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FINAL REPORT

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REMEDIATION of SYNTHETIC ORGANIC POLLUTION in WASTEWATER by PHOTOCATALYTIC MINERALIZATION

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3 EXECUTIVE SUMMARY

The project was aimed at the removal of toxic organic chemicals from water and effluents Many of these chemicals are non-biodegradable and their elimination by the conventional wastewater treatment is unsatisfactory The solar photocatalytic degradation (**SPD**), based on TiO_2, a non-toxic photcatalyst, and on sunlight, a clean and abundant energy source, offers a process of powerful oxidation, leading to complete mineralization of these pollutants The studies have focussed on the remediation of rinse waters of agricultural aircraft sprayers (Muszkat et al , 1995), on treatment of polluted ground-water from a well in the Ashdod area (Israel), and treatment of effluents in the Alarchin reservoir, (Kyrgyzstan) SPD of selected nitro-phenols and of textile dyes, studied at the Volcani Center has shown satisfactory removal of these pollutants from water In addition, SPD of the herbicides metribuzin and bromacil has been examined and compared with other photooxidative degradation patterns (Muszkat et al , 1998a) Bromacil, metribuzin and some nitro-phenol derivatives are widely used herbicides in both Israel and Kyrgyzstan They have also been detected in Israeli groundwater Further to these studies, a *constant flow minireactor* (30 liter) for SPD was constructed and its factor analysis allowed the carrying out of field studies, where the effect of selected oxidants on had been examined The Kyrgyz group conducted laboratory and field studied of SPD Major water resources in the Chu Valley were sampled and subjected to solar photocatalytic degradation In selected cases the extracts of samples were sent to Israel and analyzed in the ARO laboratory The following organic chemicals have been studied in pure and in drainage water Lindan, DDE and Metaphos, the detergent TBS, humic acids In addition, the coating of TiO_2 photocatalyst on solid surfaces was examined The solid supports were polyethylene tubes, polypropylene balls and stainless steel porous membranes, "Ultram" (Moscow) The regeneration of titanium dioxide catalyst and the effect of light intensity on photocatalytic degradation were also examined The results indicate the practical value of SPD in the purification of highly polluted groundwater and agricultural rinse waters The value of SPD as a supplementary technique for improving the existing treatment methods has also been shown Further, the results of direct (non-photocatalytic) photooxidation of pesticides revealed the specific role of oxygen in some of the non catalytic reactions while, in other non-catalytic processes the unique role of hydrogen peroxide could be demonstrated (Muszkat et al , 1998b) The results have been presented in international symposia and documented in proceedings and international journals (AID/CAR acknowledged) Close collaboration between the Israeli and the Kyrgyz groups was maintained At the initial level the Kyrgyz scientists were trained at the laboratory of Volcani Center in novel analytical methods and in the application of solar photocatalysis for the treatment of effluents and polluted water Further to their training, the purchase of modern analytical equipment, including capillary-GC, with FID and NPD, has been ordered by the Israeli partner and sent from the USA to the Kyrgyz laboratory This machine been put into operation due to the dedicated training provided by Dr L Feigelson (ARO group), who traveled to Bishkek on August 1995

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Names and boundary representation are not necessarily authoritative.
KAZAKHSTAN
Burylbaytal
Zhanatas
Turkestan
Karatau
Dzhambul
Chu
Kara Balty
Bishkek (Frunze)
Tokmak
Kaskelen
Alma-Ata
Kapchagay
Saryozek
Arys'
Chimkent
Talas
Issyk Kul' (Rybach'ye)
Przheva
ISSYK KUL'SK OBLAST'
Kara Say
Naryn
Chirchik
Tashkent
UZBEKISTAN
Angren
Namangan
Kara Kul
Tash Kumyr
Kok Yangak
Dzhalal-Abad
Syrdar'
Gulistan
Khudzhand (Leninabad)
Kokand
Andizhan
Fergana
Osh
Kyzyl-Kiya
Sulyukta
Ura-Tyube
Ayni
CHINA
Kyrgyzsta
International bound
Oblast boundary
National capital
Oblast center
Railroad
Road
Information on the 1990 reorganization
divisions is incomplete. It is not clear wh
administrative center of Issyk-Kul skaya
or Przheval'sk. An oblast is named only
differs from that of its administrative cen
0 50 100 150 Kilom
0 50 100
Lambert Conformal Conic Projectio
TAJIKISTAN
Dushanbe
Ordzhonikidzeabad
Kulyab
Kurgan-Tyube
Murgab
Tashkorgan
AFGHANISTAN
Khorog
Feyzabad
Kondüz
Lasht
PAKISTAN

4 RESEARCH OBJECTIVES

The overall aim of the project consisted of the field application and evaluation of TiO_2 photodegradation for the remediation of water pollution by organosynthetic contaminants in semi-arid areas
The specific objectives were the following

1 Field studies for improvement of catalyst photoefficiency,
2 Study of the kinetics of selected organic pollutants,
3 Identification of intermediates (if any) in the photocatalytic process
4 Study of non-photocatalytic processes for degradation of organic pollutants

5 METHODS AND RESULTS

A ***Survey on water resources in Kyrgyzstan***

The major water resources in Kyrgyzstan are the runoff of rivers The average supply is ca 42,3 Cubic Km per year About 9 Cubic Km of this amount is used for irrigation In the last few years there has been a decrease in abundance of the industrial and irrigation wastewater, because of common economic stagnation However today the irrigation by waste water ranges up to 1 54 Cubic Km half of which is discharged to river system without any purification Another part with salinity, of about 1-5 g/l is re-circulated for irrigation Typical data on minerals and organic contaminants in waste water are given in Tables 1 and 2 Data on pesticides used in the Chuy Valley (valid for 1993/4) are given in Table 3 These show that ca 50,000 kg of pesticides and herbicides were utilized during 1993 in the Chuy Valley, major agricultrual area in Kyrgyzstan This included the use of 30,000 kg/year organophosphates (with 20,000 kg/year of parathion and malathion), and ca 25,000 kg/year of organochlorines, with the herbicides 2,4-DB (6,300 kg/year), trifluralin (5,600 kg/year) Many of the pesticides listed in Table 3 are known as water pollutants due to their persistence and water solubility Further, the examination of drainage and river waters in the Chuy Valley (Karmanchuk et al , 1994) revealed the presence of phenol derivatives (0 15 mg/L), oil components (0 5 mg/L) and residues of DDT and lindane The organochlorine pesticides may result from use in former times when the use of lindane and DDT was very popular These data clearly demonstrate the significant use of pesticides in Kyrgyzstan However, the information available today on possible water pollution in this country is limited

Good quality water with salinity to 1 0 g/l is essentially used for irrigation, but in some regions of Kyrgyzstan drainage water is used because of considerable shortage of unsalted water Until today more than 200 names of pesticides have been applied in Kyrgysztan agriculture with concentration 2 5-3 0 Kg/hectare The pesticides accumulate in the soil and by the irrigation water they are transfered to all bodies of water This includes DDT, Lindan, Methaphos and Carbophos, which were founded in dangerous

concentrations The purification of drainage water had not been conducted Industrial and domestic wastewater had undergone treatment The efficiency of purification averaged between 70% and 90% of COD Pesticides, detergents, petroleum products, humic acids and other organic pollutants do not decompose entirely The water contamination in water sources is above the permissible level because of an uncompleted wastewater purification and the lack of drainage water purification The above listed factors were the reasons for crises in the of Aral-Sea The deterioration in the ecological situation has motivated an active search for more effective methods of water treatment for full mineralization of soluble organic substances In 1993 in the Volcani Center (Israel) had started in Bishkek a research of solar photo-catalytic process for water purification, exceptionally interesting in Kyrgyz conditions The following methods have been applied (Kyrgyz laboratory) Crystallizers of 5L 2L of the sample were placed into each of the crystallizers, the catalyst TiO_2 with concentration50 mg/l was added into one of the vessels Crystallizers were exposed to the sun light The stirring of solutions was performed by electric stirrer The samples were periodically analyzed In the years 1993-1994 we used the gas-chromatograph "Zvet-500" for pesticides concentration measurement before and during the experiment But the sensitivity of this device was very poor Since 1995 all the measurements were conducted by gas-chromatograph "Varian", that has high sensitivity The concentration of detergent and humic acid was determined colorimetrically, using photo-colorimeter T→K-56 The general quantity of organic substances was determined by the chemical oxygen demand (oxidation with $KMnO_4$ and $K_2Cr_2O_7$) The salinity and ionic concentrations were also evaluated In the drainage and waste water samples The samples volume change due to evaporation when exposed to sunlight was taken into account

B Field Studies of Solar TiO_2-photocatalytic degradation, conducted in ARO, Israel

1 TiO_2-SPD in the absence of H_2O_2

Field studies of the polluted well water point to the possibility of inhibition of the photodegradation by some unknown factors This inhibitory effect is prevented by hydrogen peroxide (Muszkat et al , 1995, CAR acknowledged), which leads to effective solar photodegradation, presumably because of oxidation of inhibitory constituents in the polluted water In the absence of hydrogen peroxide significant degradation occurred only during the first hour Then the process underwent a strong retardation and the level of pollutants stabilized, owing to system deactivation The photodegradation of malathion and atrazine solutions was also effective in the absence of H_2O_2 Comparison with the non-catalytic photodecomposition emphasizes the decisive contribution of TiO_2

2 *Purification of rinse water from agricultural spray containers*

The potential of photocatalytic oxidation carried out in the absence of hydrogen peroxide has been examined in the study of purification of rinse water from agricultural spray containers, mainly from aircraft sprayers, These

waters are significantly polluted with pesticide formulations at levels of 10-100 ppm Thus treatment is required prior to the disposal of such rinse waters To simulate such conditions, the photocatalytic treatment of pesticides in their formulation mixtures was examined Results in Table 4 are from the photocatalysis of malathion, an organophosphate pesticide, used in spray treatment of a wide range of crops While 90% decomposition was achieved within less than 5 hours of solar exposure, while sub-ppm level were reached in 18 hours Satisfactory results have also been obtained in closed systems covered with polyethylene film The covering of sun-irradiated basins with a polyethylene films provides a simple solution to problems inherent in semivolatile contaminants such as pesticide formulations (Muszkat et al , 1998b, CAR acknowledged)

3 *Reaction patterns in photooxidative degradation of the herbicides metribuzin and bromacil (Muszkat et al , 1998a)*

Different reaction patterns of photooxidation have been witnessed for the herbicides metribuzin, (4-amino-6-tert-butyl-4,5 dihydro-3-methylthio-1,2,4 triazine-5-one) and bromacil (5-bromo-3-sec-butyl-6-methyluracil) In the first case oxygen has a pronounced effect on the rate of photooxidation while the influence of hydrogen peroxide is quite moderate The photolytic process in this case would apparently start through a reaction of the excited herbicide molecule with hydrogen peroxide or with oxygen In another case, exemplified by bromacil, oxygen does not have a pronounced effect on the rate of photooxidation which, however, is considerably enhanced by hydrogen peroxide The reaction is initiated by hydroxyl radicals generated by hydrogen peroxide photolysis These conclusions are supported by the different effects of isopropanol inhibition The recognition that several direct photooxidation mechanisms could be used in the treatment of polluted water is of significant, practical importance It may allow the tailoring of the exact photooxidation procedure to a specific case of pollutant

4 *Minireactor*

A constant flow minireactor was constructed It operates in a closed cycle and includes three containers of 30 L each and a shallow bath tray, where the solar photocatalytic reaction takes place The conical structure allows the photocatalyst powder to settle and be separated from the solution (Fig 5) This allows the optimization of the primary experimental conditions for the photocatalytic process

5 *Solar TiO_2-photocatalytic mineralization of nitroaromatics* [2]

The nitroaromatic pesticides DNOC (dinitro-o-cresol), dinoseb and dinobuton have been studied, as well as the ortho-, meta- and para- nitrophenols In Israel dinoseb and DNOC have been identified in ground-water The nitro phenols are of wide use as agrochemicals They are also used in production of pesticides and dyes and some of them are formed as intermediates in the chemical industry Being hazardous chemicals, their removal from polluted water and effluents is important However, their removal by conventional methods is a difficult task, due to their persistence and ready water solubility In

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the treatment-plant they are toxic to natural biomass, which excludes the option of their biodegradation by activated sludge The present study demonstrates the feasibility of destruction of these pollutants by solar TiO_2-photocatalytic degradation Figs 1-4 present data on the photocatalytic decomposition of nitrophenols under different conditions (in the presence and absence of hydrogen peroxide), compared with blank experiments, without the addition of photocatalyst The average half life values for solar photocatalysis in the presence of hydrogen peroxide were 32 - 34 minutes The follow-up of the decomposition process was conducted by chemical analysis including spectophotometric and HPLC, and also by toxicological measurments using Microtox tests Significant decrease in the solution toxicity has been observed after an irradiation period of 90 minutes

[1] Muszkat L , Feigelson L , Bir L and Muszkat K A Chemosphere, 1998,
[2] L Ashkenazi and L Muszkat, unpublished results

C ***Studies on Photocatalytic Degradation Conducted in KSRII***

1 The following substances were studied
Pesticides Lindan, DDE, Metaphos (in pure water and drainage water)
Detergents TBS in pure water
Humic acids in pure water
Bishkek sewage water
Satisfactory destruction has also been observed in effluents sampled in Bishkek and in model solutions of TBS detergent
In addition, our results indicate the decomposition of humic acids present in the runoff water and decrease in the COD data (Table 5)

2 Catalyst coating to the solid surfaces The photocatalytic degradation rate of pollutants depends on the form and activity of the catalyst Titanium dioxide had been used in the laboratory experiments in a powdered form The use of suspension may be problematic To overcome this problem we examined different methods of applying catalyst coating to the solid surfaces Polyethylene tubes, polypropylene balls have been coated with suspension of titanium dioxide in oil and have been dried In addition to this we tested catalytic properties of porous membranes with selected layer of titanium dioxide The membranes were produced in the firm "Ultram" (Moscow) The plate is a flat porous membrane 20×30 cm made from stainless steel coated with titanium dioxide layer 5 mg/cm^2 The size of the pores is 0 8 micrometer In case of samples of pesticide Methaphos it has been showed that application of polyethylene tubes, polypropylene balls and porous plates with TiO_2-layer in comparison to TiO_2-suspensions increased the time of photodegradation The catalytic properties of titanium dioxide in crystalline form with different specific surfaces were checked 100% Anataze G-25 (specific surface 65 m^2/g)
H-4 (specific surface 95 m^2/g) H-17 (specific surface 130 m^2/g)
The TiO_2 - powder degussa P-25 is the most active catalyst
3 *Regeneration of titanium dioxide catalyst* After the termination of the photodegradation reaction, the solution involving the remaining pollutants and the catalyst was subjected to centrifugation The catalyst was

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separated, washed several times with distilled water and treated with 0 1% solution of hydrochloric acid and dried The re-usable catalyst was applied for photodegradation of detergent TBS (Table 6)

4 Effect of light intensity The photodegradation rate of pollutants depends on the intensity of ultraviolet radiation The employment of high pressure mercuri-quartz lamp as a source of UV radiation (in the spectrum UV beams with wave length 238-298 nm comprise 60% of radiation), increases the photodegradation rate of pesticide Methaphos into 10-12 times in comparison with solar radiation (Table 7)

6 IMPACT, RELEVANCE and TECHNOLOGY TRANSFER

The joint studies on remediation of organic pollutants (in water and effluents) by solar photocatalysis has significantly improved the scientific abilities of the Kyrgyz partners First, it introduced to them the novel domain of environmental chemical research, including the problems of organic micropollutants in water Second, the KSRII group became familiar with the technologies of photochemical and solar-photocatalytic water treatment Third, Dr Karmanshuk and her group were trained by the Israeli partners in techniques of residue analysis, in the use of analytical equipment and in the conducting of field experiments for water treatment by solar photocatalysis Furthermore, the project focussed on the environmental problems relevant to Kyrgyzstan For example, treatment of water polluted by organochlorine substances It is to be recalled that the economic crisis in Kyrgyzstan has led to the use of cheap pesticides, like the organochlorines, which were banned in Europe and the USA The removal of these substances from the waters is therefore of high significance in this area In addition to the organochlorines, other pesticides and pollutants (Table 3) of major interest have been examined Malathion was efficiently degraded by photocatalysis, the herbicides atrazine and metribuzin, applied in the treatment of corn and tomatos and the nitro-phenolic substances, broadly used in Kyrgyzstan The results of the joint Israeli-Kyrgyz study, documented in Para 6, demonstrate the promising potential of the method and lead to the continuation in the research subject by the KSRII group The main directions of development include the scaling-up of the process and improvement of the catalyst application (regeneration and fixation) The experience and scientific expertise acquired due to the project provides a solid basis for their future scientific work

7 PROJRCT ACTIVITIES/ OUTPUTS

1 Meetings and visits

1993 Dr Karmanchuk in Israel

1993 Internatl CAR/CDR Meeting, Volcani Center, Bet Dagan

Dec 1994 Dr Karmanchuk in Israel Two weeks training

Aug 1995 Visit of D L Feigelson, ARO, to the KRSII, Bishkek,

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Two weeks training

2 Lectures in Internatl Conferences , Dr Lea Muszkat

1994 American Chemical Society (ACS) Meeting, Washington, D C , Co-Chairman of session, and invited lecturer in the Environmental Division

1994 Internatl Conference on Modern Agriculture and the Environment, Rehovot, Israel

1994 Internatl Conference on "The environmental challenges facing Israel, the West Bank and Gaza", Jerusalem Opening lecturer, Subject Minimization of Water Pollution

1994 Internatl Conference on Groundwater, Brighton, UK

1995 Internatl Conference on Photochemistry, London, England

1996 Internatl Conference of the Israeli Society for Ecology, Jerusalem

1996 Invited lecture, Bremen University, Dept Environ Chem *Subject* Mineralization of pesticides by TiO_2- solar photocatalytic oxidation

3 Publications

1 Muszkat L, 1994
Horizontal spread of organic pollutants in groundwater
ACS 208th Meeting, *Book of Preprints, Division of Environmental Chemistry,* Washington, *D C* 34(2) 580- 585

2 Muszkat L, Bir L and Feigelson L, 1995
Solar photocatalytic mineralization of pesticides in polluted waters
J Photochem Photobiol A Chem 87 85-88

3 Muszkat L and Feigelson L, 1996
Solar photodegradation of pesticides in polluted water
In *Preservation of our world, Proceeding of Intern Congress on Environmental Quality Sciences* , Steinberger Y , Ed pp 828-831

4 Muszkat L, Feigelson L, Bir L and Muszkat K A ,1998a
Reaction patterns in photooxidative degradation of two herbicides
Chemosphere, 36 1485-1492

5 Muszkat L, 1998b
Photocatalytic degradation processes
In *Pesticide remediation in soil and water*, Kearney and Roberts (Eds), *Wiley series in Plant Protection*, John Wiley and Sons, pp 307-337

8 PROJRCT PRODUCTIVITY

The study closely followed the research objectives, outlined in Para 4 Special attention was paid to field studies Solar Photocatalytic Degradation (SPD) has been applied for the removal of toxic organic chemicals from water Natural samples of polluted ground-water and rinse waters from agricultural spray containers were efficiently purified by this technique The studies were carried out in a pilot plant constructed in our laboratory, particularly suitable for field experiments Selected herbicides, nitro-phenols and other abundant pollutants have been degraded by the SPD Several approaches for the improvement of the catalyst efficiency have been

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examined Further, the results of non-catalytic photooxidation of pesticides revealed the existence of different degradation patterns and the specific role of oxygen and of hydrogen peroxide
Most of the rsearch goals were adequately fulfilled, whereas some part was only partially carried out and deserves future efforts This category includes the subjects of catalyst regeneration, prevention of catalyst fouling, and the identification of intermediates These important and broad subjects were beyond the possibilities of the present project and deserve extended studies in the future

9 FUTURE WORK

The joint project has significantly stengthened the scientific capabilities of our Kyrgyz partners The promising results, the availability of modern equipment and the experience acquired has led the Israeli and Kyrgyz groups to plan a continuation of the study for the development of the SPD technology The future work is aimed at the scaling-up of the process and construction of a pilot plant, Detailed examination of oxidative additives, to achieve enhanced degradation and to prevent photocatalyst fouling, and the combination of the photocatalytic process with conventional treatment facilities The study will allow the Kyrgyz group to establish and develop a research program on water pollution and water treatment, and to conduct basic and applied studies on photocatalytic degradation This activity will fulfill the objectives of AID/CAR program and provide some answers to real the needs of the Kyrgyz Republic

10 LITERATURE CITED

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J Photochem & Photobiol , A Chem , 65, 409-417
Solar photocatalytic degradation of xenobiotic contaminants in polluted well-water
2 Muszkat L, D Raucher, M Magaritz and D Ronen, 1993,
Ground Water 31, 556-565
Groundwater contamination by organic pollutants in a sewage-effluent irrigated site
3 Karmanchuk A 1994, Private communication
4 Muszkat, L Bir and L Feigelson, 1995,
J Photochem & Photobiol , A Chem , 87, 85-88
5 Muszkat L, L Feigelson and K A Muszkat, 1998a,
Chemosphere, 36 1485-1492
6 Muszkat L, 1998b Photocatalytic degradation of pesticides in water, pp 307-339 in *Pesticide Remediation in Soil and Water,* Kearney and Roberts (Eds), John Wiley & Sons
7 Ashkenazi L and L Muszkat, 1998, unpublished results

Table 1 - The pollutants concentrations in the sewage (waste water) from Bishkek (after purification) and drainage from Atbashinsk system

Indexes and pollutants	Bishkek sewage ppm	Atbashinsk system's drainage ppm
Salinity	680-893	646-1763
Chemical oxygen demand	14-275	62-252 8
Biogenic elements (P, N, S)	1 2-17 6	1 49-3 21
Petroleum products	0 6-7 0	0 1-0 2
Phenol	0 1-1 4	no
Detergents	0 4-1 8	no
Pesticides	no	01-0 05
pH	8 2-8 4	8 10-8 65

Table 2 – Chemical composition of sewage and collector-drainage water (1995)

Water source	PH	Mineral-als Mg/L	Chemical composition Mg/L							Permnga-n ate mg O_2/L	Bichromat mg O_2/L
			CO_3^{2}	HCO_3	SO_4^{2}	Cl	Ca^{2+}	Mg^{2+}	Na^{+} K^{+}		
Researv "Spartak"	8 54	816 5	6 0	250 1	9	3	52 1	60 8	97 3	57 9	35 2
Rollector K-2	8 89	1434 4	36 0	6	0	6	96 2	92 4	200 0	3 32	26 05
At-Bashy channel	8 60	496 3	12 0	158 6	2	6	40 1	34 0	56 8	4 86	40 25
Sewage after cleansing	7 85	380 6	no	195 2	59 1	3	48 1	24 3	21 6	10 24	32 0

Table 3

Pesticides use in Chuy valley (Kyrghizia, 1993/94)

Pesticide common name	Rate, kg/hectare	amount used kg/year	Crops
1. malathion	0.7-1 2	9342	Beets, cabbage, cucumbers, rape vegetable marrow, garden plants
2 Parathion	0 5-1 0	10219	Beets, rapc, crops, grapes, lucerne
3 Phoxim	1 0-1 5	575	cabbage, lucerne, tomatoes
4 Nitrofen	43 0-60 0	14597	vegetables
5 Phosalone	2 0	1635	Cabbage, tomatoes
6 Dimethoate	1 6	6369	Beets, garden plants
7. Trichlorphon	8 0	1440	Garden plants
8 Decis	0 15-1 0	2743	potatoes, lucerne, tomatoes, cabbage
9 Metribuzin	1 4	350	tomatoes
10 2,4-DB	1 9	6294	Crops, grass
11 Glyphosate		796	Fields
12 Trifluralin	4 0	5640	tomatoes, cabbage, rape

		kg/year	
13 Fuselad	1 0-2 0	946	beets, onion
14 Chloridazon	4 0-8 0	5279	beets
15 Polyram	2 3-6 0	6089	onion, grapes, beets
16 zineb	3 2-8 0	1384	onion, grapes, beets
17 Pynacarbolid	3 0	2722	beets
18. Agelon	4 0	2765	corn
19 Phenmedipham	6 0	3891	beets
20 Eradicane	4 0	4889	corn
21 Dialen	1 75	3788	crops, corn
22 Penitran	3 4	3975	onion
23. Atrazine	3 0	1146	corn

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Table 4 Effect of solar irradiation through polyethylene film on TiO_2-photocatalyzed decomposition of malathion (70 ppm)[a,b,c]

Exposure (h)	Residual concentration (ppm)	
	Open[d]	Polyethylene cover
1	34	35
3	9	13
6	2 5	4 5
12	0 2	0 3
18	>0 2 ppb	0 8 ppb

[a] Polyethylene film, 100 μm thick
[b] In the presence of 1 15 mg L^{-1} detergent TPBS Detergent is decomposed completely after 1 h of irradiation
[c] Irradiation in crystallizer (diameter, 22 5 cm), solution volume, 2 l , in the absence of H_2O_2
[d] Concentrations corrected for evaporation

Table 5

SPD of organic contaminants in drainage waters, Kyrgyzstan

Substrate	**Substrat initial , ppm**	**TiO_2 concentration ppm**	**Half life, min**	**Blank, half life (without catalyst), min**
	Solar degradation			
1 Lindan	1 121	5 0	95 8	392 3
2 DDE	0 00244	5 0	161 2	1351 0
3 Metaphos in drainage water	1 10	Ultram * membranes TiO_2 amount 76 5 mg/2L Sol	166 3	315 8
4 TBS	1 98	50 0		378 0
undrainage water	1 032	50 0	52 1 48 3	202 0
5 Humic acids	7 3	50 0	84 3	352 4
6 Bishkek sewage water COD with KM_nO_4	4 86	2 5	603 5	820
COD with $K_2Cr_2O_7$	12 42	2 5	843 4	1039
	UV degradation (mercury Lamp with max 358nm)			
1 Lindan	0 97	50 0	299 0	771 0
2 Metaphos	8 8	50 0	247 5	1039 0

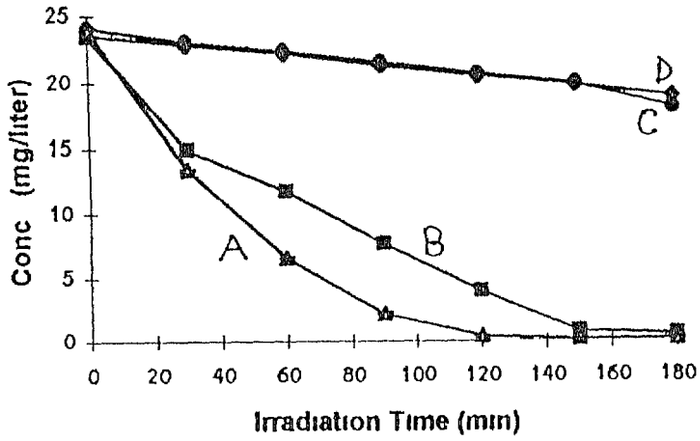
Table 6 - Photolysis of detergent TBS with re-used catalyst

	Blank (without catalyst)		Catalyst TiO_2 50 mg/l		Re-used catalyst TiO_2 50 mg/l	
ion, min	Concentration mg/l	half life time min	Concentration mg/l	half life time min	Concentration mg/l	half life time min
0	1 032		1 032		1 032	
20	0 584	24 34	0 047	4 39	0 327	12 07
40	0 288	22 72	0 024	7 57	0 163	15 02
60	0 176	23 60	0 012	9 37	0 081	16 42
90	0 117	28 68	no		0 033	18 14
120	0 077	32 23			0 009	17 54
150	0 053	35 05			no	
180	0 028	34 65				
210	0 015	34 65				
240	0 008	34 65				
300	0 005	39 15				
330	no					

Table 7 Photodegradation of Methaphos, induced by solar- and by UV-lamp irradiation

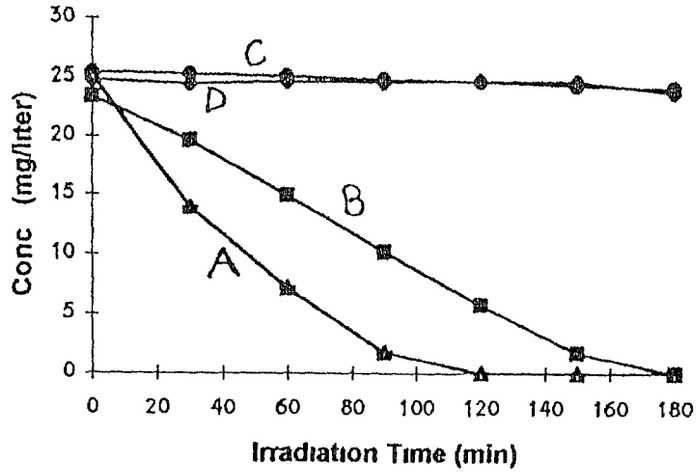
Photolysis time, min	Solar radiation without catalyst		Solar radiation with catalyst TiO_2, 50 mg/l		Mercuri-quartz lamp with catalyst TiO_2, 50 mg/l	
	on mg/l	Half life time, min	oncentrati on mg/l	Half life time, min	oncentratio n mg/l	Half life time, min
0	8 80		8 80		8 80	
120	8 50	2406 25	7 12	387 58	3 50	90 23
240	8 02	1795 33	4 96	290 2	1 03	75 55
360	7 40	1446 76	3 65	292 4	-	
540	6 80	1358 83	2 22	209 9		
720	5 35	1010 20	-			
900	4 81	1034 32				
1080	4 25	1029 71				
1260	3 72	1018 65				
1440	3 10	1021 32				

Fig 1
Solar photocatalytic degradation of o- Nitrophenol



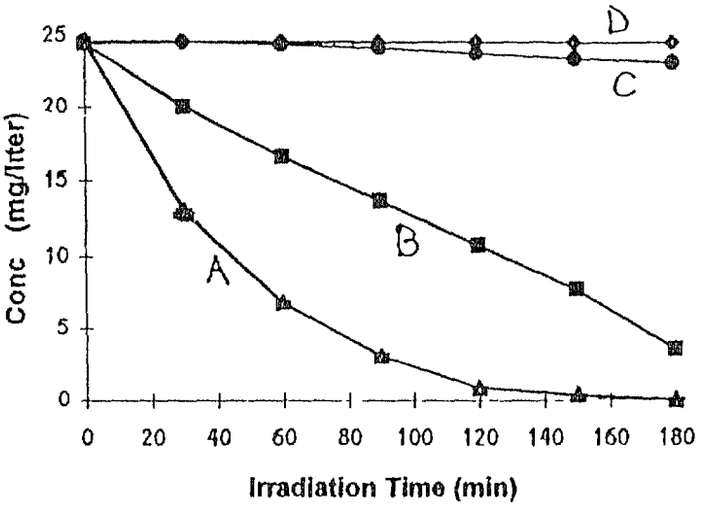
A Photocatalyst + H_2O_2 *B* Photocatalyst
C H_2O_2 *D* No additives

Fig 2
Solar photocatalytic degradation of m-Nitrophenol



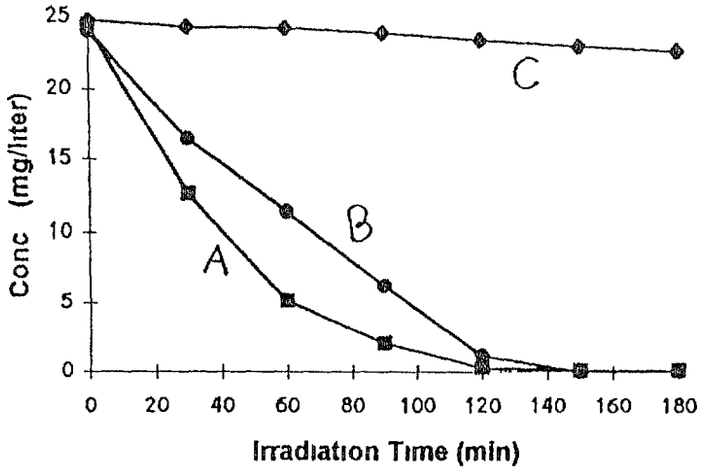
A Photocatalyst + H_2O_2 *B* Photocatalyst
C H_2O_2 *D* No additives

Fig 3.
Solar photocatalytic degradation of p-Nitrophenol



A Photocatalyst + H_2O_2 *B* Photocatalyst
C H_2O_2 *D* No additives

Fig 4
Solar photocatalytic degradation of Dinitro-o-cresol



A Photocatalyst + H_2O_2 *B* Photocatalyst
C H_2O_2

Fig 5

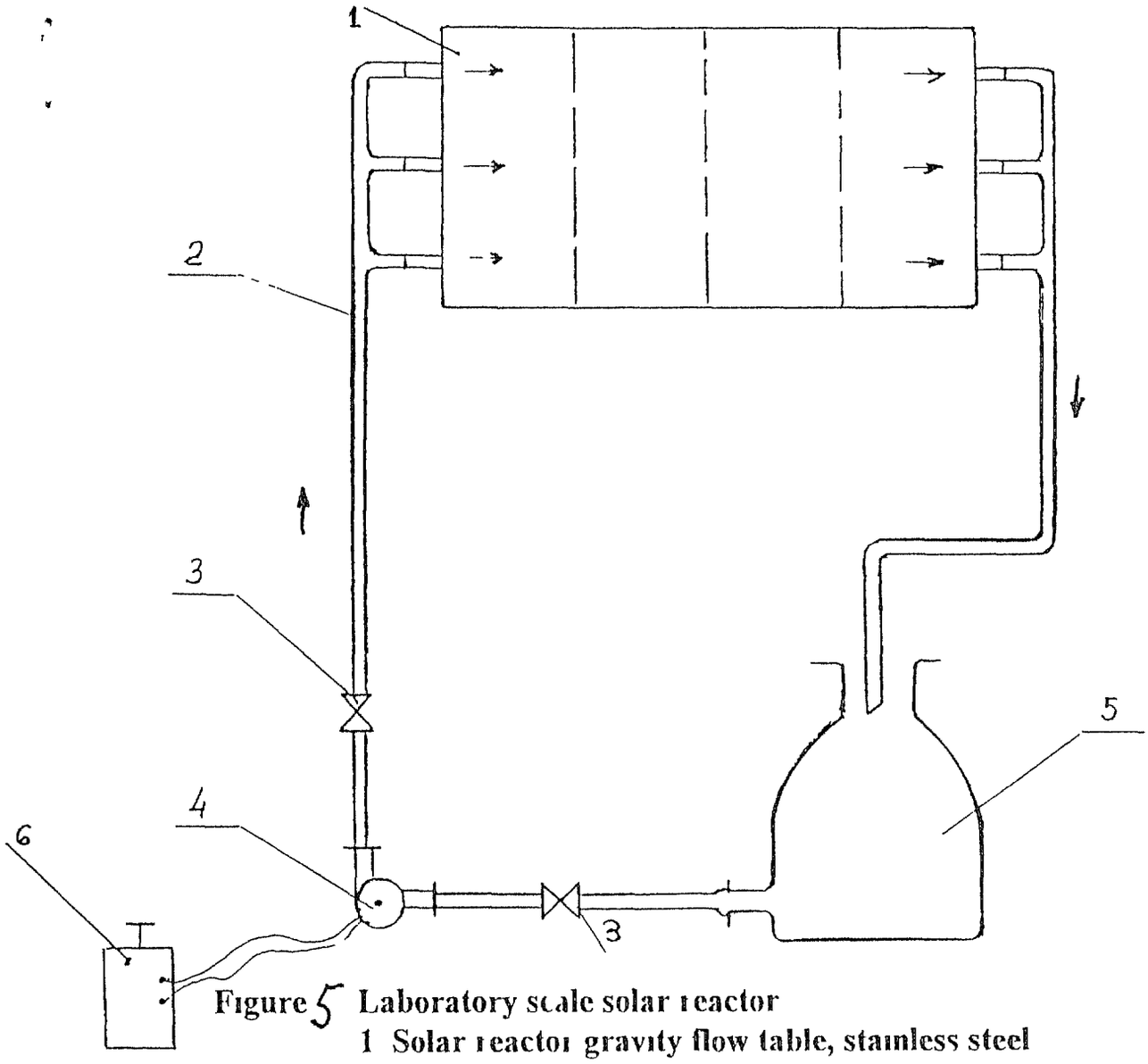


Figure 5 Laboratory scale solar reactor

1 Solar reactor gravity flow table, stainless steel
2 In-flow tube (teflon)
3 valves
4 pump
5 collection vessel
6 flow control variac