat Humus	5 45	296 5	314	6768 (91 3)	7412 (94 4)
4	Alder Peat Humus	5 40	418	423	9445 (90 4)	9780 (92 5)
5	Alder Peat Humus	5 38	501	509	10830 (86 5)	11572 (90 9)
6	Alder Peat Humus	5 35	598	598	12360 (82 7)	12850 (85 9)
7	Alder Peat Humus	5 55	94 8	0	2295 2 (96 8)	-<0 12
8	Alder Peat Humus	5 51	198 2	0	4080 (96 9)	-<0 12
9	Alder Peat Humus	5 50	299 5	0	7079 5 (94 6)	-0 25
10	Alder Peat Humus	5 46	420	0	9798 (93 3)	-0 25
11	Alder Peat Humus	5 40	492	0	11338 (92 2)	-0 25
12	Alder Peat Humus	5 38	608	0	13560 (89 2)	-2 25
13	Alder Peat Humus	5 66	0	98	-<0 12	2382 5 (97 2)
14	Alder Peat Humus	5 60	0	207	-<0 12	5044 (97 5)
15	Alder Peat Humus	5 55	0	308	-<0 12	7432 (96 5)
16	Alder Peat Humus	5 49	0	429	-<0 12	10348 (96 5)
17	Alder Peat Humus	5 45	0	496	-<0 12	11815 (95 3)
18	Alder Peat Humus	5 45	0	595	-<0 12	13970 (93 9)
1	Brushwood Peat Humus	5 80	95 2	102 2	2304 7 (96 8)	2506 2 (98 1)
2	Brushwood Peat Humus	5 51	211 5	208	4994 (94 4)	4997 (96 1)
3	Brushwood Peat Humus	5 44	296 5	314	6824 5 (92 1)	7444 (94 8)
4	Brushwood Peat Humus	5 40	418	423	9315 (89 1)	9770 (92 4)
5	Brushwood Peat Humus	5 38	501	509	11240 (89 7)	11440 (89 9)
6	Brushwood Peat Humus	5 38	598	598	12310 (82 3)	12895 (86 2)
7	Brushwood Peat Humus	5 62	94 8	0	2278 7 (96 1)	-<0 12
8	Brushwood Peat Humus	5 51	198 2	0	4622 (95 7)	-0 25
9	Brushwood Peat Humus	5 60	299 5	0	7131 5 (95 2)	-0 25
10	Brushwood Peat Humus	5 48	420	0	9945 (94 7)	-0 25
11	Brushwood Peat Humus	5 40	492	0	11585 (94 1)	-<0 12
12	Brushwood Peat Humus	5 38	608	0	12485 (88 7)	-2 25
13	Brushwood Peat Humus	5 55	0	98	-<0 12	2390 5 (97 6)
14	Brushwood Peat Humus	5 46	0	207	-<0 12	5013 (96 9)
15	Brushwood Peat Humus	5 45	0	308	-<0 12	7395 (96 3)
16	Brushwood Peat Humus	5 46	0	429	<0 12	10336 (96 4)
17	Brushwood Peat Humus	5 45	0	496	-<0 12	11863 (95 7)
18	Brushwood Peat Humus	5 35	0	595	-<0 12	13940 (93 7)

No	Substrat	pH	Added Zn ppm	Added Cd ppm	Adsorbed Zn µg/g (%)	Adsorbed Cd µg/g (%)
1	Rush (Reed-Sedge) Peat	5 26	95 2	102 2	2151 5 (90 4)	2326 5 (91 1)
2	Rush (Reed-Sedge) Peat	5 35	211 5	208	4655 (88 0)	4467 (85 9)
3	Rush (Reed-Sedge) Peat	5 35	296 5	314	5795 (78 2)	6232 5 (79 4)
4	Rush (Reed-Sedge) Peat	5 20	418 0	423	8060 (77 1)	8455 (79 9)
5	Rush (Reed-Sedge) Peat	5 25	501	509	93 85 (74 9)	10030 (78 8)
6	Rush (Reed-Sedge) Peat	5 30	598	598	8800 (58 9)	10140 (67 8)
7	Rush (Reed-Sedge) Peat	5 44	94 8	0	2246 7 (94 8)	-<0 12
8	Rush (Reed-Sedge) Peat	5 36	198 2	0	4514 (93 5)	-<0 12
9	Rush (Reed-Sedge) Peat	5 45	299 5	0	6790 (90 7)	-1 00
10	Rush (Reed-Sedge) Peat	5 40	420	0	94775 (90 2)	-0 50
11	Rush (Reed-Sedge) Peat	5 38	492	0	10895 (88 6)	-0 25
12	Rush (Reed-Sedge) Peat	5 35	608	0	12925 (85 0)	-2 75
13	Rush (Reed-Sedge) Peat	5 50	0	98	-<0 12	2385 2 (97 4)
14	Rush (Reed-Sedge) Peat	5 48	0	207	-<0 12	4972 (96 1)
15	Rush (Reed-Sedge) Peat	5 46	0	308	-<0 12	7296 (95 1)
16	Rush (Reed-Sedge) Peat	5 44	0	429	-<0 12	10216 (95 1)
17	Rush (Reed-Sedge) Peat	5 52	0	496	-<0 12	11700 (94 3)
18	Rush (Reed-Sedge) Peat	5 44	0	595	-<0 12	13800 (92 77)

Table 20 Sequential fractionation of Zn^{2+} and Cd^{2+} ions sorbed from $Me\text{-}SO_4$ solution in mono-metal and binary system onto pretreated low-moor peat at fixed pH 5 5,

Batch experiments, $c_0 = 600$ mg Me dm^3, pH 5 5, S/L=1 25,
Peat samples adjusted to pH 5 5 Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge)Peat (W9c)
Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

SAMPLE Alder Peat Humus W1 (DR 70%), INPUT CONCENTRATION c_0 = 600 mg/dm^3					
		Zn without Cd	Cd without Zn	Zn with Cd	Cd with Zn
SORPTION mg/kg		13560	13970	12360	12850
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	56 2 (0 41)	27 8 (0 20)	120 8 (0 98)	65 0 (0 52)
Most labile	F1 (EXC)	2720 (20 06)	3830 (27 42)	2592 (20 97)	3552 (27 64)
Labile	F2 (CARB)	4740 (34 96)	5160 (36 94)	3928 (31 78)	4624 (35 98)
Easily reducible	F3 (ERO)	424 (3 13)	538 (3 85)	393 (3 18)	476 (3 70)
Moderately reducible	F4 (MRO)	5100 (37 61)	910 (6 51)	4290 (34 71)	675 (5 25)
Strongly bound	F5 (OM)	519 8 (3 83)	3504 2 (25 08)	1036 2 (8 38)	3458 (26 91)
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)

SAMPLE Brushwood Peat Humus W9b (DR 55%), INPUT CONCENTRATION c_0 = 600 mg/dm^3					
		Zn without Cd	Cd without Zn	Zn with Cd	Cd with Zn
SORPTION mg/kg		13485	13940	12310	12895
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	65 0 (0 48)	23 4 (0 17)	110 4 (0 90)	55 0 (0 43)
Most labile	F1 (EXC)	3462 (25 67)	4383 4 (31 44)	2870 (23 31)	3704 (28 72)
Labile	F2 (CARB)	4190 (31 07)	4752 (34 08)	3870 (31 44)	4472 (34 68)
Easily reducible	F3 (ERO)	416 8 (3 09)	532 (3 82)	449 (3 65)	620 (4 81)
Moderately reducible	F4 (MRO)	4785 (35 48)	820 (5 88)	4315 (35 05)	750 (5 82)
Strongly bound	F5 (OM)	566 2 (4 20)	3429 2 (24 60)	695 6 (5 65)	3293 8 (25 54)
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)

Sample Rush (Reed-Sedge)Peat W9c (DR 55%), INPUT CONCENTRATION c_o = 600 mg/dm^3					
SORPTION mg/kg		12925	13800	8800	10140
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	152 4	23 9	290 0	165 9
		(1 18)	(0 18)	(3 29)	(1 64)
Most labile	F1 (EXC)	3685	5000	2960	4064
		(28 5)	(36 23)	(33 64)	(40 08)
Labile	F2 (CARB)	4080	4768	2570	3248
		(31 57)	(34 55)	(29 20)	(32 03)
Easily reducible	F3 (ERO)	444	514	284	334
		(3 43)	(3 72)	(3 23)	(3 29)
Moderately reducible	F4 (MRO)	3965	930	2040	555
		(30 68)	(6 74)	(23 18)	(5 47)
Strongly bound	F5 (OM)	598 6	2564 1	656	1773 1
		(4 63)	(18 58)	(7 45)	(17 49)
Residual fraction	F6 (R)	0 0	0 0	0 0	0 0
		(0 0)	(0 0)	(0 0)	(0 0)

Table 21 Sorption of Zn^{2+} on Brushwood Peat Humus from the mono-metal Zn-SO_4 solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Zn/dm^3 (2) c_0 = 250 mg Zn/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9b, mass 90 g , water retention capacity S/L = 1 2

	C_o 500mg Zn/dm^3 pH 4				C_o 250mgZn/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	6 98	124	<0 001	1020	7 28	121	<0 001	540
2	7 40	713	<0 001	2040	6 95	626	<0 001	1080
3	6 71	1194	<0 001	3060	6 60	753	<0 001	1620
4	6 54	1205	<0 001	4080	6 35	758	<0 001	2160
5	6 41	1240	<0 001	5100	6 36	750	<0 001	2700
6	6 23	1208	<0 001	6120	6 23	751	<0 001	3210
7	6 01	1246	<0 001	7140	6 19	748	<0 001	3780
8	6 26	1248	<0 001	8160	6 60	784	<0 001	4320
9	6 20	1242	<0 001	9180	6 53	765	<0 001	4860
10	6 03	1237	<0 001	10200	6 55	752	<0 001	5400
11	6 25	1189	<0 001	11220	6 42	747	<0 001	5940
12	6 06	1239	<0 001	12240	6 14	749	<0 001	6480
13	6 00	1259	<0 001	13260	6 22	753	<0 001	7020
14	5 68	1255	<0 001	14280	6 80	780	<0 001	7560
15	6 07	1258	<0 001	15300	6 60	762	<0 001	8100
16	6 21	1282	<0 001	16320	7 05	804	<0 001	8750
17	6 09	1242	<0 001	17340	6 97	757	<0 001	9400
18	6 12	1260	<0 001	18360	6 60	721	<0 001	10050
19	6 48	1210	<0 001	19620	6 56	755	<0 001	10700
20	6 48	1212	<0 001	20880	6 40	803	<0 001	11350
21	5 94	1238	<0 001	22140	6 49	716	1 67	11998
22	6 08	1247	<0 001	23400	6 30	707	2 25	12646
23	6 19	1239	<0 001	24660	6 10	705	3 57	13293
24	6 19	1257	<0 001	25920	5 82	697	4 38	13939
25	5 68	1293	<0 001	27180	6 20	742	4 90	14584
26	5 71	1241	<0 001	28440	6 25	720	9 05	15224
27	5 67	1240	<0 001	29700	6 67	829	2 77	15868 5
28	6 11	1248	<0 001	30960	6 54	750	2 87	16512 8
29	6 36	1343	<0 001	32220	6 30	700	4 47	17153 9
30	6 06	1228	<0 001	33480	6 36	687	6 94	17790
31	5 89	1230	<0 001	34740	5 91	686	8 18	18423 6
32	5 66	1238	<0 001	36000	6 20	714	7 78	19058 0
33	5 48	1128	<0 001	37260	6 00	695	9 38	19689 2

	C_o 500mg Zn/dm^3, pH 4				C_o 250mgZn/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
34	5 43	1276	0 14	38520	6 29	696	10 57	20318 1
35	5 60	1388	0 62	39780	6 22	711	10 76	20946 6
36	6 18	1196	18 1	41003 8	6 24	725	3 38	21483 8
37	6 18	1204	33 3	42197 2	6 90	726	4 75	22018 3
38	5 92	1199	62 7	43331 8	6 42	690	7 64	22547 0
39	5 70	1143	91 3	44251 8	6 31	650	9 55	23071 9
40	4 95	1146	93 8	45165 6	5 90	634	10 45	23595 0
41	5 17	1146	91 3	46085	5 75	630	13 99	24111 0
42	4 66	1137	122	46943	5 83	638	17 38	24620 2
43	4 54	1115	181	47683	5 26	628	19 11	25125 9
44	4 20	1149	293	48199	4 44	635	22 2	25625 5
45	4 41	1250	225	48851	4 75	632	21 6	26126 3
46	4 53	1203	251	49451	5 92	671	13 0	26644 3
47	4 49	1178	248	50057	6 17	658	16 0	27156 3
48	4 34	1209	311	50537	5 82	685	12 5	27675 3
49	4 44	1246	352	50935	5 10	656	16 5	28186 3
50	4 34	1166	310	51417	5 98	657	16 5	28697 3
51	4 45	1156	324	51871	5 33	669	22 5	29196 3
52	4 49	1184	353	52267	5 83	667	24 0	29692 3
53	4 45	1161	364	52641	5 29	704	26 0	30184 3
54	4 34	1166	347	53049	5 47	692	26 0	30676 3
55	4 36	1159	377	53397	5 65	691	25 0	31166 3
56	4 41	1341	211	54077	5 25	693	29 0	31652 3
57	4 87	1265	447	54285	5 51	699	32 4	32131 5
58	4 87	1197	271	54845	5 60	868	52 6	32570 4
59	4 70	1174	441	55065	5 16	776	63 5	32987 4
60	4 78	1161	475	55217	4 76	732	67 9	33395 6
61	4 65	1177	347	55624	4 96	725	74 1	33791 4
62	4 57	1152	498	55730	4 99	720	96 3	34142 8
63	4 56	1151	510	55730	5 14	720	85 8	34515 1
64	4 49	1146	510	55730	5 11	720	86 6	34885 9
65					4 90	723	97 2	35235 4
66					4 75	811	53 6	35672 3
67					5 34	732	54 9	36106 4
68					5 31	721	70 3	36509 8
69					4 85	753	71 4	36911 0
70					4 86	751	76 0	37303 0
71					4 68	746	72 5	37702 0
72					4 83	783	86 8	38072 4

	C_o 500mg Zn/dm^3, pH 4				C_o 250mgZn/dm^3, pH 4			
ER	pH	EC (µS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (µS/s)	C (mg/dm^3)	Load (mg/kg)
73					4 74	743	86 8	38442 8
74					4 60	744	99 0	38788 8
75					4 50	751	89 0	39154 8
76					4 71	787	98 0	39502 8
77					4 63	756	98 0	39850 8
78					4 70	737	94 0	40206 8
79					4 74	741	117 8	40511 2
80					4 94	748	107 7	40839 8
81					4 90	754	101 5	41180 8
82					4 60	759	104 7	41515 4
83					4 04	751	107	41845 4
84					4 46	755	110	42169 4
85					4 59	762	116	42481 4
86					4 40	766	121	42783 4
87					4 60	764	129	43069 4
88					4 63	768	133	43347 4
89					4 73	763	130	43631 4
90					4 75	759	135	43905 4
91					4 49	756	136	44177 4
92					4 50	754	140	44441 4
93					4 50	751	133	44719 4
94					4 50	758	141 5	44980 4
95					4 50	754	148 5	45227 4
96					4 60	755	149	45473 4
97					4 32	749	149	45719 4
98					4 70	745	146	45971 4
99					4 62	747	163	46189 4
100					4 29	749	163	46407 4
101					4 10	750	161	46629 4
102					4 25	756	175	46823 4
103					4 21	761	184	46999 4
104					4 18	764	198	47147 4
105					4 16	765	212	47267 4
106					4 15	768	243	47321 4
107					4 18	770	270	47321 4
108					4 16	755	270	47321 4

Table 22 Sorption of Zn^{2+} on Rush (Reed-Sedge) Peat from the mono-metal Zn-SO_4 solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Zn/dm^3 (2) c_0 = 250 mg Zn/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1

	C_o 500 mgZn/dm^3, pH 4				C_o 250 mgZn/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	6 85	63 5	<0 001	550	7 08	108	<0 001	255
2	6 74	62 8	<0 001	1100	6 89	300	<0 001	510
3	6 80	111 7	<0 001	1650	6 64	494	<0 001	765
4	6 60	672	<0 001	2200	6 59	857	<0 001	1020
5	6 20	455	<0 001	2750	6 96	756	<0 001	1275
6	5 95	497	<0 001	3300	6 84	718	<0 001	1530
7	5 87	1229	<0 001	3850	6 20	716	<0 001	1785
8	6 15	1246	<0 001	4400	5 95	713	<0 001	2040
9	6 20	1268	<0 001	4950	6 67	743	<0 001	2291
10	6 09	1251	<0 001	5500	6 50	740	<0 001	2550
11	6 27	1326	<0 001	6050	6 38	726	<0 001	2805
12	6 00	1279	<0 001	6600	6 21	782	<0 001	3060
13	6 17	1268	<0 001	7150	6 77	737	<0 001	3315
14	6 07	1278	<0 001	7700	6 65	722	<0 001	3570
15	6 24	1272	<0 001	8250	6 60	722	<0 001	3825
16	6 15	1270	<0 001	8800	6 49	726	<0 001	4080
17	6 21	1266	<0 001	9350	6 40	717	<0 001	4335
18	6 05	1273	<0 001	9900	6 18	716	<0 001	4590
19	6 03	1279	<0 001	10450	6 30	709	<0 001	4845
20	6 20	1279	<0 001	11000	6 20	791	<0 001	5100
21	6 07	1333	<0 001	11550	6 59	728	<0 001	5355
22	6 04	1287	<0 001	12100	6 32	724	<0 001	5610
23	6 25	1284	<0 001	12650	6 15	716	<0 001	5865
24	6 04	1282	<0 001	13200	6 36	713	<0 001	6120
25	6 10	1285	<0 001	13750	6 31	711	<0 001	6375
26	6 10	1269	<0 001	14300	6 65	852	<0 001	6630
27	6 20	1487	<0 001	14850	6 87	746	<0 001	6885

	C_o 500 mgZn/dm^3, pH 4				C_o 250 mgZn/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
28	6 15	1318	<0 001	15400	6 91	730	<0 001	7140
29	6 20	1296	<0 001	15950	6 38	722	<0 001	7395
30	6 20	1284	<0 001	16500	6 55	723	<0 001	7650
31	6 20	1283	<0 001	17050	6 21	724	<0 001	7905
32	6 20	1287	<0 001	17600	6 53	752	<0 001	8160
33	6 21	1349	<0 001	18110	6 44	722	<0 001	8415
34	6 17	1289	<0 001	18620	6 44	714	<0 001	8670
35	6 18	1283	<0 001	19130	6 16	711	<0 001	8925
36	6 22	1275	<0 001	19640	6 20	713	<0 001	9180
37	6 14	1241	<0 001	20150	5 90	706	<0 001	9435
38	6 18	1202	<0 001	20660	6 13	774	<0 001	9690
39	6 20	1227	<0 001	21170	6 63	712	<0 001	9945
40	6 09	1231	<0 001	21680	6 12	717	<0 001	10200
41	5 88	1229	<0 001	22190	6 04	1021	<0 001	10451
42	6 40	1225	<0 001	22700	6 03	741	<0 001	10702
43	6 28	1291	<0 001	23210	6 70	771	<0 001	10953
44	6 15	1254	<0 001	23720	6 88	692	<0 001	11204
45	6 46	1232	<0 001	24230	6 43	675	<0 001	11455
46	6 32	1234	<0 001	24740	6 40	668	<0 001	11706
47	6 30	1237	<0 001	25250	6 40	661	<0 001	11957
48	6 32	1251	<0 001	25760	6 46	821	<0 001	12208
49	6 28	1250	<0 001	26270	6 70	698	<0 001	12459
50	6 00	1240	<0 001	26780	6 00	684	<0 001	12710
51	6 16	1249	<0 001	27290	6 32	739	<0 001	12961
52	6 06	1235	<0 001	27800	6 30	694	<0 001	13212
53	6 11	1253	0 4	28309 6	6 33	697	<0 001	13463
54	5 83	1245	2 2	28817 4	6 20	670	<0 001	13714
55	6 35	1249	6 7	29320 7	6 18	649	<0 001	13963
56	6 20	1404	4 7	29826 0	5 94	660	<0 001	14216
57	6 50	1277	7 3	30328 7	6 72	647	<0 001	14467
58	6 41	1254	1 03	30825 7	6 03	647	<0 001	14718
59	6 53	1252	20 4	31315 3	6 10	642	<0 001	14969
60	5 81	1245	33 0	31792 3	5 36	642	<0 001	15220

C_o 500 mgZn/dm^3, pH 4					C_o 250 mgZn/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
61	5 77	1241	40 3	32262 0	5 75	645	<0 001	15471
62	5 84	1255	54 8	32717 2	6 04	700	<0 001	15722
63	5 80	1243	63 6	33163 6	6 10	697	<0 001	15973
64	5 92	1293	58 8	33614 8	5 53	680	<0 001	16224
65	5 98	1236	94 4	34030 4	6 13	667	<0 001	16475
66	5 72	1230	115	34425 4	6 18	667	<0 001	16726
67	5 78	1221	140	34795 4	5 96	825	<0 001	16977
68	5 56	1232	177	35128 4	5 80	855	<0 001	17228
69	5 28	1219	210	35428 4	6 18	741	<0 001	17479
70	5 25	1226	234 5	35703 9	6 40	748	<0 001	17730
71	5 50	1188	288	35925 9	6 33	743	<0 001	17981
72	5 65	1243	324	36111 9	6 08	731	<0 001	18232
73	5 46	1188	358	36263 9	5 60	728	0 35	18482 7
74	5 50	1187	390	36383 9	5 04	779	3 86	18730 1
75	5 50	1180	420	36473 9	5 30	774	4 42	18976 7
76	4 31	1240	425	36558 9	5 82	732	7 51	19220 2
77	5 46	1395	499	36569 9	5 47	737	8 02	19463 1
78	5 60	1202	441	36638 9	5 70	756	3 69	19710 5
79	5 41	1155	445	36703 9	5 03	740	6 26	19955 2
80	5 34	1141	459	36754 9	5 66	754	13 7	20192 5
81	5 25	1140	446	3618 9	5 90	738	13 9	20429 6
82	5 22	1131	500	36819 9	5 30	689	14 3	20666 3
83	5 20	1378	550	36819 9	5 20	772	15 2	20902 1
84	5 30	1205	550	36819 9	4 57	696	12 06	21141 0
85	5 60	1147	550	36819 9	5 10	688	14 15	21377 9
86	4 95	1109	550	36819 9	5 49	694	15 45	21613 4
87	4 96	1075	550	36819 9	5 50	698	16 0	21848 4
88					5 50	700	18 2	22081 2
89					5 47	712	19 6	22312 6
90					5 45	730	20 4	22543 2
91					5 40	724	21 6	22772 6
91					5 41	729	24 1	22999 5
93					5 44	734	26 8	23223 7

C_o 500 mgZn/dm^3, pH 4					C_o 250 mgZn/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
94					5 40	733	30 1	23444 6
95					5 38	740	31 0	23664 6
96					5 39	739	32 3	23883 3
97					5 36	743	33 2	24101 1
98					5 30	746	41 1	24311 0
99					5 32	752	42 3	24519 7
100					5 28	749	44 7	24726 0
101					5 29	755	46 1	24930 9
102					5 20	753	49 5	25132 4
103					5 22	752	50 0	25333 4
104					5 20	758	53 4	25531 0
105					5 18	759	58 9	25723 1
106					5 19	756	60 7	25913 4
107					5 15	753	62 4	26102 0
108					5 14	755	62 6	26290 4
109					5 10	760	65 4	26476 0
110					5 15	762	68 3	26658 7
111					5 13	769	71 2	26838 5
112					5 12	754	85 3	27004 2
113					5 10	749	91 4	27163 8
114					5 00	748	93 5	27321 3
115					5 11	759	98 6	27473 7
116					5 10	763	106 2	27618 5
117					5 11	766	111 2	27758 3
118					5 09	769	136 4	27872 9
119					5 07	760	120 4	28003 5
120					5 06	764	124 1	28130 4
121					5 08	769	131 4	28250 0
122					5 10	770	138 6	28362 4
123					5 04	774	138 9	28474 5
124					5 01	767	142 4	28583 1
125					5 00	759	146 2	28687 9
126					4 98	768	147 9	28791 0

C_o 500 mgZn/dm^3, pH 4					C_o 250 mgZn/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
127					5 00	744	152 1	28889 9
128					4 99	756	156 4	28984 5
129					4 96	759	159 2	29076 3
130					4 95	769	163 4	29163 9
131					4 90	768	171 3	29243 6
132					4 88	767	174 8	29319 8
133					4 92	760	179 2	29391 6
134					4 93	766	179 9	29462 7
135					4 92	768	184 1	29529 6
136					4 90	765	189 4	29591 2
137					4 88	761	198 3	29643 9
138					4 89	759	204 8	29690 1
139					4 85	764	212 4	29728 7
140					4 86	763	232 8	29746 9
141					4 85	768	249 4	29748 5
142					4 83	774	255	29748 5
143					4 87	771	255	29748 5

Table 23 Sorption of Cd^{2+} on Brushwood Peat Humus from the mono-metal Cd-SO_4 solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Zn/dm^3 (2) c_0 = 250 mg Zn/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9b, mass 90 g , water retention capacity S/L = 1 2

C_o 500mg Cd/dm^3 pH 4					C_o 250mg Cd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	7 13	620	<0 001	920	7 00	79 8	<0 001	510
2	6 88	745	<0 001	1840	7 03	234	<0 001	1020
3	6 64	760	<0 001	2760	6 74	402	<0 001	1530
4	6 56	753	<0 001	3680	6 42	429	<0 001	2040
5	6 34	732	<0 001	4600	6 25	427	<0 001	2550
6	6 53	755	<0 001	5520	6 35	416	<0 001	3060
7	6 44	752	<0 001	6440	6 12	415	<0 001	3570
8	6 86	791	<0 001	7360	6 58	440	<0 001	4080
9	6 78	750	<0 001	8280	6 70	460	<0 001	4590
10	6 40	770	<0 001	9200	6 48	428	<0 001	5100
11	6 51	759	<0 001	10120	6 38	424	<0 001	5610
12	6 37	749	<0 001	11040	6 45	440	<0 001	6120
13	6 36	741	<0 001	11960	6 26	425	<0 001	6630
14	6 65	782	<0 001	12880	6 56	460	<0 001	7140
15	6 40	756	<0 001	13800	6 48	450	<0 001	7650
16	6 73	750	<0 001	14720	6 54	430	<0 001	8160
17	6 34	748	<0 001	15640	7 09	514	<0 001	8826
18	6 70	829	<0 001	16560	7 30	489	<0 001	9492
19	6 89	836	<0 001	17490	6 89	449	<0 001	10158
20	6 92	783	<0 001	18420	6 49	440	<0 001	10824
21	6 54	768	<0 001	19350	6 77	445	<0 001	11490
22	6 56	764	<0 001	20280	6 82	464	<0 001	12156
23	6 50	788	<0 001	21210	6 55	440	<0 001	12822
24	6 40	766	<0 001	22140	6 33	439	<0 001	13488
25	6 44	769	<0 001	23070	6 35	447	<0 001	14154
26	6 30	762	<0 001	24000	6 80	466	<0 001	14820
27	6 35	779	<0 001	24930	6 77	459	<0 001	15486
28	6 90	898	<0 001	25860	6 60	588	<0 001	16152
29	7 02	815	<0 001	26790	6 40	508	<0 001	16818
30	6 64	763	<0 001	27720	6 48	441	<0 001	17484
31	6 40	745	<0 001	28650	6 45	428	<0 001	18150
32	6 00	741	<0 001	29580	6 23	428	<0 001	18816
33	6 02	777	<0 001	30510	6 50	451	<0 001	19482

C_o 500mg Cd/dm^3 pH 4					C_o 250mg Cd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
34	6 20	867	<0 001	31440	6 45	431	<0 001	20148
35	6 20	780	<0 001	32370	6 50	430	<0 001	20814
36	6 30	795	<0 001	33300	6 71	649	<0 001	21310
37	7 10	801	<0 001	34230	6 84	576	<0 001	21806
38	6 40	753	<0 001	35160	6 80	468	<0 001	22302
39	6 50	733	<0 001	36090	6 28	426	<0 001	22798
40	6 30	734	<0 001	37020	6 47	420	<0 001	23294
41	6 48	716	<0 001	37950	6 11	419	<0 001	23790
42	5 64	719	<0 001	39034	5 90	416	<0 001	24286
43	5 80	724	<0 001	40118	6 13	414	<0 001	24782
44	4 44	756	<0 001	41202	6 33	406	<0 001	25278
45	6 30	742	<0 001	42286	6 33	395	<0 001	25774
46	5 93	812	<0 001	43370	6 20	413	<0 001	26270
47	5 92	810	<0 001	44454	6 12	417	<0 001	26766
48	6 19	787	<0 001	45538	5 48	418	<0 001	27262
49	6 18	818	<0 001	46622	6 54	505	<0 001	27758
50	5 93	770	<0 001	47706	6 60	467	<0 001	28254
51	5 90	807	<0 001	48790	5 43	449	<0 001	28750
52	5 69	799	<0 001	49874	5 81	443	<0 001	29246
53	5 50	791	<0 001	50958	5 65	443	<0 001	29742
54	5 45	889	33 4	51975 2	6 04	483	<0 001	30238
55	5 32	897	38 4	52982 2	6 45	463	<0 001	30734
56	4 65	831	54 6	53957	6 10	448	<0 001	31230
57	5 02	796	76 3	54888 4	5 40	445	<0 001	31726
58	5 17	792	89 5	55793 4	6 18	459	<0 001	32222
59	4 99	801	73 7	56730	6 25	442	<0 001	32718
60	5 34	788	101 2	57611 6	6 28	441	<0 001	33214
61	5 18	791	119 4	58456 8	6 10	445	<0 001	33710
62	4 88	824	78 5	59383 8	5 75	438	<0 001	34206
63	5 79	793	121 6	60224 6	5 57	808	7 41	34687 2
64	5 6	799	109 7	61089 2	5 72	579	14 7	35153 8
65	5 21	802	124 5	61925 2	6 19	582	9 18	35631 4
66	5 17	811	173 4	62662 4	5 95	536	19 9	36087 6
67	4 80	813	201 0	63344 4	5 98	540	13 52	36556 6
68	5 61	822	68 5	64127 4	5 60	523	22 87	37006 8
69	5 93	840	75 2	64897 0	5 53	552	40 66	37421 4
70	5 79	834	99 4	65618 2	5 50	585	58 0	37801 4
71	5 23	845	81 5	66375 2	5 09	543	63 9	38169 4
72	4 99	840	86 8	67121 6	6 45	703	14 88	38635 6

	C_o 500mg Cd/dm^3, pH 4				C_o 250mg Cd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
73	4 86	836	118 7	67804 2	6 41	589	28 8	39074 0
74	4 81	844	120 0	68484 2	6 22	545	14 3	39541 4
75	4 79	829	124 0	69156 2	5 98	536	22 4	39992 6
76	4 75	811	130 0	69816 2	5 60	549	16 8	40455 0
77	4 76	840	168 0	70400 2	5 18	538	16 45	40918 0
78	4 72	839	192 0	70936 2	5 15	549	29 6	41354 6
79	4 65	827	231 0	71394 2	4 86	549	38 5	41773 6
80	4 70	818	254 0	71806 2	5 46	546	36 2	42197 2
81	4 61	819	286 0	72154 2	5 49	550	27 8	42615 6
82	4 50	824	360 0	72354 2	5 39	549	35 8	43018 0
83	4 52	833	411 0	72452 2	5 40	547	46 8	43398 4
84	4 53	838	434 0	72504 2	5 40	548	51 0	43770 4
85	4 50	841	455 0	72514 2	5 80	553	52 7	44139 0
86	4 52	844	460 0	72514 2	5 85	550	59 8	44494 2
87	4 51	843	460 0	72514 2	5 42	553	61 4	44845 4
88					5 40	552	49 1	45221 2
89					5 70	555	64 0	45567 2
90					5 71	557	73 3	45894 6
91					5 34	560	77 1	46214 4
92					5 22	561	64 5	46559 4
93					5 60	564	58 6	46916 2
94					5 40	567	62 4	47265 4
95					5 50	569	82 4	47574 6
96					5 60	571	58 0	47932 6
97					5 40	575	68 3	48270 0
98					6 18	576	72 8	48598 4
99					5 70	577	79 4	48913 6
100					5 88	587	82 1	49223 4
101					5 75	589	84 4	49528 6
102					5 77	588	88 8	49825 0
103					5 72	586	91 4	50116 2
104					5 74	582	96 5	50397 2
105					5 70	580	98 7	50673 8
106					5 65	576	99 9	50948 0
107					5 69	577	104 6	51212 8
108					5 68	579	105 9	51475 0
109					5 70	574	111 4	51726 2
110					5 63	570	119 6	51961 0
111					5 60	568	126 3	52182 4

C_o 500mg Cd/dm^3, pH 4					C_o 250mg Cd/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
112					5 58	569	139 2	52378 0
113					5 56	566	145 4	52561 2
114					5 54	568	158 8	52717 6
115					5 50	565	171 2	52849 2
116					5 48	560	189 3	52944 6
117					5 49	562	196 0	53026 6
118					5 50	565	212 4	53076 2
119					5 42	567	228 8	53092 6
120					5 51	564	240 1	53122 4
121					5 49	562	255 0	53122 4
122					5 50	564	255 0	53122 4

Table 24 Sorption of Cd^{2+} on Rush (Reed-Sedge) Peat from the mono-metal $Zn\text{-}SO_4$ solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Cd/dm^3 (2) c_0 = 250 mg Cd/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1

	C_o 500 mgCd/dm$_3$, pH 4				C_o 250 mgCd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	6 55	66 2	<0 001	525	6 68	51 0	<0 001	268
2	6 73	54 3	<0 001	1050	6 75	55 3	<0 001	536
3	7 10	96	<0 001	1575	6 64	109 6	<0 001	804
4	6 64	422	<0 001	2100	6 42	327	<0 001	1072
5	6 24	706	<0 001	2625	6 09	433	<0 001	1340
6	6 23	844	<0 001	3150	6 04	453	<0 001	1608
7	6 12	806	<0 001	3675	6 05	458	<0 001	1876
8	6 12	809	<0 001	4200	6 00	457	<0 001	2144
9	6 24	804	<0 001	4725	6 30	453	<0 001	2412
10	6 13	799	<0 001	5250	6 22	452	<0 001	2680
11	6 06	801	<0 001	5775	6 11	480	<0 001	2948
12	6 20	805	<0 001	6300	6 22	467	<0 001	3216
13	6 56	808	<0 001	6825	6 40	462	<0 001	3484
14	6 18	805	<0 001	7350	6 43	459	<0 001	3752
15	6 39	802	<0 001	7875	6 32	456	<0 001	4020
16	6 24	800	<0 001	8400	6 32	457	<0 001	4288
17	6 15	801	<0 001	8925	6 33	457	<0 001	4556
18	6 25	818	<0 001	9450	6 44	459	<0 001	4824
19	6 22	800	<0 001	9975	6 28	456	<0 001	5092
20	6 40	799	<0 001	10500	6 09	456	<0 001	5360
21	5 98	805	<0 001	11025	6 31	481	<0 001	5628
22	5 74	800	<0 001	11550	6 20	484	<0 001	5896
23	6 40	802	<0 001	12075	6 14	464	<0 001	6164
24	6 33	806	<0 001	12600	6 29	439	<0 001	6432
25	6 23	805	<0 001	13125	6 33	449	<0 001	6700
26	6 22	790	<0 001	13650	6 22	464	<0 001	6968
27	6 30	801	<0 001	14175	6 20	485	<0 001	7236
28	6 47	803	<0 001	14700	6 30	477	<0 001	7504
29	6 29	825	<0 001	15225	6 28	475	<0 001	7772
30	6 20	811	<0 001	15750	6 30	466	<0 001	8040
31	6 29	806	<0 001	16275	6 15	452	<0 001	8308
32	6 23	804	<0 001	16800	6 16	460	<0 001	8576
33	6 37	786	<0 001	17325	6 45	460	<0 001	8844

	C_o 500 mgCd/dm$_3$, pH 4				C_o 250 mgCd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
34	6 08	789	<0 001	17850	6 27	458	<0 001	9112
35	6 08	785	<0 001	18375	6 15	450	<0 001	9380
36	6 74	848	<0 001	18890	6 21	462	<0 001	9648
37	6 26	812	<0 001	19405	6 11	452	<0 001	9916
38	6 50	797	<0 001	19920	6 42	487	<0 001	10163
39	6 38	797	<0 001	20435	6 37	473	<0 001	10410
40	6 29	772	<0 001	20950	6 50	459	<0 001	10657
41	6 21	758	<0 001	21465	6 33	462	<0 001	10904
42	6 31	740	<0 001	21980	6 32	451	<0 001	11151
43	6 28	759	<0 001	22495	6 30	457	<0 001	11398
44	6 45	756	<0 001	23010	6 26	450	<0 001	11645
45	6 42	745	<0 001	23525	6 30	460	<0 001	11892
46	6 25	794	<0 001	24040	6 36	451	<0 001	12139
47	6 52	785	<0 001	24555	6 27	460	<0 001	12386
48	6 45	767	<0 001	25070	6 40	466	<0 001	12633
49	6 45	764	<0 001	25585	6 34	459	<0 001	12880
50	6 45	764	<0 001	26100	6 34	460	<0 001	13127
51	6 22	763	<0 001	26615	6 15	507	<0 001	13374
52	6 20	770	<0 001	27130	6 15	482	<0 001	13621
53	6 04	770	<0 001	27645	6 15	460	<0 001	13868
54	6 25	770	<0 001	28160	6 45	462	<0 001	14115
55	6 29	770	<0 001	28675	6 33	461	<0 001	14362
56	6 48	922	<0 001	29190	6 28	462	<0 001	14609
57	6 70	800	<0 001	29705	6 55	628	<0 001	14856
58	6 72	764	<0 001	30220	6 50	504	<0 001	15103
59	6 75	812	<0 001	30735	6 76	500	<0 001	15350
60	6 17	830	<0 001	31250	6 34	491	<0 001	15597
61	6 42	765	<0 001	31765	6 32	486	<0 001	15844
62	6 50	765	<0 001	32280	6 08	474	<0 001	16091
63	6 37	771	<0 001	32795	6 03	468	<0 001	16338
64	6 51	830	<0 001	33310	6 08	508	<0 001	16585
65	6 58	775	<0 001	33825	6 38	484	<0 001	16832
66	6 52	784	<0 001	34340	6 44	476	<0 001	17079
67	6 37	780	<0 001	34855	6 38	479	<0 001	17326
68	6 15	768	<0 001	35370	6 36	477	<0 001	17573
69	6 20	764	<0 001	35885	5 91	484	<0 001	17820
70	6 16	764	<0 001	36400	6 22	474	<0 001	18067
71	6 09	774	<0 001	36915	6 15	471	<0 001	18314
72	6 12	827	<0 001	37430	6 10	485	<0 001	18561

	C_o 500 mgCd/dm_3 pH 4				C_o 250 mgCd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
73	5 50	791	<0 001	37945	6 17	516	<0 001	18808
74	5 49	777	<0 001	38460	6 40	495	<0 001	19055
75	6 20	945	<0 001	38975	6 15	490	<0 001	19302
76	6 97	793	<0 001	39490	6 20	476	<0 001	19549
77	6 85	772	<0 001	40005	6 26	579	<0 001	19779
78	6 44	763	<0 001	40520	6 40	541	<0 001	20009
79	5 83	760	<0 001	41035	6 52	484	<0 001	20239
80	6 34	761	<0 001	41550	6 60	461	<0 001	20469
81	6 03	898	<0 001	42090	6 35	452	<0 001	20699
82	5 98	813	<0 001	42630	5 56	447	<0 001	20929
83	5 96	779	<0 001	43170	6 28	577	<0 001	21159
84	6 00	700	<0 001	43710	6 34	470	<0 001	21389
85	6 00	683	<0 001	44250	6 10	457	<0 001	21619
86	5 57	682	<0 001	44790	6 10	451	<0 001	21849
87	6 40	688	<0 001	45330	6 11	454	<0 001	22079
88	5 95	682	<0 001	45870	6 18	425	<0 001	22309
89	6 08	677	<0 001	46410	6 03	579	<0 001	22539
90	6 30	682	<0 001	46950	6 13	524	<0 001	22769
91	5 96	671	<0 001	47490	6 16	509	<0 001	22999
92	5 77	678	<0 001	48030	5 80	456	<0 001	23229
93	5 92	681	<0 001	48570	6 19	439	<0 001	23459
94	5 60	889	<0 001	49110	6 25	433	<0 001	23689
95	6 01	911	<0 001	49650	5 85	425	<0 001	23919
96	5 38	751	<0 001	50190	5 59	437	<0 001	24149
97	5 25	725	<0 001	50730	5 59	431	<0 001	24379
98	5 77	709	<0 001	51270	6 20	427	<0 001	24609
99	5 35	708	0 33	51810	5 80	427	<0 001	24839
100	5 20	708	1 01	52349	5 80	425	<0 001	25069
101	5 55	850	1 01	52888	5 85	428	<0 001	25299
102	5 90	795	0 13	53427 9	5 83	430	<0 001	25529
103	5 18	786	0 65	53967 3	5 90	430	<0 001	25759
104	5 30	749	1 48	54506 4	6 02	512	<0 001	25989
105	5 25	734	2 70	55043 7	4 94	512	<0 001	26219
106	5 02	724	4 90	55578 8	5 13	477	<0 001	26449
107	4 89	725	7 53	56111 3	5 08	447	<0 001	26679
108	4 80	721	12 36	56638 9	6 23	455	<0 001	26909
109	4 89	721	19 75	57159 1	5 69	517	<0 001	27139
110	4 81	803	29 1	57670 0	6 30	476	<0 001	27369
111	4 71	725	38 3	58171 7	6 25	469	<0 001	27599

	C$_o$ 500 mgCd/dm$_3$ pH 4				C$_o$ 250 mgCd/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
112	4 85	737	32 4	58679 3	5 69	448	<0 001	27829
113	4 78	727	49 1	59170 2	5 50	455	<0 001	28059
114	5 18	717	74 6	59636 1	5 06	450	<0 001	28289
115	4 42	708	94 4	60081 7	6 00	469	<0 001	28519
116	4 81	705	113 7	60508 0	5 85	528	<0 001	28749
117	4 80	708	140 4	60907 6	5 69	510	<0 001	28979
118	4 90	705	159 0	61288 6	5 75	531	<0 001	29255
119	4 50	707	192 2	61636 4	5 93	507	<0 001	29531
120	4 41	698	180 6	61995 8	5 89	483	<0 001	29803
121	4 71	736	172 2	62363 6	5 30	528	<0 001	30083
122	4 70	704	219 0	62685 6	5 37	533	<0 001	30359
123	4 68	691	249 7	62975 0	5 28	541	<0 001	30635
124	4 80	910	449 8	63042 2	4 94	541	<0 001	30911
125	4 96	781	420 2	63139 2	4 79	568	<0 001	31187
126	5 40	794	413 8	63242 4	5 60	546	<0 001	31463
127	4 85	783	433 5	63325 9	5 48	547	<0 001	31739
128	4 85	762	431 0	63411 9	5 28	538	<0 001	32015
129	5 23	814	437 0	63491 9	5 51	558	<0 001	32291
130	4 82	790	470 0	63538 9	5 45	547	<0 001	32567
131	4 81	780	461 0	63594 9	5 11	544	<0 001	32843
132	4 85	767	424 0	63687 9	5 66	542	<0 001	33119
133	4 95	900	444 0	63760 9	4 58	539	<0 001	33395
134	4 54	810	477 0	63800 9	5 36	541	<0 001	33671
135	4 78	757	484 0	63833 9	6 31	639	<0 001	33947
136	4 53	765	487 0	63863 9	6 30	615	<0 001	34223
137	4 53	757	502 0	63878 9	6 70	584	<0 001	34499
138	4 44	759	479 0	63916 9	6 20	553	<0 001	34775
139	4 49	749	475 0	63958 9	5 37	611	<0 001	35051
140	4 65	931	520 0	63958 9	5 46	562	<0 001	35327
141	4 66	802	520 0	63958 9	5 43	578	<0 001	35603
142	4 65	761	520 0	63958 9	5 40	558	<0 001	35879
143					6 13	581	<0 001	36155
144					6 13	562	<0 001	36431
145					5 91	560	<0 001	36707
146					5 78	563	2 65	36980 4
147					5 11	599	2 70	37253 6
148					4 99	548	2 70	37526 9
149					5 06	541	2 90	37800 1
150					4 92	544	3 10	38072 9

C_o 500 mgCd/dm_3, pH 4					C_o 250 mgCd/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
151					4 85	547	3 40	38345 5
152					4 77	549	4 60	38616 9
153					4 81	555	5 10	38887 8
154					4 80	552	5 80	39158 0
155					4 75	558	6 40	39427 6
156					4 72	550	7 00	39696 6
157					4 70	568	7 50	39965 1
158					4 81	570	8 10	40233 6
159					4 95	567	8 90	40500 7
160					4 88	575	9 40	40767 3
161					4 79	563	11 3	41032 0
162					4 85	560	14 7	41293 3
163					4 86	553	19 5	41549 8
164					4 83	550	24 6	41801 2
165					4 82	547	26 9	42050 3
166					4 80	542	29 4	42296 9
167					4 75	544	35 4	42537 5
168					4 74	540	41 5	42772 0
169					4 73	538	67 8	42980 2
170					4 70	537	75 4	43176 8
171					4 74	538	88 8	43364 0
172					4 71	539	90 3	43549 7
173					4 69	546	95 4	43730 3
174					4 70	543	109 1	43897 2
175					4 67	540	126 4	44046 8
176					4 65	547	1111 3	44211 5
177					4 63	541	121 2	44366 3
178					4 66	549	134 3	44508 0
179					4 65	550	158 9	44625 1
180					4 64	540	171 4	44729 7
181					4 62	551	186 4	44819 3
182					4 60	553	199 9	44895 4
183					4 58	556	211 4	44960 0
184					4 59	551	226 8	45009 2
185					4 55	559	245	45032 2
186					4 57	556	268	45032 2
187					4 55	552	268	45032 2

Table 25 Sorption of Cu^{2+} on Brushwood Peat Humus from the mono-metal Cu-SO_4 solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Cu/dm^3 (2) c_0 = 250 mg Cu/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9b, mass 90 g , water retention capacity S/L = 1 2

C_o 500 mgCu/dm^3 pH 4					C_o 250 mgCu/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	7 27	144	<0 001	930	6 94	131	<0 001	470
2	7 15	666	<0 001	1860	7 32	334	<0 001	940
3	6 65	1174	<0 001	2790	6 75	633	<0 001	1410
4	6 38	1213	<0 001	3720	6 55	703	<0 001	1880
5	6 40	1219	<0 001	4650	6 28	710	<0 001	2350
6	6 34	1216	<0 001	5580	6 00	711	<0 001	2820
7	6 70	1213	<0 001	6510	6 15	711	<0 001	3290
8	6 68	1240	<0 001	7440	6 30	709	<0 001	3760
9	6 45	1218	<0 001	8370	6 44	742	<0 001	4230
10	6 26	1214	<0 001	9300	6 48	720	<0 001	4700
11	6 30	1220	<0 001	10230	6 20	688	<0 001	5170
12	6 12	1190	<0 001	11160	5 88	687	<0 001	5640
13	6 26	1199	<0 001	12090	6 11	686	<0 001	6110
14	6 42	1244	<0 001	13020	6 37	721	<0 001	6580
15	6 60	1195	<0 001	13950	6 47	704	<0 001	7050
16	6 36	1195	<0 001	14880	6 70	846	<0 001	7522
17	5 78	1207	<0 001	15810	6 78	733	<0 001	7994
18	6 80	1396	<0 001	16810	6 59	684	<0 001	8466
19	6 81	1303	<0 001	17810	6 50	673	<0 001	8938
20	6 48	1207	<0 001	18810	6 50	670	<0 001	9410
21	6 33	1147	<0 001	19810	6 40	652	<0 001	9882
22	6 15	1158	<0 001	20810	5 87	666	<0 001	10354
23	6 44	1178	<0 001	21810	5 62	663	<0 001	10826
24	6 53	1158	<0 001	22810	6 45	685	<0 001	11298
25	6 33	1156	<0 001	23810	6 51	665	<0 001	11770
26	6 08	1156	<0 001	24810	6 42	686	<0 001	12242
27	6 40	1211	<0 001	25810	7 07	767	<0 001	12714
28	6 26	1152	<0 001	26810	6 93	677	<0 001	13186
29	6 60	1287	<0 001	27810	6 36	630	<0 001	13658
30	6 42	1138	<0 001	28810	6 40	615	<0 001	14130
31	6 40	1082	<0 001	29810	6 15	613	<0 001	14602
32	6 22	1093	<0 001	30810	6 21	647	<0 001	15074
33	6 21	1130	<0 001	31810	6 60	627	<0 001	15546

	C_o 500 mgCu/dm^3, pH 4				C_o 250 mgCu/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
34	6 21	1116	<0 001	32810	6 56	527	<0 001	16018
35	5 73	1132	0 1	33810	6 77	819	<0 001	16490
36	6 50	1163	0 17	34810	6 62	737	<0 001	16960
37	6 40	1138	0 95	35808	6 80	699	<0 001	17430
38	6 01	1097	1 49	36805	6 45	649	<0 001	17900
39	5 54	1080	7 25	37791	6 12	625	<0 001	18370
40	4 66	1080	2<0 001	38751	5 99	606	<0 001	18840
41	4 82	1111	20 2	39711	6 10	598	<0 001	19310
42	4 48	1110	49 1	40613	5 44	605	<0 001	19780
43	4 44	1084	75 2	41463	5 22	600	<0 001	20250
44	4 44	1081	68 8	42259	5 80	600	<0 001	20720
45	4 31	1099	105	42983	5 34	605	<0 001	21190
46	4 17	1078	132	43653	4 90	620	<0 001	21660
47	4 16	1062	164	44259	6 90	689	<0 001	22130
48	4 08	1074	156	44881	6 51	660	<0 001	22600
49	4 48	1204	156	45503	6 39	643	<0 001	23070
50	4 11	1204	258	45921	5 38	640	<0 001	23540
51	4 04	1254	193	46469	6 17	763	<0 001	24010
52	3 90	1201	125	47153	6 26	648	<0 001	24480
53	3 80	1140	128	47831	6 08	670	<0 001	24950
54	3 72	1173	194	48377	6 13	639	<0 001	25420
55	3 63	1196	241	48829	5 85	636	<0 001	25890
56	3 67	1210	292	49179	5 61	648	<0 001	26360
57	3 64	1260	311	49491	5 54	918	0 27	26838
58	3 92	1382	373	49680	5 27	722	2 27	27311 5
59	3 55	1246	359	49896	4 22	686	16 36	27756 8
60	3 57	1134	372	50086	4 58	670	27 33	28180 1
61	3 58	1104	381	50258	4 3	663	39 6	28578 9
62	3 56	1090	372	50448	4 1	659	58 6	28939 7
63	3 31	1116	438	50506	4 04	663	71 9	29273 7
64	3 54	1102	465	50506	4 19	672	50 7	29650 3
65	3 52	1103	465	50506	4 01	662	82 15	29964
66					4 00	667	84 4	30273 2
67					3 85	667	90 4	30570 4
68					3 83	667	104 1	30838 2
69					3 80	667	116 5	31081 2
70					4 22	702	66 8	31423 6
71					4 92	973	14 2	31873 2
72					4 93	836	10 5	32330 2

C_o 500 mgCu/dm^3, pH 4					C_o 250 mgCu/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
73					4 89	786	11 7	32784 8
74					4 47	826	12 2	33238 4
75					4 36	789	16 5	33683 4
76					4 90	767	22 8	34115 8
77					4 17	751	30 7	34532 4
78					4 10	810	28 3	34953 8
79					4 35	773	35 6	35308 6
80					4 04	759	42 1	35650 4
81					4 00	728	47 9	35980 4
82					4 04	714	57 1	36292 2
83					3 96	791	42 0	36634 2
84					3 93	739	50 0	36960 2
85					3 85	748	54 3	37277 6
86					3 81	750	56 3	37591 0
87					3 71	757	68 0	37881 0
88					4 15	754	76 3	38154 4
89					3 76	758	79 4	38422 4
90					3 90	759	91 4	38665 6
91					3 75	762	105 5	38880 6
92					3 65	765	119	39068 6
93					3 66	768	116	39262 6
94					3 56	770	121	39446 6
95					3 60	772	129	39614 6
96					3 60	774	127	39786 6
97					3 60	777	132	39948 6
98					3 51	781	127	40120 6
99					3 57	784	138	40270 6
100					3 59	785	141	40414 6
101					3 58	780	146	40548 6
102					3 60	779	159	40656 6
103					3 55	770	162	40758 6
104					3 57	779	178	40828 6
105					3 56	783	189	40876 6
106					3 60	787	211	40880 6
107					3 58	780	213	40924 6
108					3 56	784	235	40924 6

Table 26 Sorption of Cu^{2+} on Rush (Reed-Sedge) Peat from the mono-metal Cu-SO_4 solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Cu/dm^3 (2) c_0 = 250 mg Cu/dm^3, pH 4 0, flow rate q=0 1 cm^3/s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1

	C_o 507 mgCu/dm^3, pH 4				C_o 245 mgCu/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	6 49	54 3	<0 001	507	6 93	59 9	<0 001	245
2	6 74	62 7	<0 001	1014	6 95	66 6	<0 001	490
3	6 35	183	<0 001	1521	6 81	110 6	<0 001	735
4	5 99	797	<0 001	2028	6 29	363	<0 001	980
5	5 90	1084	<0 001	2535	6 12	589	<0 001	1225
6	5 81	1148	<0 001	3042	6 06	679	<0 001	1470
7	5 93	1164	<0 001	3549	6 03	697	<0 001	1715
8	5 79	1167	<0 001	4057	6 42	698	<0 001	1960
9	6 00	1165	<0 001	4563	6 12	698	<0 001	2205
10	5 82	1165	<0 001	5070	6 20	696	<0 001	2450
11	6 03	1217	<0 001	5577	6 07	766	<0 001	2695
12	6 00	1182	<0 001	6084	6 07	698	<0 001	2940
13	6 18	1174	<0 001	6591	6 17	704	<0 001	3185
14	5 98	1173	<0 001	7098	6 17	695	<0 001	3430
15	6 10	1172	<0 001	7605	6 11	697	<0 001	3675
16	6 16	1277	<0 001	8112	6 15	688	<0 001	3920
17	6 10	1183	<0 001	8619	6 20	684	<0 001	4165
18	6 25	1167	<0 001	9126	6 04	804	<0 001	4410
19	6 11	1172	<0 001	9633	6 11	719	<0 001	4655
20	6 00	1167	<0 001	10140	6 15	708	<0 001	4900
21	5 93	1168	<0 001	10647	6 64	698	<0 001	5145
22	5 88	1203	<0 001	11154	6 54	656	<0 001	5390
23	5 98	1201	<0 001	11661	6 46	664	<0 001	5635
24	5 65	1166	<0 001	12168	6 33	696	<0 001	5880
25	5 99	1170	<0 001	12675	6 30	697	<0 001	6125
26	5 98	1179	<0 001	13182	6 26	690	<0 001	6370
27	6 04	1213	<0 001	13689	6 21	680	<0 001	6615
28	6 15	1250	<0 001	14196	6 63	730	<0 001	6860
29	6 09	1210	<0 001	14703	6 55	720	<0 001	7105
30	6 05	1240	<0 001	15210	6 56	730	<0 001	7350
31	5 90	1207	<0 001	15717	6 55	650	<0 001	7595
32	5 98	1190	<0 001	16224	6 30	670	<0 001	7840
33	6 05	1193	<0 001	16731	6 30	670	<0 001	8085
34	6 20	1191	<0 001	17238	6 32	660	<0 001	8330
35	5 95	1187	<0 001	17745	6 30	680	<0 001	8575

C_o 507 mgCu/dm^3, pH 4					C_o 245 mgCu/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
36	6 15	1232	<0 001	18167	6 20	670	<0 001	8820
37	6 13	1221	<0 001	18589	6 21	650	<0 001	9065
38	6 19	1199	<0 001	19011	6 15	680	<0 001	9310
39	6 15	1170	<0 001	19433	6 19	650	<0 001	9555
40	6 13	1135	<0 001	19855	6 18	620	<0 001	9800
41	6 10	1120	<0 001	20277	6 21	719	<0 001	10045
42	6 09	1097	<0 001	20699	6 23	700	<0 001	10366
43	6 08	1086	<0 001	21121	6 45	692	<0 001	10687
44	6 03	1111	<0 001	21543	6 48	666	<0 001	11008
45	6 05	1112	<0 001	21965	6 39	664	<0 001	11329
46	5 95	1116	<0 001	22387	6 05	642	<0 001	11650
47	5 96	1109	<0 001	22809	6 38	649	<0 001	11971
48	6 04	1114	<0 001	23231	6 08	646	<0 001	12292
49	5 99	1109	<0 001	23653	6 30	649	<0 001	12613
50	6 01	1119	<0 001	24075	6 05	646	<0 001	12934
51	5 93	1110	<0 001	24497	6 29	646	<0 001	13255
52	6 03	1110	<0 001	24919	6 15	646	<0 001	13576
53	6 20	1090	<0 001	25341	6 32	649	<0 001	13897
54	6 53	1089	<0 001	25763	6 07	646	<0 001	14218
55	6 03	1087	<0 001	26185	6 20	641	<0 001	14539
56	6 00	1091	<0 001	26607	6 70	908	<0 001	14860
57	6 09	1272	0 5	27028 5	6 80	689	<0 001	15181
58	6 20	1149	1 0	27449 5	6 78	688	<0 001	15502
59	6 08	1127	2 1	27869 4	6 75	672	<0 001	15823
60	6 11	1096	4 3	28287 1	6 48	649	<0 001	16144
61	6 01	1086	6 1	28703 0	6 19	655	<0 001	16465
62	5 80	1086	8 2	29116 8	6 09	649	<0 001	16786
63	5 27	1089	18 1	29520 7	6 23	644	<0 001	17107
64	5 11	1100	28 2	29914 5	6 49	691	<0 001	17428
65	4 98	1086	45 9	30290 6	6 55	660	<0 001	17749
66	5 18	1087	19 8	30692 8	6 55	654	<0 001	18070
67	5 41	1138	31 8	31083 0	6 38	665	<0 001	18391
68	5 18	1102	57 5	31447 5	6 40	656	<0 001	18712
69	4 97	1088	82 1	31787 4	5 99	644	<0 001	19033
70	4 94	1085	94 2	32115 2	6 10	660	<0 001	19354
71	4 62	1077	117 0	32420 2	6 12	651	<0 001	19675
72	4 52	1080	129 2	32713 0	5 99	647	<0 001	19996
73	3 63	1080	145 0	3299<0 001	6 25	722	<0 001	20317

	C_o 507 mgCu/dm^3, pH 4				C_o 245 mgCu/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
74	4 51	1075	149 4	33262 6	6 13	663	<0 001	20638
75	4 40	1085	171 2	33513 4	6 48	655	<0 001	20959
76	4 70	1076	89 5	33845 9	5 98	650	<0 001	21280
77	4 60	1151	122 8	34145 1	6 15	678	<0 001	21601
78	4 48	1104	151 2	34415 9	6 30	785	<0 001	21922
79	4 45	1088	189 4	34648 5	6 05	648	<0 001	22243
80	4 39	1069	194 7	34875 8	7 08	640	<0 001	22564
81	4 30	1071	220 5	35077 3	6 42	623	<0 001	22885
82	4 77	1064	83 2	35462 1	6 23	613	<0 001	23206
83	4 67	1102	87 7	35842 4	6 03	604	<0 001	23527
84	4 51	1061	125 8	36184 6	6 21	756	<0 001	23765
85	4 41	1037	184 7	36467 9	6 70	651	<0 001	24003
86	4 35	1039	204	36731 9	6 30	640	<0 001	24241
87	4 31	1030	246 5	36953 4	6 16	624	<0 001	24479
88	3 90	1285	181	37240 4	6 20	587	<0 001	24717
89	3 87	1130	180	37528 4	6 18	666	<0 001	24955
90	3 83	1087	200	37796 4	6 22	890	<0 001	24193
91	3 81	1055	239	38025 4	6 22	950	<0 001	25431
92	3 77	1036	259	38234 4	5 84	711	<0 001	25669
93	3 72	1015	284	38418 4	6 22	703	<0 001	25907
94	3 63	1030	327	38559 4	6 13	637	<0 001	26145
95	3 64	1024	336	38691 4	5 83	647	<0 001	26383
96	3 62	1029	345	38814 4	5 98	624	<0 001	26621
97	3 61	1020	355	38927 4	5 87	622	<0 001	26859
98	3 62	1020	381	39014 4	5 90	619	<0 001	27097
99	3 65	1031	398	39084 4	5 91	621	<0 001	27335
100	3 62	1035	412	39140 4	5 95	620	<0 001	27573
101	3 64	1120	443	39165 4	6 25	715	<0 001	27811
102	3 67	1080	441	39192 4	6 30	715	<0 001	28049
103	3 67	1070	435	39225 4	6 33	674	<0 001	28287
104	3 71	1110	432	39261 4	6 2	661	<0 001	28525
105	3 72	1080	443	39286 4	6 23	651	<0 001	28763
106	3 75	1200	445	39309 4	5 81	738	<0 001	29001
107	3 8	1050	435	39342 4	6 43	765	<0 001	29239
108	3 6	1050	435	39375 4	6 40	662	<0 001	29477
109	3 8	1040	440	39403 4	6 11	658	<0 001	29715
110	3 64	1050	441	39431 4	5 38	653	<0 001	29953
111	3 72	1070	450	39449 4	5 62	677	<0 001	30191
112	3 84	1070	460	39457 4	5 65	660	<0 001	30429

	C_o 507 mgCu/dm^3, pH 4				C_o 245 mgCu/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
113	3 8	1080	507	39465 4	5 58	657	<0 001	30667
114	3 81	1087	507	39465 4	4 87	643	<0 001	30905
115	3 8	1090	507	39465 4	4 63	670	<0 001	31143
116	3 79	1085	507	39465 4	5 86	718	<0 001	31381
117	3 79	1080	507	39465 4	5 64	692	<0 001	31619
118	3 81	1085	507	39465 4	5 65	695	<0 001	31857
119					5 22	674	<0 001	32095
120					5 26	676	<0 001	32333
121					4 35	671	0 99	32570
122					4 70	676	1 78	32806 2
123					4 46	674	3 74	33040 5
124					4 26	673	5 86	33272 6
125					4 44	669	9 35	33501 3
126					4 63	697	1 94	33737 4
127					4 80	683	7 04	33968 3
128					4 33	674	20 2	34186 1
129					4 50	675	34 7	34389 4
130					4 06	676	46 5	34580 9
131					4 11	669	55 6	34763 3
132					4 01	669	70 7	34930 6
133					3 95	660	81 8	35086 8
134					3 90	660	86 1	35238 7
135					4 43	795	31 0	35445 7
136					4 25	809	66 0	35617 7
137					3 96	784	82 0	35773 7
138					3 90	813	11 0	35901 7
139					3 84	783	88 0	36051 7
140					3 90	783	95 0	36194 7
141					4 02	843	44 0	36388 7
142					4 08	810	77 0	36549 7
143					4 01	818	165	36622 7
144					3 87	828	180	36680 7
145					3 88	766	196	36722 7
146					3 39	768	196	36764 7
147					4 04	792	198	36804 7
148					4 25	734	199	36843 7
149					4 45	776	245	36843 7
150					4 02	730	245	36843 7

Table 27 Sorption of Cr^{3+} on Brushwood Peat Humus from the mono-metal Cr-Cl solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Cr/dm^3 (2) c_0 = 250 mg Cr/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9b, mass 90 g , water retention capacity S/L = 1 2

	C_o 500 mgCr/dm^3 pH 4				C_o 250 mgCr/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	6 91	148	<0 001	910	7 20	103 3	<0 001	400
2	7 30	1179	<0 001	1820	7 35	418	<0 001	800
3	6 50	2220	<0 001	2730	6 55	1051	<0 001	1200
4	6 44	2280	<0 001	3640	6 22	1157	<0 001	1600
5	6 25	2250	<0 001	4550	6 06	1156	<0 001	2000
6	6 11	2250	<0 001	5460	6 00	1165	<0 001	2400
7	6 40	2250	<0 001	6370	6 23	1161	<0 001	2800
8	6 45	2250	<0 001	7280	6 55	1228	<0 001	3200
9	6 30	2330	<0 001	8190	6 76	1199	<0 001	3600
10	6 44	2240	<0 001	9100	6 18	1183	<0 001	4000
11	6 28	2240	<0 001	10010	6 65	1164	<0 001	4400
12	6 20	2250	<0 001	10920	6 14	1160	<0 001	4800
13	6 22	2260	<0 001	11830	6 22	1148	<0 001	5200
14	6 20	2210	<0 001	12740	6 20	1170	<0 001	5600
15	6 45	2230	<0 001	13650	6 65	1130	<0 001	6000
16	6 43	2400	<0 001	14560	6 72	1130	<0 001	6400
17	6 45	2180	<0 001	15470	6 20	1120	<0 001	6800
18	6 43	2260	<0 001	16380	6 88	1280	<0 001	7244
19	6 50	2360	<0 001	17402	6 99	1180	<0 001	7688
20	6 70	2390	<0 001	18424	6 69	1150	<0 001	8132
21	6 45	2350	<0 001	19446	6 26	1120	<0 001	8576
22	6 09	2310	<0 001	20486	6 41	1140	<0 001	9020
23	6 29	2280	<0 001	21490	6 49	1080	<0 001	9464
24	6 37	2290	<0 001	22512	6 46	1060	<0 001	9906
25	6 29	2430	<0 001	23534	6 36	1154	<0 001	10352
26	6 15	2450	<0 001	24556	5 98	1138	<0 001	10796
27	5 80	2450	0 55	25578	6 40	1195	<0 001	11240
28	5 55	2450	0 60	26600	6 34	1156	<0 001	11684

	C_o 500 mgCr/dm^3 pH 4				C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
29	5 60	2510	0 35	27622	7 07	1362	<0 001	12128
30	5 25	2330	7 30	28627 4	6 90	1161	<0 001	12572
31	4 55	2300	8 30	29638 2	6 64	1084	<0 001	13016
32	4 89	2310	10 14	30640	6 23	1065	<0 001	13460
33	4 40	2210	30 82	31600 4	5 89	1052	<0 001	13904
34	3 97	2260	66 15	32490 1	6 30	1115	<0 001	14348
35	3 84	2260	76 4	33359 3	6 70	1060	<0 001	14792
36	3 83	2220	92 4	34196 5	6 56	1168	<0 001	15236
37	3 57	2220	73 3	35071 9	6 28	1380	<0 001	15630
38	3 54	2220	81	35931 9	6 60	1547	<0 001	16024
39	3 43	2250	136 4	36681 1	6 55	1217	<0 001	16418
40	3 42	2350	192 4	37318 3	6 83	1136	<0 001	16812
41	3 16	2580	12 6	38315 1	6 23	1092	<0 001	17206
42	3 13	2360	60 4	39216 3	5 81	1109	<0 001	17600
43	3 16	2260	135	39968 3	6 30	1122	<0 001	17994
44	3 20	2260	179	40632 3	5 55	1125	<0 001	18388
45	3 01	2260	142	41344 3	6 01	1108	<0 001	18788
46	3 03	2220	161	42014 3	6 19	1077	<0 001	19176
47	3 02	2280	209	42592 3	5 61	1079	<0 001	19570
48	3 06	2290	242	43104 3	5 80	1099	<0 001	19964
49	2 88	2600	108	43616 3	5 85	1098	<0 001	20358
50	2 86	3070	167	44396 3	5 45	1105	<0 001	20752
51	2 90	2690	169	45054 3	6 28	1240	<0 001	21146
52	2 93	2590	268	45514 3	6 29	1150	<0 001	21540
53	2 78	2750	299	45870 3	6 04	1130	<0 001	21934
54	2 80	2690	297	46230 3	6 22	1250	<0 001	22320
55	2 90	2750	299	46590 3	6 10	1150	<0 001	22722
56	2 88	2920	300	46944 3	6 02	1140	<0 001	23116
57	2 31	3640	202	47494 3	5 70	1150	<0 001	23510
58	2 35	3370	253	47942 3	6 24	1150	<0 001	23904
59	2 40	3110	261	48374 3	6 10	1150	<0 001	24298
60	2 40	3080	289	48750 3	5 65	1160	<0 001	24692
61	2 45	3140	399	48906 3	5 95	1160	<0 001	25086

C_0 500 mgCr/dm^3, pH 4					C_0 250 mgCr/dm^3 pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
62	2 02	3150	320	49494 3	6 22	1635	<0 001	25494
63	2 00	3011	326	49758 3	5 82	1416	<0 001	25902
64	2 15	3003	345	50052 3	5 64	1360	<0 001	26310
65	2 18	2989	330	50324 3	5 95	1264	<0 001	26718
66	2 16	2978	341	50698 3	5 65	1313	<0 001	27126
67	2 24	2988	290	51050 3	5 91	1345	<0 001	27534
68	2 20	2845	301	51374 3	5 63	1389	<0 001	27942
69	2 21	2870	315	51680 3	5 44	1398	<0 001	28350
70	2 28	2835	324	51932 3	5 53	1470	<0 001	28758
71	2 21	2790	351	52158 3	6 35	1439	<0 001	29166
72	2 18	2750	364	52374 3	5 37	1453	<0 001	29574
73	2 15	2830	369	52586 3	5 97	1392	<0 001	29982
74	2 14	2800	371	52810 3	5 72	1387	<0 001	30390
75	2 20	2780	365	53008 3	5 69	1346	<0 001	30798
76	2 22	2760	378	53164 3	5 45	1383	<0 001	31206
77	2 20	2755	399	53296 3	5 75	1442	<0 001	31614
78	2 18	2769	411	53394 3	5 62	1363	<0 001	32022
79	2 20	2730	428	53528 3	5 26	1435	<0 001	32430
80	2 25	2710	410	53616 3	5 43	1410	<0 001	32838
81	2 23	2690	433	53626 3	5 41	1377	<0 001	33246
82	2 20	2734	450	53626 3	4 83	1416	<0 001	33654
83	2 21	2670	455	53626 3	4 89	1417	<0 001	34062
84	2 19	2680	455		5 04	1420	0 12	34469 8
85					4 97	1418	0 15	34877 5
86					4 63	1430	0 11	35285 3
87					4 82	1434	0 33	35692 6
88					4 89	1440	3 80	36093 0
89					4 00	1447	13 7	36473 6
90					3 64	1460	24 1	36833 4
91					3 57	1439	31 2	37179 0
92					3 26	1440	38 9	37553 2
93					3 19	1444	45 2	37914 8
94					3 40	1457	40 2	38286 4

C_o 500 mgCr/dm^3, pH 4					C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
95					3 24	1480	36 7	38665 0
96					3 10	1489	52 3	39012 4
97					3 02	1470	25 9	39412 6
98					2 93	1486	31 4	39801 9
99					2 88	1479	55 3	40143 2
100					2 84	1491	65 5	40464 2
101					2 80	1494	64 1	40788 0
102					2 75	1499	70 8	41098 4
103					2 75	1497	76 9	41396 6
104					2 74	1495	80 0	41688 6
105					2 70	1510	70 0	42000 6
106					2 70	1527	97 0	42258 6
107					2 71	1520	92 4	42525 8
108					2 70	1530	69 4	42839 0
109					2 76	1534	88 9	43113 2
110					2 70	1547	52 1	43461 0
111					2 65	1542	76 5	43760 0
112					2 67	1537	82 1	44047 8
113					2 60	1498	89 4	44321 0
114					2 59	1491	99 4	44574 2
115					2 52	1489	103 6	44819 0
116					2 50	1499	111 5	45048 0
117					2 65	1511	124 3	45251 4
118					2 67	1521	127 4	45448 6
119					2 63	1529	132 6	45635 4
120					2 60	1533	134 9	45817 6
121					2 58	1539	140 1	45989 4
122					2 54	1543	156 0	46129 4
123					2 56	1539	169 3	46242 8
124					2 54	1544	188 5	46317 8
125					2 53	1530	196 7	46376 4
126					2 51	1521	200	46376 4
127					2 52	1519	200	46376 4

Table 28 Sorption of Cr^{3+} on Rush (Reed-Sedge) Peat from the mono-metal Cr-Cl solutions under dynamic flow conditions

Column experiments, Input solution (1) c_o = 500 mg Cd/dm^3 (2) c_0 = 250 mg Cd/dm^3, pH 4 0, flow rate q = 0 1 cm^3/s, Adsorbent W9c, mass 90 g, water retention capacity S/L = 1 1

	C_o 500 mgCr/dm^3, pH 4				C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
1	6 86	41 7	0 0	455	6 60	88 6	0 0	220
2	6 97	48 9	0 0	910	6 64	66	0 0	440
3	6 55	267	0 0	1365	6 50	226	0 0	660
4	6 4	1278	0 0	1820	6 43	713	0 0	880
5	5 74	2260	0 0	2275	6 09	1167	0 0	1100
6	5 84	2450	0 0	2730	6 03	1286	0 0	1320
7	5 78	2510	0 0	3185	5 92	1309	0 0	1540
8	5 8	2490	0 0	3640	6 01	1321	0 0	1760
9	5 98	2500	0 0	4095	5 98	1319	0 0	1980
10	5 63	2500	0 0	4550	6 05	1323	0 0	2200
11	5 95	2610	0 0	5005	6 11	1452	0 0	2420
12	5 92	2560	0 0	5460	6 11	1355	0 0	2640
13	6	2500	0 0	5915	6 15	1343	0 0	2860
14	5 79	2500	0 0	6370	6 18	1332	0 0	3080
15	5 96	2500	0 0	6825	6 18	1336	0 0	3300
16	5 98	2510	0 0	7280	5 98	1330	0 0	3520
17	5 94	2500	0 0	7735	6 06	1340	0 0	3740
18	5 99	2480	0 0	8190	6 10	1330	0 0	3960
19	5 96	2500	0 0	8645	6 05	1334	0 0	4180
20	5 99	2480	0 0	9100	6 08	1326	0 0	4400
21	5 95	3560	0 0	9585	5 68	1437	0 0	4620
22	6 05	2580	0 0	10070	6 28	1797	0 0	4850
23	6 04	2480	0 0	10555	6 30	1380	0 0	5080
24	6	2550	0 0	11040	6 34	1362	0 0	5310
25	6 01	2600	0 0	11525	6 43	1345	0 0	5540
26	6 03	2770	0 0	12010	6 38	1359	0 0	5770
27	6	2590	0 0	12495	6 38	1346	0 0	6000
28	6 05	2430	0 0	12980	6 28	1416	0 0	6230
29	6 1	2500	0 0	13465	6 23	1334	0 0	6460
30	6	2580	0 0	13950	6 50	1288	0 0	6690
31	5 91	2540	0 0	14435	6 49	1309	0 0	6920
32	5 93	2510	0 0	14920	6 32	1320	0 0	7150
33	5 9	2520	0 0	15405	6 22	1321	0 0	7380

C_o 500 mgCr/dm^3, pH 4					C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
34	5 99	2510	0 0	15890	6 36	1313	0 0	7610
35	5 96	2510	0 0	16375	6 14	1312	0 0	7840
36	5 94	2510	0 0	16860	6 29	1309	0 0	8070
37	5 96	2630	0 0	17345	6 15	1311	0 0	8300
38	6 04	2460	0 0	17830	6 20	1307	0 0	8530
39	6 06	2410	0 0	18315	6 26	1311	0 0	8760
40	6 04	2500	0 0	18800	6 20	1284	0 0	8990
41	5 8	2430	1 4	19283 6	6 22	1299	0 0	9220
42	5 7	2380	3 5	19765 1	6 11	1301	0 0	9450
43	5 6	2380	6 1	20244	6 18	1308	0 0	9680
44	5 45	2290	8 1	20720 9	6 23	1308	0 0	9910
45	5 13	2390	9 1	21196 8	6 25	1294	0 0	10140
46	4 97	2360	10 6	21671 2	6 15	1359	0 0	10370
47	4 78	2310	10 8	22145 4	6 15	1315	0 0	10600
48	4 6	2250	11 4	22619	6 44	1293	0 0	10830
49	6 13	2210	1 8	23102 2	6 00	1307	0 0	11060
50	6 15	2190	1 2	23586	6 10	1298	0 0	11290
51	5 76	2130	4 7	24066 3	6 15	1317	0 0	11520
52	4 81	2300	17 4	24533 9	5 98	1310	0 0	11750
53	4 36	2420	34 8	24984 1	6 11	1305	0 0	11980
54	4 27	2400	61 3	25407 8	6 06	1307	0 0	12210
55	4 21	2370	58 0	25834 8	6 00	1336	0 0	12440
56	4 2	2480	20 6	26299 2	6 31	1470	0 0	12670
57	3 93	2280	57 0	26727 2	6 20	1210	0 0	12900
58	3 84	2270	102	27110 2	6 31	1130	0 0	13130
59	3 74	2400	91 5	27503 7	6 33	1180	0 0	13360
60	3 65	2430	105	27896 7	6 36	1220	0 0	13590
61	3 6	2590	88 6	28306 1	6 46	1220	0 0	13820
62	3 58	2570	106	28698 1	5 99	1220	0 0	14050
63	3 59	2510	109	29086 6	6 07	1200	0 0	14280
64	3 6	2550	116	29468 6	6 02	1310	0 0	14510
65	3 55	2580	95 0	29871 6	6 03	1190	0 0	14744
66	3 45	2350	134	30235 6	6 30	1140	0 0	14978
67	3 39	2310	147	30586 6	6 04	1280	0 0	15212
68	3 34	2430	187	30901 6	6 14	1340	0 0	15446
69	3 09	2910	86 2	31313 4	6 12	1460	0 0	15680
70	3 04	2340	120 2	31691 2	6 05	1440	0 0	15914
71	3 04	2320	169	32020 2	6 00	1410	0 0	16148
72	2 96	2510	252	32266 2	5 84	1410	0 0	16382

C_o 500 mgCr/dm^3, pH 4					C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
73	2 92	2590	285	32479 2	5 75	1390	0 0	16616
74	2 9	2580	282	32695 2	6 03	1530	0 0	16850
75	2 91	2590	279	32914 2	6 10	1370	0 0	17084
76	2 5	2720	87 7	33324 5	6 04	1340	0 0	17318
77	2 53	2690	150 1	33672 4	6 10	1350	0 0	17552
78	2 54	2650	212	33958 4	6 04	1430	0 0	17786
79	2 58	2690	264 2	34192 2	5 90	1430	0 0	18020
80	2 55	2660	265	34425 2	6 14	1733	0 0	18254
81	2 5	2690	264	34659 2	6 25	1344	0 0	18488
82	2 55	2650	265	34892 2	6 00	1189	0 0	18722
83	2 56	2610	280	35110 2	5 39	1314	0 1	18955 9
84	2 55	2630	310	35298 2	5 41	1345	0 0	19189 9
85	2 55	3210	234	35562 2	6 10	1330	0 0	19423 9
86	2 57	2920	245	35815 2	6 01	1533	0 0	19657 9
87	2 6	2840	266	36047 2	6 21	1263	0 1	19891 8
88	2 6	2940	312	36233 2	6 29	1198	0 1	20125 7
89	2 6	3830	409	36322 2	6 34	1292	0 0	20359 7
90	2 61	3020	266	36554 2	6 10	1296	0 1	20593 6
91	2 7	2840	298	36714 2	6 22	1287	0 0	20827 6
92	2 77	3010	382	36849 2	6 32	1240	0 2	21061 4
93	2 75	3300	382	36944 2	6 28	1248	0 2	21295 1
94	2 75	3170	387	37034 2	5 93	1301	0 25	21528 9
95	2 8	3060	152	37359 2	5 53	1364	0 1	21762 8
96	2 28	3070	239	37597 2	5 50	1350	0 1	21996 7
97	2 35	2940	261	37813 2	5 75	1352	0 0	22230 7
98	2 35	2980	332	37958 2	5 05	1365	0 08	22464 6
99	2 44	3050	427	38008 2	5 60	1276	0 11	22698 5
100	2 44	3070	403	38082 2	5 55	1332	0 14	22932 4
101	2 45	3010	417	38142 2	5 31	1710	0 07	23166 4
102	2 5	2940	432	38187 2	5 85	1520	0 0	23400 4
103	2 5	2930	423	38241 2	6 15	1360	0 16	23634 4
104	2 5	2830	433	38285 2	5 95	1400	0 2	23868 4
105	2 5	2830	435	38328 2	5 79	1460	0 14	24102 4
106	2 5	2870	432	38330 2	5 75	1690	0 01	24336 4
107	2 5	2890	450	38377 2	6 00	1420	0 3	24570 1
108	2 5	2890	455	38399 2	5 18	1370	0 15	24804 0
109	2 51	2900	455	38399 2	4 25	1490	6 9	25032 1
110	2 49	2910	455	38399 2	4 26	1530	128	25253 1
111					4 48	1580	5 4	25481 9

C_o 500 mgCr/dm^3, pH 4					C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
112					4 11	1510	17 5	25698 4
113					3 81	1440	21 5	25970 9
114					3 85	1470	27 8	26118 4
115					3 58	1500	34 0	26317 1
116					3 80	1500	27 8	26523 3
117					3 78	1490	36 7	26720 6
118					3 74	1690	33 0	26921 6
119					3 34	1580	1 32	27154 3
120					3 84	1314	3 4	27384 9
121					3 58	1366	13 4	27605 5
122					3 22	1459	24 0	27815 5
123					3 37	1488	34 0	28015 5
124					3 34	1480	41 0	28208 5
125					3 13	1500	46 0	28396 5
126					3 30	1502	49 0	28581 5
127					3 18	1507	55 0	28760 5
128					3 05	1510	62 0	28932 5
129					3 05	1564	41 0	29125 5
130					3 04	1482	58 0	29301 5
131					2 95	1499	65 0	29470 5
132					2 92	1557	75 0	29629 5
133					2 88	1596	81 0	29782 5
134					2 80	1608	85 0	29931 5
135					2 78	1617	91 0	30074 5
136					2 68	1668	64 0	30244 5
137					2 69	1622	71 0	30407 5
138					2 66	1670	84 0	30557 5
139					2 60	1758	120	30671 5
140					2 59	1772	133	30772 5
141					2 60	1793	151	30855 5
142					2 60	1796	155	30934 5
143					2 53	1850	113	31055 5
144					2 53	1800	91 0	31198 5
145					2 54	1809	126	31306 5
146					2 54	1822	137	31403 5
147					2 55	1830	136	31501 5
148					1 99	1833	119	31616 5
149					1 88	1840	171	31680 5
150					2 01	1856	135	31780 5

C_o 500 mgCr/dm^3, pH 4					C_o 250 mgCr/dm^3, pH 4			
ER	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)	pH	EC (μS/s)	C (mg/dm^3)	Load (mg/kg)
151					2 02	1868	166	31849 5
152					2 01	1870	159	31925 5
153					2 05	1890	164	31996 5
154					2 08	1888	168	32063 5
155					2 05	1891	140	32158 5
156					2 10	1900	143	32250 5
157					2 08	1901	146	32339 5
158					2 05	1910	151	32423 5
159					2 08	1914	135	32523 5
160					2 03	1924	145	32613 5
161					2 10	1941	153	32695 5
162					2 10	1950	145	32785 5
163					2 05	1948	153 5	32867 0
164					2 05	1955	166	32936 0
165					2 06	1960	148 5	33022 5
166					2 10	1965	171	33086 5
167					2 14	1976	178	33143 5
168					2 12	1959	182	33196 5
169					2 10	1954	195	33236 5
170					2 08	1962	201	33270 5
171					2 06	1959	208	33297 5
172					2 09	1964	220	33297 5
173					2 07	1955	220	33297 5

Table 29 Binding of metal ions onto low-moor peat under batch and dynamic conditions in the mono-metal systems Comparison of sorption capacity and parameters

	Batch experiment C_o 5000 mg Me/dm^3	Column experiment C_o 500 Me/dm^3		Column experiment C_o 250 Me/dm^3	
		full	total	full	total
Brushwood Humus Peat - W9b					
Zn - SO_4					
Sorption mg/kg (%)	36370 (82 8%)	39780	55730 (87 08%)	13293	47321 (87 63%)
Solid solution ratio	1 10	1 70	1 128	1 46	1 216
Changes of pH	6 70 - 5 18	6 98 - 5 60/5 43	6 98 - 4 57	7 28 - 6 10/5 82	7 28 - 4 18
Desorption mg/kg (%)	28176 (77 47%)	32080 (57 49%)			
Cd - SO_4					
Sorption mg/kg (%)	45029 (93 1%)	51975	72514 (83 35%)	34687	53122 (87 08%)
Solid solution ratio	1 10	1 108	1 174	1 126	1 244
Changes of pH	6 93 - 5 57	7 13 - 5 45	7 13 - 5 51	7 00 - 5 75/5 57	7 00 - 5 50
Desorption mg/kg (%)	36408 (80 85%)	36642 (57 29%)			
Cu - Cl		Cu - SO_4			
Sorption mg/kg (%)	45540 (91 1%)	33810 (67 0%)	50506 (78 91%)	26838	40924 (76 48%)
Solid solution ratio	1 10	1 70	1 128	1 114	1 214
Changes of pH	7 60 - 3 77	7 27 - 6 21/5 73	7 27 - 3 54	6 94 - 5 61	6 94 - 3 58
Desorption mg/kg (%)	27100 (59 51%)	14080 (27 89%)			
Cr - Cl					
Sorption mg/kg (%)	47620 (95 2%)	24556	53626 (63 84%)	34062	46376 (73 03%)
Solid solution ratio	1 10	1 52	1 168	1 166	1 254
Changes of pH	6 95 - 3 11	6 91 - 6 15/5 55	6 91 - 2 21	7 20 - 5 40/4 89	7 20 - 2 52
Desorption mg/kg (%)	2911 (6 11%)	554 5 (1 03%)			

Rush (Reed-Sedge) Peat - W9c					
Zn - SO_4					
Sorption mg/kg (%)	36264 (82 5%)	30880	36820 (88 72%)	18730	29748 (83 21%)
Solid solution ratio	1 10	1 58	1 83	1 74	1 143
Changes of pH	5 98 - 5 10	6 85 -6 41/5 81	6 85 - 4 16	7 08 - 6 08/5 60	7 08 - 4 83
Desorption mg/kg (%)	25096 (69 2%)	27748 (75 36%)			
Cd - SO_4					
Sorption mg/kg (%)	45889 (94 9%)	51810	63958 (90 72%)	36707	45032 (96 32%)
Solid solution ratio	1 10	1 99	1 141	1 145	1 187
Changes of pH	5 99 - 5 38	6 55 - 5 77/5 35	6 55 - 4 66	6 68 - 5 91/5 78	6 68 - 4 55
Desorption mg/kg (%)	29352 (63 96%)	36642 (57 29%)			
Cu - Cl		Cu - SO_4			
Sorption mg/kg (%)	47390 (94 8%)	27028	39465 (69 23%)	32333	36844 (68 25%)
Solid solution ratio	1 10	1 57	1 114	1 120	1 149
Changes of pH	7 54 - 4 44	6 90 - 6 09/5 30	6 90 - 3 80	6 93 - 5 26/4 70	6 93 - 3 09
Desorption mg/kg (%)	29100 (61 41%)	20040 (50 78%)			
Cr - Cl					
Sorption mg/kg (%)	49380 (98 8%)	18800	38399 (71 11%)	20827	33297(76 99%)
Solid solution ratio	1 10	1 40	1 108	1 91	1 173
Changes of pH	7 65 - 3 22	6 98 - 6 04/5 00	6 98 - 2 50	6 60 - 6 22/5 53	6 60 - 2 07
Desorption mg/kg (%)	3150 (6 38%)	872 5 (2 27%)			

Table 30 Sorption and recovery of metals bound under dynamic flow conditions from the peat matrix

Sorption Column experiments, Input solution (1) c_o = 500 mg Me dm^3, pH 4 0, flow rate q = 0 1 cm^3 s, Adsorbent (1) Brushwood Peat Humus W9b, S/L = 1 2 , (2) Rush (Reed-Sedge) Peat W9c, S/L = 1 1
Desorption 1% HCl

SAMPLE Brushwood Peat Humus W9b (DR 55%), INPUT CONCENTRATION c_o = 500 mg/dm^3						
Metal	Sorption		Desorption		Desorption	
	pH	S (mg/kg)	pH	Distilled water pH 6	pH	1% HCl
Cr	2 21	53626	2 60	35 52 (0 066%)	1 30	554 5 (1 03%)
Cu	3 52	50506	3 91	1156 4 (2 29%)	1 40	14080 (27 88%)
Cd	4 52	72514	5 14	2210 1 (3 05%)	1 46	23785 (32 80%)
Zn	4 49	55730	4 70	2786 1 (4 99%)	1 35	32040 (57 49%)
SAMPLE Rush (Reed-Sedge) Peat W9c (DR 55%), INPUT CONCENTRATION c_o = 500 mg/dm^3						
Metal	Sorption		Desorption		Desorption	
	pH	S (mg/kg)	pH	Distilled water pH 6	pH	1% HCl
Cr	2 49	38399	2 62	89 13 (0 23%)	1 23	872 5 (2 27%)
Cu	3 80	39465	3 64	1622 0 (4 11%)	1 43	20040 5 (50 78%)
Cd	4 65	63959	4 81	3310 0 (5 17%)	1 32	36642 (57 29%)
Zn	4 96	36820	4 57	2401 5 (6 52%)	1 33	27748 (75 36%)

Table 31 Sequential fractionation of Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} ions sorbed from mono-metal solution under dynamic conditions, at c_0 = 500 mg Me dm^3 and pH 4 0 onto low-moor peat

Peat samples (1) Brushwood Peat Humus (W9b), (2) Rush (Reed-Sedge)Peat (W9c), Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

SAMPLE Brushwood Peat Humus W9b (DR 55%), INPUT CONCENTRATION c_0 = 5000 mg/dm^3					
		Cr	Cu	Cd	Zn
SORPTION mg/kg		53626	50506	72514	55730
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	35 52 (0 07)	1156 4 (2 29)	2210 1 (3 05)	2786 1 (4 99)
Most labile	F1 (EXC)	269 9 (0 50)	6853 5 (13 57)	14574 6 (20 10)	24507 (43 97)
Labile	F2 (CARB)	1321 6 (2 46)	6156 (12 19)	8360 (11 53)	7125 (12 78)
Easily reducible	F3 (ERO)	270 9 (0 51)	963 9 (1 91)	1000 9 (1 38)	1593 (2 86)
Moderately reducible	F4 (MRO)	4962 6 (9 25)	10608 (21 00)	864 (1 19)	1073 7 (1 93)
Strongly bound	F5 (OM)	46765 7 (58 03)	24768 2 (49 04)	45504 5 (62 75)	19383 1 (34 78)
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)
SAMPLE Rush (Reed-Sedge) Peat W9c (DR 55%), INPUT CONCENTRATION c_0 = 500 mg/dm^3					
		Cr	Cu	Cd	Zn
SORPTION mg/kg		38399	39465 4	63959	36820
FRACTION mg/kg (%)					
Pore solution	F0 (PS)	89 13 (0 23)	1622 0 (4 11)	3310 (5 17)	2401 5 (6 52)
Most labile	F1 (EXC)	2167 2 (5 64)	11306 8 (28 65)	25032 (39 14)	20013 (54 30)
Labile	F2 (CARB)	1445 2 (3 76)	5982 9 (15 16)	9270 (14 49)	6200 (16 84)
Easily reducible	F3 (ERO)	412 8 (1 07)	1162 2 (2 95)	1983 (3 10)	1939 2 (5 27)
Moderately reducible	F4 (MRO)	5772 6 (15 03)	5933 (15 03)	2087 4 (3 26)	1016 7 (2 76)
Strongly bound	F5 (OM)	28512 07 (74 25)	13457 5 (34 1)	22276 5 (34 83)	5249 5 (14 01)
Residual fraction	F6 (R)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)	0 0 (0 0)

Table 32 Equilibrium mass adsorption/desorption isotherms for metal ions bound from electroplating waste onto Alder Peat Humus (W1) and pH of equilibrated solutions,

Batch experiments, Input liquid waste Me-SO$_4$, pH 1 47, c$_0$ 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Sample	Alder Peat Humus - W1						
	SORPTION			DESORPTION by distilled water pH 6		DESORPTION by 1% HCl	
c$_0$ mg/dm^3	pH	c$_{eq}$ mg/dm^3	S mg/kg (%)	pH	D mg/kg (%)	pH	D mg/kg (%)
Cd							
17 2	4 40	0 27	169 3 (98 4%)	3 80	2 17 (1 28%)	2 60	64 87 (38 32%)
34 4	3 13	2 79	316 0 (91 8%)	3 61	17 87 (5 65%)	2 41	105 3 (33 32%)
51 5	2 43	11 10	404 0 (78 4%)	3 38	47 07 (3 38%)	2 20	87 60 (21 68%)
68 7	2 05	20 40	483 0 (70 3%)	3 08	66 40 (13 74%)	2 08	59 55 (12 33%)
85 9	1 90	29 40	565 0 (65 8%)	2 99	72 81 (12 89%)	2 01	55 59 (9 84%)
103 1	1 84	37 60	655 0 (63 5%)	2 98	75 48 (11 53%)	2 00	51 60 (7 88%)
120 1	1 79	44 60	756 0 (62 9%)	2 91	96 27 (12 73%)	1 88	65 76 (8 60%)
137 4	1 75	49 80	876 0 (63 8%)	2 88	112 10 (12 79%)	1 67	52 14 (5 95%)
154 6	1 71	52 30	1023 0 (66 2%)	2 86	148 24 (14 49%)	1 62	76 41 (7 47%)
171 8	1 67	65 40	1064 0 (61 9%)	2 86	133 23 (12 52%)	1 49	79 11 (7 43%)
Cr							
23 5	4 40	0 03	234 7 (99 8%)	3 80	0 28 (0 12%)	2 60	24 36 (10 38%)
47 0	3 13	0 10	469 0 (99 8%)	3 61	0 55 (0 12%)	2 41	56 91 (12 13%)
70 5	2 43	0 44	700 6 (99 4%)	3 38	1 68 (0 24%)	2 20	99 12 (14 15%)
94 0	2 05	1 15	928 5 (98 8%)	3 08	5 25 (0 56%)	2 08	94 00 (10 12%)
117 5	1 90	6 20	1113 0 (94 7%)	2 99	13 25 (1 19%)	2 01	119 8 (10 76%)
141 0	1 84	9 10	1319 0 (93 5%)	2 98	19 38 (1 46%)	2 00	108 09 (8 19%)
164 5	1 79	13 10	1514 0 (92 0%)	2 91	33 12 (2 19%)	1 88	129 51 (8 55%)
188 0	1 75	16 80	1712 0 (91 1%)	2 88	45 40 (2 65%)	1 67	112 59 (6 58%)
211 5	1 71	21 70	1898 0 (89 7%)	2 86	65 60 (3 46%)	1 62	160 04 (8 44%)
235 0	1 67	31 20	2038 0 (86 7%)	2 86	63 37 (3 12%)	1 49	169 11 (8 29%)
Fe							
1498 5	4 40	1 01	14975 (99 9%)	3 80	2 76 (0 018%)	2 60	12080 (80 67%)
2997 0	3 13	4 23	29928 (99 8%)	3 61	11 57 (0 039%)	2 41	15276 (51 04%)
4495 5	2 43	143	43525 (96 8%)	3 38	163 95 (0 38%)	2 20	24272 (55 77%)
5994 0	2 05	999	49950 (83 3%)	3 08	801 2 (1 60%)	2 08	26512 (53 08%)
7492 5	1 90	1571	59215 (79 0%)	2 99	1696 8 (2 86%)	2 01	34680 (58 57%)
8991 0	1 84	1781	72100 (80 2%)	2 98	3102 0 (4 30%)	2 00	36366 (50 44%)
10489 5	1 79	2135	83545 (79 6%)	2 91	4863 0 (5 82%)	1 88	38826 (46 47%)
11988 0	1 75	2800	91880 (76 6%)	2 88	5939 0 (6 46%)	1 67	30960 (33 70%)
13486 5	1 71	3761	97255 (72 1%)	2 86	6366 0 (6 54%)	1 62	39138 (40 24%)
14985 0	1 67	4516	104690 (69 9%)	2 86	8522 0 (8 14%)	1 49	41233 (39 38%)

Sample	Alder Peat Humus - W1						
	SORPTION			DESORPTION by distilled water, pH 6		DESORPTION by 1% HCl	
c_0 mg/dm^3	pH	c_{eq} mg/dm^3	S mg/kg (%)	pH	D mg/kg (%)	pH	D mg/kg (%)
Mn							
12 2	4 40	4 07	81 3 (66 7%)	3 80	2 39 (2 43%)	2 60	37 10 (45 63%)
24 4	3 13	14 26	101 4 (41 6%)	3 61	3 89 (3 84%)	2 41	46 20 (45 56%)
36 6	2 43	24 9	117 0 (31 9%)	3 38	4 79 (4 41%)	2 20	57 60 (49 23%)
48 8	2 05	35 4	134 0 (27 4%)	3 08	8 79 (6 56%)	2 08	64 30 (47 98%)
61 0	1 90	45 9	151 0 (24 7%)	2 99	10 29 (6 82%)	2 01	77 20 (51 12%)
73 2	1 84	52 8	204 0 (27 9%)	2 98	12 83 (6 29%)	2 00	99 40 (48 72%)
85 4	1 79	63 2	222 0 (25 9%)	2 91	15 36 (6 92%)	1 88	115 2 (51 98%)
97 6	1 75	73 8	238 0 (24 4%)	2 88	20 99 (8 82%)	1 67	126 4 (53 11%)
109 8	1 71	80 8	290 0 (26 4%)	2 86	26 85 (9 26%)	1 62	149 6 (51 58%)
122 0	1 67	88 2	338 0 (27 7%)	2 86	32 14 (9 51%)	1 49	166 8 (49 35%)
Zn							
280 7	4 40	24 4	2563 (91 3%)	3 80	13 92 (0 54%)	2 60	2222 (86 70%)
561 4	3 13	211	3504 (62 4%)	3 61	115 86 (3 31%)	2 41	3156 (90 07%)
842 1	2 43	475	3672 (43 6%)	3 38	183 20 (4 99%)	2 20	1721 2 (46 87%)
1122 8	2 05	743	3797 (23 8%)	3 08	218 49 (5 75%)	2 08	1355 1 (35 86%)
1403 5	1 90	1015	3889 (27 7%)	2 99	242 32 (6 23%)	2 01	1104 9 (28 41%)
1684 2	1 84	1291	3936 (23 4%)	2 98	304 65 (7 74%)	2 00	1121 4 (28 49%)
1964 9	1 79	1566	3993 (20 3%)	2 91	383 70 (9 61%)	1 88	1591 2 (39 85%)
2245 6	1 75	1839	4064 (18 1%)	2 88	397 80 (9 78%)	1 67	1379 1 (33 93%)
2526 3	1 71	2117	4093 (16 2%)	2 86	386 40 (9 44%)	1 62	2031 6 (49 64%)
2807 0	1 67	2448	3590 (12 7%)	2 86	323 60 (9 01%)	1 49	1456 9 (40 58%)

Table 33 Equilibrium mass adsorption/desorption isotherms for metal ions bound from electroplating waste onto Brushwood Peat Humus (W9b) and pH of equilibrated solutions,

Batch experiments, Input liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Sample	Brushwood Peat Humus - W9b						
	SORPTION			DESORPTION by distilled water pH 6		DESORPTION by 1% HCl	
c_0 mg/dm³	pH	c_{eq} mg/dm³	S mg/kg (%)	pH	D mg/kg (%)	pH	D mg/kg (%)
Cd							
17 2	4 41	0 60	166 0 (96 5%)	3 68	3 23 (1 94%)	2 55	65 18 (39 27%)
34 4	2 47	9 39	250 1 (72 7%)	3 40	34 99 (13 99%)	2 49	56 40 (22 55%)
51 5	2 05	16 55	349 5 (67 9%)	3 07	45 87 (13 12%)	2 19	30 81 (8 82%)
68 7	1 95	24 32	443 8 (64 6%)	2 99	62 57 (14 10%)	2 07	38 73 (8 73%)
85 9	1 85	30 60	553 0 (64 4%)	2 94	71 07 (12 85%)	2 00	37 62 (6 80%)
103 1	1 85	34 80	683 0 (66 2%)	2 93	89 85 (13 16%)	1 98	60 57 (8 87%)
120 1	1 80	41 70	785 0 (65 3%)	2 89	105 36 (13 42%)	1 88	82 41 (10 50%)
137 4	1 75	51 40	860 0 (62 6%)	2 87	117 71 (13 69%)	1 65	62 64 (7 28%)
154 6	1 71	58 20	964 0 (62 3%)	2 86	145 32 (15 07%)	1 60	69 87 (7 25%)
171 8	1 67	66 50	1053 0 (61 3%)	2 86	147 50 (14 01%)	1 38	77 55 (7 36%)
Cr							
23 5	4 41	0 06	234 4 (99 7%)	3 68	0 00 (0 00%)	2 55	27 83 (11 87%)
47 0	2 47	0 42	465 8 (99 1%)	3 40	0 81 (0 34%)	2 49	60 87 (13 07%)
70 5	2 05	2 58	679 2 (96 3%)	3 07	6 79 (0 99%)	2 19	67 56 (9 95%)
94 0	1 95	6 33	876 7 (93 3%)	2 99	12 90 (1 47%)	2 07	85 60 (9 76%)
117 5	1 85	9 49	1080 1 (91 9%)	2 94	19 72 (1 82%)	2 00	93 68 (8 67%)
141 0	1 85	11 10	1299 0 (92 1%)	2 93	27 97 (2 15%)	1 98	122 58 (9 44%)
164 5	1 80	13 30	1512 0 (91 9%)	2 89	40 49 (2 68%)	1 88	137 19 (9 07%)
188 0	1 75	17 80	1702 0 (90 5%)	2 87	66 92 (3 93%)	1 65	129 90 (7 63%)
211 5	1 71	28 70	1828 0 (86 4%)	2 86	73 32 (4 01%)	1 60	169 52 (9 27%)
235 0	1 67	34 60	2004 0 (85 3%)	2 86	77 96 (3 89%)	1 38	177 11 (8 84%)
Fe							
1498 5	4 41	0 33	14981 7 (99 9%)	3 68	4 03 (0 027%)	2 55	13134 (87 67%)
2997 0	2 47	11 90	29851 (99 6%)	3 40	48 57 (0 16%)	2 49	19068 (63 88%)
4495 5	2 05	316 0	41795 (92 9%)	3 07	777 60 (1 86%)	2 19	25928 (62 04%)
5994 0	1 95	818 6	51754 (86 3%)	2 99	1395 8 (2 69%)	2 07	36256 (70 05%)
7492 5	1 85	1488	60045 (80 1%)	2 94	3476 0 (5 79%)	2 00	31440 (52 36%)
8991 0	1 85	2014	69770 (77 6%)	2 93	4007 0 (5 74%)	1 98	35880 (51 43%)
10489 5	1 80	2436	80535 (76 8%)	2 89	5793 0 (7 19%)	1 88	45582 (52 87%)
11988 0	1 75	3336	86520 (72 2%)	2 87	8174 0 (9 45%)	1 65	35790 (41 37%)
13486 5	1 71	4096	93905 (69 6%)	2 86	9046 0 (9 63%)	1 60	48786 (51 95%)
14985 0	1 67	4876	101090 (67 5%)	2 86	15036 0 (14 87%)	1 38	49586 (49 05%)

Sample	Brushwood Peat Humus - W9b						
	SORPTION			DESORPTION by distilled water, pH 6		DESORPTION by 1% HCl	
c_o mg/dm^3	pH	c_{eq} mg/dm^3	S mg/kg (%)	pH	D mg/kg (%)	pH	D mg/kg (%)
Mn							
12 2	4 41	4 88	73 2 (60 0%)	3 68	5 61 (7 66%)	2 55	28 4 (38 79%)
24 4	2 47	13 76	106 4 (43 6%)	3 40	6 46 (6 07%)	2 49	46 6 (43 80%)
36 6	2 05	24 8	118 0 (32 2%)	3 07	10 73 (9 09%)	2 19	55 5 (47 03%)
48 8	1 95	34 9	139 0 (28 5%)	2 99	9 76 (7 02%)	2 07	68 1 (48 99%)
61 0	1 85	44 6	164 0 (26 9%)	2 94	10 61 (6 47%)	2 00	73 8 (45 00%)
73 2	1 85	55 3	179 0 (24 4%)	2 93	10 24 (5 72%)	1 98	88 1 (49 22%)
85 4	1 80	60 6	248 0 (29 0%)	2 89	21 40 (8 63%)	1 88	111 6 (45 00%)
97 6	1 75	70 2	274 0 (28 1%)	2 87	21 21 (7 74%)	1 65	128 5 (46 89%)
109 8	1 71	80 9	289 0 (26 3%)	2 86	27 14 (9 39%)	1 60	140 1 (48 48%)
122 0	1 67	86 5	355 0 (29 1%)	2 86	36 38 (10 25%)	1 38	169 4 (47 72%)
Zn							
280 7	4 41	53 9	2268 (80 7%)	3 68	24 28 (0 74%)	2 55	2128 2 (93 84%)
561 4	2 47	287	2744 (48 9%)	3 40	138 02 (5 03%)	2 49	1095 5 (39 92%)
842 1	2 05	554	2881 (34 2%)	3 07	169 78 (5 89%)	2 19	813 60 (28 24%)
1122 8	1 95	818	3048 (27 1%)	2 99	214 50 (7 04%)	2 07	988 8 (32 44%)
1403 5	1 85	1080	3235 (23 1%)	2 94	244 16 (7 55%)	2 00	1186 5 (36 68%)
1684 2	1 85	1346	3380 (20 1%)	2 93	347 25 (10 27%)	1 98	1503 6 (44 49%)
1964 9	1 80	1613	3517 (17 3%)	2 89	414 55 (11 79%)	1 88	1902 9 (54 11%)
2245 6	1 75	1880	3656 (16 3%)	2 87	458 90 (12 55%)	1 65	1853 2 (50 69%)
2526 3	1 71	2140	3863 (15 3%)	2 86	506 60 (13 11%)	1 60	2099 6 (54 35%)
2807 0	1 67	2455	3520 (12 5%)	2 86	548 00 (15 57%)	1 38	2041 1 (57 98%)

Table 34 Equilibrium mass adsorption/desorption isotherms for metal ions bound from electroplating waste onto Rush Reed-Sedge Peat (W9c) and pH of equilibrated solutions,

Batch experiments, Input liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Sample	Rush (Reed-Sedge) Peat - W9c						
	SORPTION			DESORPTION by destilled water pH 6		DESORPTION by 1% HCl	
c_o mg/dm^3	pH	c_{eq} mg/dm^3	S mg/kg (%)	pH	D mg/kg (%)	pH	D mg/kg (%)
Cd							
17 2	4 21	0 66	165 4 (96 2%)	3 64	6 06 (3 66%)	2 58	53 30 (32 22%)
34 4	2 95	7 38	270 2 (78 5%)	3 49	30 67 (11 36%)	2 40	91 90 (34 01%)
51 5	2 13	14 41	370 9 (72 0%)	3 16	54 11 (14 59%)	2 19	58 45 (15 76%)
68 7	2 01	23 86	448 4 (65 3%)	3 03	72 22 (16 11%)	2 05	47 01 (10 48%)
85 9	1 92	30 38	555 2 (64 6%)	2 99	89 37 (16 10%)	1 99	55 23 (9 95%)
103 1	1 87	37 26	658 0 (63 8%)	2 98	100 29 (15 24%)	1 87	56 91 (8 65%)
120 1	1 82	48 60	716 0 (59 6%)	2 95	132 18 (18 97%)	1 65	57 78 (8 07%)
137 4	1 76	52 68	847 0 (61 6%)	2 91	141 54 (16 71%)	1 58	72 72 (8 59%)
154 6	1 73	54 24	1004 0 (64 9%)	2 88	179 13 (17 89%)	1 48	71 73 (7 14%)
171 8	1 68	63 00	1088 0 (63 3%)	2 88	184 29 (16 94%)	1 44	72 96 (6 71%)
Cr							
23 5	4 21	0 38	231 2 (98 4%)	3 64	0 079 (0 034%)	2 58	17 22 (7 22%)
47 0	2 95	0 98	460 2 (97 9%)	3 49	0 43 (0 09%)	2 40	52 71 (11 45%)
70 5	2 13	1 12	693 8 (98 4%)	3 16	2 86 (0 41%)	2 19	80 68 (11 63%)
94 0	2 01	3 45	905 5 (96 3%)	3 03	12 53 (1 38%)	2 05	93 20 (10 29%)
117 5	1 92	9 04	1084 6 (92 3%)	2 99	22 69 (2 09%)	1 99	73 29 (6 76%)
141 0	1 87	16 20	1248 0 (88 5%)	2 98	36 23 (2 90%)	1 87	106 20 (8 81%)
164 5	1 82	16 70	1478 0 (89 8%)	2 95	59 90 (4 05%)	1 65	129 66 (8 77%)
188 0	1 76	19 80	1682 0 (89 9%)	2 91	86 00 (5 11%)	1 58	146 88 (8 73%)
211 5	1 73	28 90	1826 0 (86 3%)	2 88	87 00 (4 80%)	1 48	150 36 (8 23%)
235 0	1 68	36 80	1982 0 (84 3%)	2 88	83 85 (4 23%)	1 44	158 11 (7 98%)
Fe							
1498 5	4 21	1 10	14974 (99 9%)	3 64	2 85 (0 019%)	2 58	7623 (50 91%)
2997 0	2 95	5 06	29919 (99 8%)	3 49	24 44 (0 082%)	2 40	13068 (43 68%)
4495 5	2 13	409 6	40859 (90 9%)	3 16	1009 6 (2 47%)	2 19	20692 (50 64%)
5994 0	2 01	624 2	53698 (89 6%)	3 03	1565 2 (2 92%)	2 05	34624 (64 48%)
7492 5	1 92	1002	64903 (86 6%)	2 99	2823 6 (4 35%)	1 99	30438 (46 90%)
8991 0	1 87	2060	69310 (77 1%)	2 98	4338 5 (6 26%)	1 87	30978 (44 69%)
10489 5	1 82	2471	80185 (76 4%)	2 95	8653 0 (10 79%)	1 65	36060 (44 97%)
11988 0	1 76	3424	85644 (71 4%)	2 91	9942 0 (11 61%)	1 58	40578 (47 38%)
13486 5	1 73	3845	96415 (71 5%)	2 88	11150 0 (11 54%)	1 48	48468 (50 27%)
14985 0	1 68	4252	107330 (71 6%)	2 88	12378 0 (11 53%)	1 44	49677 (46 28%)

Sample	Rush (Reed-Sedge) Peat - W9c						
	SORPTION			DESORPTION by destilled water, pH 6		DESORPTION by 1% HCl	
c_o mg/dm³	pH	c_{eq} mg/dm³	S mg/kg (%)	pH	D mg/kg (%)	pH	D mg/kg (%)
Mn							
12 2	4 21	4 97	72 3 (59 2%)	3 64	5 02 (6 95%)	2 58	28 1 (38 86%)
24 4	2 95	10 60	138 0 (56 6%)	3 49	8 34 (6 04%)	2 40	59 1 (42 83%)
36 6	2 13	21 70	149 0 (40 7%)	3 16	10 67 (7 16%)	2 19	61 8 (41 48%)
48 8	2 01	31 80	170 0 (34 8%)	3 03	11 46 (7 69%)	2 05	74 5 (43 82%)
61 0	1 92	41 50	195 0 (31 9%)	2 99	12 30 (6 31%)	1 99	88 9 (45 59%)
73 2	1 87	47 20	260 0 (35 5%)	2 98	19 63 (7 55%)	1 87	118 9 (45 73%)
85 4	1 82	57 00	284 0 (33 2%)	2 95	18 18 (6 40%)	1 65	126 8 (44 60%)
97 6	1 76	62 60	350 0 (35 9%)	2 91	19 71 (5 63%)	1 58	156 1 (44 60%)
109 8	1 73	73 20	366 0 (26 9%)	2 88	26 53 (7 25%)	1 48	161 8 (44 20%)
122 0	1 68	84 90	371 0 (30 4%)	2 88	28 90 (7 79%)	1 44	188 1 (50 70%)
Zn							
280 7	4 21	54 9	2258 (80 4%)	3 64	28 55 (1 26%)	2 58	2102 1 (93 10%)
561 4	2 95	314	2472 (44 0%)	3 49	114 80 (4 64%)	2 40	1687 5 (68 26%)
842 1	2 13	545	2974 (35 3%)	3 16	202 8 (6 82%)	2 19	1334 0 (44 86%)
1122 8	2 01	823	3002 (26 7%)	3 03	246 66 (8 22%)	2 05	1208 1 (40 24%)
1403 5	1 92	1102	3020 (21 5%)	2 99	321 56 (10 65%)	1 99	1407 6 (46 61%)
1684 2	1 87	1372	3122 (18 5%)	2 98	347 25 (11 12%)	1 87	1527 6 (48 93%)
1964 9	1 82	1738	3271 (11 5%)	2 95	464 25 (14 19%)	1 65	1666 8 (50 96%)
2245 6	1 76	1912	3336 (14 8%)	2 91	536 00 (16 07%)	1 58	2316 0 (69 42%)
2526 3	1 73	2182	3443 (13 6%)	2 88	593 00 (17 22%)	1 48	2181 6 (63 36%)
2807 0	1 68	2474	3330 (11 9%)	2 88	649 00 (19 48%)	1 44	2065 1 (62 01%)

Table 35 Sorption of metal ions onto Brushwood Humus Peat (W9b) from electroplating waste under dynamic flow conditions

Column experiments, flow rate q = 0 1 cm^3 s, peat mass 90 g, water retention capacity S/L = 1 2
Input liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Electroplating waste											
Brushwood Peat Humus - W9b											
ER	pH	Cr		Cd		Fe		Mn		Zn	
		C_o 235 mg/dm^3		C_o 171 mg/dm^3		C_o 14985 mg/dm^3		C_o 122 mg/dm^3		C_o 2807 mg/dm^3	
		C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)
1	6 82	<0 0010	470	<0 0010	342	0 61	29969	<0 0017	244	<0 0010	5612
2	6 21	<0 0010	940	<0 0010	684	0 95	59937	3 12	482	0 10	11223
3	5 85	0 10	1410	0 10	1026	129	89649	14 0	698	10 2	16815
4	4 25	0 74	1878 6	10 2	1347 6	576	118467	79 4	783	435 0	21557
5	4 00	0 8	2347	28 5	1632 6	11280	125877	122	783	1640	23889
6	4 29	0 11	2817	58 8	1857	14985	12587	122	783	2800	23889
7	3 56	0 12	3287	102	1995	14985	125877	122	783	2800	23889
8	2 24	0 19	3757	117	2103	14985	125877	122	783	2800	23889
9	2 19	0 23	4227	139	2167						
10	1 93	0 31	4696	171	2167						
11	1 77	0 33	5167	171	2167						
12	1 80	0 36	5637	171	2167						
13	1 78	0 39	6106								
14	1 71	0 41	6575								
15	1 68	0 44	7044								
16	1 69	0 45	7513								
17	1 70	0 46	7982								
18	1 66	0 46	8451								
19	1 70	0 49	8920								
20	1 70	0 49	9389								

21	1 72	0 48	9858								
22	1 70	0 49	10327								
23	1 60	46 8	10703 4								
24	1 64	42 2	11089								
25	1 62	42 7	11473 6								
26	1 65	42 5	11858 6								
27	1 61	43 2	12242 2								
28	1 67	44	12624 2								
29	1 66	47 5	12999 2								
30	1 63	45 4	13378 4								
31	1 65	45 1	13758 2								
32	1 63	47 9	14132 4								
33	1 64	47 9	14506 8								
34	1 67	48 5	14879 8								
35	1 70	49	15251 8								
36	1 66	48 5	15624 8								
37	1 29	50 0	15994 8								
38	1 50	56 5	16352 8								
39	1 46	70 5	16680 8								
40	1 42	86 0	16978 8								
41	1 72	104	17240 8								
42	1 69	174	17362 8								
43	1 74	201	17362 8								
44	1 83	235	17430 8								
45	1 77	235	17430 8								
46	1 68	235	17430 8								
47	1 63	235	17430 8								

Table 36 Sorption of metal ions onto Rush (Reed-Sedge) Peat (W9c) from electroplating waste under dynamic flow conditions

Column experiments, flow rate q = 0.1 cm^3 s, peat mass 90 g, water retention capacity S/L = 1 1
Input liquid waste Me-SO_4, pH 1.47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

Electroplating waste											
Rush (Reed Sedge) Peat W9c											
ER	pH	Cr		Cd		Fe		Mn		Zn	
		C_o 235 mg/dm^3		C_o 171 mg/dm^3		C_o 14985 mg/dm^3		C_o 122 mg/dm^3		C_o 2807 mg/dm^3	
		C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)	C (mg/dm^3)	Load (mg/kg)
1	6.33	0.13	234.9	<0.0010	171	<0.0015	14985	<0.0013	122	<0.0010	2807
2	6.45	0.16	469.7	<0.0010	342	0.14	29970	<0.0013	244	<0.0010	5614
3	6.02	0.15	704.5	<0.0010	513	0.27	44955	0.16	365.8	<0.0011	8421
4	5.81	0.18	939.4	<0.0010	684	1.1	59939	5.11	482.7	<0.0011	11228
5	5.40	0.20	1174.2	<0.0012	885	71.2	74853	12.1	592.6	0.12	14035
6	4.90	1.40	1407.8	<0.0013	1026	1723	88115	89.4	625.2	200.8	16641
7	4.07	2.90	1639.9	0.17	1196.8	12948	90152	120	627.2	1325	18124
8	3.87	2.90	1872	0.23	1367.6	14849	90288	122	627.2	1925	19006
9	4.21	2.70	2104.3	5.70	1532.9	14985	90288	122	627.2	2807	19006
10	3.76	2.80	2336.5	19.2	1684.7	14985	90288	122	627.2	2807	19006
11	4.25	2.70	2568.9	21.5	1834.2	14985	90288	122	627.2	2807	19006
12	4.14	2.90	2800.9	76.8	1928.4	14985	90288	122	627.2	2807	19006
13	4.30	3.40	3032.5	102.6	1996.8						
14	3.81	0.35	3267.1	136.8	2031						
15	2.38	18.9	3483.2	171	2031						
16	2.50	13.2	3705	171	2031						
17	2.05	22.6	3917.4	171	2031						
18	1.83	27.6	4124.8	171	2031						
19	1.71	29.2	4330.6								

20	1 60	3<0 001	4535 6								
21	1 71	28 4	4742 2								
22	1 66	30 7	4946 5								
23	1 60	32 8	5148 7								
24	1 65	35 2	5348 5								
25	1 62	29 0	5554 5								
26	1 60	33 0	5756 5								
27	1 65	32 0	5959 5								
28	1 65	32 0	6162 5								
29	1 63	34 0	6363 5								
30	1 66	34 5	6564								
31	1 70	33 5	6765 5								
32	1 67	32 5	6968								
33	1 70	37 1	7165 9								
34	1 46	43 3	7357 6								
35	1 65	34 9	7557 7								
36	1 64	37 3	7755 4								
37	1 64	38 3	7952 1								
38	1 64	40 1	8147								
39	1 64	39 2	8342 8								
40	1 65	39 4	8538 4								
41	1 54	41 5	8731 9								
42	1 58	34 5	8932 4								
43	1 61	39 9	9127 5								
44	1 59	40 7	9321 8								
45	1 60	40 1	9516 7								
46	1 62	54 8	9696 9								
47	1 65	43 0	9888 9								
48	1 65	40 4	10083 5								

49	1 65	41 5	10277								
50	1 70	41 0	10471								
51	1 70	44 0	10662								
52	1 35	50 0	10847								
53	1 44	54 0	11028								
54	1 60	60 5	11202 5								
55	1 60	64 0	11373 5								
56	1 50	66 5	11542								
57	1 55	73 0	11704								
58	1 57	85 0	11854								
59	1 50	92 0	11997								
60	1 52	105	12127								
61	1 57	112	12250								
62	1 60	120	12365								
63	1 67	150	12450								
64	1 77	185	12500								
65	1 89	200	12535								
66	1 85	205	12565								
67	1 84	235	12565								
68	1 80	235	12565								
69	1 81	235	12565								
70	1 80	235	12565								

Table 37/1 Comparison of the sorption capacity of Alder Peat Humus W1 for Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} ions sorbed in batch and dynamic (fixed-bed) process in monometallic, binary and polymetallic systems from synthetic solutions and real electroplating wastes

	Cr		Cu		Cd		Zn	
	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)
Alder Humus Peat - W1 (DR 70%)								
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me-Cl, mono-metal system	47370 (94 7%)	3013 (6 36%)	47150 94 3%)	29328 7 (62 20%)	35100 (70 2%)	33225 (94 66%)	32500 (65 0%)	26227 (80 7%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me Cl, binary system	32660 (76 8%)	2002 (6 07%)	21030 (52 7%)	12764 (60 69%)	24340 (52 4%)	18192 (74 74%)	26214 (56 7%)	16882 (64 4%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me-SO_4, mono-metal system					46285 (95 7%)	34492 (74 52%)	37208 (84 7%)	34149 (91 8%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1 5000 mg/dm^3, Me-SO_4, binary system					38365 (82 6%)	30588 (79 73%)	35500 (69 1%)	25847 (72 8%)
Batch experiment Peat samples adjusted to pH 5 5, input solution pH 5 5, c_0=1-600 mg/dm^3, S/L=1 25, Me SO_4, mono-metal system					13970 (93 9%)		13560 (89 2%)	
Batch experiment Peat samples adjusted to pH 5 5, input solution pH 5 5, c_0=1-600 mg/dm^3, S/L=1 25, Me SO_4, binary system					12850 (85 9)		12360 (82 7%)	
Batch experiment electroplating wastes	2038 (86 72%)				1064 (61 93%)		3590 (12 79%)	

	Cı		Cu		Cd		Zn	
	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3, q=0 1 cm^3/s, S/L=1 2 total	46376 (73 03%)		40924 76 48%)		53122 (87 08%)		47321 (87 63%)	
Batch experiment electroplating wastes	2004 (85 28%)				1053 (61 29%)		3520 (12 54%)	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 2 full	1410				1026		11223	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 2 total	17430 8 (84 28%)				2167 (70 40%)		23889 (85 11%)	
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3, q=0 1 cm^3/s, S/L=1 1 total	33297 (76 99%)		36844 (68 25%)		45032 (96 32%)		29748 (83 21%)	
Batch experiment electroplating wastes	1982 (84 34%)				1088 (63 33%)		3330 (11 86%)	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 1 full	1174				1026		14035	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 1 total	12565 (82 26%)				2031 (84 84%)		19006 (84 64%)	

Table 37/2 Comparison of the sorption capacity of Brushwood Peat Humus W9b for Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} ions sorbed in batch and dynamic (fixed-bed) process in monometallic, binary and polymetallic systems from synthetic solutions and real electroplating wastes

	Cr		Cu		Cd		Zn	
	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)
Brushwood Humus Peat W9b (DR 55%)								
Batch experiment Input solution pH 4 0, S/L=1 10 c_0=1 5000 mg/dm^3, Me-Cl, mono-metal system	47620 (95 2%)	2954 6 (6 20)	45540 (91 1%)	27305 (59 96%)	33200 (66 4%)	32294 (97 27%)	32050 (64 1%)	27403 (85 5%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1 5000 mg/dm^3, Me-Cl, binary system	32058 (75 4%)	2006 (6 88%)	21122 (52 9%)	12132 (57 44%)	27004 (58 2%)	18088 (66 98%)	28390 (61 4%)	15075 (53 1%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me-SO_4, mono-metal system					45029 (93 1)	38202 6 (84 84%)	36370 (82 8%)	29882 (82 16%)
Batch experiment Input solution pH 4 0 S/L=1 10, c_0=1-5000 mg/dm^3, Me-SO_4, binary system					34700 (74 70%)	26668 (76 85%)	35484 (69 1%)	26608 (74 98%)
Batch experiment Peat samples adjusted to pH 5 5, input solution pH 5 5 c_0=1 600 mg/dm^3, S/L=1 25, Me SO_4 mono metal system					13940 (93 7%)		12485 (89 7%)	
Batch experiment Peat samples adjusted to pH 5 5, input solution pH 5 5, c_0=1-600 mg/dm^3, S/L=1 25, Me-SO_4, binary system					12895 (86 2%)		12310 (82 3%)	
Column experiment Input solution pH 4 0, c_0=500 mg/dm^3, q=0 1 cm^3/s, S/L=1 2 full	24556		33810		51975		39780	
Column experiment Input solution pH 4 0, c_0=500 mg/dm^3, q=0 1 cm^3/s, S/L=1 2 total	53626 (63 84%)	554 5 (1 03%)	50506 (78 91%)	14080 (27 89%)	72514 (83 35%)	36642 (57 29%)	55730 (87 08%)	32080 (57 49%)

	Cr		Cu		Cd		Zn	
	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3, q=0 1 cm^3/s, S/L=1 2 full	34064		26838		34687		13293	
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3, q=0 1 cm^3/s, S/L=1 2 total	46376 (73 03%)		40924 76 48%)		53122 (87 08%)		47321 (87 63%)	
Batch experiment electroplating wastes	2004 (85 28%)				1053 (61 29%)		3520 (12 54%)	
Column experiment electroplating wastes q=0 1 cm^3/s, S/L=1 2 full	1410				1026		11223	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 2 total	17430 8 (84 28%)				2167 (70 40%)		23889 (85 11%)	
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3, q=0 1 cm^3/s, S/L=1 1 total	33297 (76 99%)		36844 (68 25%)		45032 (96 32%)		29748 (83 21%)	
Batch experiment electroplating wastes	1982 (84 34%)				1088 (63 33%)		3330 (11 86%)	
Column experiment electroplating wastes, q=0 1 cm^3/s S/L=1 1 full	1174				1026		14035	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 1 total	12565 (82 26%)				2031 (84 84%)		19006 (84 64%)	

Table 37/3 Comparison of the sorption capacity of Rush (Reed-Sedge) Peat for Zn^{2+}, Cd^{2+} Cu^{2+} and Cr^{3+} ions sorbed in batch and dynamic (fixed-bed) process in monometallic, binary and polymetallic systems from synthetic solutions and real electroplating wastes

	Cr		Cu		Cd		Zn	
	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)	S mg/kg (%)	D mg/kg (%)
Rush (Reed-Sedge) Peat W9c (DR 55%)								
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me-Cl, mono-metal system	49380 (98 8%)	3189 7 (6 46%)	47390 (94 8%)	29696 (62 66%)	37520 (75 0%)	35736 (95 24%)	32700 (65 4%)	30854 (94 35%)
Batch experiment Input solution pH 4 0, S/L=1 10 c_0=1-5000 mg/dm^3, Me-Cl, binary system	35234 (82 8%)	2272 (6 45%)	19486 (48 8%)	11908 (61 11%)	25504 (54 9%)	16038 (62 88%)	25480 (55 15%)	14646 (57 48%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me-SO_4, mono-metal system					45889 (94 9%)	31208 (68 01%)	36264 (82 5%)	26510 (73 10%)
Batch experiment Input solution pH 4 0, S/L=1 10, c_0=1-5000 mg/dm^3, Me-SO_4, binary system					39261 (84 5%)	29892 (76 14%)	36776 (71 6%)	21456 (58 34%)
Batch experiment Peat samples adjusted to pH 5 5 input solution pH 5 5, c_0=1-600 mg/dm^3, S/L=1 25, Me SO_4, mono-metal system					13800 (92 77%)		12925 (85 0%)	
Batch experiment Peat samples adjusted to pH 5 5, input solution pH 5 5, c_0=1-600 mg/dm^3, S/L=1 25, Me SO_4, binary system					10140 (67 8%)		8800 (58 9%)	
Column experiment Input solution pH 4 0, c_0=500 mg/dm^3, q=0 1 cm^3/s, S/L=1 1 full	18800		27028		51810		30880	

Column experiment Input solution pH 4 0, c_0=500 mg/dm q=0 1 cm^3/s, S/L=1 1 total	38399 (71 11%)	872 5 (2 27%)	39465 (69 23%)	20040 (50 78%)	63958 (90 72%)	36642 (57 29%)	36820 (88 72%)	27748 (75 36%)
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3, q=0 1 cm^3/s S/L=1 1 full	20827		32333		36707		18730	
Column experiment Input solution pH 4 0, c_0=250 mg/dm^3 q=0 1 cm^3/s, S/L=1 1 total	33297 (76 99%)		36844 (68 25%)		45032 (96 32%)		29748 (83 21%)	
Batch experiment electroplating wastes	1982 (84 34%)				1088 (63 33%)		3330 (11 86%)	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 1 full	1174				1026		14035	
Column experiment electroplating wastes, q=0 1 cm^3/s, S/L=1 1 total	12565 (82 26%)				2031 (84 84%)		19006 (84 64%)	

FIGURES

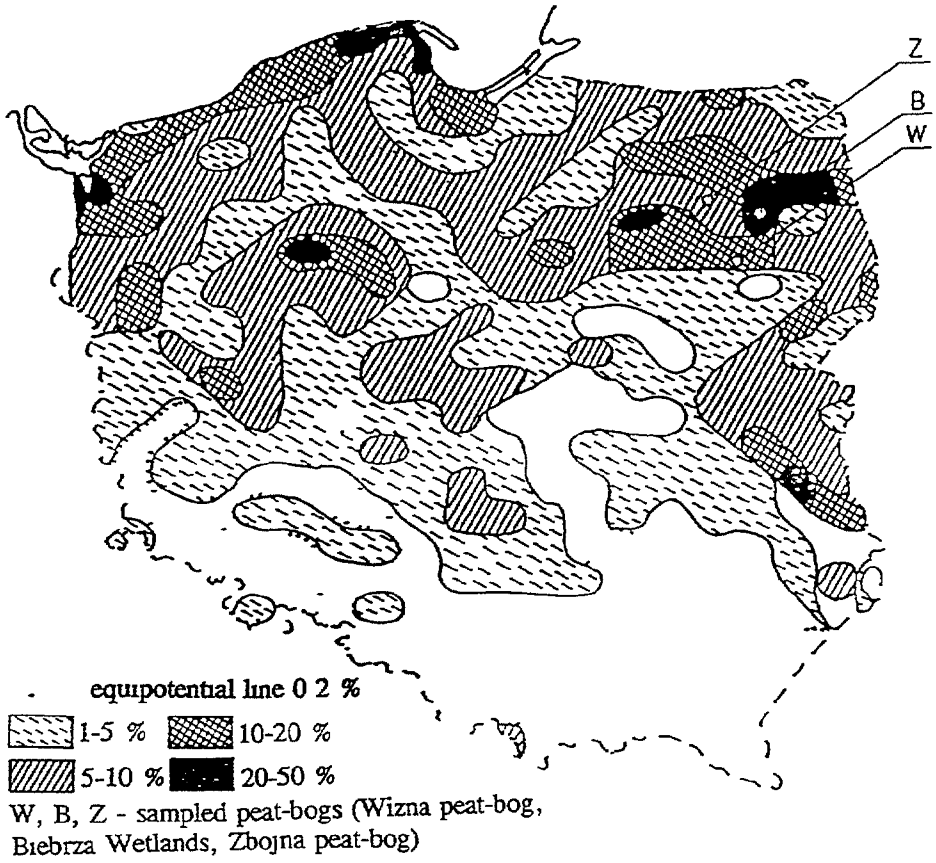


Figure 1 Distribution of peatlands in Poland (after K Bitner, 1958) and location of peatbogs selected for sampling

Card numbers in the square network of the Institute of Melioration and Grassland Database

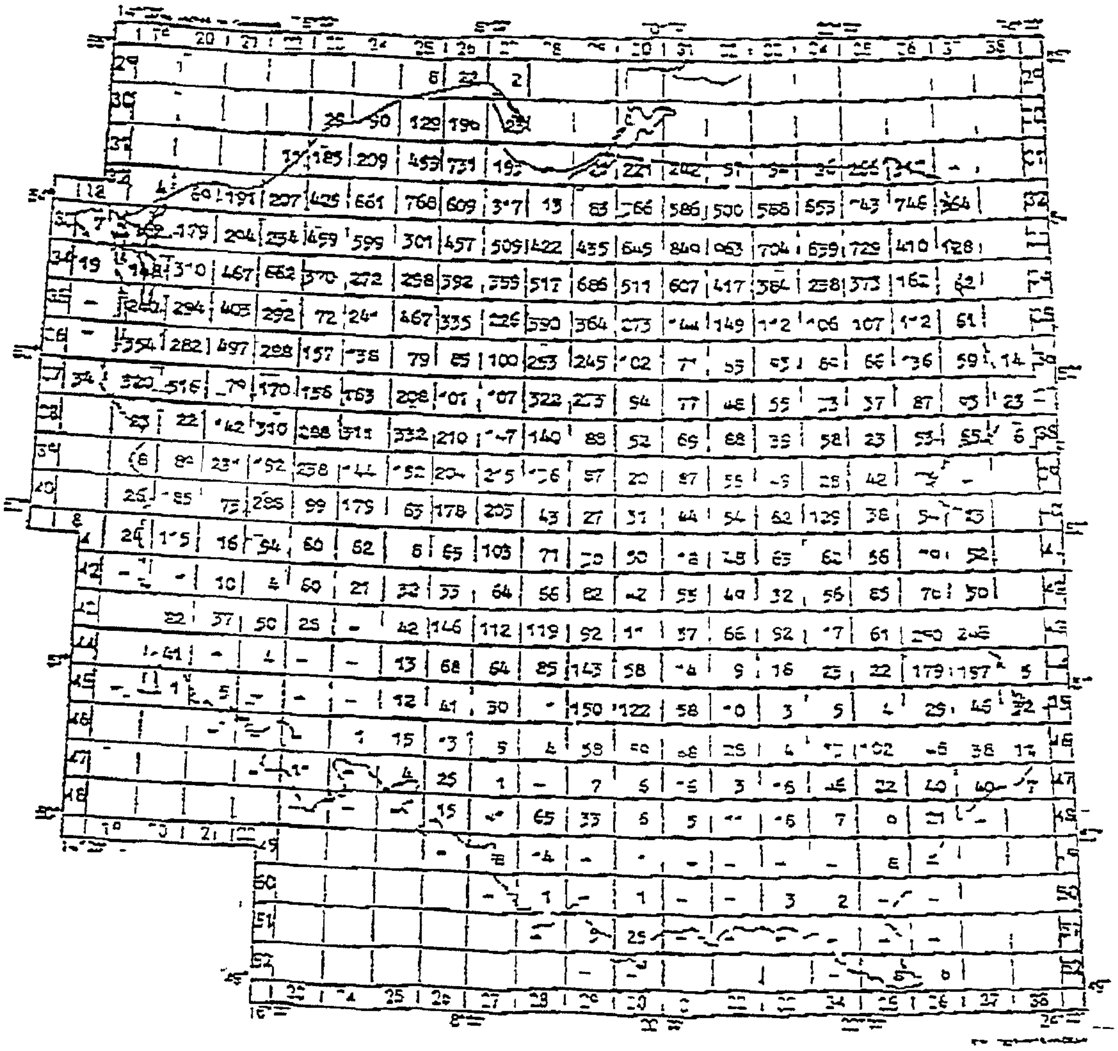


Figure 2 Peatland database of the Institute for Land Reclamation and Grassland Farming (IMUZ) Card numbers in the square network

a Sedgeous Peat
b Sedgeous Peat on Reed Peat
c Sedgeous Peat on Peat Humus
d Deep Moss - Turf Peat
e Moss-Turf Peat on Sedgeous Peat
f Moss-Turf Peat on Reed-Sedge Peat
g Wood Peat Humus
h Brushwood Peat Humus

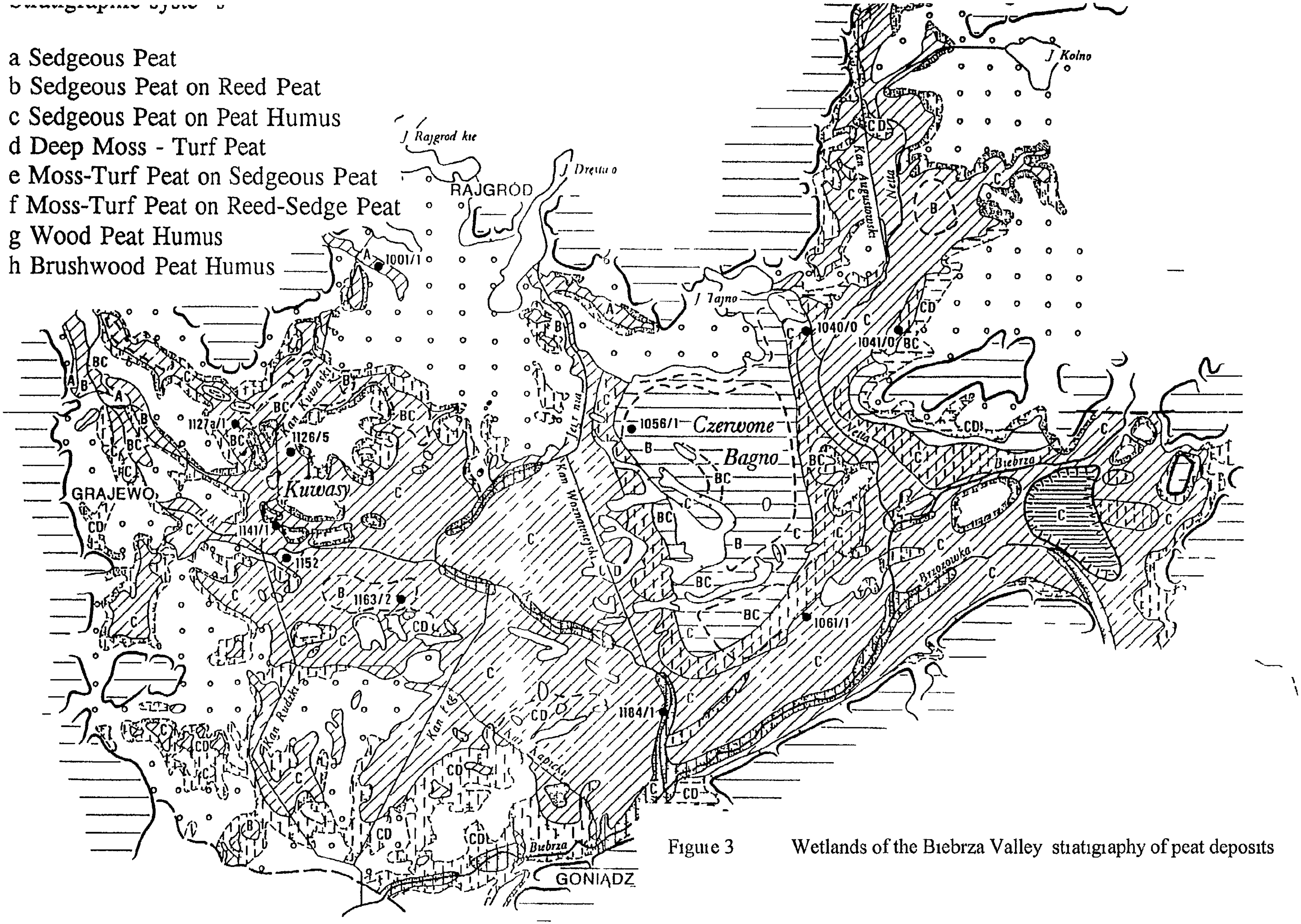


Figure 3 Wetlands of the Biebrza Valley stratigraphy of peat deposits

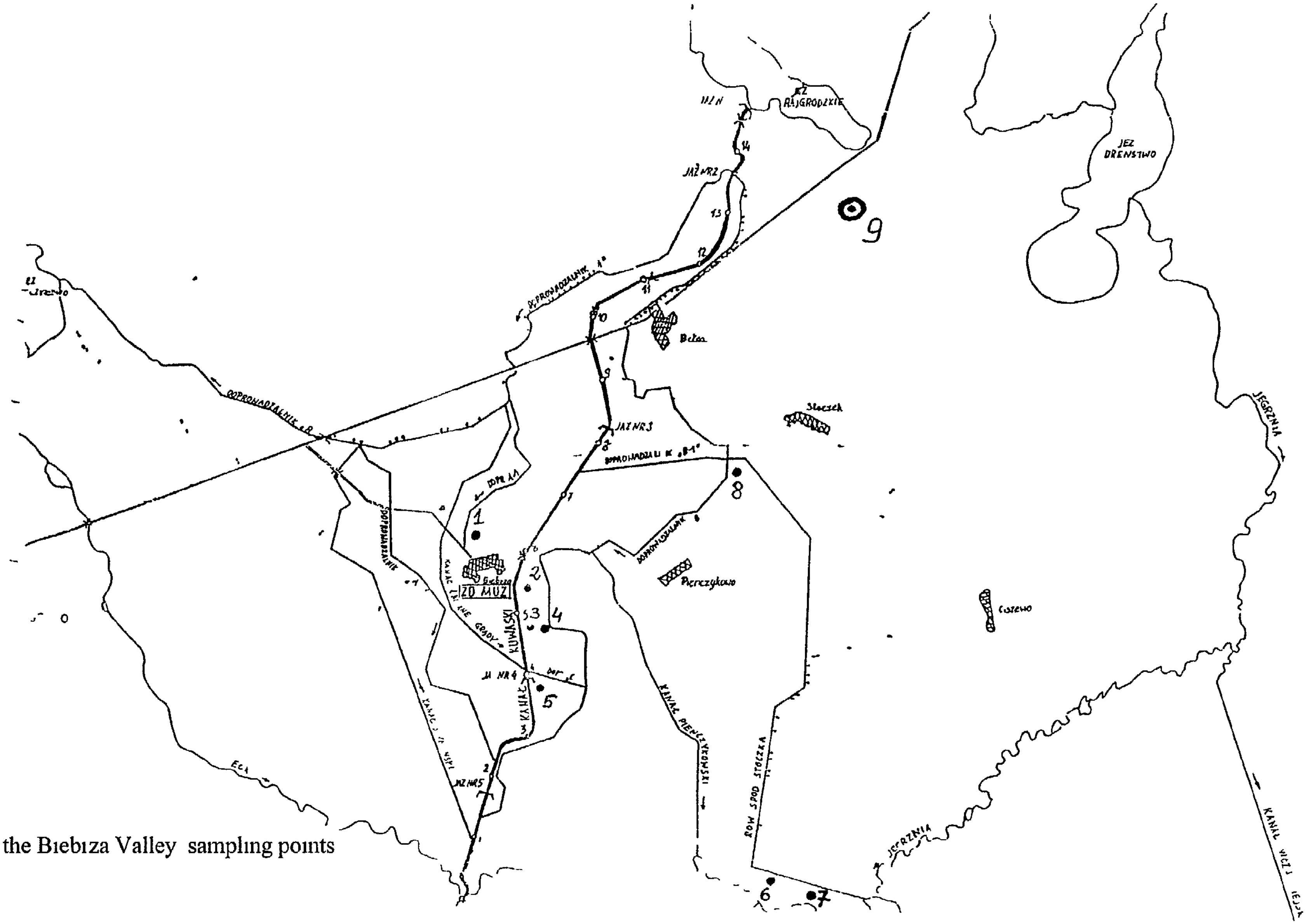


Figure 4 Wetlands of the Biebrza Valley sampling points

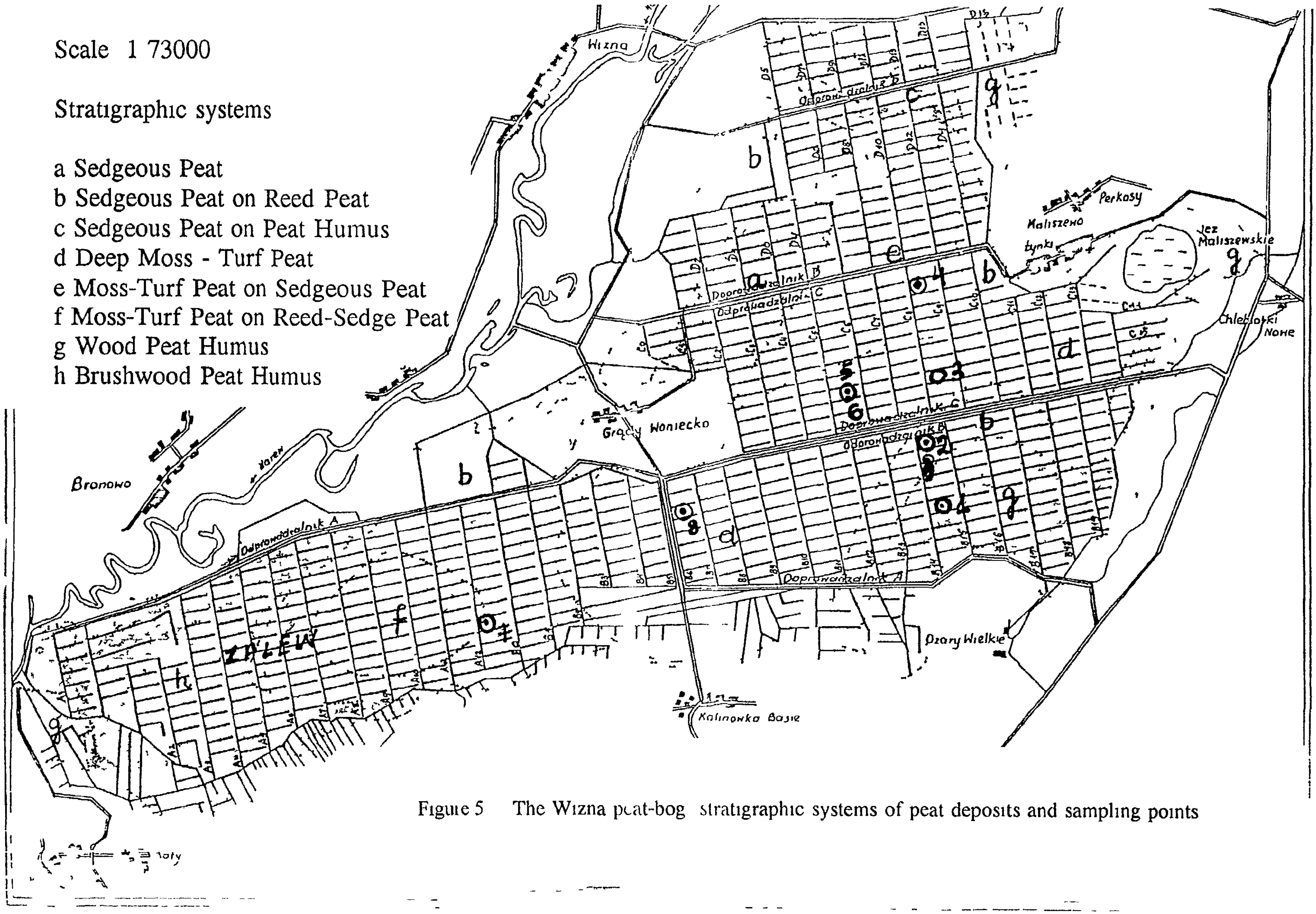


Figure 5 The Wizna peat-bog stratigraphic systems of peat deposits and sampling points

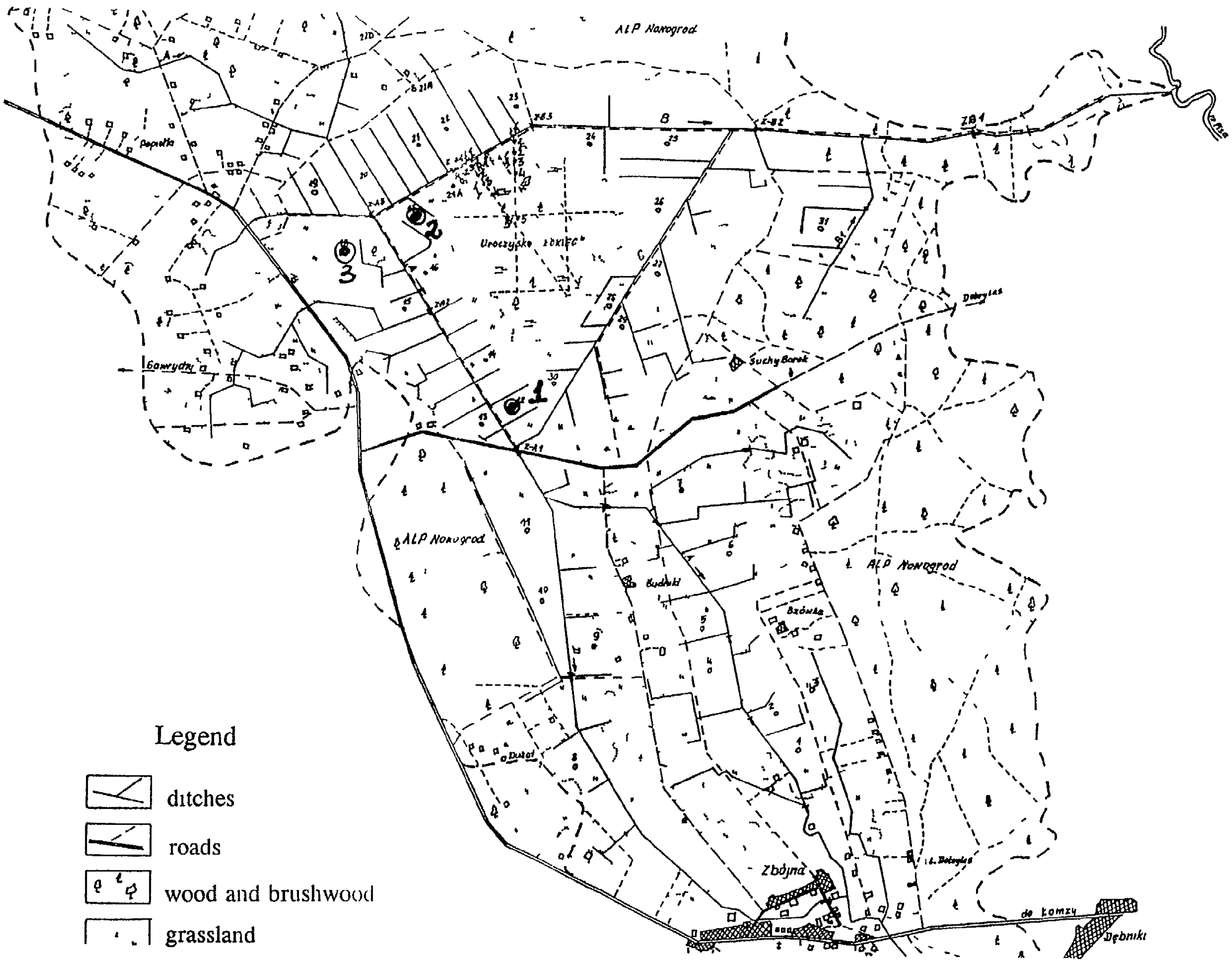


Figure 6 The Zbojna Site sampling points

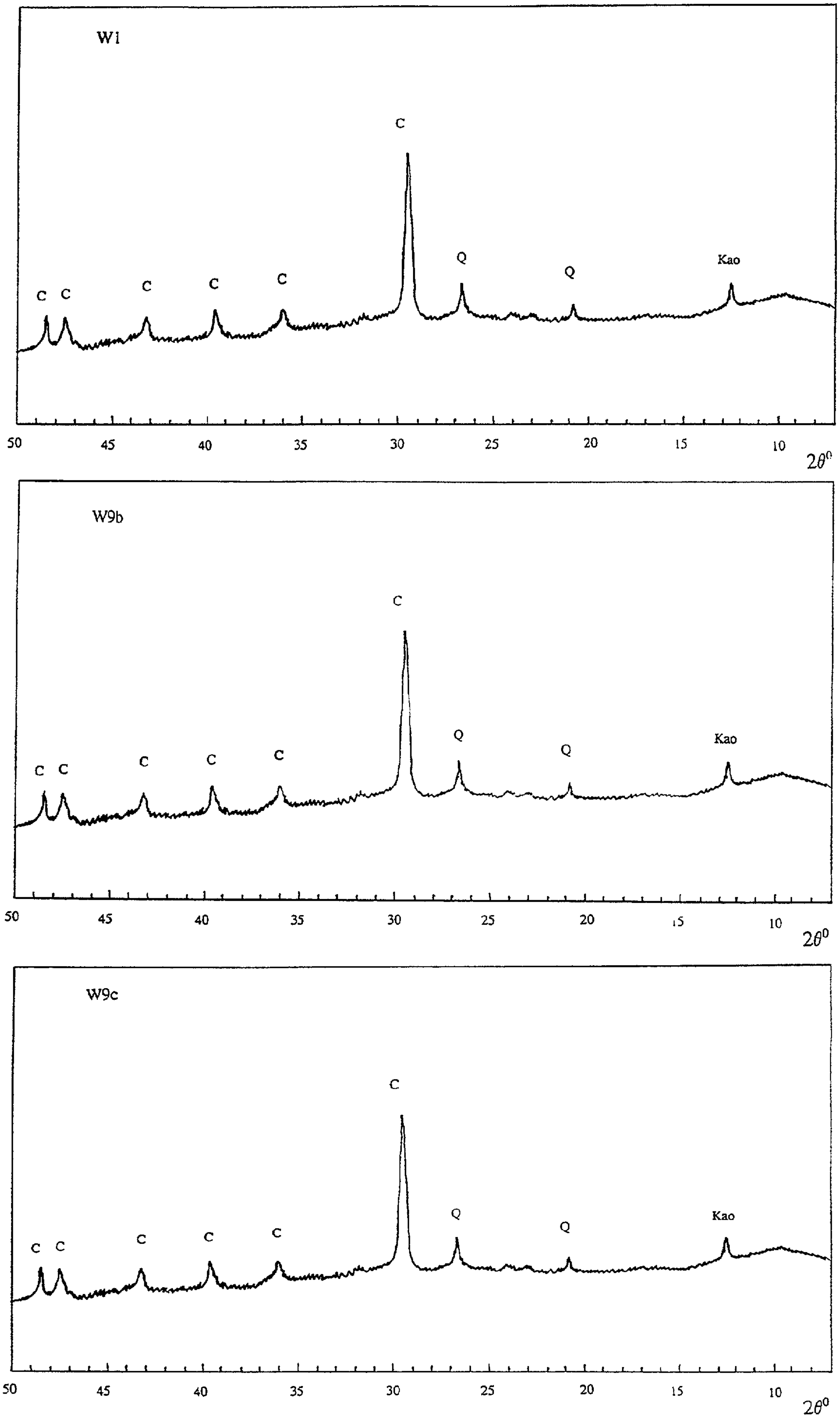


Figure 7 Phase composition of mineral fraction in the representative peat samples of different kind (x-ray diffractograms)

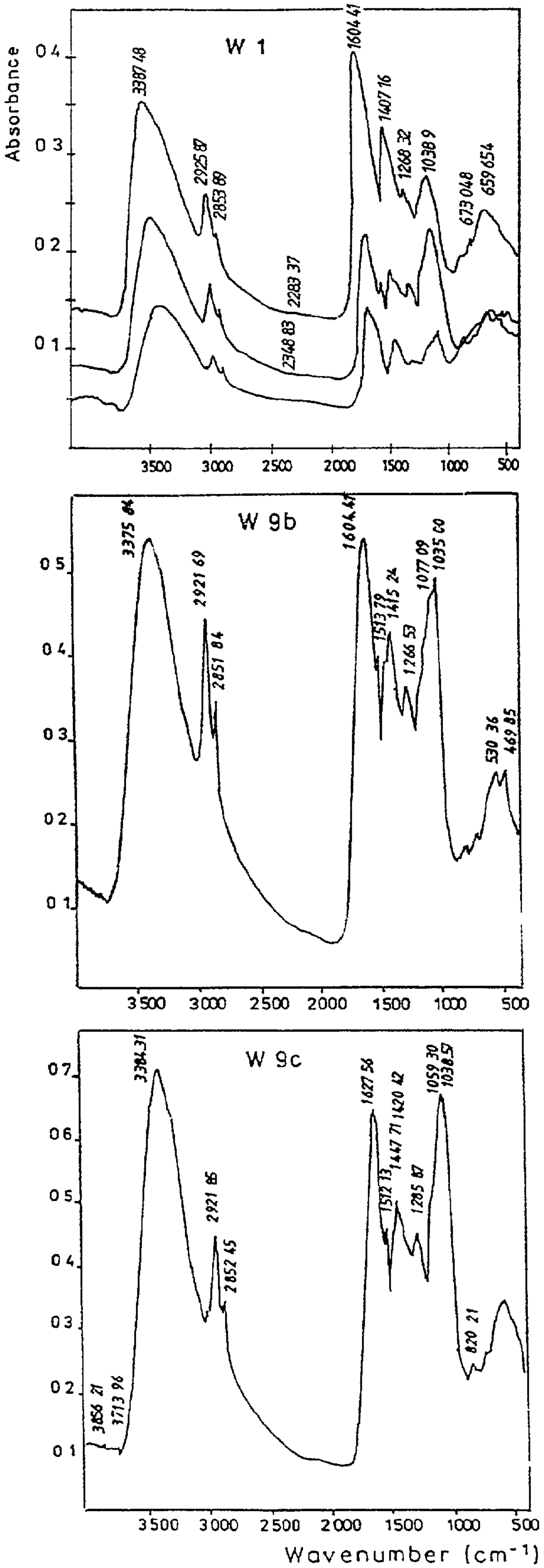


Figure 8/1 FTIR spectra of the representative peat samples of different kind
Peat matter (I) Alder Peat Humus (W1), a – unfractionated, b – fraction > 0.2µm, c – fraction < 0.2µm, (II) Brushwood Peat Humus (W9b), (III) Rush Reed-Sedge Peat (W9c), Bands 1600-1630, close to 1400 and to 1040 cm^{-1} - carboxylic groups of humic and fulvic acids, 3380 and 1620 cm^{-1} - water, 2850 and 2920 cm^{-1} - CH_2 and CH_3 groups, 1512 and 1266 cm^{-1} - organic compounds containing nitrogen (amides),

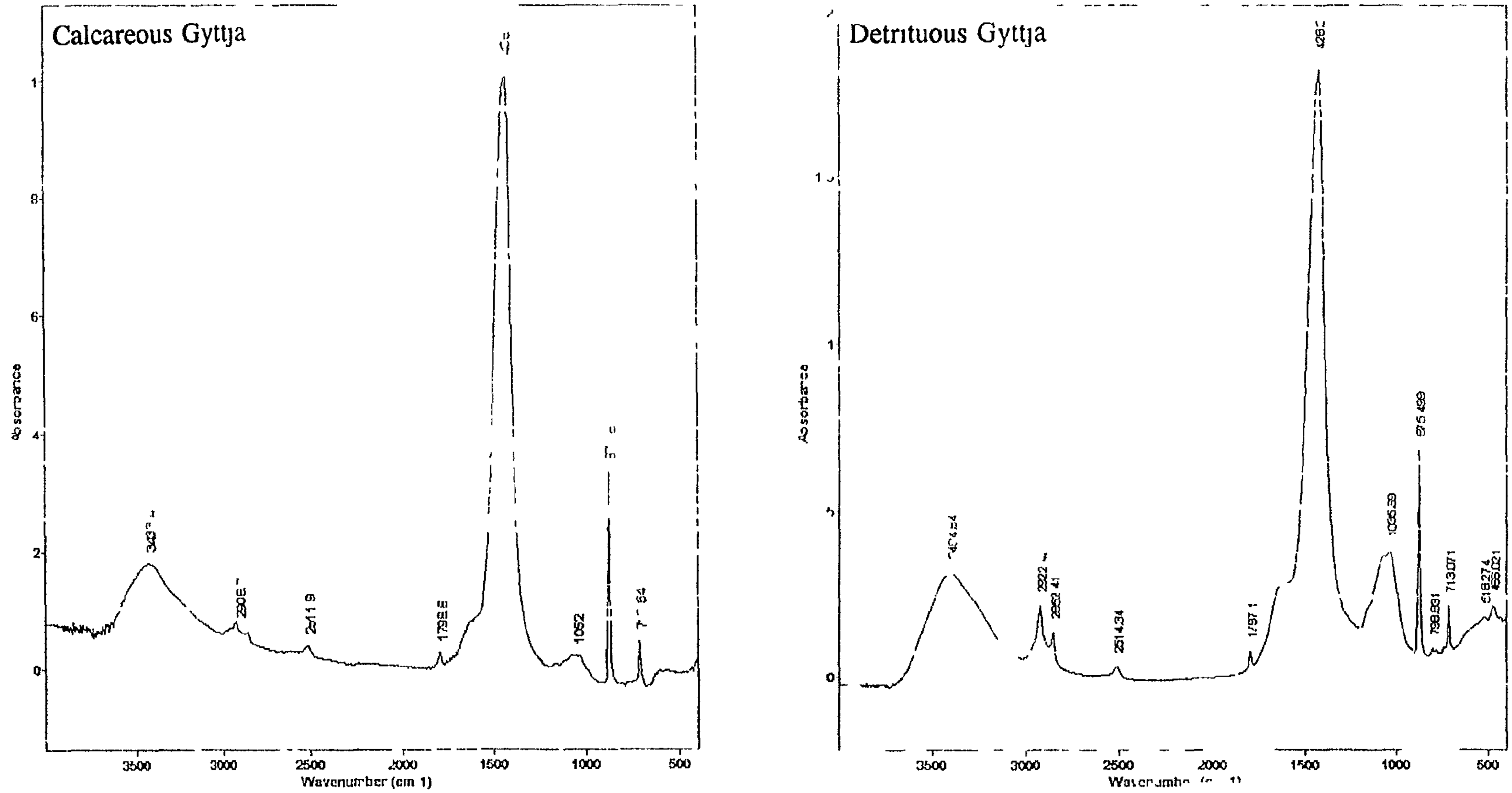
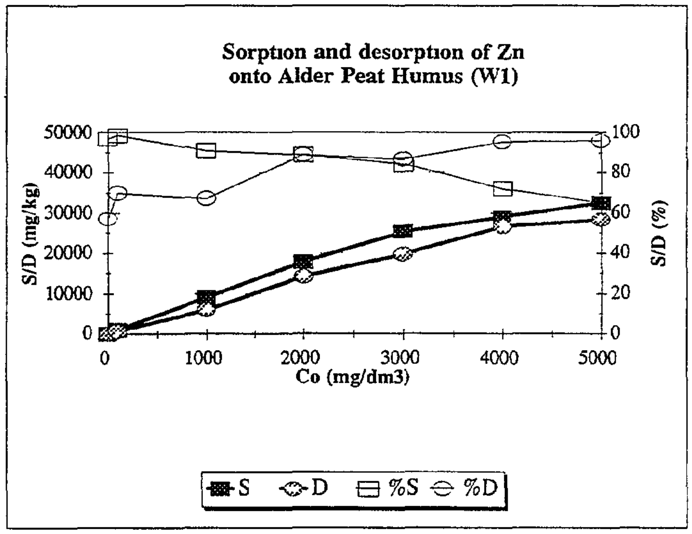
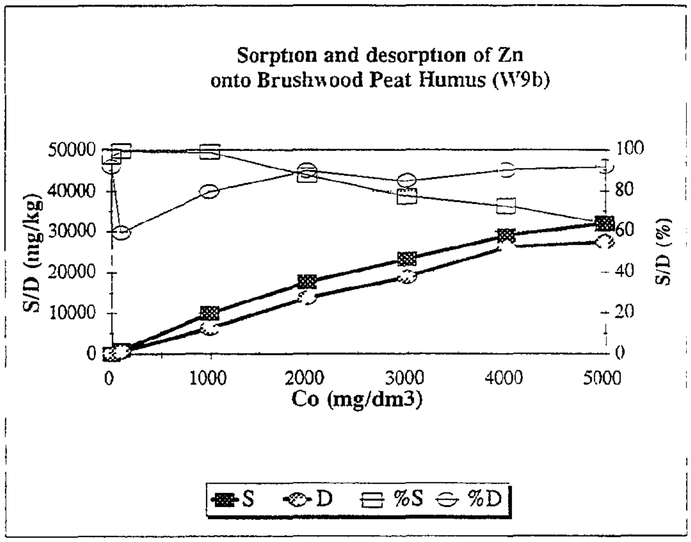


Figure 8/2 FTIR spectra of the representative peat samples of different kind
Peat matter (IV) Calcareous Gyttia, (V) Detrituous Gyttia, Bands 1600-1630, close to 1400 and to 1040 cm^{-1} - carboxylic groups of humic and fulvic acids, 3380 and 1620 cm^{-1} - water, 2850 and 2920 cm^{-1} - CH_2 and CH_3 groups, 1512 and 1266 cm^{-1} - organic compounds containing nitrogen (amides),





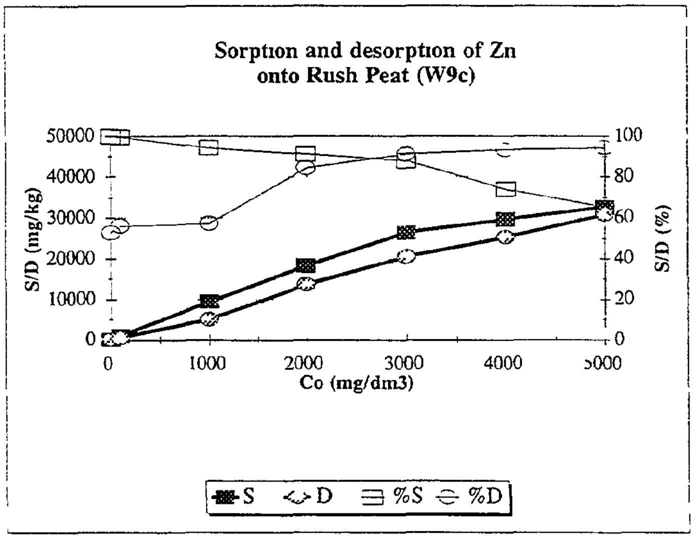


Figure 9 Equilibrium mass sorption/desorption isotherms for Zn on low-moor peats (Rush Peat, Alder and Brushwood Peat Humus) in mono-metal systems Zn-Cl, S/L=1 10 and sorption/desorption rate (in %), Input solution pH 4 0, c_0 = 1 - 5000 mgZn dm^{3}, Desorption 1% HCl 1 10

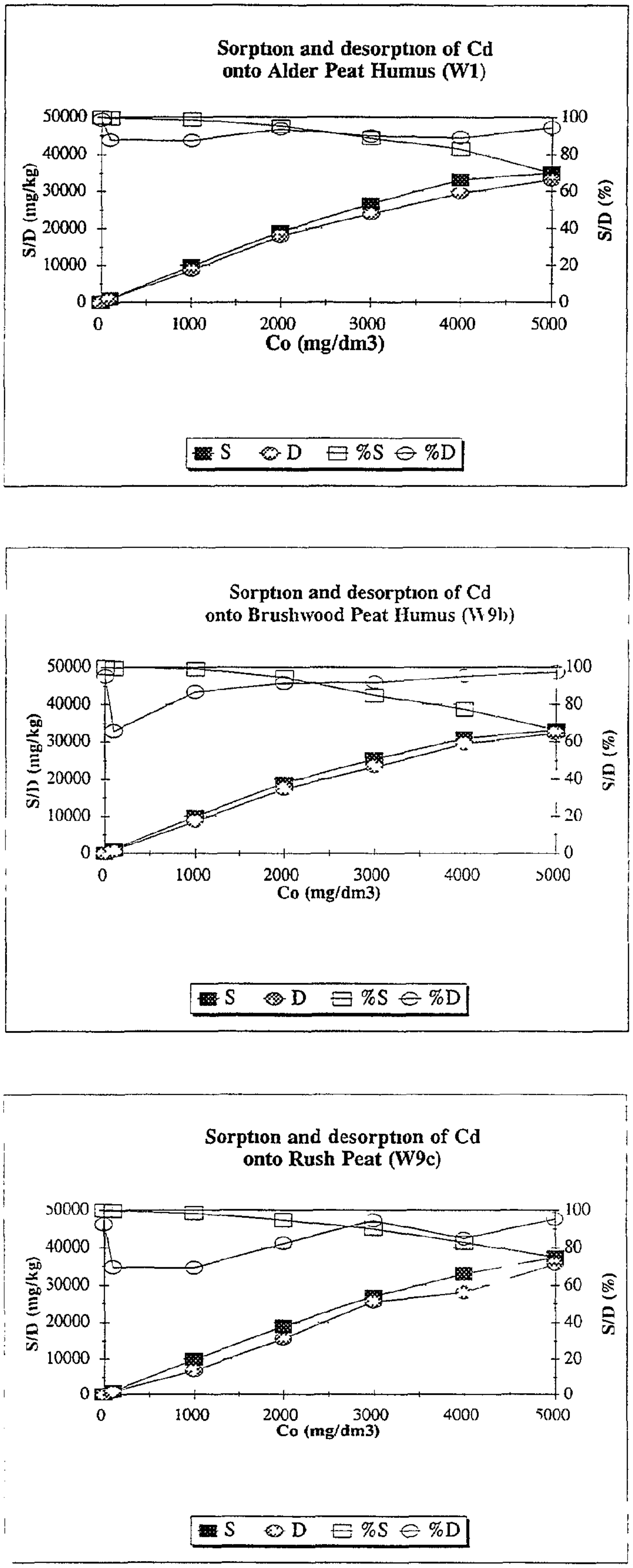
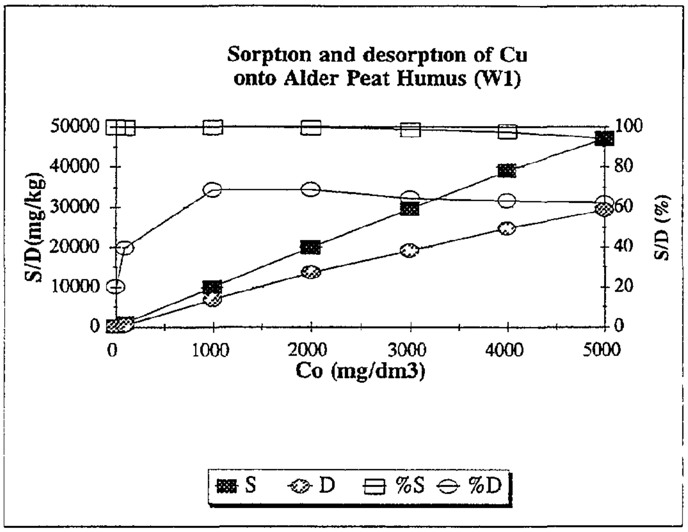
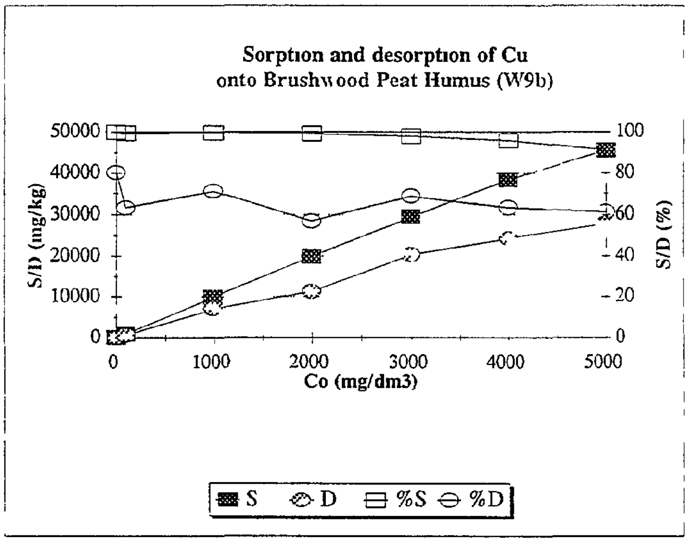


Figure 10 Equilibrium mass sorption/desorption isotherms for Cd on low-moor peats (Rush Peat Alder and Brushwood Peat Humus) in mono-metal systems Cd-Cl, S/L=1 10 and sorption/desorption rate (in %), Input solution pH 4 0, c_0 = 1 - 5000 mgCd dm^{3}, Desorption 1% HCl, 1 10





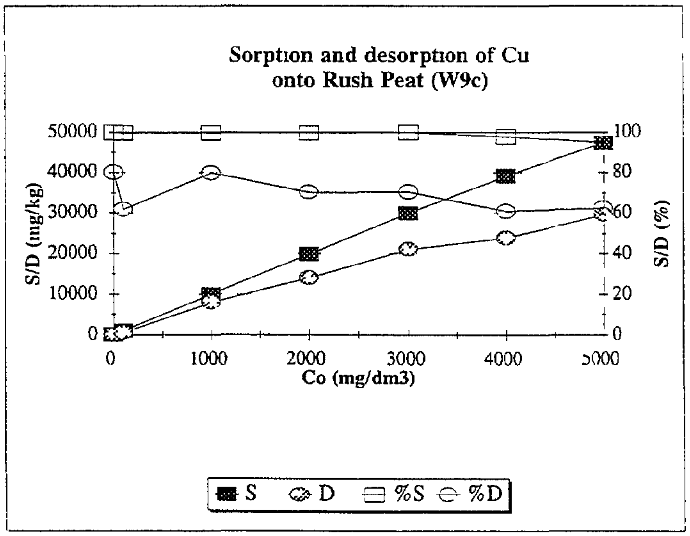


Figure 11 Equilibrium mass sorption/desorption isotherms for Cu on low-moor peats (Rush Peat, Alder and Brushwood Peat Humus) in mono-metal systems Cu-Cl, S/L=1 10 and adsorption/desorption rate (in %), Input solution pH 4 0, c_0 = 1 - 5000 mgCu dm^{-3}, Desorption 1% HCl, 1 10

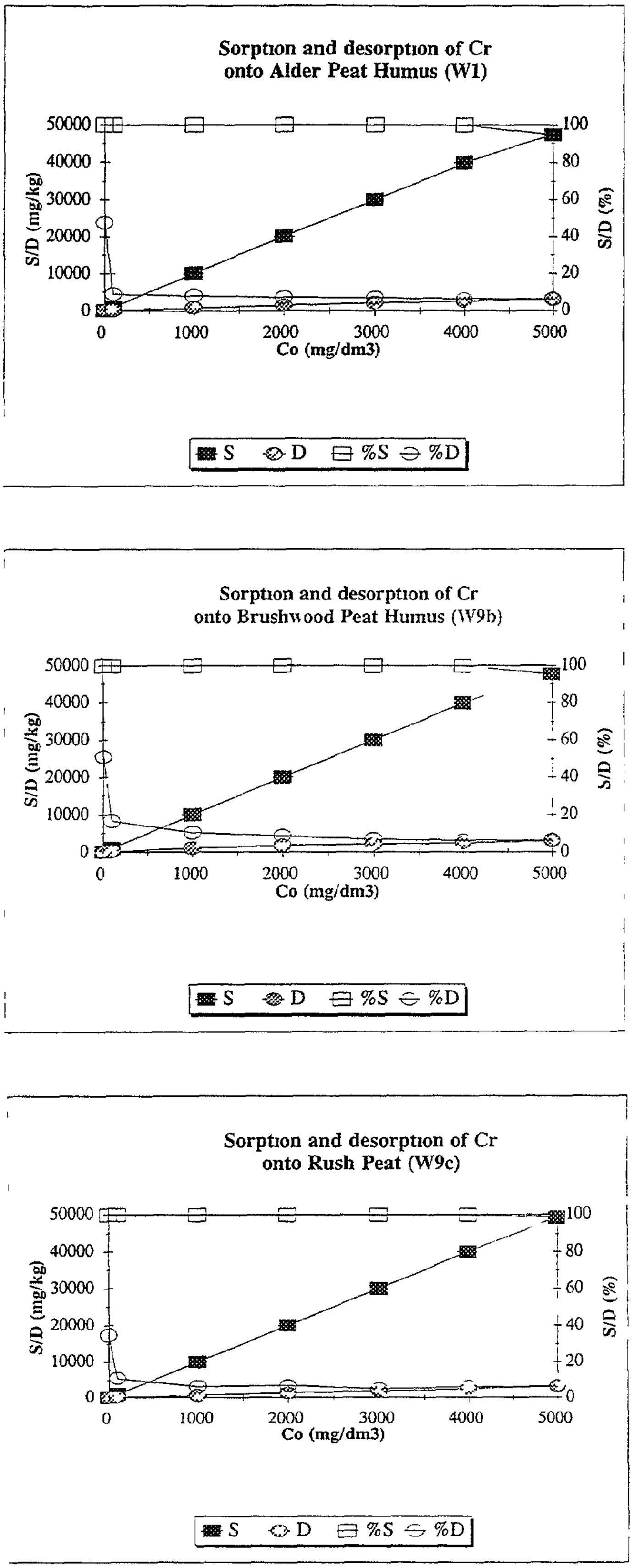


Figure 12 Equilibrium mass sorption/desorption isotherms for Cr on low-moor peats (Rush Peat, Alder and Brushwood Peat Humus) in mono-metal systems Cu-Cl, S/L=1 10 and sorption/desorption rate (in %), Input solution pH 4 0, c_0 = 1 - 5000 mgCu dm^{-3}, Desorption 1% HCl, 1 10

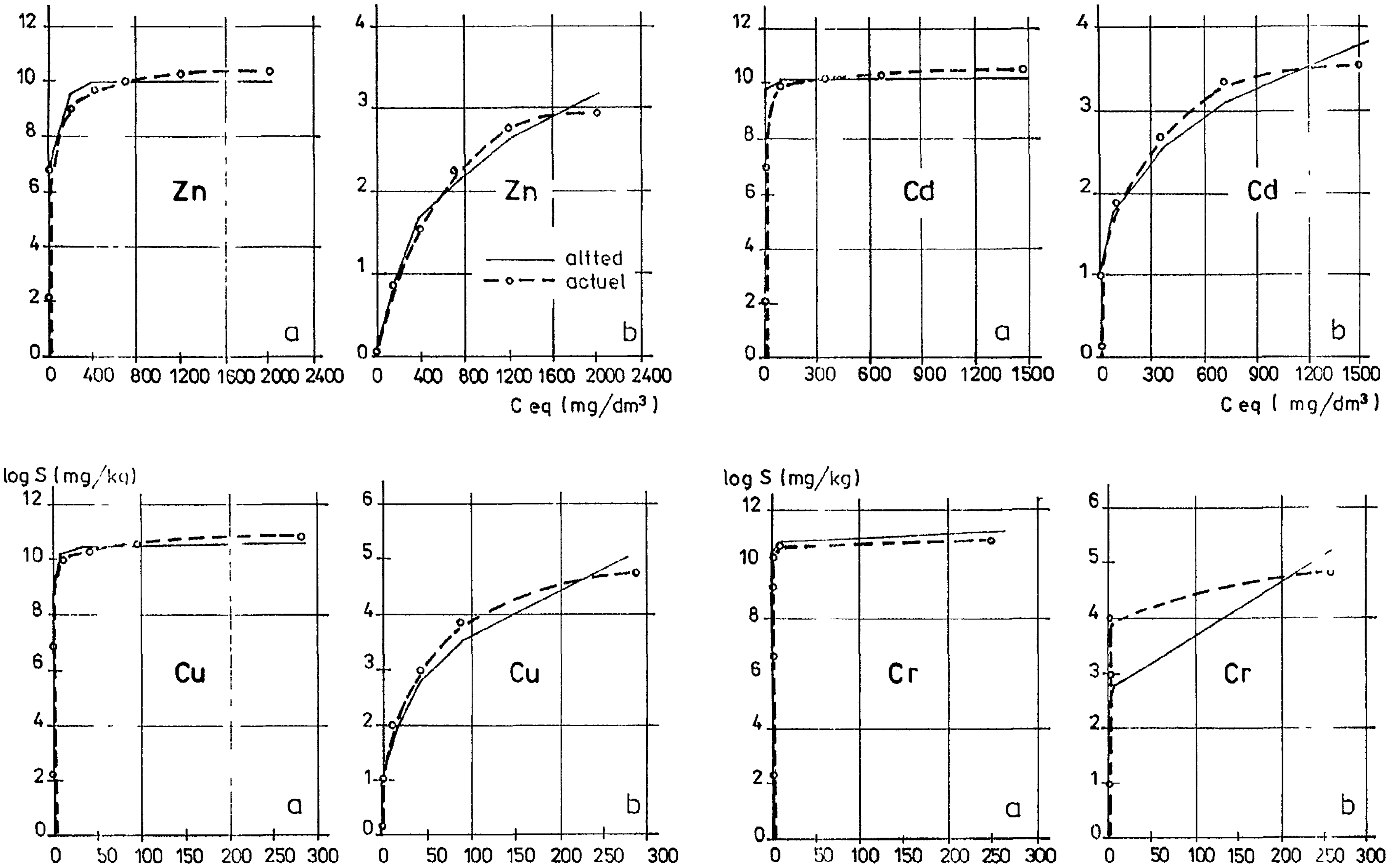
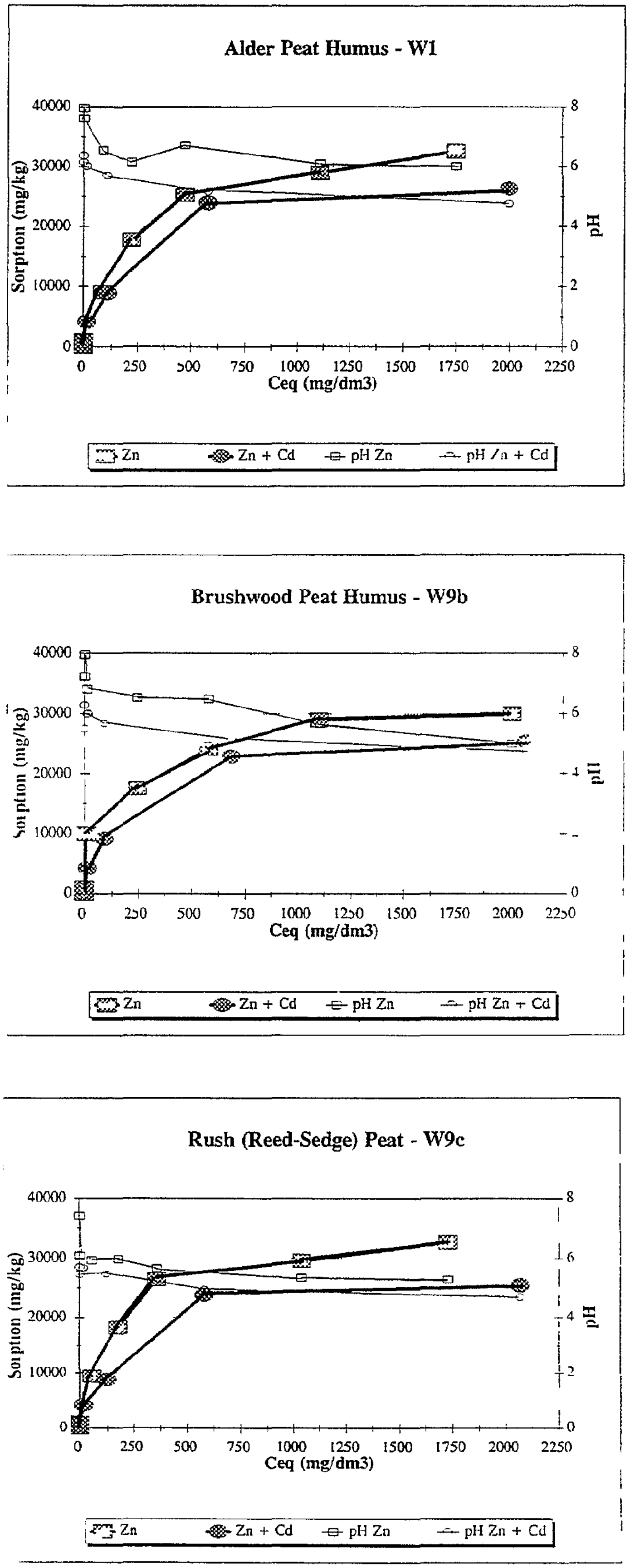


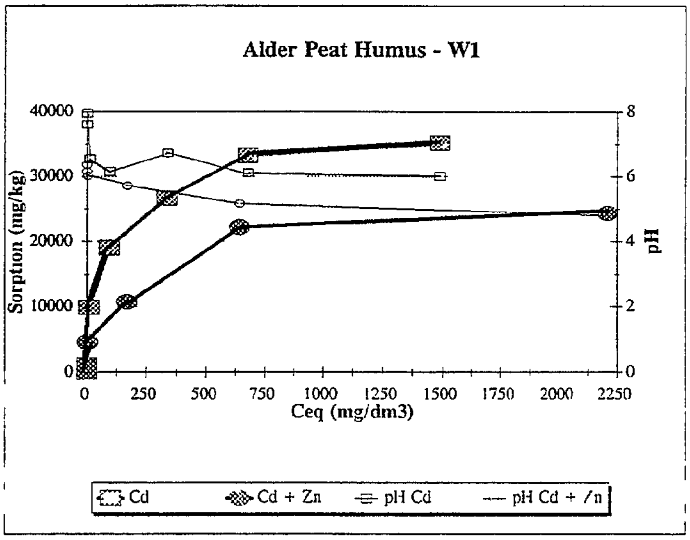
Figure 13 Langmuir (a) and Freundlich (b) equilibrium isotherms for Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} adsorption onto Alder Peat Humus (Sample W1)

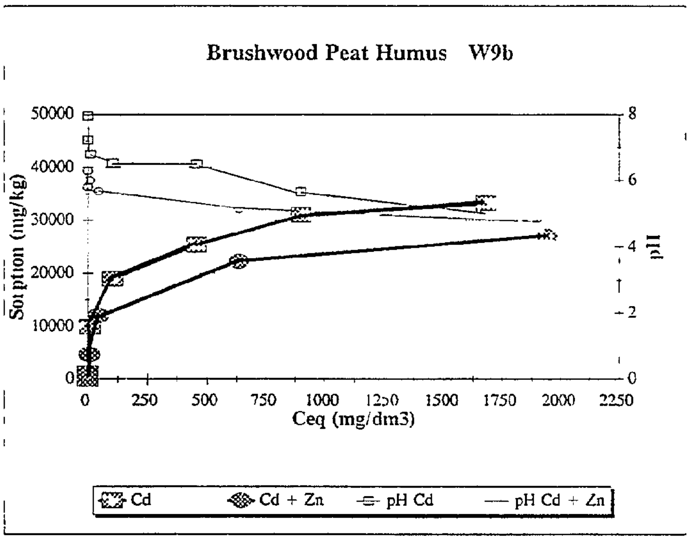

Alder Peat Humus - W1

Brushwood Peat Humus - W9b

Rush (Reed-Sedge) Peat - W9c

Figure 14 Equilibrium mass isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl, S/L=1 10, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3},





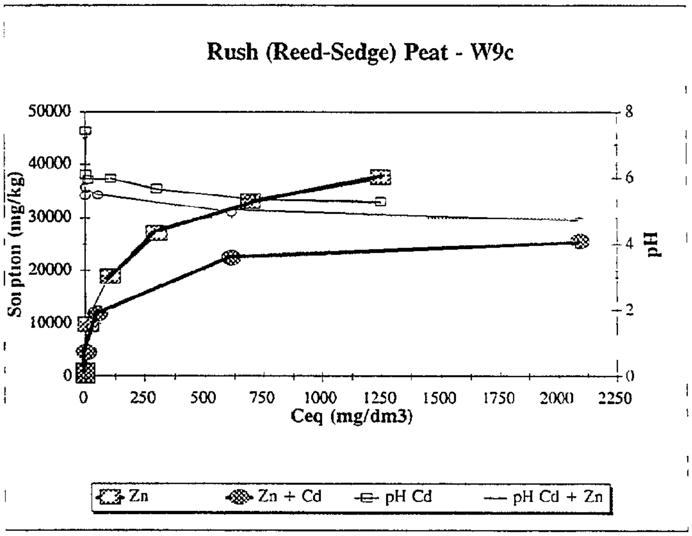
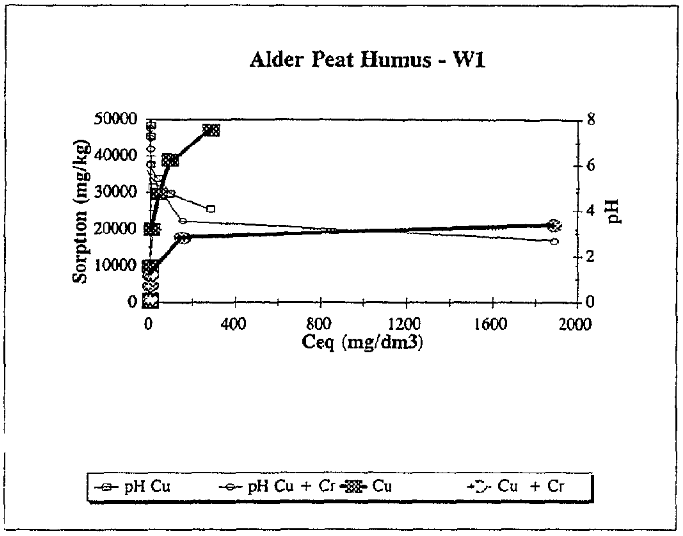
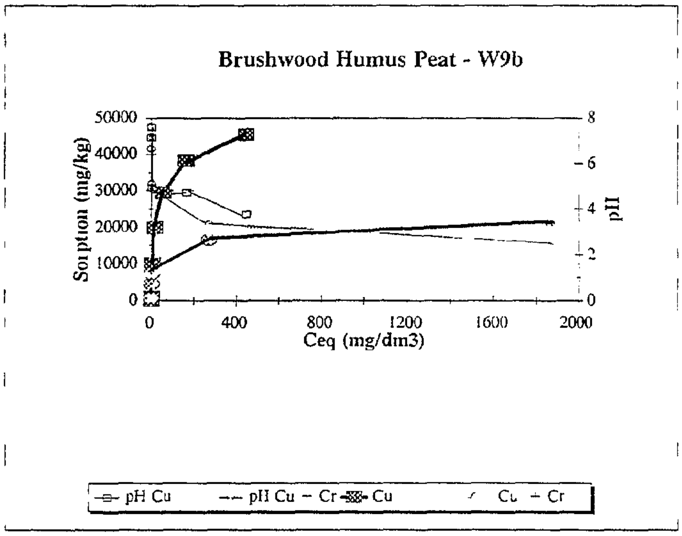


Figure 15 Equilibrium mass isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in mono-metal Cd-Cl and binary systems (Cd+Zn)-Cl, S/L=1:10, Input solution pH 4.0, c_0 = 1 - 5000 mgMe dm^{-3},





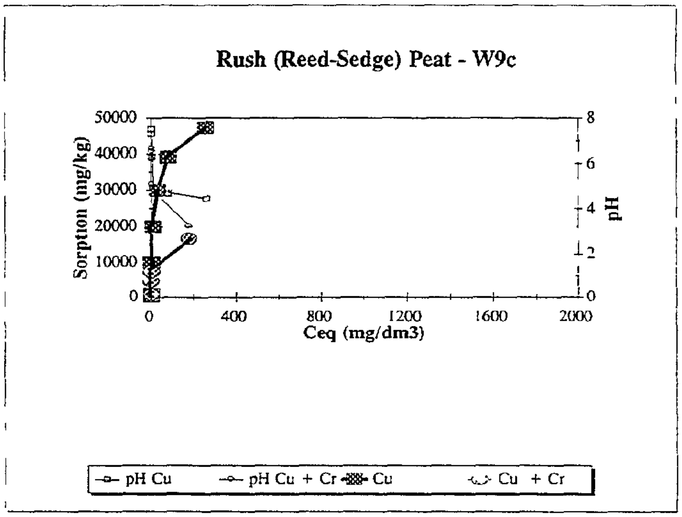


Figure 16 Equilibrium mass isotherms for Cu^{2+}on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in mono-metal Cu-Cl and binary systems (Cu+Cd)-Cl, S/L=1:10, Input solution pH 4.0, c_0 = 1 - 5000 mgMe dm^{-3},

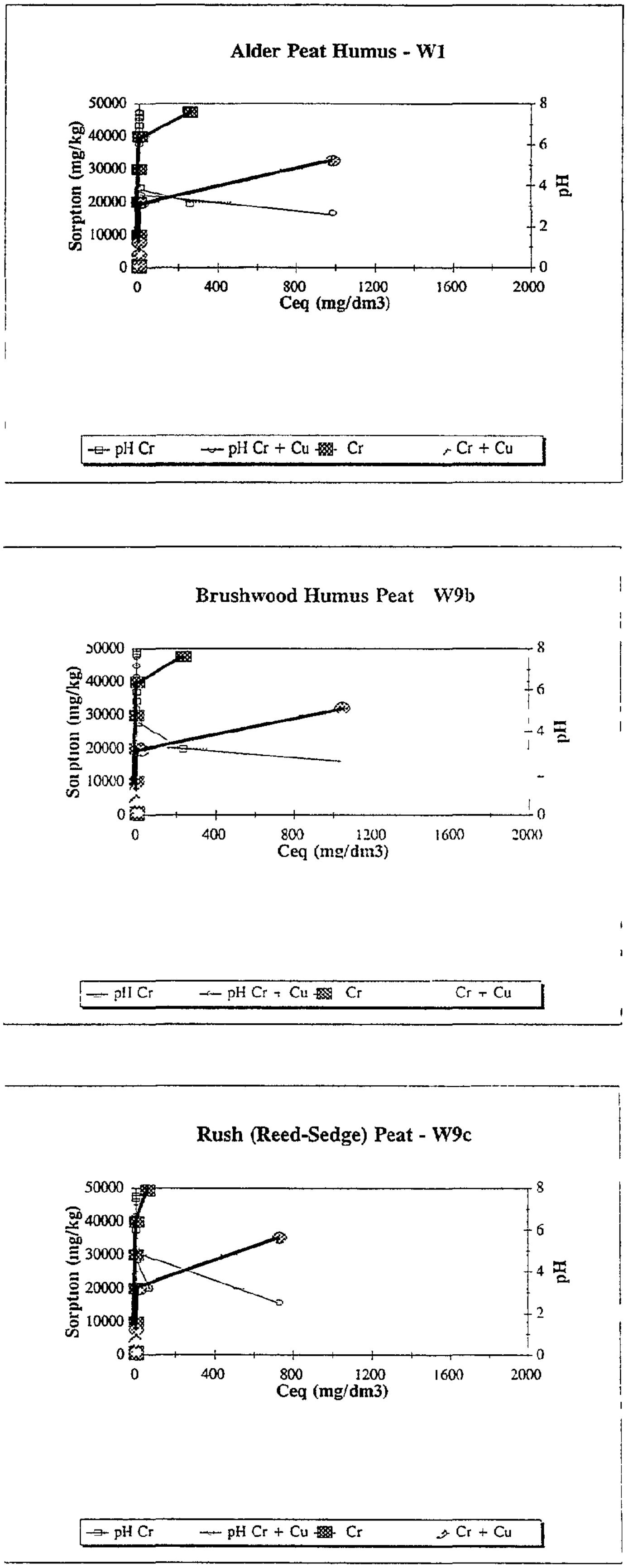


Figure 17 Equilibrium mass isotherms for Cr^{3+} on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl, at S/L=1 10, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3},

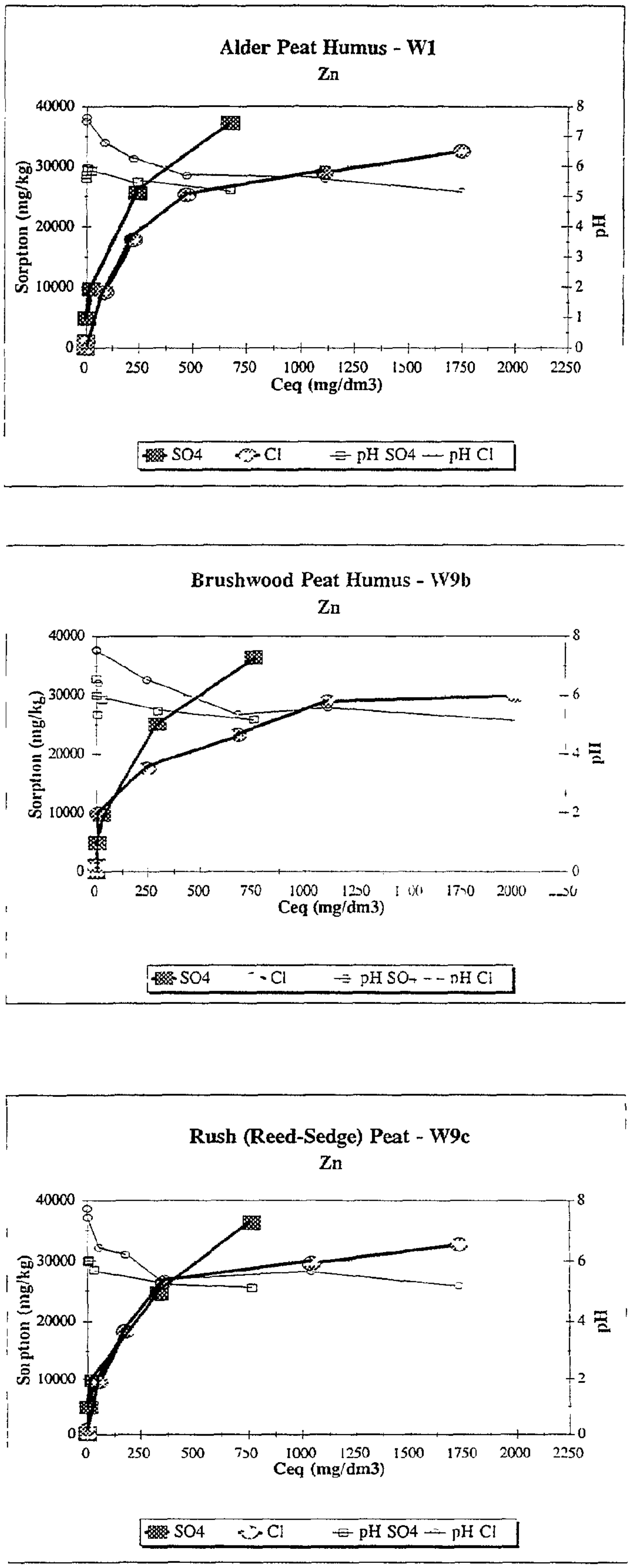


Figure 18 Equilibrium mass isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Peat) and and pH of equilibrated solutions in mono-metal systems Zn-Cl and Zn-SO_4^{2}, S/L=1 10, Input solution pH 4 0, c_0 = 1 - 5000 mgZn dm^{3},

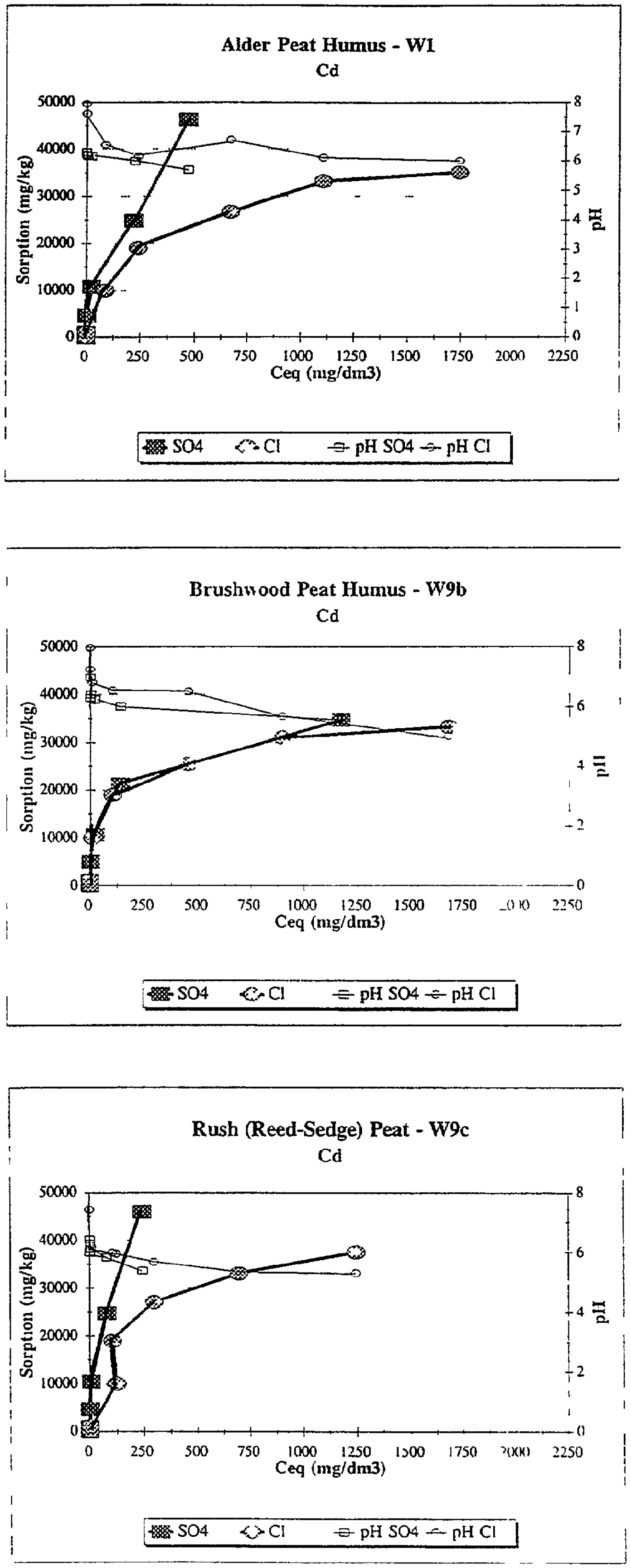


Figure 19 Equilibrium mass isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Peat) and and pH of equilibrated solutions in mono-metal systems Cd-Cl and Cd-SO_4^{2-}, S/L=1:10, Input solution pH 4.0, c_0 = 1 - 5000 mgCd dm^{-3},

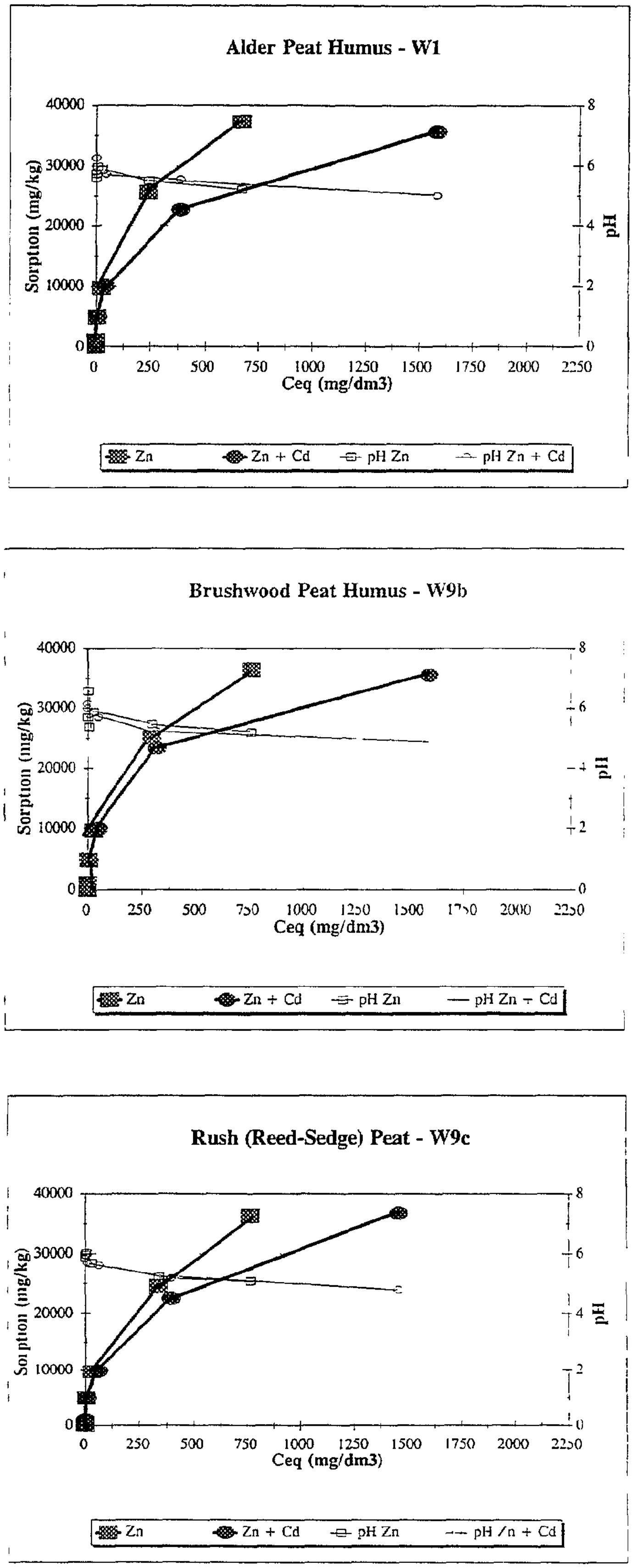


Figure 20 Equilibrium mass isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in mono-metal Zn-SO_4 and binary systems (Zn+Cd)-SO_4, S/L=1 10, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3},

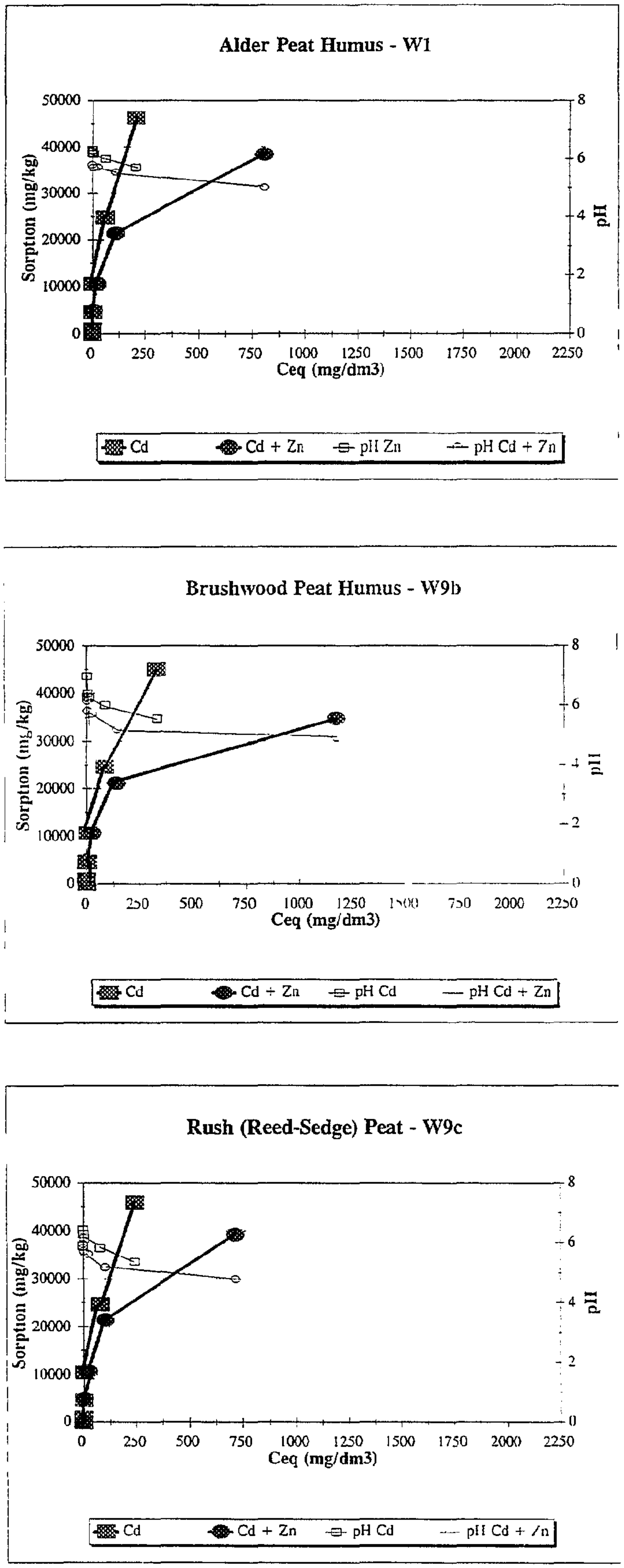


Figure 21 Equilibrium mass isotherms for Cd^{2+}on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in mono-metal Cd-SO$_4$ and binary systems (Cd+Zn)-SO$_4$, S/L=1 10, Input solution pH 4 0 c_0 = 1 - 5000 mgMe dm^{-3}

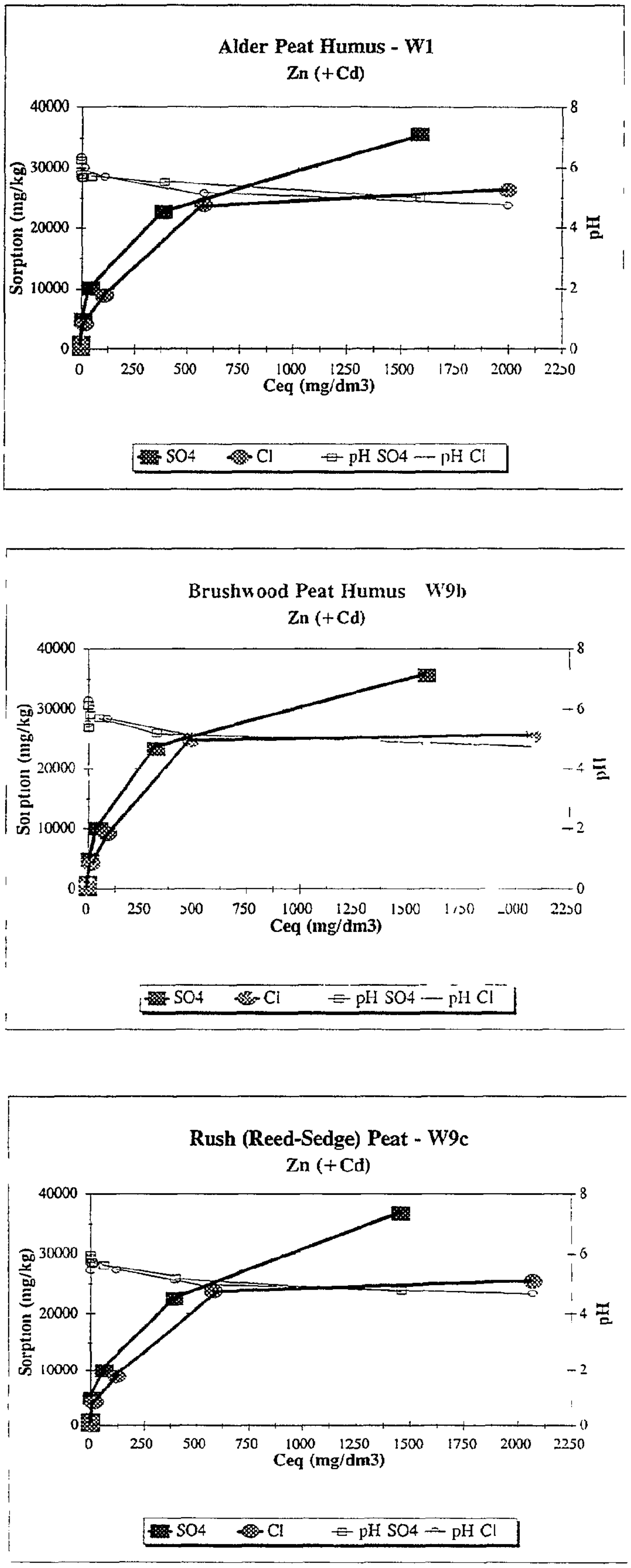


Figure 22 Equilibrium mass isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in binary systems (Zn+Cd)-Cl and (Zn+Cd)-SO_4, S/L=1 10, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{-3},

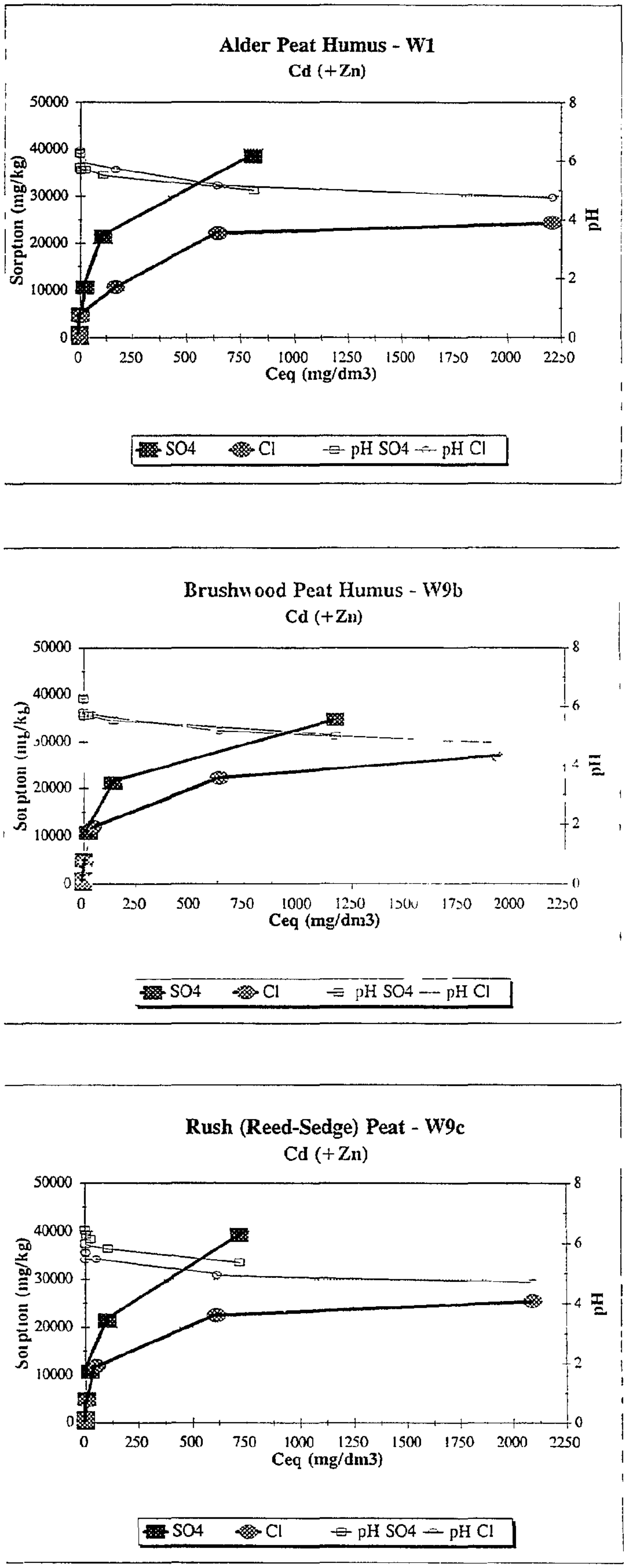


Figure 23 Equilibrium mass isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Peat) and pH of equilibrated solutions in binary systems (Cd+Zn)-Cl and (Cd+Zn)-SO_4, S/L=1 10, Input solution pH 4 0, c_0 = 1 - 5000 mgMe dm^{3},

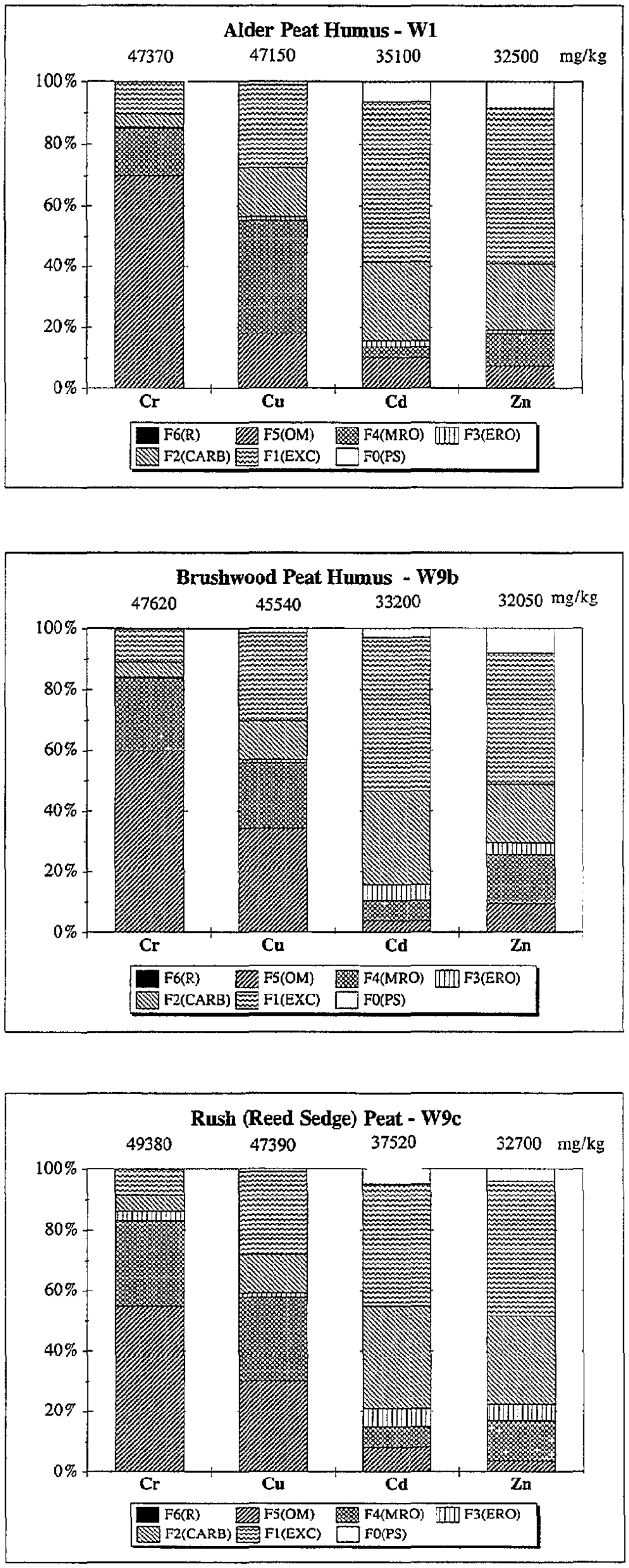


Figure 24 Sequential fractionation of Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} bound from mono-metal Me-Cl solution under batch conditions, at c_0 = 5000 mgMe dm^3 and pH 4 0 onto Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) according to the increasing binding strength Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

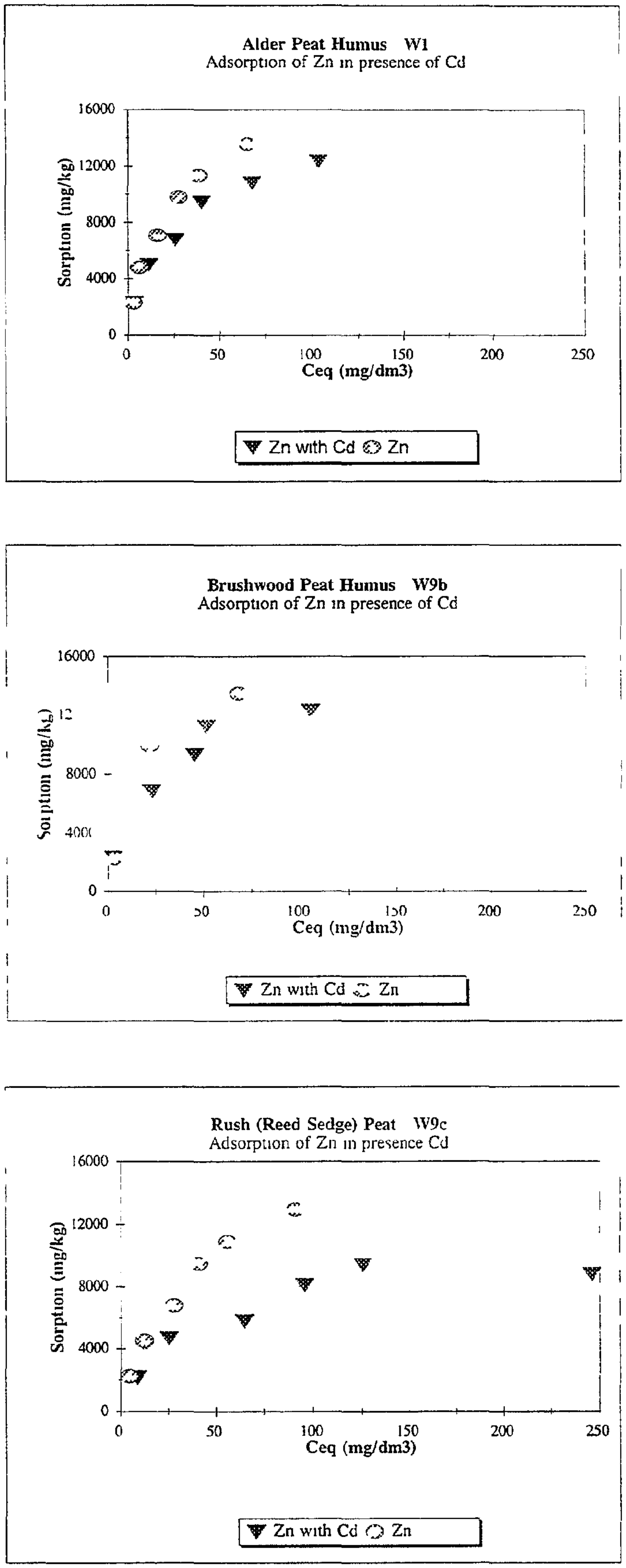


Figure 25 Equilibrium mass isotherms for Zn^{2+} on low-moor peats (Peat Humus and Rush Peat) at fixed pH 5 5 of substrate and input solution in mono-metal Zn-Cl and binary systems (Zn+Cd)-Cl, c_0 = 1 - 600 mgMe dm^{3}, S/L = 1 25

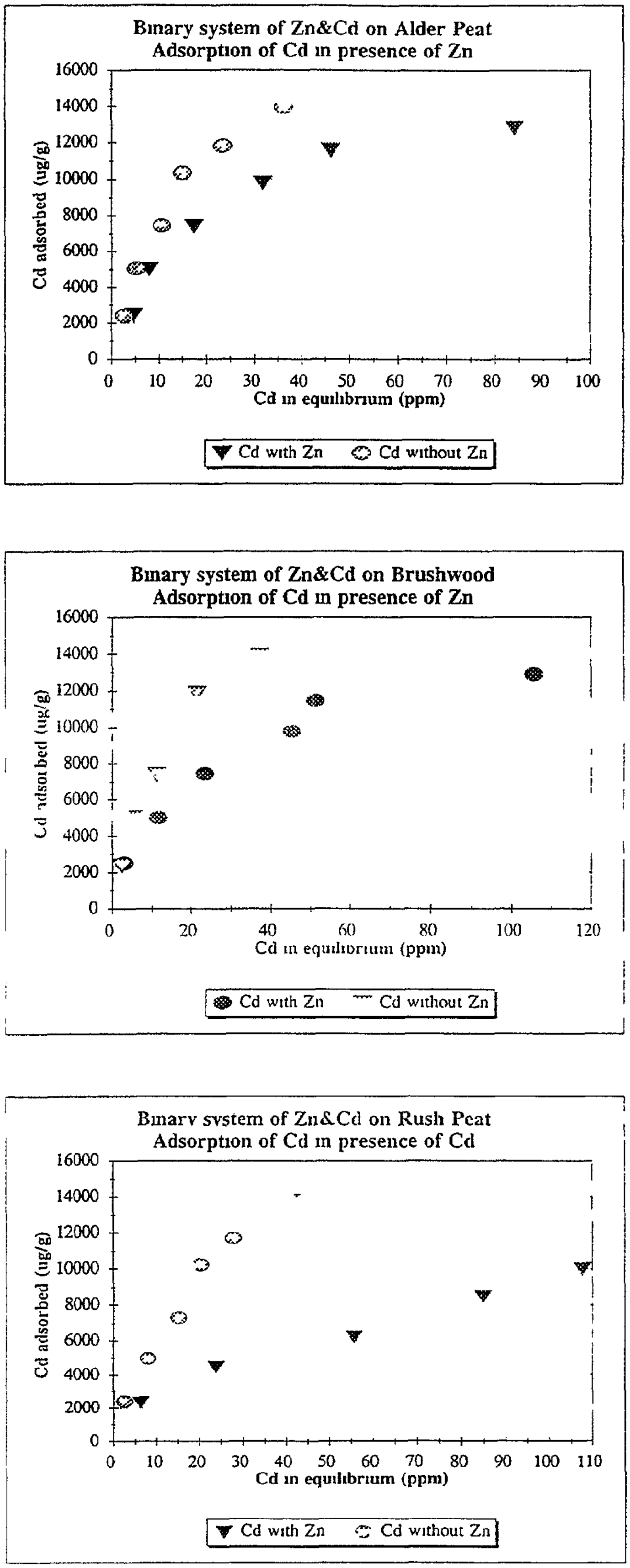


Figure 26 Equilibrium mass isotherms for Cd^{2+} on low-moor peats (Peat Humus and Rush Peat) at fixed pH 5 5 of substrate and input solution in mono-metal Cd-Cl and binary systems (Cd+Zn)-Cl, c_0 = 1 - 600 mgMe dm^{-3}, S/L = 1 25

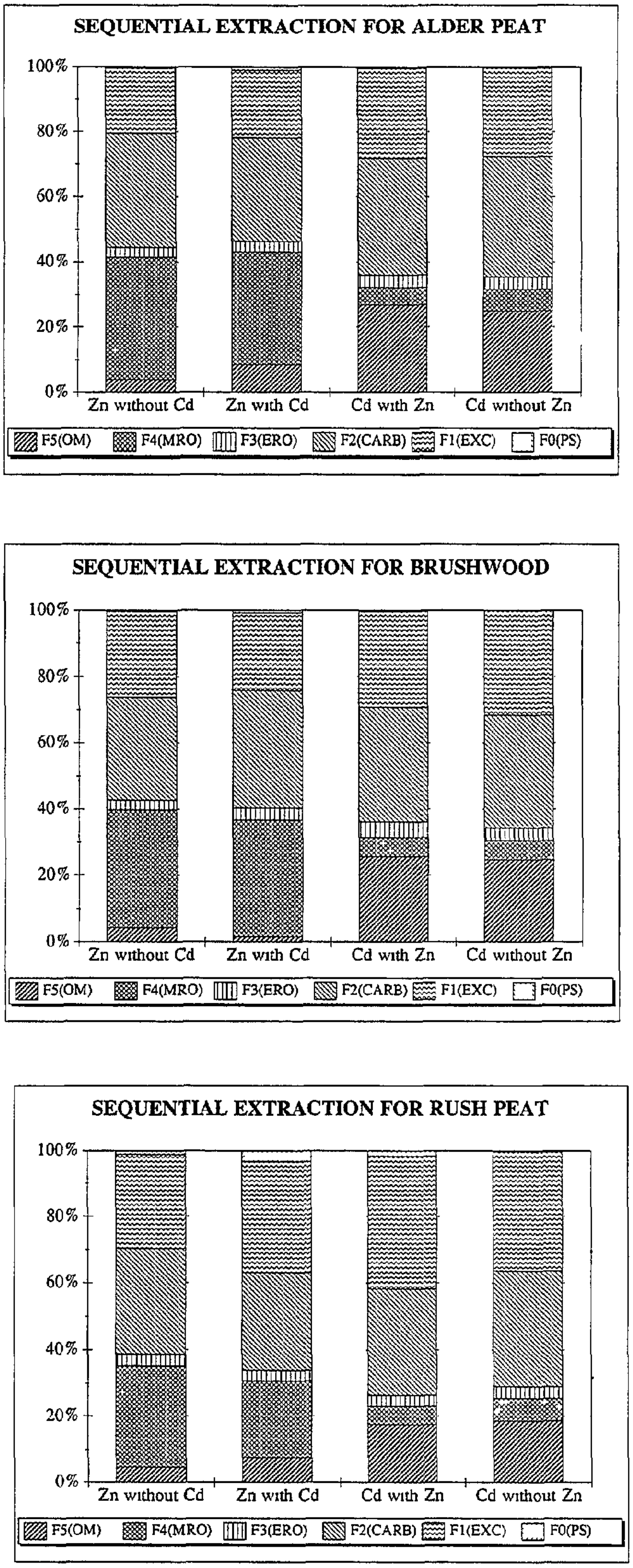
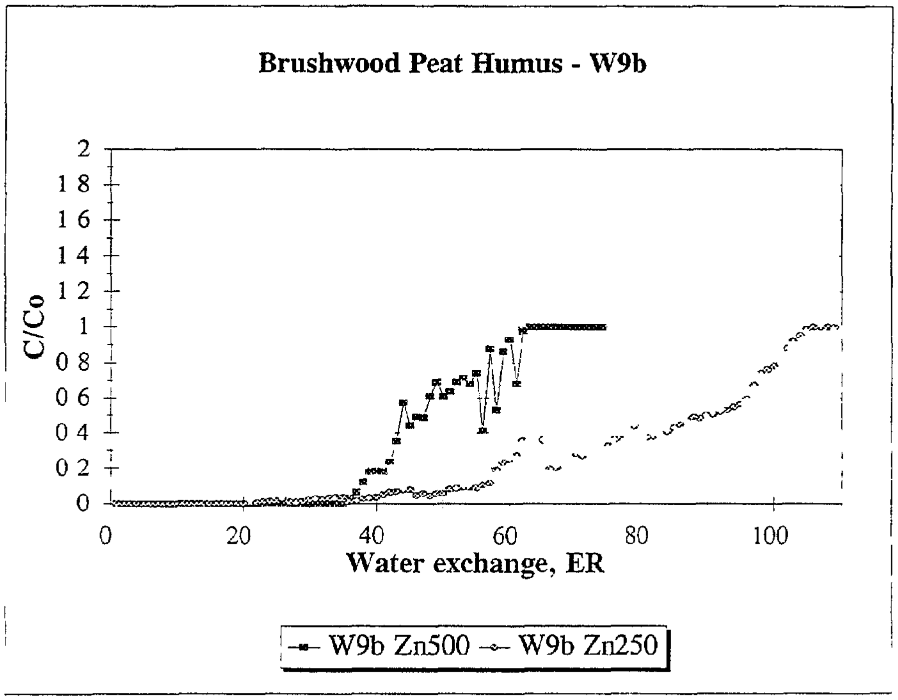


Figure 27 Sequential fractionation of Zn^{2+} and Cd^{2+} bound under batch conditions from the pre-treated mono-metal Zn-Cl and binary (Zn+Cd)-Cl solutions onto Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) according to the increasing binding strength Fixed pH 5 5 of substrate and input solution, c_0 = 600



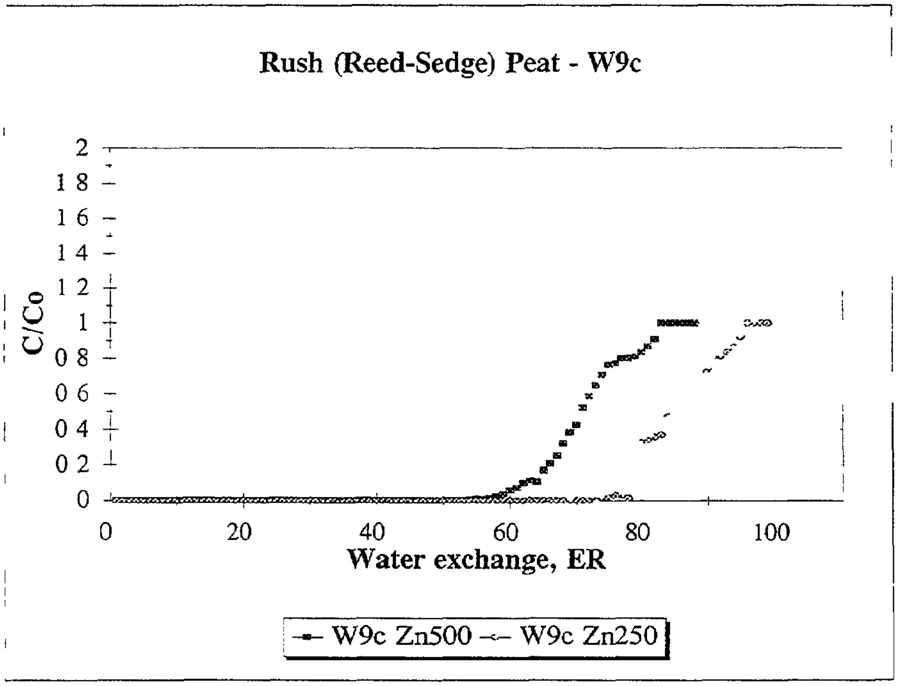


Figure 28 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Zn^{2+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,

Working parameters Column φ 48 mm, H = 285 mm

Input solutions Zn-SO_4, c_0 = 500 mgZn dm^{3} and 250 mgZn dm^{3}, pH 4 0, flow rate 0 1 cm^3/s saturated zone flow conditions, Substrate solution ratio 1 10

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

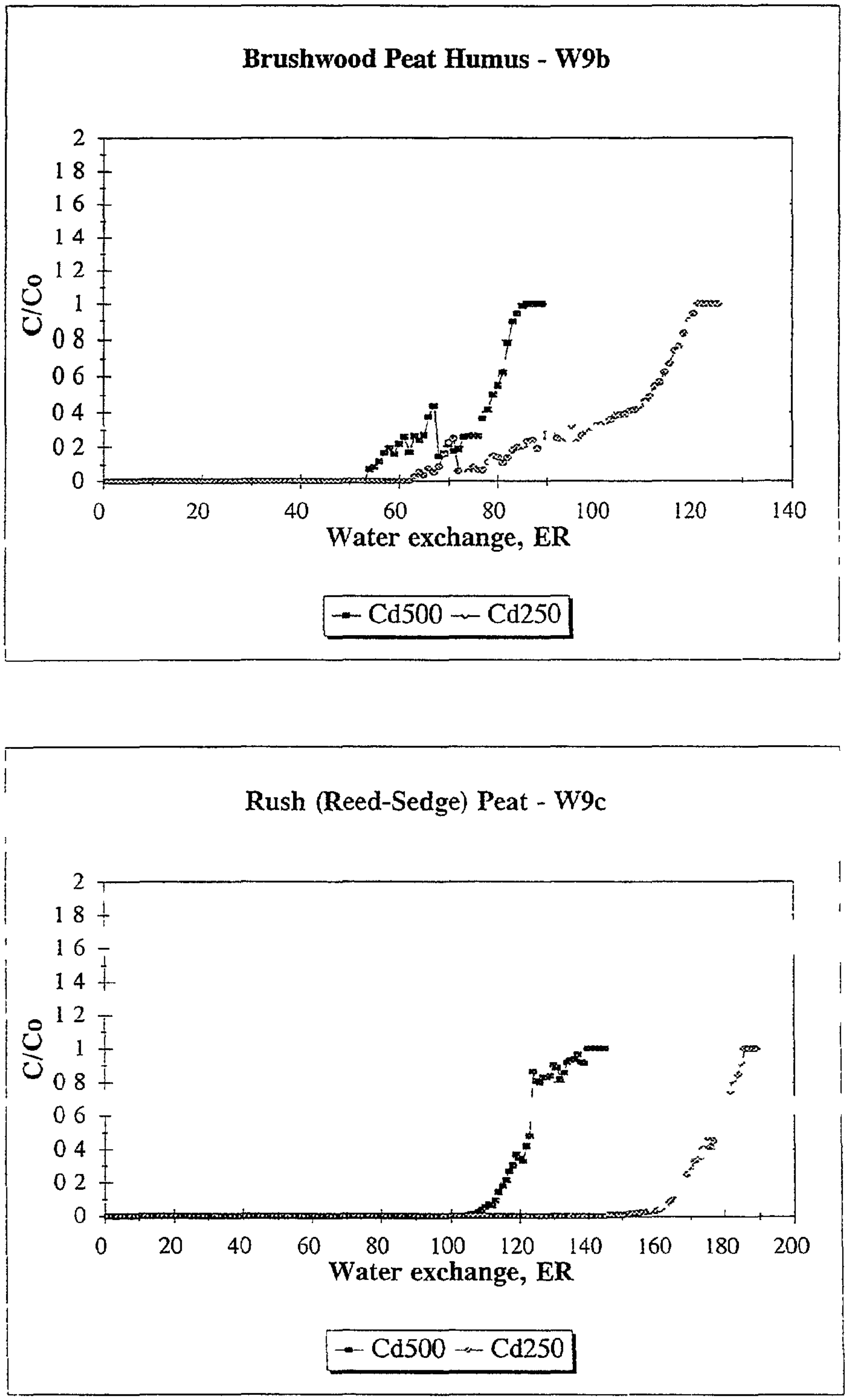


Figure 29 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Cd^{2+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,

Working parameters Column φ 48 mm, H = 285 mm

Input solutions Cd-SO_4, c_0 = 500 mgCd dm^{3} and 250 mgCd dm^{3}, pH 4.0, flow rate 0.1 cm^{3}/s, saturated zone flow conditions, Substrate solution ratio 1 10

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

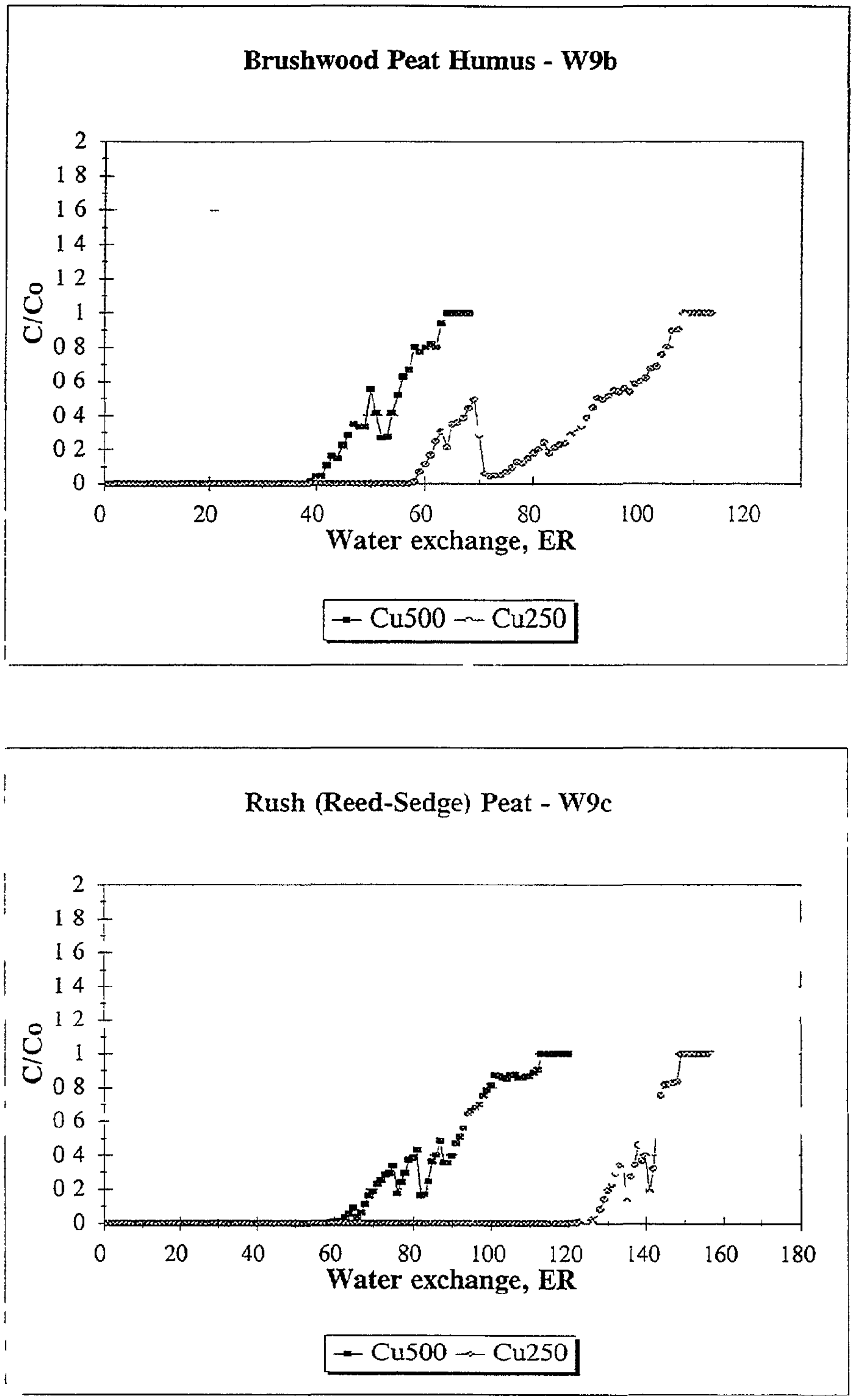


Figure 30 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Cu^{2+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,

Working parameters Column φ 48 mm, H = 285 mm

Input solutions Cu-SO$_4$, c$_0$ = 500 mgCu dm^{3} and 250 mgCu dm^{3}, pH 4 0, flow rate 0 1 cm^{3}/s, saturated zone flow conditions, Substrate solution ratio 1 10

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

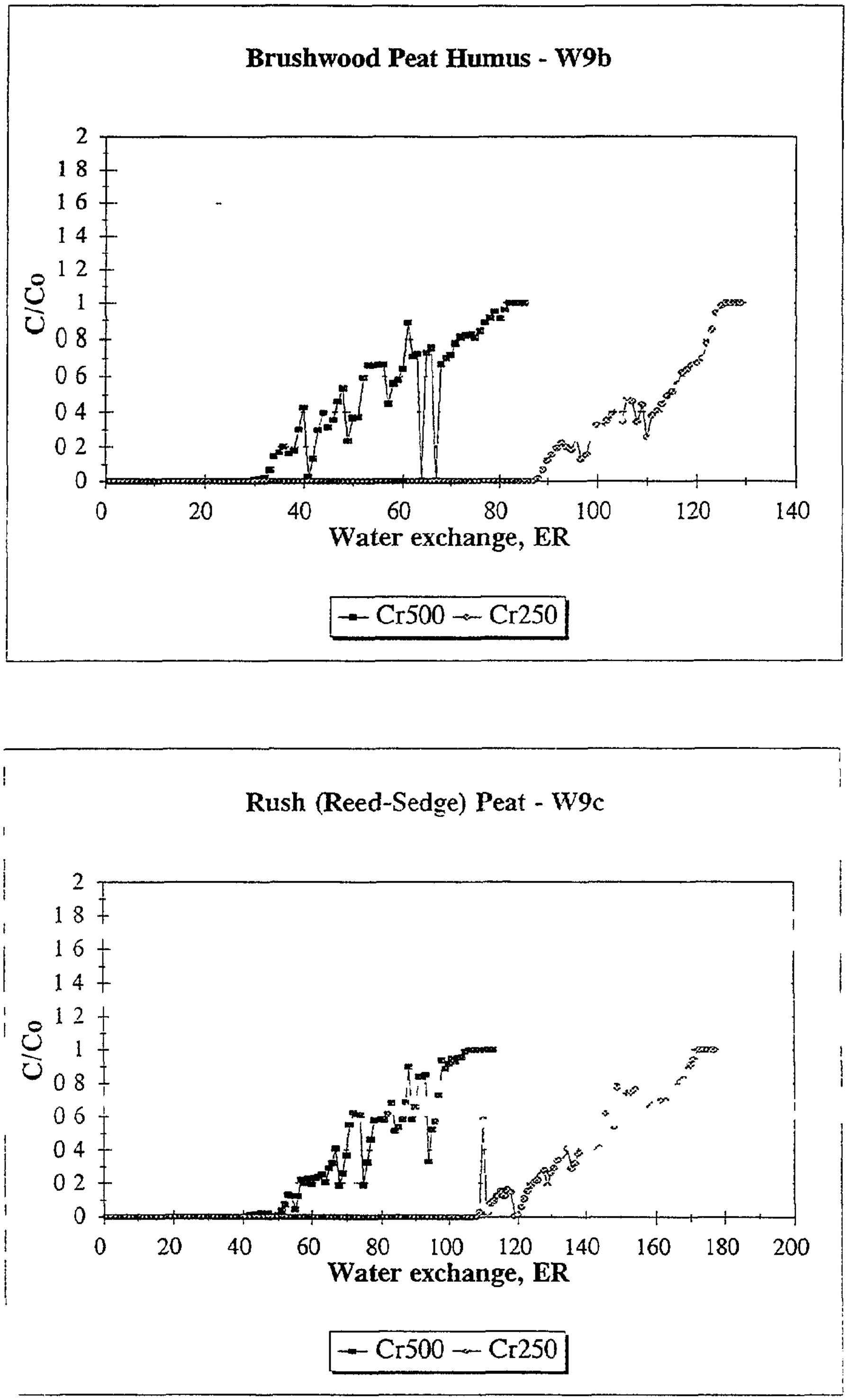


Figure 31 Fixed bed (column) dimensionless liquid phase concentration against water exchange rate (ER) for Cr^{3+} on Brushwood Peat Humus W9b and Rush (Reed-Sedge) Peat W9c,

Working parameters Column φ 48 mm, H = 285 mm

Input solutions Cr-Cl, c_0 = 500 mgCr dm^{-3} and 250 mgCr dm^{-3}, pH 4 0, flow rate 0 1 cm^3/s, saturated zone flow conditions, Substrate solution ratio 1 10

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L = 1 1 (W9c)

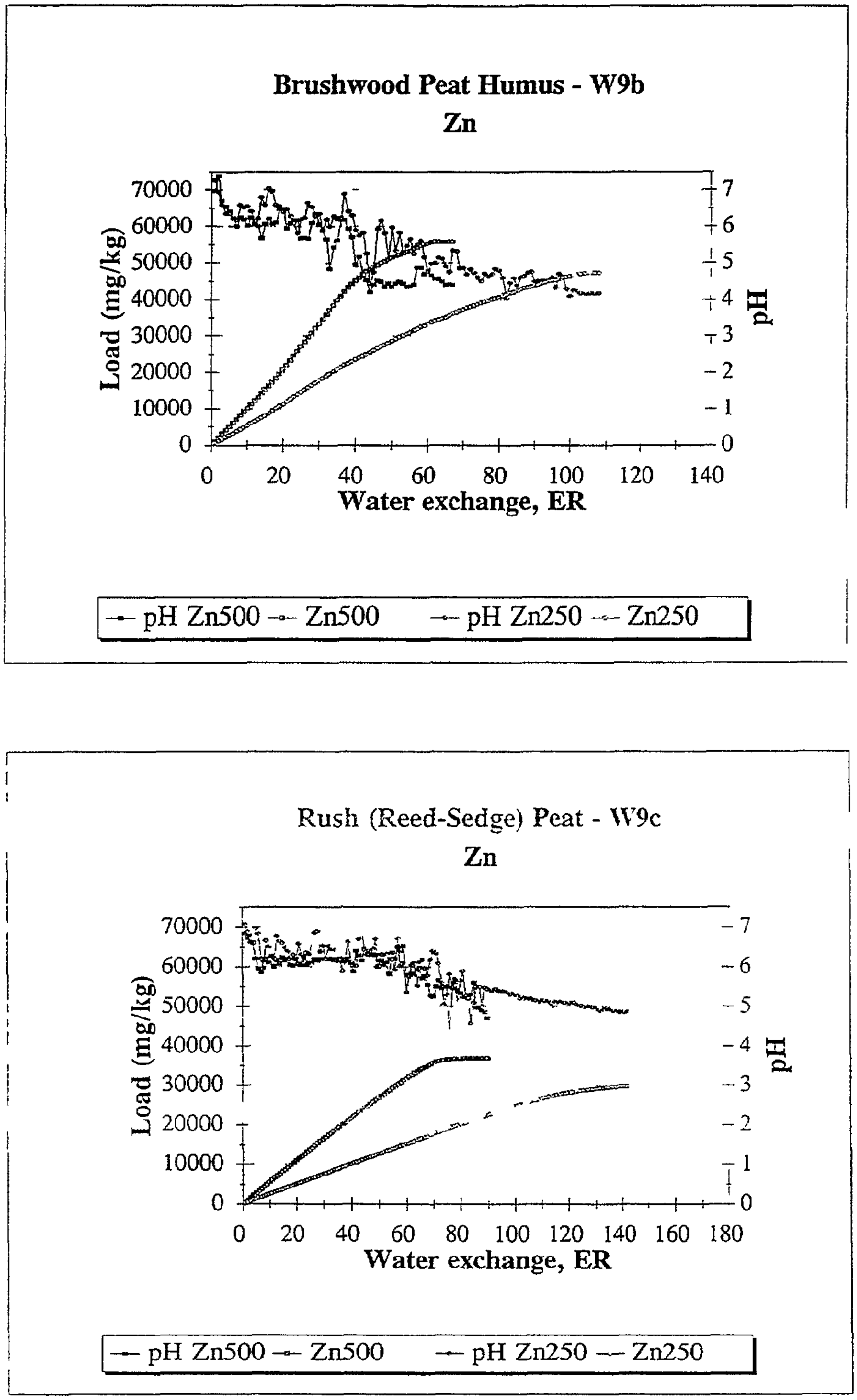


Figure 32 Sorption of Zn^{2+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Zn concentration in the input solution

<u>Working parameters</u> as in Fig 28,

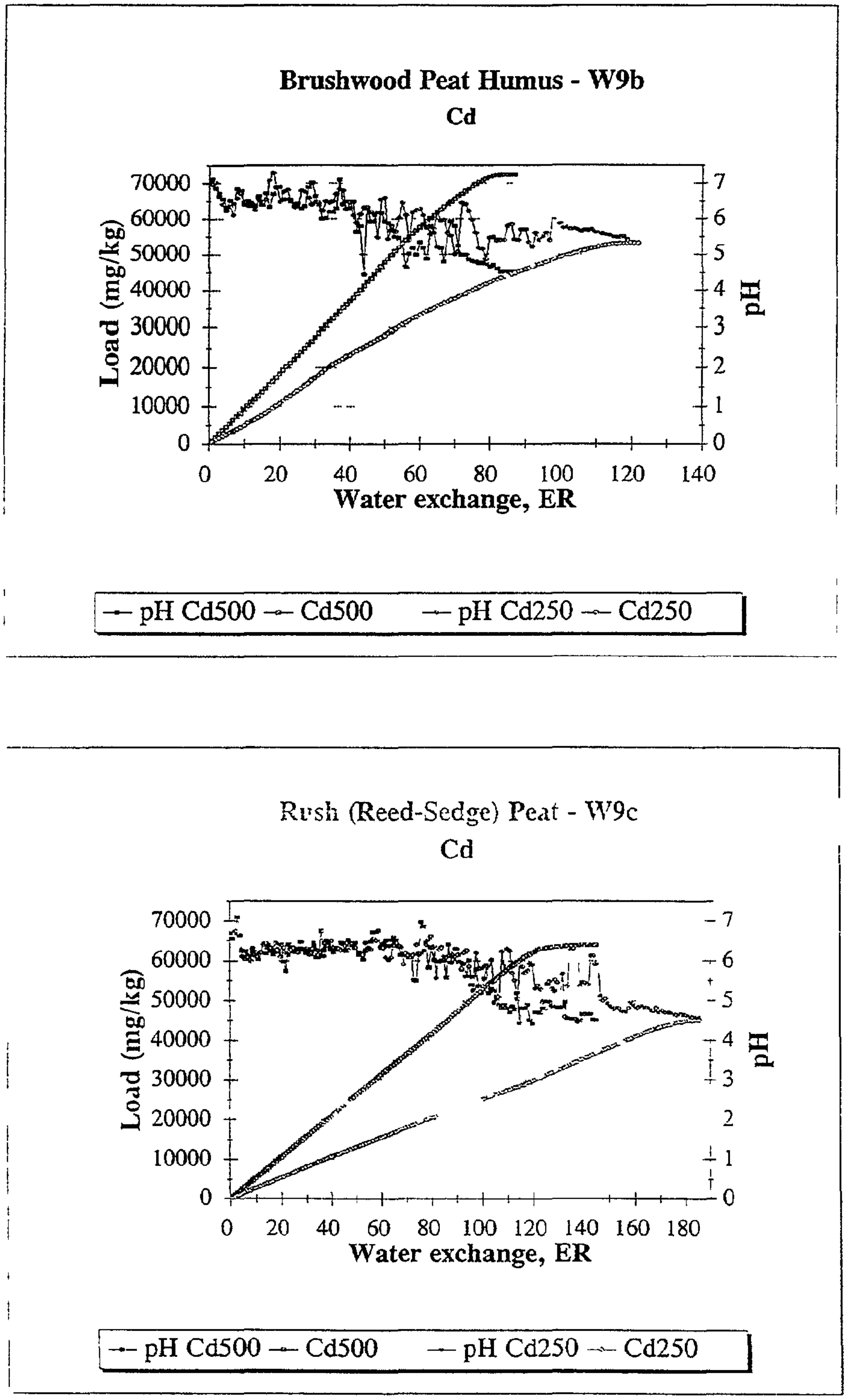


Figure 33 Sorption of Cd^{2+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Cd concentration in the input solution
<u>Working parameters</u> as in Fig 29,

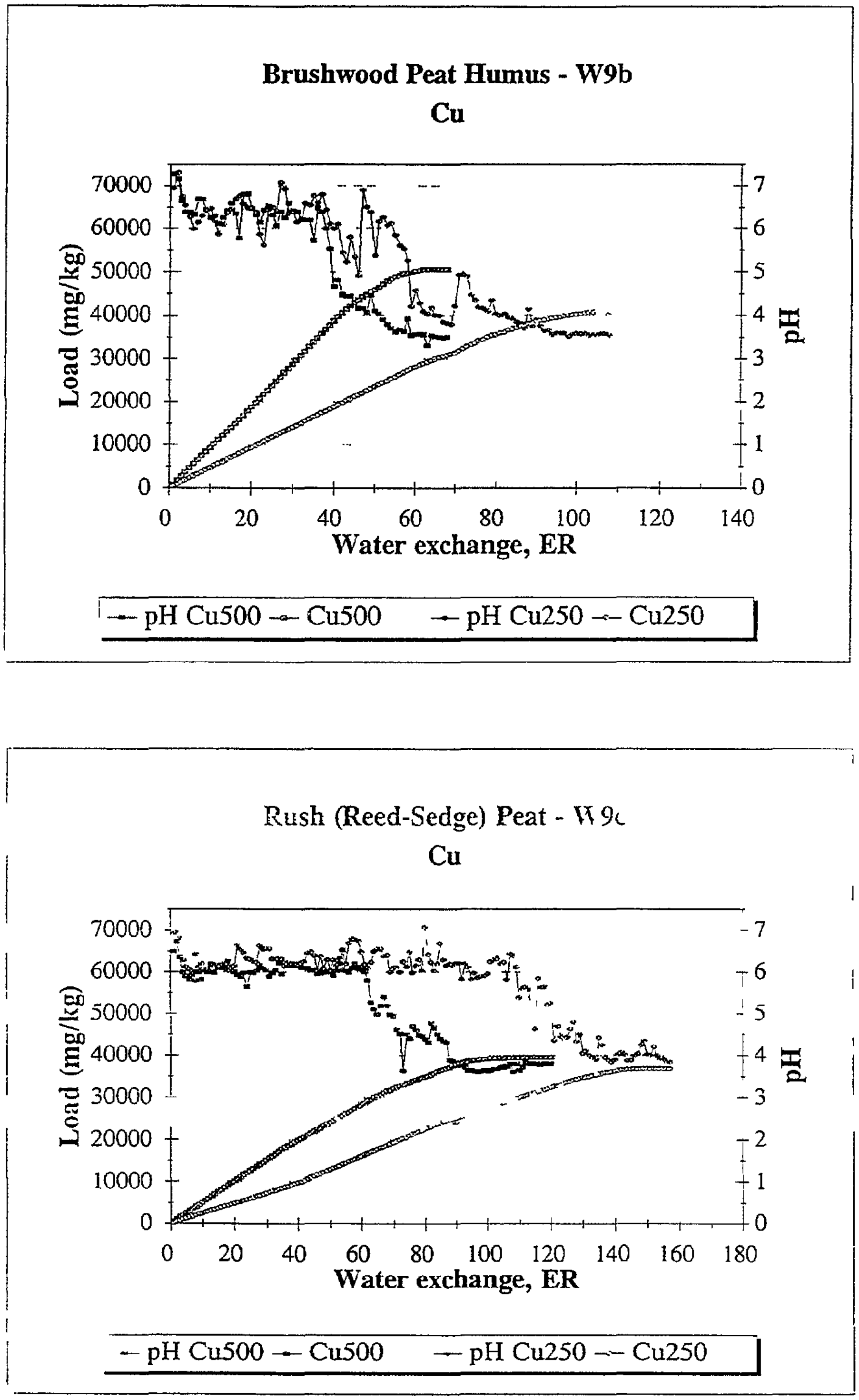


Figure 34 Sorption of Cu^{2+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Cu concentration in the input solution
Working parameters as in Fig 30,

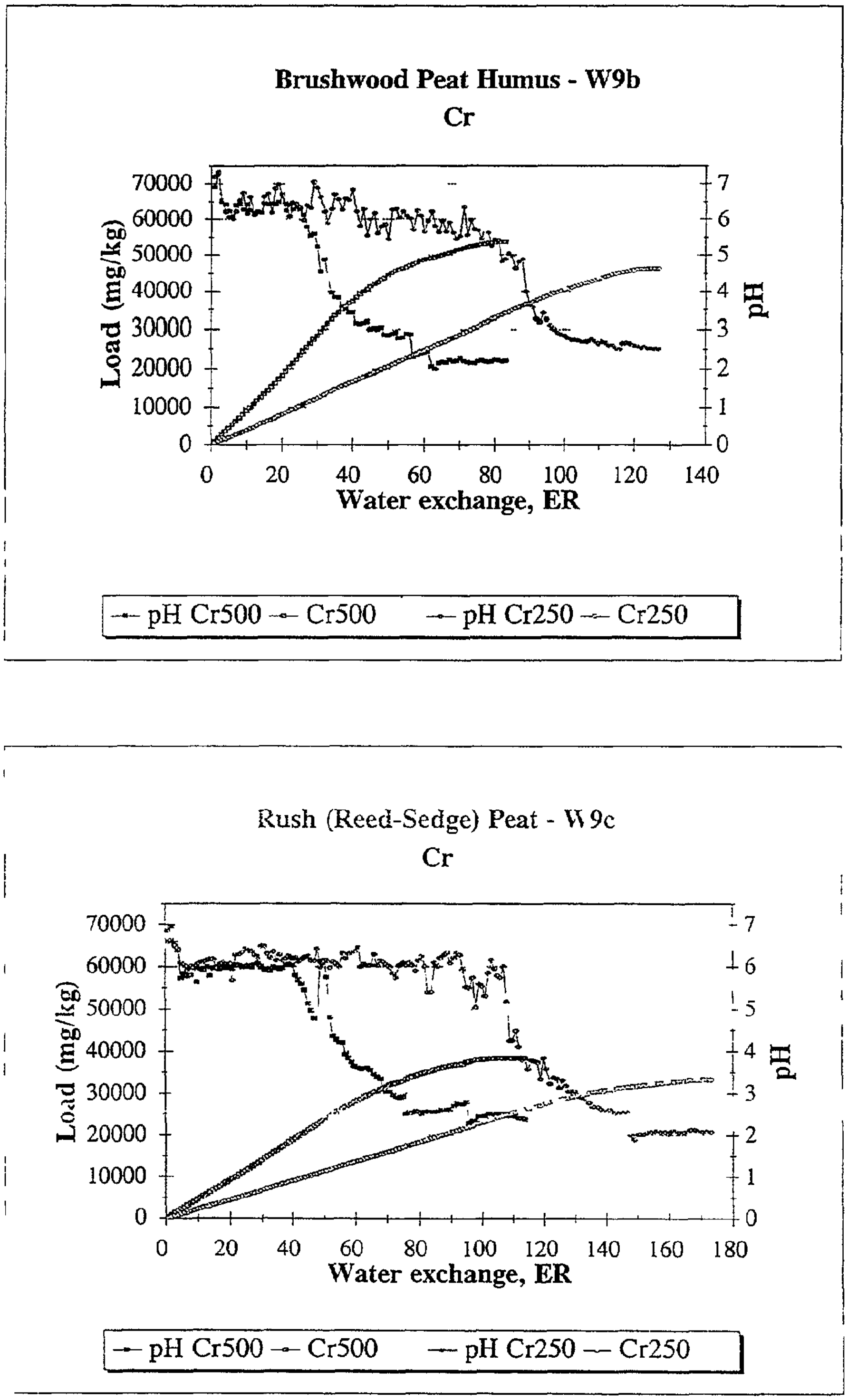


Figure 35 Sorption of Cr^{3+} onto low-moor peats (Peat Humus and Rush Peat) and pH of output solutions under dynamic flow conditions *vs* water exchange rate and Cr concentration in the input solution

Working parameters as in Fig 31,

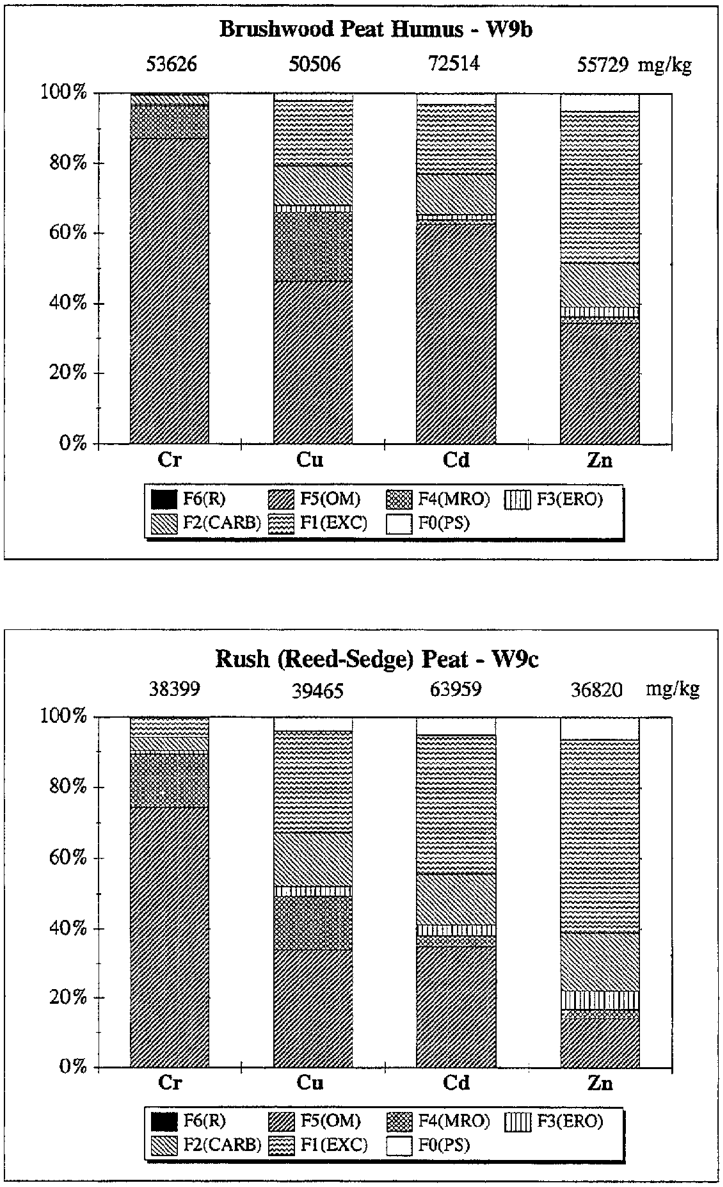


Figure 36 Sequential fractionation according to the increasing binding strength of Zn^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+} bound from the mono-metal Me-SO_4 (Cr-Cl) solution under dynamic (saturated zone) flow conditions, at c_0 = 500 mgMe dm^{3} and pH 4 0 onto Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual

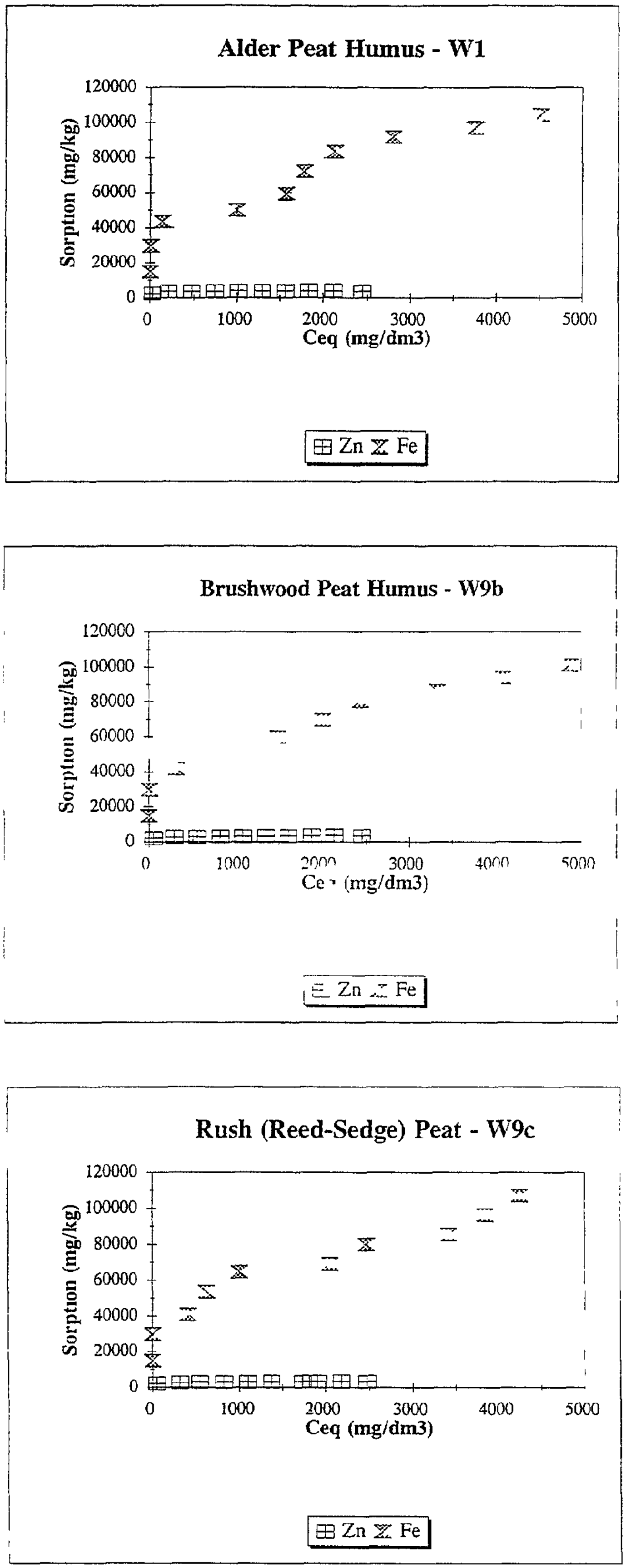


Figure 37 Equilibrium mass sorption isotherms for Fe and Zn on low-moor peats (Peat Humus and Rush Peat) from liquid waste from electroplating process
Batch experiments, Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

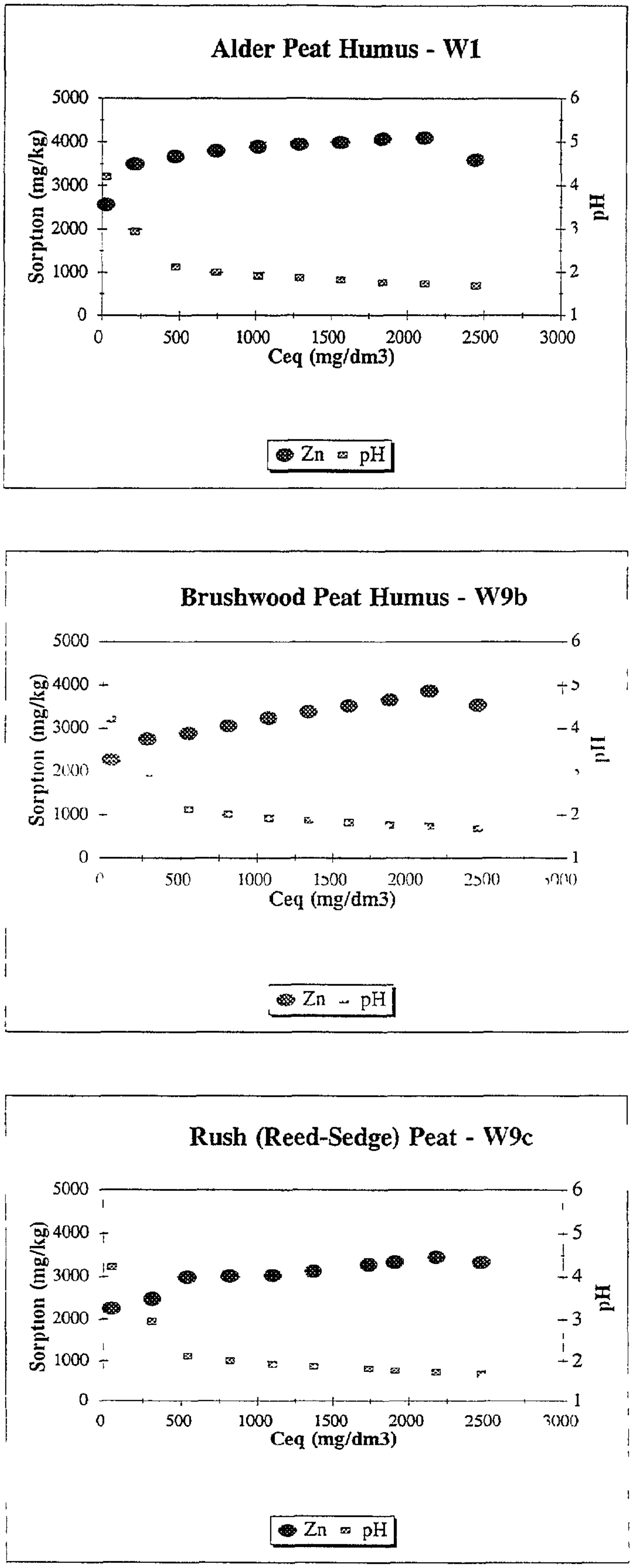


Figure 38 Equilibrium mass sorption isotherms for Zn on low-moor peats (Peat Humus and Rush Peat) from liquid waste from electroplating process and pH of the equilibrated solution
Batch experiments, Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{-3} > 122 mgMn dm^{3}

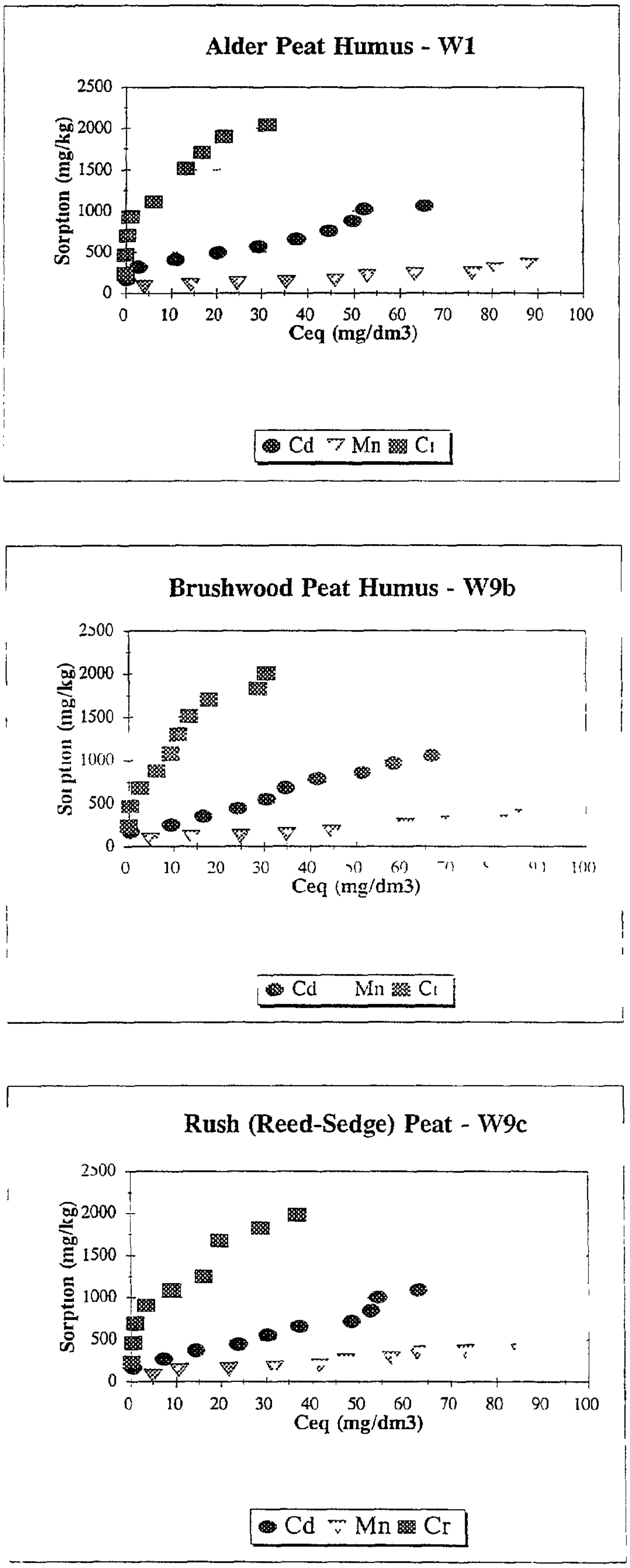
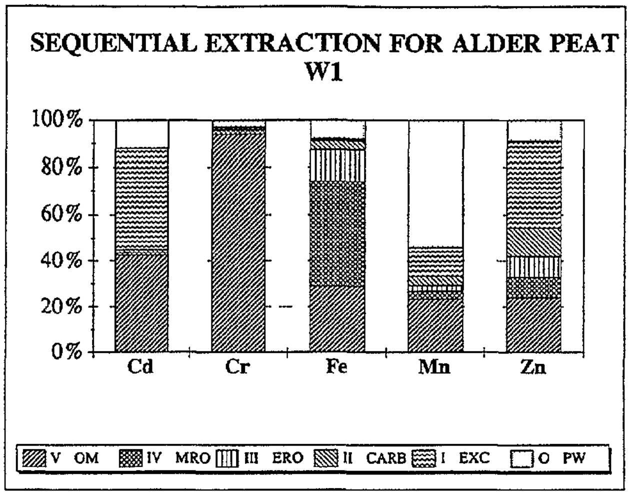
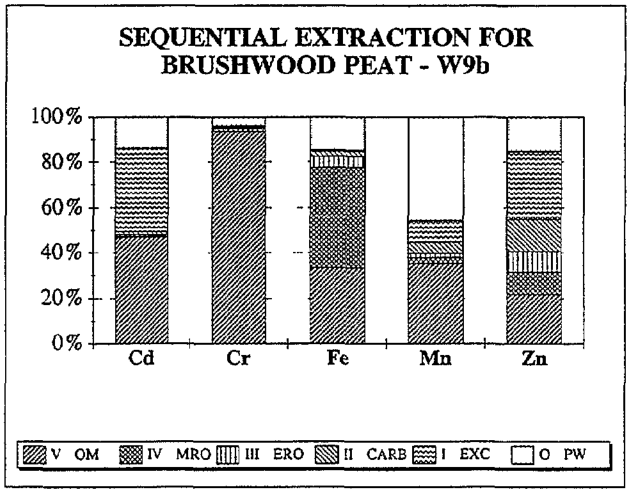


Figure 39 Equilibrium mass sorption isotherms for Cd, Mn and Cr on low-moor peats (Peat Humus and Rush Peat) from liquid waste from electroplating process
Batch experiments, Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}


SEQUENTIAL EXTRACTION FOR ALDER PEAT W1


SEQUENTIAL EXTRACTION FOR BRUSHWOOD PEAT - W9b

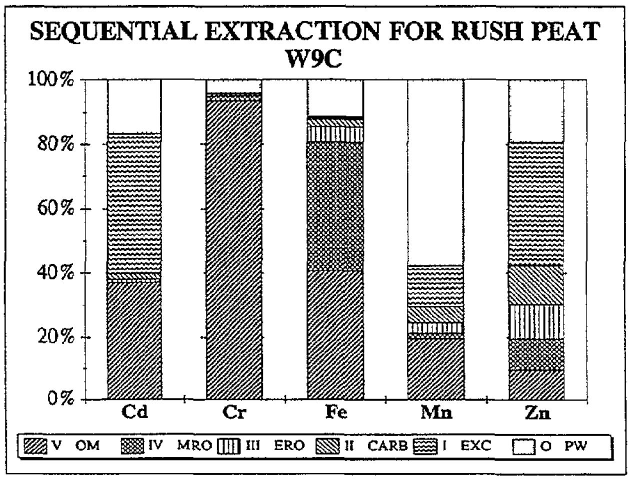

SEQUENTIAL EXTRACTION FOR RUSH PEAT W9C

Figure 40 Sequential fractionation according to the increasing binding strength of Cd, Cr, Fe, Mn and Zn bound from the electroplating liquid waste onto Alder Peat Humus (W1), Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c)
Fractions F0(PS) - pore solution, F1(EXC) - most labile, F2(CARB) - labile, F3(ERO) - easily reducible, F4(MRO) - moderately reducible, F5(OM) - strongly bound, F6(R) - residual
Batch experiments, Liquid waste Me-SO$_4$, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

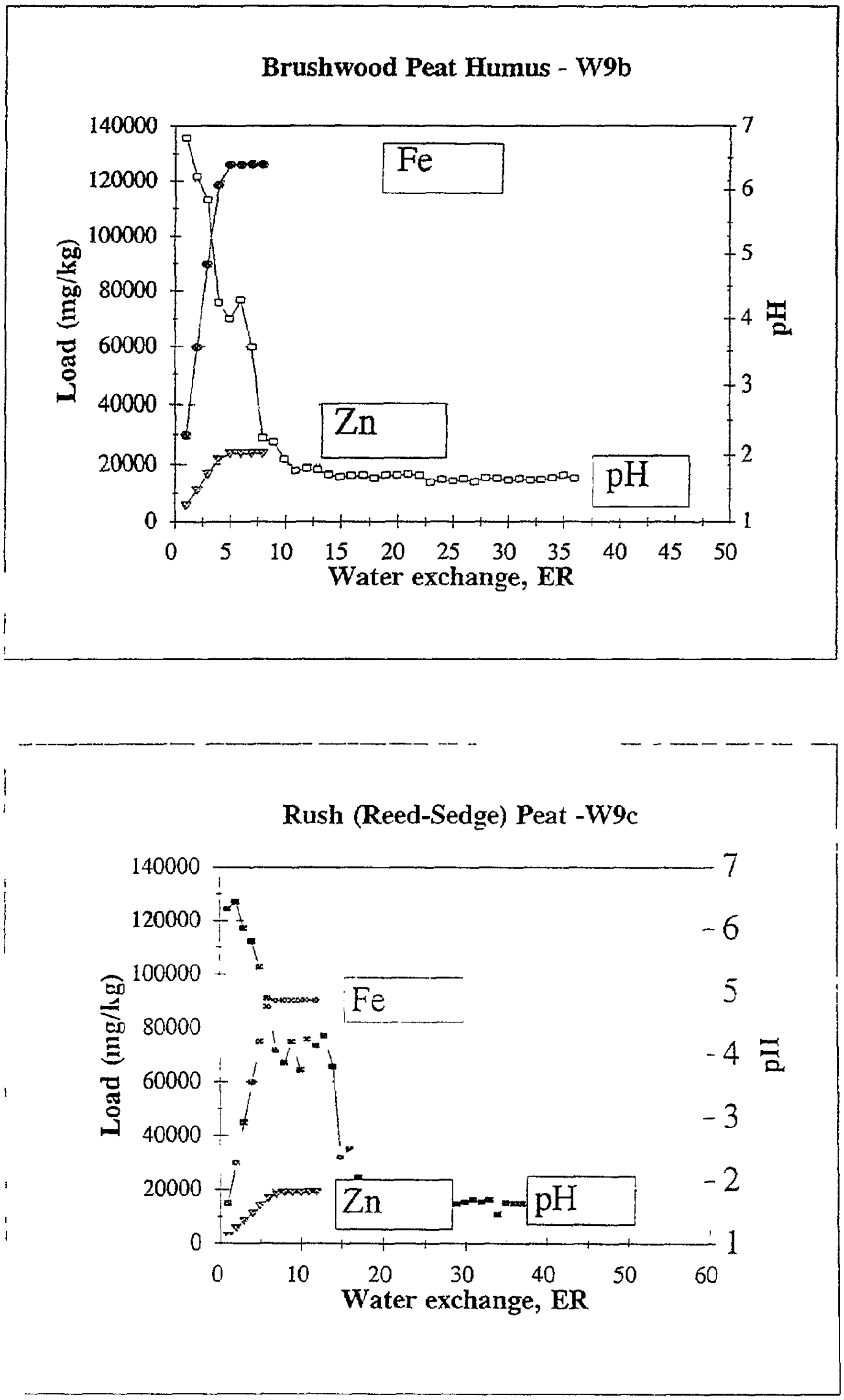


Figure 41 Sorption of Fe and Zn from the electroplating liquid waste onto low-moor peats (Brushwood Peat Humus and Rush Peat) and pH of the effluent under dynamic flow conditions *vs* water exchange rate

Working parameters Column φ 48 mm, H = 285 mm

Flow rate 0 1 cm^3/s, saturated zone flow conditions,

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L=1 1 (W9c)

Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^3 > 2807 mgZn dm^3 > 235 mgCr dm^3 > 171 mgCd dm^3 > 122 mgMn dm^3

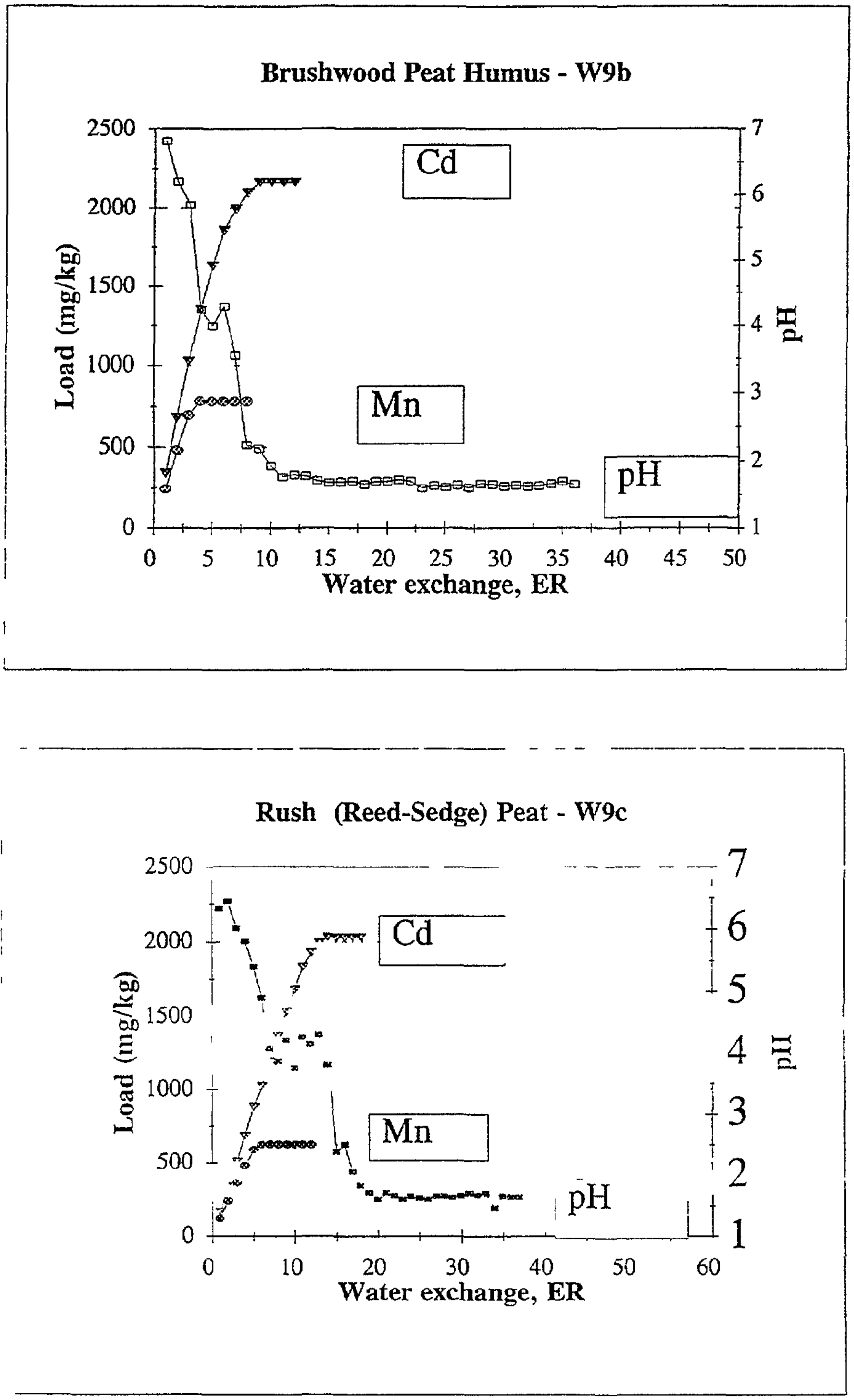


Figure 42 Sorption of Cd and Mn from the electroplating liquid waste onto low-moor peats (Brushwood Peat Humus and Rush Peat) and pH of the effluent under dynamic flow conditions *vs* water exchange rate

<u>Working parameters</u> Column φ 48 mm, H = 285 mm

Flow rate 0 1 cm^3/s, saturated zone flow conditions,

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L=1 1 (W9c)

Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{3} > 2807 mgZn dm^{3} > 235 mgCr dm^{3} > 171 mgCd dm^{3} > 122 mgMn dm^{3}

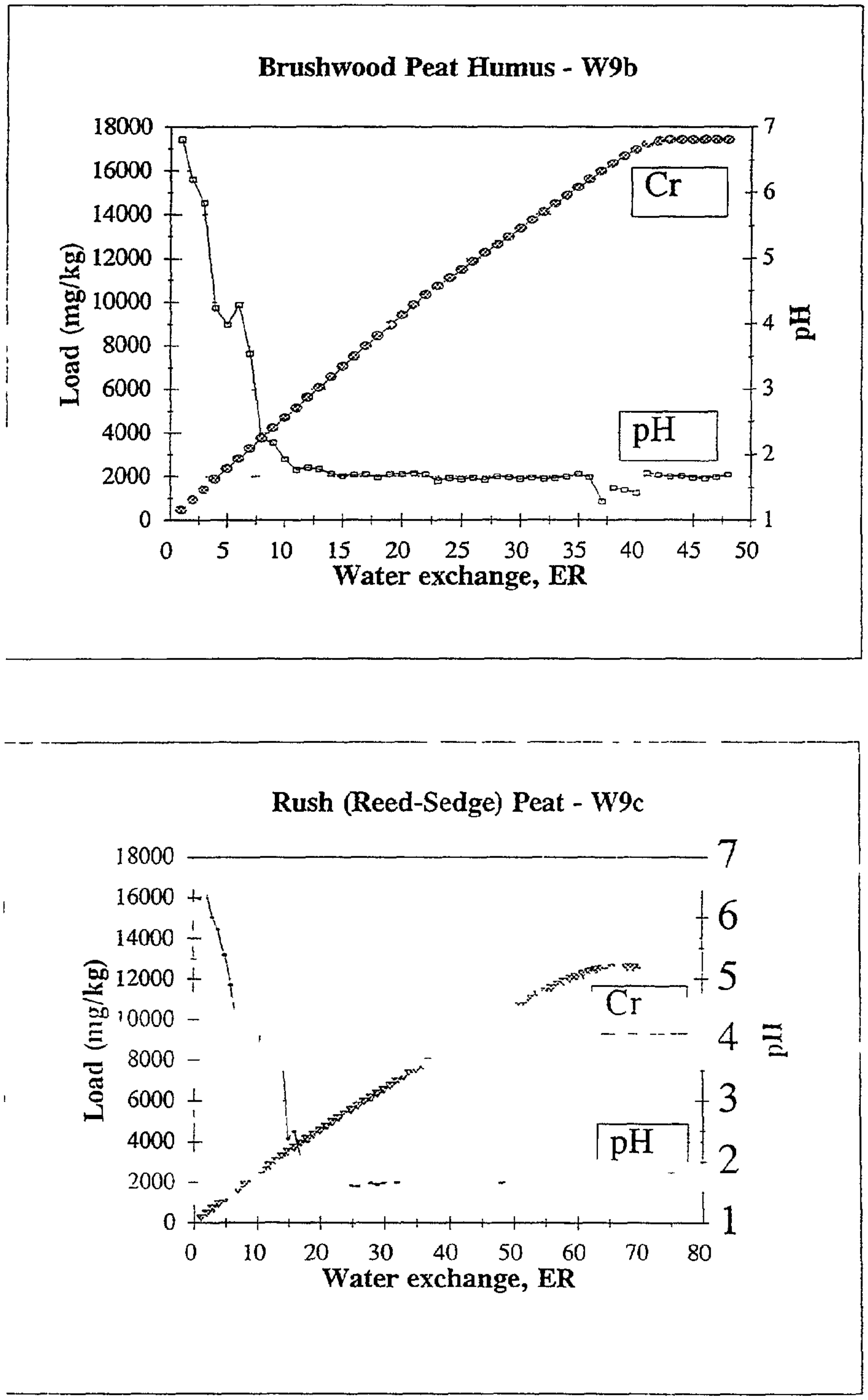


Figure 43 Sorption of Cr from the electroplating liquid waste onto low-moor peats (Brushwood Peat Humus and Rush Peat) and pH of the effluent under dynamic flow conditions *vs* water exchange rate

<u>Working parameters</u> Column φ 48 mm, H = 285 mm

Flow rate 0 1 cm^3/s, saturated zone flow conditions,

Adsorbent mass 90 g, water retention capacity S/L= 1 2 (W9b), S/L=1 1 (W9c)

Liquid waste Me-SO_4, pH 1 47, c_0 14985 mgFe dm^{-3} > 2807 mgZn dm^{-3} > 235 mgCr dm^{-3} > 171 mgCd dm^{-3} > 122 mgMn dm^{-3}