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POLYMER SUPPORTED LIGANDS FOR ECOLOGICAL PROBLEMS

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Project duration: August 10, 1993 to August 31, 1997

Executive Summary:

The purpose of the project is to develop new, selective adsorbents for separation of specific metals from aqueous solutions, especially in environment protection, by the immobilization of selective ligands on polymer carriers (solvent impregnated resins - SIR). In the past (third) year of the project there was made a great progress in characterization of the SIR's based on reactive supports (poly-vinylpyridine and anion exchangers). Thanks to the strong interaction with the support the ligand is absorbed into the polymer functioning as a "solid solvent". It was found that the uptake of metal ions changes this situation considerably. Metal uptake severs the ligand-support bond and the ligand is "squeezed-out" from the polymer mass into the pore system of the adsorbent particles where it is held by similar capillary forces like in the non-functional XAD supports. Preliminary assessment of the metal extraction properties suggest that there exist substantial differences between SIR's based on non-functional and functional supports, both in capacity depending on the accessibility of the supported ligand and in selectivity towards various metals.

The collaboration of Rehovot and Prague laboratories proceeds without problems. In Rehovot are investigated mainly the problems concerning chemistry of the solvent impregnated resins while the Prague laboratory examines chiefly the process of ligand immobilization and morphology of the resulting SIR. Mutual communication is greatly facilitated by Internet.

In the next stages of the project will be quantitatively characterized influences of the immobilization of the ligand on its activity and accessibility. For this purpose will be used as the ligand di-(2-ethylhexyl) phosphoric acid (DEHPA), which chemically more stable than the previously used di-(2-ethylhexyl) dithiophosphoric acid (DEHTPA). The purpose of this work will be an assessment of the influence of nature of the support on the degree of utilization of the immobilized ligand and on the microenvironment in the SIR beads.

Section I

A) Research Objectives: In the third year of the project we wanted to investigate further the immobilization of DEHTPA on reactive supports, including commercial anion exchange resins, as well as properties of so obtained SIR's. Another planned task was to attempt a synthesis of selective adsorbents with covalently bonded dithiophosphoric acid groups. Another objective was to start studies of the properties of the prepared selective adsorbents under dynamic conditions in column metal extraction experiments.

B) Research Accomplishments:

Additional measurements of DEHTPA adsorption on Amberlite XAD resins.

All the pereviously reported investigations [1,2] of the physical adsorption of DEHTPA on Amberlite XAD-2 and XAD-4 were performed from solvents in which these polymers does not swell (mainly alcohols). There was found that under these condition DEHTPA does not penetrate inside of the polymer skeleton and fills the pore space only. The experiences with the deposition of the ligand into the interior of the polymer skeleton of the Reillex resins induced consideration whether it could not be possible to introduce at least a part of the ligand into the polymer skeleton of the XAD-type resin too. For this purpose was investigated sorption of DEHTPA on the Amberlite XAD-2 and XAD-4 resins from tetrahydrofuran (THF), which is know to be a good swelling solvent for this type of the resins. Together with these experiments was also determined DEHTPA adsorption isotherm from acetonitrile (ACN) as the solvent from which the sorptions on the Reillex resins were performed. Results of these experiments are shown in Fig. 1. For comparison, into the plot were also included the previously determined [1] DEHTPA sorption isotherms from methanol and ethanol.

Sorption from ACN was found to be similar like that from the alcohols. In all of these solvents Amberlist XAD-2 does not swell. On the other hand, the sorption from THF was much weaker and the adsorption reached the saturation already at very low equilibrium concentration of DEHTPA in solution. This difference indicate a different mechanism of adsorption than that acting in non-swelling solvents.The measurements of the surface area of the resins with supported DEHTPA are shown in table 1.

Table 1. Sorption of DEHTPA on Amberlite XAD-2 from THF and surface area of resulting SIR's as determined by Nelson-Eggertsen method (for details see [1]).

Equil. DEHTPA concentration	DEHTPA sorption from THF	Specific surface area

wt. %	g/g of the support	m^2/g
0	0	336
1.92	0.040	219
4.64	0.052	163
7.39	0.056	124
11.32	0.058	125

Loading of DEHTPA from THF diminished the surface of the resin support quite similarly like the sorption from the non-swelling solvents. For example, the surface area of Amberlite XAD-2-based SIR's prepared from methanol solution was found to be 222,141 and 118 m^2/g for the ligand loading 0.005, 0.048 and 0.102 g/g of the support, respectively. It means that even if some ligand in the presence of THF penetrated into the swollen polymer skeleton, after THF removal it was squeezed-out into the pore space and resulting SIR morphology was similar like that prepared from the non-swelling solvents.

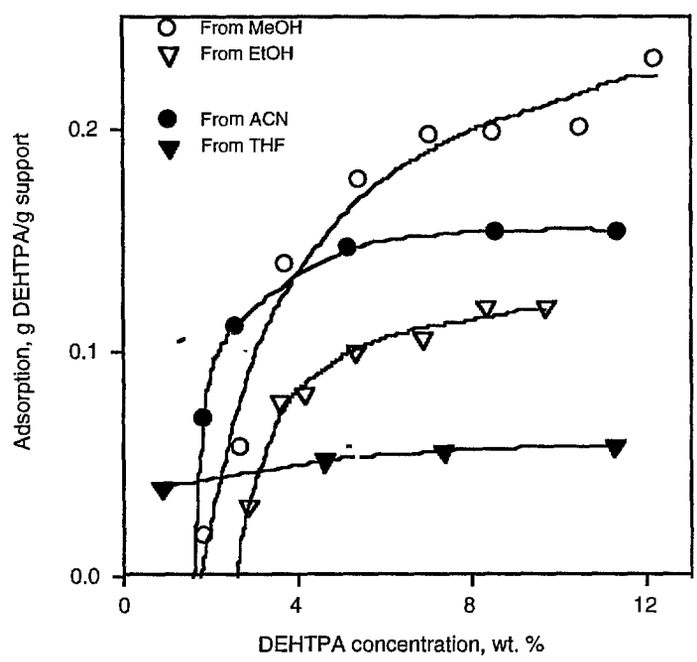


Fig. 1. Sorption isotherms of DEHTPA on Amberlite XAD-2 from various solvents.

Measurements of DEHTPA adsorption on commercial anion exchange resins.

Commercial anion exchange resin could be an alternative and cost-effective supports for the chemisorption immobilization of the ligand. They exhibit a more hydrophilic and swellable skeleton than the poly-vinylpyridine Reillex resins. We examined the ligand sorption on the

anion exchange resins produced by Bayer A.G., Leverkusen, Germany: Lewatit MP-62 - weak-basic macroreticular type; Lewatit MP-600 - strong-basic macroreticular type and Lewatit M-600 - strong-basic gel type. In the sorption experiments weighed amount of the resin in the basic form was suspended in acetonitrile (ACN) and then there was added an weighed amount of DEHTPA. After 20 hours of equilibration (with occasional stirring) the residual equilibrium concentration of DEHTPA in solution above the resin was determined as evaporation residuum. Sorbed amount was then determined from material balance.

Like in the case of the Reillex resins [2], the character of the adsorption isotherms corresponds to the chemisorption character of the interaction of the ligand with the support the starting portion of the isotherm is very steep but it soon achieve a plateau. The utilization of the exchange capacity of anion exchangers by the DEHTPA sorption (the position of the plateau of the adsorption isotherm) is shown in Table 2.

DEHTPA sorption corresponds to the exchange capacity of the anion exchanger support only for the macroreticular resins. In the gel resin DEHTPA ca occupy only about 35 % of the basic groups. There was found that the highest capacity for DEHTPA has the weakly basic resin Lewatit MP-62.

Table 2. Comparison of the exchange capacity of the anion exchanger supports and the highest achieved DEHTPA sorption.

Support	Exchange capacity meq/g	Capacity for DEHTPA, mmol/g
Lewatit MP-62.	6.0	5.4
Lewatit MP-600	4.3	4.5
Lewatit M-600	4.9	1.4

Measurements of metal adsorption isotherms on solvent impregnated resins prepared from Reillex HP and Lewatit MP-62.

For the measurements were used freshly prepared SIR based on Reillex HP and Lewatit MP-62. The Reillex HP resin was from the new batch we got directly from Reilly S.A. and was used without any pretreatment. Lewatit MP-62 was before the impregnation transferred to carbonate form and then to OH^- form. Both resins were impregnated with DEHTPA from acetonitrile solution. For sorption of each metal were the SIR's prepared separately. For the sorption experiments the resins were taken in the water-swollen form and the exact weight of the dry sample was determined after the sorption. Sorptions were performed from solutions with different Cu, Ni or Pb concentrations but with constant ionic strength O.2 M which was made-up by addition of sodium salt (nitrate for Cu, chloride for Ni and acetate for Pb). Solutions containing Pb were stabilized against a precipitation of lead carbonate by the addition

of 6.5 ml CH_3COOH/dm^3). The residual metal concentration after the sorption was determined by AAS.

On the figures 2 and 3 is plotted saturation of the ligand (relative sorption) against the equilibrium concentration of the metal in solution.

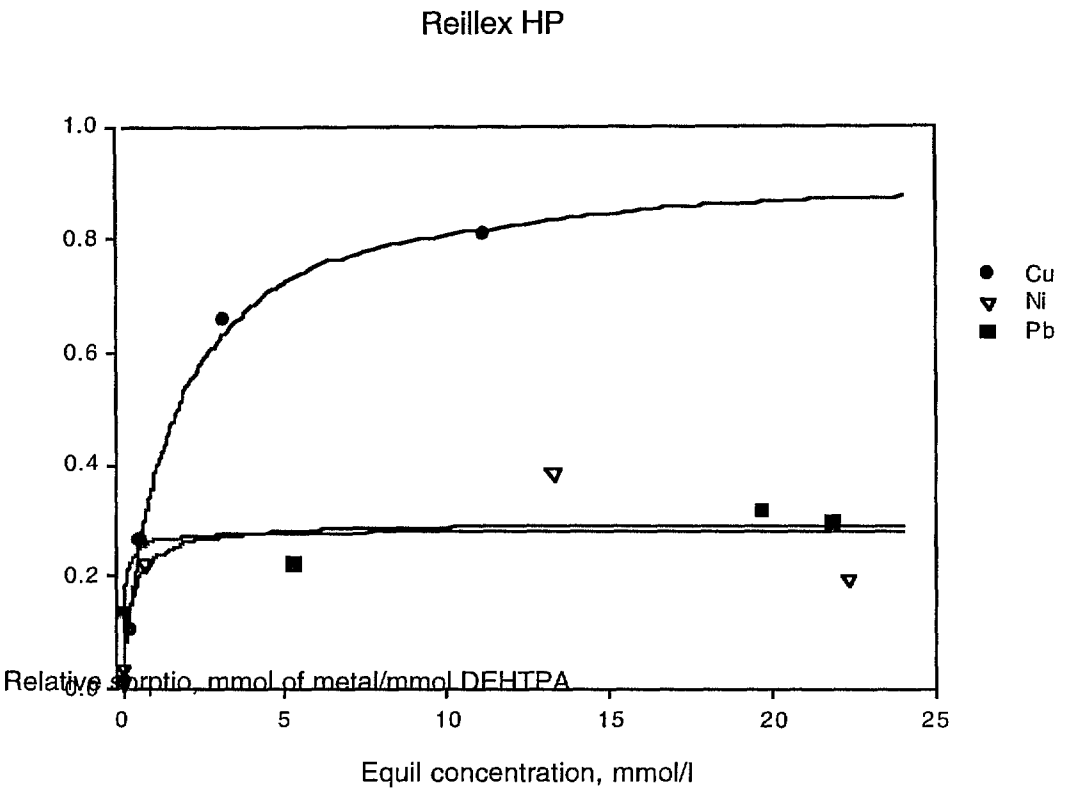


Fig. 2. Sorption of various metals on DEHTPA-impregnated Reillex HP.

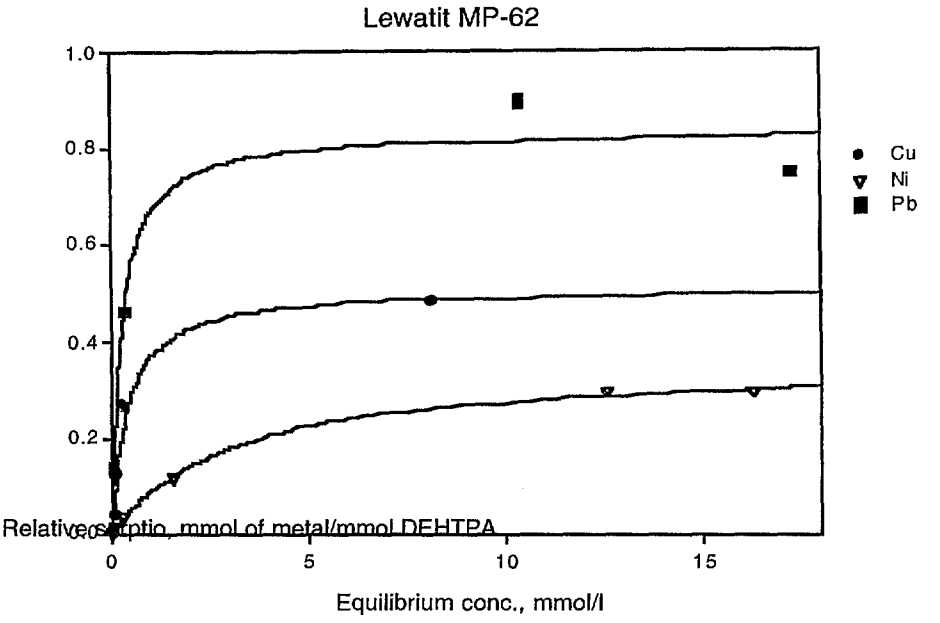


Fig. 3.. Sorption of various metals on DEHTPA-impregnated Lewatit MP-62.

There is a substantial difference in these adsorption isotherms between Reillex- and Lewatit-based resins. It seems that Ni and Pb can use only a small fraction of the supported ligand. The higher sorption of Cu is probably results of the adsorption of this metal also on the Reillex itself. However, a separate "blind" experiment shown that Pb is not sorbed by the "naked" Lewatit MP-62 and hence, the high capacity of the SIR for this cation must be attributed to the ligand itself. What is the reason for the differences in the activity of the ligand supported on Reillex HP and Lewatit MP-62 is open to debate and will be the subject of a further research.

The decrease of the surface area with the increase of the amount of sorbed metal ions (Fig. 4) indicates the exclusion of the ligand from the polymer gel phase into the pore space. The pore volume of the Reillex resin is evidently high enough for to accommodate all the excluded ligand. In the case of the Lewatit MP-62 and high metal uptake there was observed an appearance of an amount of liquid ligand outside of the resin beads (sorption of Cu and Ni) or "maps" (differently colored areas) on the surface of the resin beads (sorption of Pb).. These resins also exhibited practically zero specific surface. Volume of the pore system of Lewatit MP-62 is rather small (in water-swollen state it is about only 0.3 ml/g of the dry resin) and is evidently hardly able to accommodate all the metal-ligand complex excluded from the gel phase.

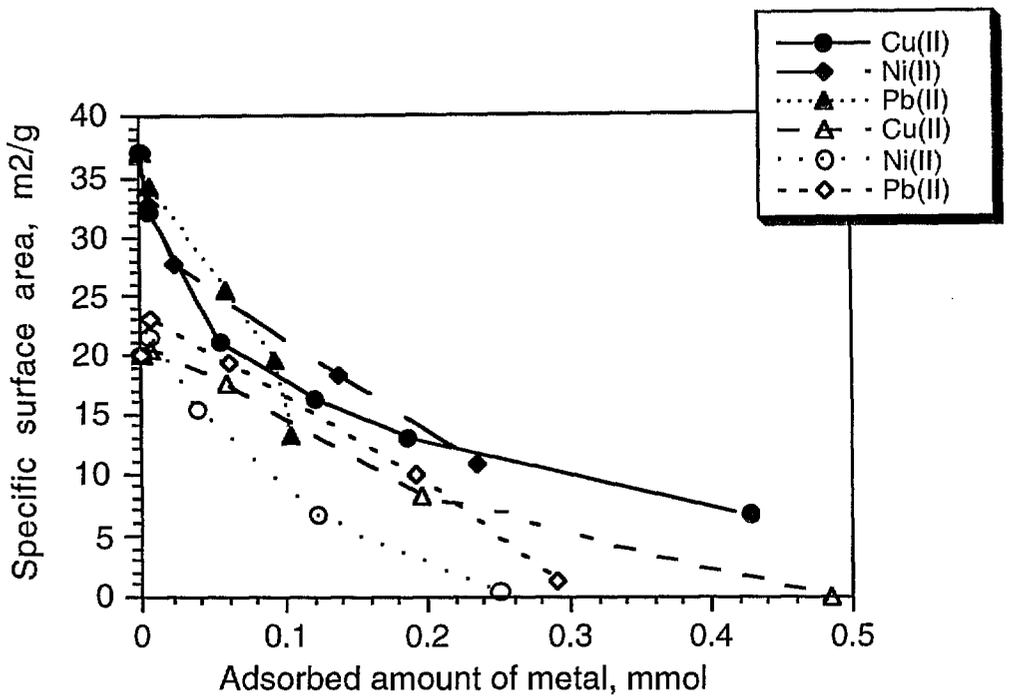


Figure 4 Reillex^{TM} HP based SIR's (filled symbols) and Levatit MP-62 based SIR's (open symbols) surface area dependence on adsorbed amount of metal. SIR loadings 0.4 g/g of SIR and 0.65 g/g of SIR, respectively.

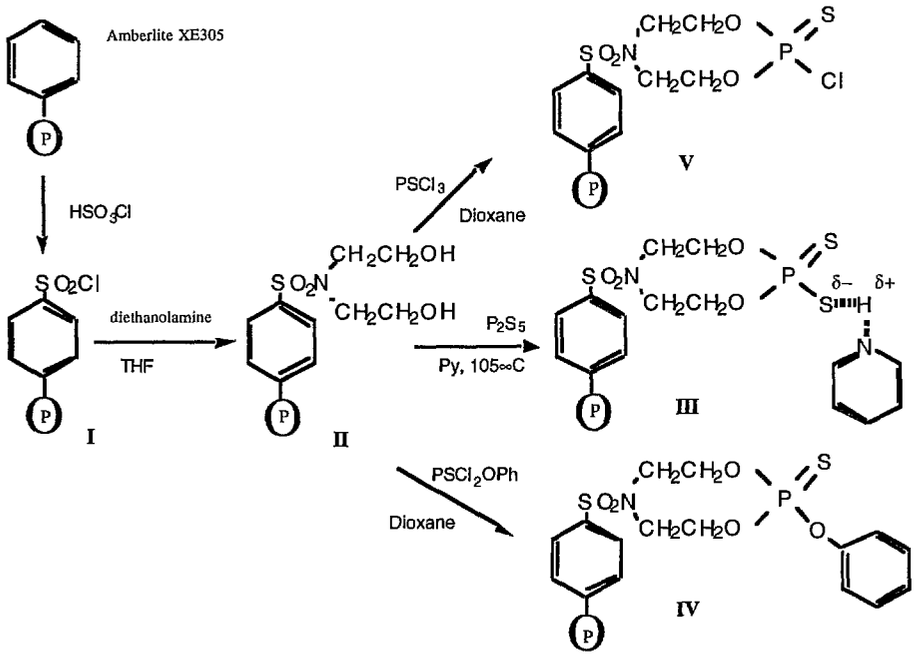
Functional polymer containing dithiophosphoric acid groups

The polymer containing diethanolsulfonamide groups was prepared on the basis of Amberlite XE 305 resin, 2% DVB crosslinked polystyrene (Scheme 1). This polymer can be a valuable intermediate product for chemical immobilization of various thiophosphoric functionalities. Two synthetic pathways have been chosen to obtain dithiophosphoric groups on the polymer. The first method leading to polymer (III) was carried out essentially in analogy to common method of dialkyldithiophosphoric acids preparation by reaction of alcohols with P_2S_5.

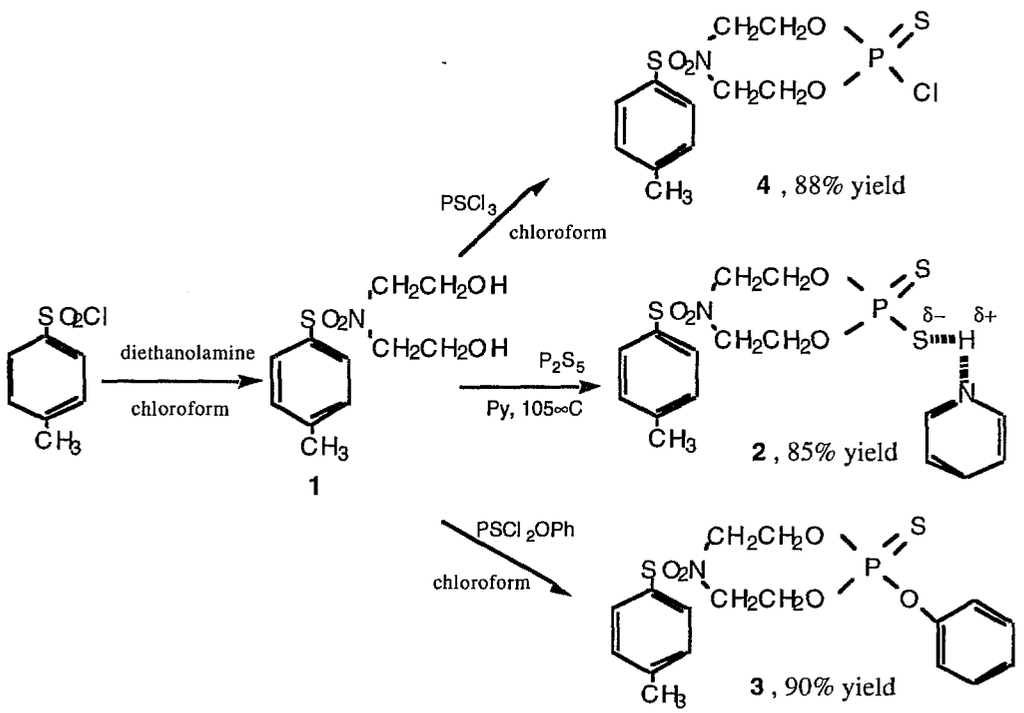
The principle difference of polymer synthesis from conventional (heterogenic) dialkyldithiophosphoric acid preparation is that P_2S_5 must be dissolved in some solvent and it is important that the reacting polymeric reagent swells well in this solvent. Pyridine, as a solvent was tried out successfully. All reactions taking place on the polymers were verified first on the model soluble analogs (Scheme 2). It was important to perform the model reactions with similar reaction conditions on the modified polymer and with high yield. In most cases, the percent of conversion of the reactions being carried out in the crosslinked polymers is reduced by the need for reagent molecule diffusion to the reactive site of the polymer. Thus the high yield of model reactions are of substantial significance. The model synthesis is essential for evaluation of the modified polymer chemical structure by comparison of IR spectra of the polymer and its soluble analog. The chemical structure of the model compound can be easily

determined from variety of methods such as NMR, MS or IR spectroscopy, while in the case of insoluble crosslinked polymer such information can be obtained only from IR spectroscopy. The detailed analysis of IR spectra of molecular and polymer analogs was used to provide prove of chemical structure of the polymer immobilized reactive groups.

Scheme 1



Scheme 2



The second method, through polymer (V), was ineffective because of unexpected resistance of Cl in (V) to thiolation. Till now it was not possible to convert the chloroanhydride to a dithiophosphoric acid by the use of NaSH as the thiolating agent. Attempts to convert chlorine atom to a SH group in compound (4) by a similar way were not successful.

Polymer (II) can be used for immobilization of various thiophosphorous derivatives, for example polymer (IV).

The ability of the new polymer (III) to selectively adsorb metal ions from aqueous solutions has been evaluated in comparison with Reillex HP based SIR containing di(2-ethylhexyl)dithiophosphoric acid (DEHTPA) as a metal extractant. Fig.5. shows a selective metal extraction from aqueous solution containing 20 metal ions. It can be clearly seen that both chemically modified resin (III) and SIR (Fig.6) preferentially extract heavy metal ions, as expected from the extractant origin.

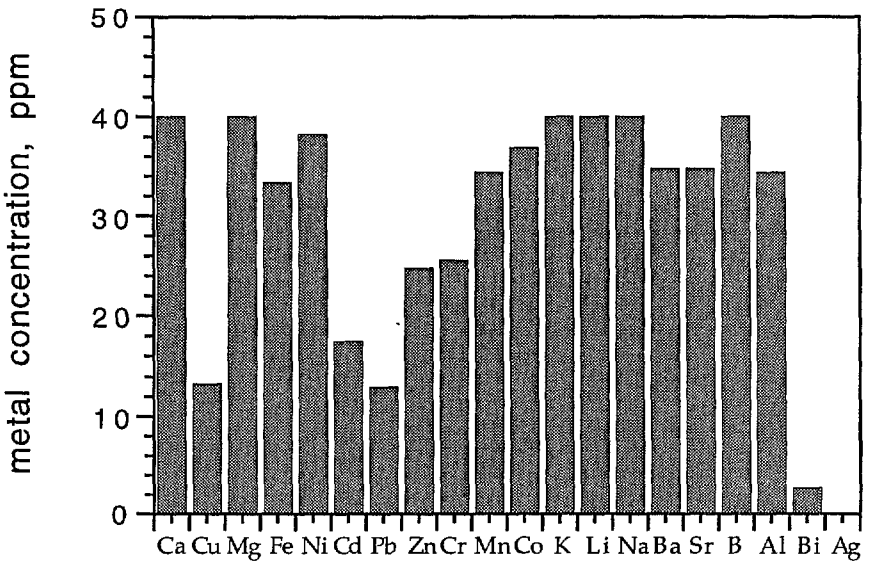


Figure 5. Selective metal sorption from 0.1N nitric acid solution on modified polymer (III).

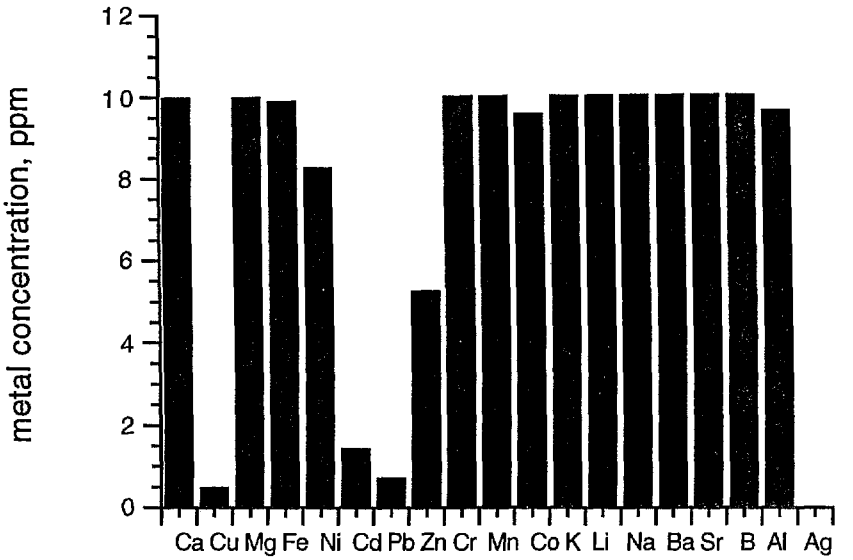


Figure 6. Selective metal sorption on Reillex™ HP based SIR, loading 0.2 g/g SIR, pH =1.92. (nitric acid).

Column metal extraction and selective metal separation

An aqueous solutions of Ag(I), Pb(II), Cd(II), Ni(II), Zn(II) and its mixtures were passed through columns containing Reillex HP polymer (free base form), Reillex HP and Amberlite XAD4 based SIRs. The results of experiments are given in Table 3. The capacity of SIRs based on the Reillex HP resin was remarkably higher than those observed with porous styrene-divinylbenzene resin (Amberlite XAD4) based SIR at nearly same DEHTPA loading.

Table 3. Metal adsorption on SIR columns.

Column number	Resin	DEHTPA loading (mmol/g support)	metal sorption capacity (mmole)	capacity ---------- loading	metal elution (mmole)
1	Reillex HP based SIR	0.65	1.74 Ag(I)	2.68	-
2	Reillex HP	-	1.28 Ag(I)	-	-
3	ReillexHP based SIR	1.10	0.44 Pb(II)	0.4	-

4	Reillex HP	-	0.01 Pb(II)	-	-
5	Reillex HP based SIR	1.48	0.63 Cd(II)	0.43	-
6	Reillex HP based SIR	1.83	0.29 Pb(II) 0.42 Ni(II)	0.44	0.2 Ni withHCl 0.19 Ni EDTA 0.28 Pb EDTA
7	Reillex HP based SIR	1.55	0.56 Pb(II) 0.11 Zn(II)	0.43	0.5 Pb(II) with EDTA
8	Amberlite XAD4 based SIR	0.93	0.089 Pb 0.032 Zn	0.13	0.031 Pb(II) with EDTA

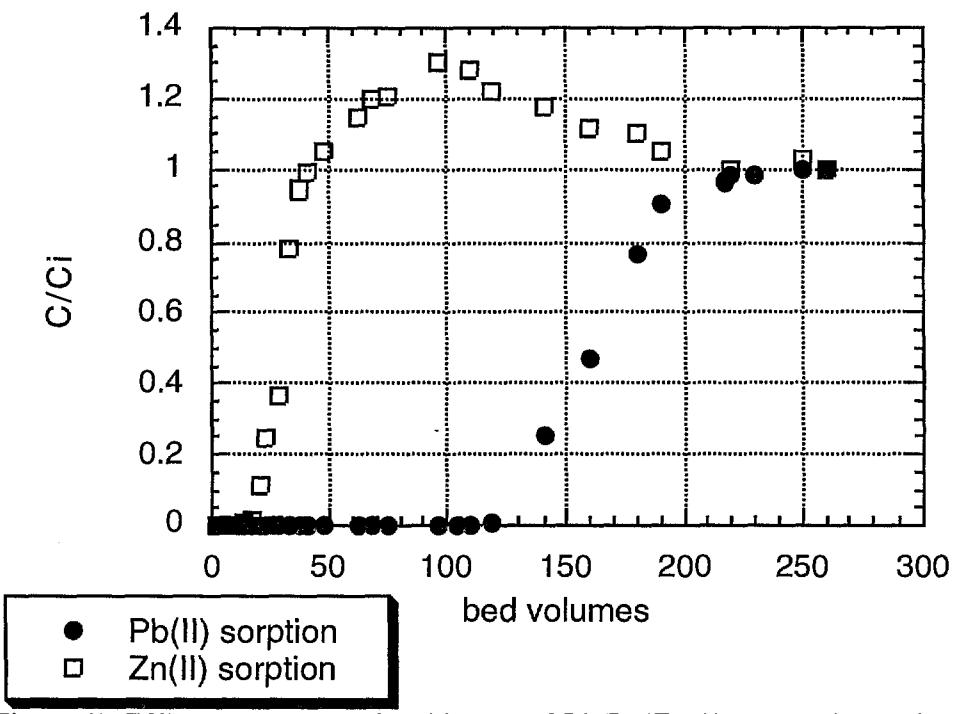


Figure 7. Effluent concentration history of Pb(II)/Zn(II) separation column experiment. DEHTPA loading: 0.55 g/g of polymeric support, pH of the influent solution: 3.8. Bed volume: 6 ml; bed height: 7.6 cm. The metal concentration in influent solution: $[Zn^{2+}]$ = 106 ppm, $[Pb^{2+}]$ = 127 ppm.

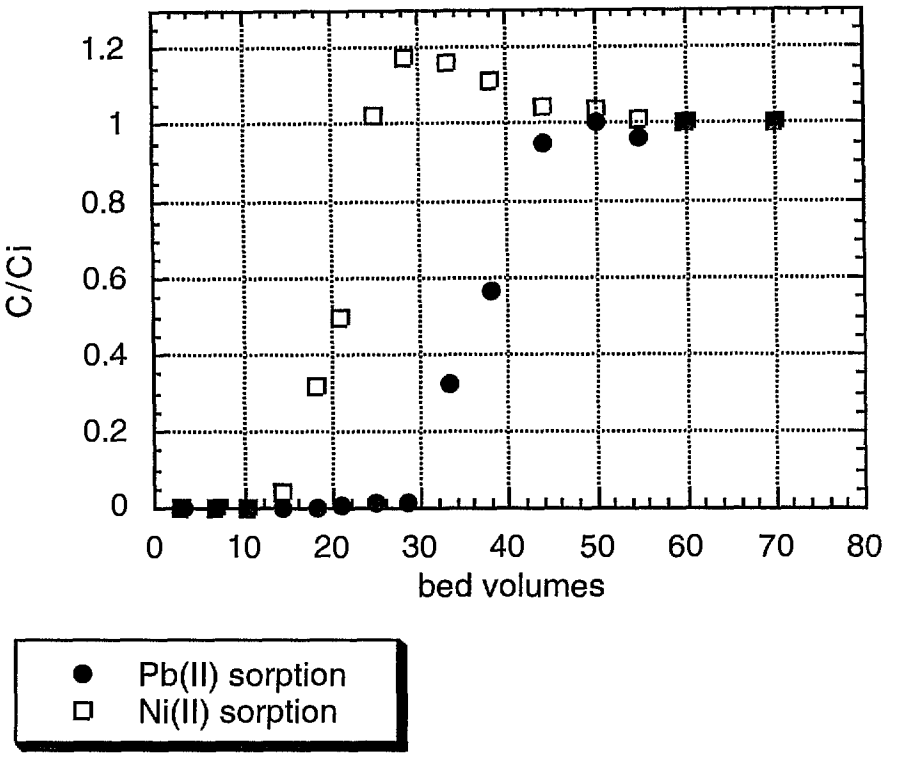


Figure 8. Effluent concentration history of Pb(II)/Ni(II) separation column experiment. DEHTPA loading: 0.65 g/g of polymeric support, pH of the influent solution: 4.1. Bed volume 6.2 ml; bed height: 7.9 cm. The metal concentration in influent solution: $[Ni^{2+}]$ = 258 ppm, $[Pb^{2+}]$ = 273 ppm.

The effluent concentration history of two selected metal separation experiments are shown in Figures 7,8. The separation factor $\alpha^{Pb}{}_{Zn}$ is equal to 36.4 and $\alpha^{Pb}{}_{Ni}$ is equal to 10.7. The metals can be readily eluted from the column by a 0.2M EDTA tetrasodium salt solution, with about 92-99% elution.

References

1. "Solvent impregnated resin (SIR) containing dialkyldithiophsphoric acid on Amberlite XAD-2: extraction of copper and comparison to the liquid-liquid extraction."
A.G. Strikovsky, K. Jerabek, J.L. Cortina, A.M. Sastre and A. Warshawsky,
Reactive & Functional Polymers, 28, (1996)149.

2. "Solvent-impregnated resins: Relation between impregnation process and polymer support morphology: 1. di-(2-ethylhexyl) dithiophosphoric acid."
K. Jerabek, L. Hankova, A.G. Strikovsky, A. Warshawsky,

Reactive & Functional Polymers, 28, (1996) 201.

3. "Solvent-impregnated resins via acid-base interaction of poly(4-vinylpyridine) resin and di(2-ethylhexyl) dithiophosphoric acid"
A.G. Strikovsky, J.L. Cortina, K. Jerabek, A. Warshawsky,
Solvent Extraction and Ion Exchange, will appear in Issue 2, Volume 15, March 1997

C) Scientific Impact of Collaboration: The co-operation of the Rehovot and Prague laboratories proceed very smoothly. The Internet communication between the laboratories makes possible very rapid exchange of ideas and flexible sharing of research tasks. This was supplemented by personal discussions during visit of Prague co-principal investigator (K.J.) in Rehovot.

D) Description of Project Impact: For to facilitate an application of the studied SIR to a practical metal separations in the Czech Republic there was commissioned from a laboratory specialized in consulting services for the Czech chemical industry a short study on special types of waste waters which could be potentially suitable for the treatment with SIR. It seems that possible candidates are mercury-containing waste waters from the electrolytic production of sodium hydroxide by the amalgam method.
Another mercury-containig waste is water from sulfonation of antrachinone where mercury ions are used as a selectivity modifier. Other possibility could be a separation of Cr 3+ ions from galvanization or leather curing plants or lead from some rechargeable batteries production or from chemical industry. However, in the contemporary legal climate in the Czech Republic, for waste producers seems to be more profitable to pay a penalty tax than to develop and operate a sophisticated water-treatment process. Serious considerations about an practical application of any sophisticated method for waste treatments will have to wait for the expected innovations of pertinent laws.

E) Strengthening of Developing Country Institutions: In the reported period there were acquired no new equipment.

F) Future work: In the next stages of the project will be quantitatively characterized influences of the immobilization of the ligand on its activity and accessibility. For this purpose will be used as the ligand di-(2-ethylhexyl) phosphoric acid (DEHPA), which chemically more stable than the previously used di-(2-ethylhexyl) dithiophosphoric acid (DEHTPA). The purpose of this work will be an assessment of the influence of nature of the support on the degree of utilization of the immobilized ligand and on the microenvironment in the SIR beads. Further effort will be extended towards testing of the selected SIR's at realistic conditions expected in solutions of practically important problems.

Section II

A) Managerial Issues: No serious managerial problems were encountered.

B) Budget: There were no major changes in the budget. Detailed Financial Statement is attached.

C) Special Concerns: No special concerns are applicable to this project

D) Collaboration, Travel, Training and Publications: The collaboration of Prague and Rehovot laboratories has been boosted by one week visit of Prague co-principal investigator (K.J.) in Rehovot. Project funds were also used for a partial financing of his trip to Spain where a part of the stay (in Barcelona) was concerned with a visit of the laboratory of J. L. Cortina, who co-operates on some aspects of the CDR project.
A paper stemming from the project (Strikovsky A.G., Jeøábek K., Cortina J.L., Warshawsky A.: Solvent Impregnated Resins via acid-base interaction of poly(4-vinylpyridine) resin and di(2-ethylhexyl) dithiophosphoric acid.) has been accepted for publication in the journal Solvent Extraction and Ion Exchange.

E) Request for A.I.D. or BOSTID Actions: No such actions are needed.