REMOVAL OF SOME HEAVY METALS AND CYANOPHOS PESTICIDE FROM WATER USING DIFFERENT ADSORBENT MATERIALS •

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ABSTRACT : The adsorption of lead and the pesticide cyanophos on six adsorbent materials with various physical and chemical properties was studied. The adsorption of zinc and manganese by cement kiln dust was studied. Also, biodegradation of cyanophos by the alga spirogyra at the level of 5 ppm was evaluated. The data showed that ,the maximum specific adsorption (ym) and the affinity ·of binding site (k) of cement kiln dust (CKD) were highly increased .as heavy metals scavenger. The ym ofCKD were 625, 588.2 and 476 μ g/gm for lead, zinc and manganese, respectively. The rice husk ash fired at 450 \mathcal{C} (amorphous) has high reactivity toward lead and cyanophos pesticide. The ym of rice husk ash were 109.89 and 909.09 μ g/gm for lead and cyanophos while K values were 9990 and 113636.4 for lead and cyanophos, respectively. Initial amount of cyanophos in water without spirogyra was 4.68 ppm while in the case of water containing spirogyra was 4.53 ppm after two hours of treatment. These amounts were decreased to be 2.68 ppm in water without spirogyra representing 46.4% dislodges after 96 hours while reached 0.65 ppm in water containing spirogyra after the same period, indicating 87% losses of the initial amounts. Medium degradation time (DT_{50}) of cyanophos in water was 7.6 days whereas in case of water containing spirogyra, DT_{50} was 2.8 days.

Key words : Heavy metals, cyanophos, adsorbent materials, Spirogyria biodegradation.

INTRODUCTION

Pollution of surface water and ground water with heavy metals and pesticides is a problem humanity can not afford to ignore. amounts of heavy Enormous mealts have been mobilized in the past century as a result of global. industrial, and in particular metalliferous mining (Kelly, 1988) as well as smelting, agricultural and waste disposal activities (Ross, 1994). The presence of heavy metals and pesticides in water often jeopardize the ecosystem stability and posses serious danger to human health (Gogoley and Wilke; 1997). Also, heavy metals remain in the sediments and are released slowely into water (Fukami, 1988). The release of large quantities of heavy metals into the natural environment has number resulted in a იf environmental problems (Hutton and Symon, 1986 and Nriaqu, 1998).

As heavy metals cannot be destroyed in the natural environment, a variety of methods to remove toxic metals from water based on ion exchange or chemical and microbiological precipitation

has been developed and used with some success (Wilde and Beneman 1993). These technologies have distinct efficiencies for different metals and may be very costly if large volumes. low metal concentrations and high cleanup standards are involved. There is a great need for reliable and inexpesive technologies that can reduce toxic metal concentrations and pesticide residues t_0 environementally acceptable levels. Such technologies might be effectively used in pollution prevention and waste reduction programs.

Recently there has been an increasing interest in the use of living and nonliving bacteria, fungi, algae and aquatic plant for the bioremediation and recovery of heavy metals from aqueous streams (Veglio and Beolchini, 1977; Summers, 1992; Wilde and Benneman. 1993). Also. bioremediation of pesticides using live cultured cells of aquatic plant, algae, bacteria and fungi are growing in importance for the clean up of contaminated soil and ground water. The technology of bioremediation is not only useful and economic but also practical. (Kuyack and Volesky 1990; Wang

al., 1996). Therefore, the *et* objectives of this study include the inexpensive capability of adsorbent materials such as cement kiln dust, kaolinite, rice husk ash, peat moss and non-living biomass of aquatic plant i.e. waterlens and the alga spirogyra for removing some heavy metals and cyanophos pesticide from aqueous solutions. moreover, the bioremediation of water polluted with cyanophos residues using live cultured cells of the alga spirogyra is studied here.

MATERIALS AND METHDOS

A. Chemicals used:

1. Cyanophos $(Cyanox)$, 50% E.C.

O-4-cyanophenyl o,o-dimethyl phosphorothioate. A formulated sample of cyanophos 50% E.C. under the trade name of cvanox was supplied by The Ministry of Agriculture, Egypt.

2. Heavy metals of lead acetate, manganese sulphate and zinc sulphate were obtained from Sigma (Germany).

b. Asorbent materials used:

- 1. Cement kiln dust (C.K.D) the components maior $are:$ alumina 7.1%, calcium oxide 43.9%, ferric oxide 4.71%, silica 21.8% and titanium oxide $1.0%$. Moreover. scanning electron microscopic analysis showed the dust was composed of spherical particles with a core of calcium carbonate, clay and an alkali (Wilson and Anable, 1986).
- 2. Rice husk ash (burned in open) air) this was there heated at 450 °C for 4 hours in a muffle furnance in a steel container and control supply air. Rice husk ash with highly active SiO₂ content was obtained. The $SiO₂$ of the ash is mostly amorphous. The maior components are silica 94.47%. calcium oxide 1.14%, alumina 2.03% . ferric oxide 0.4% magnesium oxide 0.89% and potassium oxide 1.52% (Abd El-Wahed, 1990).
- $(95%$ 3. Peat-moss organic matter)
- 4. Kaolinite. the major components are silica 46%. alumina 36%. ferric oxide

0.4%, titanium oxide 1.5%, $oxide$ 0.06% calcium and magnesium oxide 0.1%.

- 5. Aquatic plant waterlens (Lemna gibba L) was blotted then used as a dry plant hiomass.
- 6. Live and nonlive macrofilamentous agla spirogyra, (Spirogyra spp)

C. Experimental procedure :

1. Determination of adsorption capability:

A series of 50 ml of erlenmyer flask with a scew cap were prepared containing lead acetate ml) of known solution (20) concentrations in the range of 1-50 ppm. Weighed amounts of 0.5 gm of each adsorbent material (cement kiln dust, rice husk ash, peat moss $-$ kaolinite, dry waterlens and dry spirogyra) were added to each flask and the mixtures were agitated on a rotary shaker for 6 hours. The solution pH was adjusted to PH5 using 0.1 M $HNO₃$ or 0.1 M NaOH. All treatments were conducted in At the end of the triplicates.

experiment, the contents of the flask were filtered through 0.045 um membran filter (which does not adsorb the heavy metal ions) and the filterates were analysed for lead atomic absorption bv spectrometry. This experiment was repeated using only cement kiln dust as adsorbent material and manganese sulfate and zinc sulfate solution (20 ml) of known concentrations in the range of 1-50 ppm. Instead of lead acetate solution. The results of metal anlaysis was used to calculate:

- 1. Percent of metal remaining in solution.
- 2. Percent of metal recovered by adsorbent material.
- 3. Specific adsorption (ug metal) adsorbed / gm of adsorbent)

Weighed amounts of 0.5 gm of each adsorbent material (CKD, peat-moss, rice husk ash, kaolinite, dry waterlens and dry spirogyra) were added for each concentration of cyanophos insecticide. Six concentrations i.e. 1, 5, 10, 15, 20 and 25 ppm were prepared in 20 ml of water in 50 ml erlenmyer flasks equiped with a screw caps. Blank containing only the pesticide solution was included in each

determination. The flasks were agitated for 6 hours then the contents of the flask were filtered and 4 ml aliquot of the solution was taken for analysis. The amount adsorbed or specific adsorption (ug) of pesticide / gm of adsorbent) was calculated according to (Felsot and Dahm. 1979).

The maximum adsorption (Ym) and the equilibrium constant (K) of metals and cvanophos heavy pesticide were calculated by using the langmuir adsorption equation (Crist *et al* .. 1992).

2. Bioremediation of cyanophos pesticide in water using live cultured cells of alga spirogyra:

The test species spirogyra (filamentous alga) was isolated from drainge water at Aboutwala. Menia El-Kamh. Sharkia Governorate. Egypt and maintained in the laboratory in alga nutrient solution suggested in Anonymous (1980). Algal assay was conducted in triplicates in 50 ml culture flask containing 25 ml of the growth media with $0.01, 0.1$, 1, 5 and 10 ppm of cyanophos concentration. The test media were

inoculated with 0.2 gm of wet spirogyra to each concentration. The initial absorbance at 620 nm was measured for spirogyra (Joseph and Joseph, 1999). Control sets of cultures were maintained in the test medium free of cyanophos. All the test cultures were incubated for 8 days at 28 ± 3 °C under white light from fluoresent lamps. After 8 days the absorbance of spirogyra was measured and the EC_{50} was estimated. The process οf developing acclimation to cyanophos was initiated at predetermined sublethal concentration $(0.1 \tEC_{50})$. The adaptation was begun at 0.48 ppm then transfered to cyanophos free medium to check the viability (absorbance) following 8 day growth. The algal growths were exposed to successively higher concentrations of cyanophos in the order of 1, 2, 4, 6, 8 and 10 ppm each time to check the viability of the alga. At each level of exposure. absorbance was measured. At 5 ppm of cyanophos the depletion of the chemical in the cultures of the acclimated spirogyra was followed at different time intervals of 2, 4, 24, 48, 72 and 96 hours of exposure. The un-inoculated test media was the control to verify the depletion of cyanophos by alga.

3. Residue analysis techniques

a. Extraction and clean up

5 ml aliquot of cyanophos water was extracted with solution hexane, evaporated to dryness and determined using HPLC (Leppert et al., 1983).

b. Residue determination

The residues of the tested pesticide were directly determined without clean up using HPLC with the following conditions :

Dual delivery solvent system pump 406, U.V. detector 166, Integrator spectra physics 4270, attenuation 16, chart speed 1.0 cm/ min, stainless steel column (10/250) nm) packed with C 18, flow rate 0.7 ml/min, wave length 248 nm and mobile phase methanol / water 70/30.

RESULTS AND DISCUSSIONS

1. Role of certain adsorbent materials in reducing the levels of heavy metals and cvanophos pesticide from water

Data in Tables $(1, 3 \text{ and } 4)$ and figures (1 and 3) show the adsorption capacity of lead and cyanophos by cement kiln dust (CKD), rice husk ash, kaolinite, peat-moss, non living cells of aquatic plant waterlens and alga spirogyra.

The results reveal that lead and cyanophos concentrations were decreased of the tested water containing the adsorbents higher than that in the water solution without adsorbent materials, after 6 hours of treatment indicating adsorption process.

The maximum specific $(\mu$ g/gm) of adsorption. Ym adsorbent materials obtained from langmuir isotherm for lead can be descendingly arranged as follow:

CKD (625), rice husk ash (109.89), waterlens (76.92) , peat-moss (23.26) , kaolinite (16.67) and spirogyra (5.88) μ g/gm. The equilibrium constant (K) that related to the affinity of binding site were 125000, 9990, 2564, 310.13, 222.3 and 13.67 for CKD, rice husk ash, waterlens, peatmoss, kaolinite and spirogyra, respectively. Also, as can be seen in table (4) the maximum specific adsorption Ym values calculated langmuir isotherm were from higher than that of experimental data.

The maximum specific adsorption Ym and the affinity of the binding site (K) of CKD were highly increased in lead adsorption than that of the other adsorbent materials. Moreover, the roll of CKD in reducing other heavy metals *i.e.* zinc and manganese, were stuided here.

Data in tables $(1 \text{ and } 2)$ and fig and 2) cleared that, the $(1$ maximum specific adsorption (Ym) and the affinity of binding site (K) of CKD were increased higher as heavy metal scavengered. The maximum specific adsorption, Ym $(\mu \alpha/m)$

of CKD were 625, 588.2 and 476.2 for lead. ug/gm zinc and manganese, respectively while, the affinity of binding site were 125000. 98033 17007 and respectively. The maior components of CKD are alumina, calcium oxide, ferric oxide, silica and titanium oxide. Each of these components can be an ideal adsorbent. Moreover, the alkaline nature of the dust makes it a good neutralizing agent (El-Awady and Sami, 1997). El-Awady, (1996). found that use of CKD as adsorbent in waste water treatment as no cost material and clay structure. Many research have been conducted for recycling or reuse the CKD as raw material, fertilizer, constructing materials and improving the soil (Thorbjorn, 1969). Also, El-Awady and Samy (1997) mentioned that CKD could be recommended as a material for the effective removal of metal pollutants such as chromium. cobalt, iron and copper from industrial waste water.

Data in table (4) show the high capacity of rice husk ash in reducing the lead and cyanophos concentrations from liquid media. The maximum specific adsorption Ym and the affinity of binding site

(k) were $109.89 \mu g/gm$ and 9990 for lead while 909.09 μ g/g and 113 636.4 for cyanophos pesticide, Romeh respectively. (2001) showed that addition of CKD and rice straw ash each at $0.59 / kg$ to the soil caused adsorptions of carbosulfan, pirimicarb, metalaxyl and diniconazole reached (33.03, 27.70, 78.10 and 80.20%) and $(30.37, 17.57, 79.64, and 69.30\%)$ respectively.

Peat moss able to reduce cyanophos from aqueous water than that of lead. The Ym were 270.27 and 23.26 μ g/gm for cyanophos and lead while K values were 90090 310.13 and respectively, (Table-4). Our results are in agreement with many investigators, Felsot and Dahm 1979; Gosset et al., 1984; Picollo et al., 1996 and Socias – Viciana, 1999 who reported that organic matter in peat-moss are fulvic acid and humins which play a predominant part in a detoxification of xenobiotics.

Data in table (4) clear that, non living cells of waterlens was able to adsorb lead and cyanophos. The Ym of waterlens were 76.92 and 125 μ g/gm for lead and cyanophos

while K values were 2564 and 62500 respectively. On the other hand, despite the Ym and K value of non living cells of the alga spirogyra i.e. $(5.88 \text{ µg/cm}$ and 13.67) were decreased for lead, the Ym and K value reached 100 μ g/gm and 3571 for cyanophos pesticide. Shiber and Washburn, 1978; and Ho 1990) found that the concentration of lead has higher levels in sediment than Zn, the opposite occurs in the plant and seawater. This may be due to the fact that *Ulva rigida* is unable to incorporate high level of pb, has a mechanism of getting rid of it, or is able to reduce its toxicity through biochemical some processes. Moreover, the high levels of Zn in V. rigida and the seawater, in comparison to pb, could be the result because Zn, in contrast to pb was found almost totally bound weakly to the suspended particulate fraction thus increasing their biological availability (Lacerda et al., 1987; Ho, 1990 and Karez et al., 1994). From the above mentioned results it was noticed that lead and cyanophos were adsorbed on the extracellular cell surface instantaneously when these xenobiotics were added to the aquatic plant and alga. This

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association was, therefore physical in nature in a way similar to the biosorption of chemical by the plant biomass (Maeda et al., 1990, Avery et al., 1993 and Sampedro et al., 1995). Wang et al., (1998) found that bioremoval process typically exhibits two stages : an initial fast. reversible metal "biosorption" binding process followed by slow irreversible, ion sequestration "bioaccumulation". The ability of macro alga Ulva *enteromorpha* to bioaccumulate heavy metals is attributed to the formation of thioles and peptides when found under environmental stress (Haritonoidis et al., 1993; Rijstenbil et al., 1993). Metal accumulation fungi (Tobin., 1994) and two species of aquatic fern, Azolla filiculoides Lam. (Sela, 1989) and Azolla pinnata R.Br. (Jain, 1989 and EL-Kassas, 2002) been tested have as metal biosorbents capable of remediating industrial effluents. Aquatic flower plant have also been utilized for water purification. Water hyacinth (Eichornia crassipes Mart. Solms) (Falbo and Weaks, 1990; Kay., Turnquist., 1990) penny 1984; wort (Hydrocotyle umbellata L) (Dierberg 1987) and duckweed (Lemna minor L) (Mo, 1989 and EL-Kassas, 2002) can remove

various heavy metals from water. However, the efficiency of metal removal by these plants seemed to be low because of their small size and small, slow-growing roots. The high water content of aquatic plants also complicates their drving. composting and inceneration.

2. Biodegradation of cyanophos by alga the spirogyra

Data in Table (5) and fig. (4) show that the degradation of cyanophos in water containing living cells of the alga spirogyra was increased as compared with that in water only. This general trend of data was the case at any period after application i.e. 2, 4, 24, 48, 72 and 96 hours post treatment.

In water solution containing spirogyra the initial amount of cyanophos was 4.53 ppm. This amount was decreased to 0.65 ppm 96 hours of treatment. after representing 87.0% losses of the initial amount. In water solution without spirogyra the initial amount of cyanophos was 4.68

ppm. The concentration Ω£ cyanophos in the control was decreased to be 2.68 ppm after 96 hrs. indicating 46.4% dislodges from the initial amount. The rate of degradation and medium degradation time $(DT₅₀)$ value of the tested medium inoculated with spirogyra was 2.66×10^{-5} sec.⁻¹ $(DT₅₀ = 2.8 \text{ days})$ while in control was 7.55 \times 10⁻⁶ sec.⁻¹ (DT₅₀ = 7.6) days). The study clearly show that the alga can speed up the cyanophos depletion from the water. This finding may be attributed to the enzymes induction capability of the alga spirogyra. Subramanian and Uma (1997) showed that \mathbf{a} marine cvanobacterium Phormidium valderianum BDU-3050 was able to degrade phenol completely at 100 mg/ml by its intracellular oxidase and lactase enzymes. Tsang et al., (1999) and Garrison et al., (2000) found that the difference in pesticide the degradation ability may be attributed to the enzymes induction capability of the aquatic plants or algae. Aioub and Romeh (2002) reported that the degradation of oxamyl, imidacloprid and aldicarb pronounced in were water containing waterlens as compared with that in water only.

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Table (1): Specific adsorption of lead by certain adsorbent materials.

 $CB =$ Concentration of lead in water (μ g/ml)

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 $Ce = \text{concentration of lead in water with adsorbents } (\mu g/ml)$

 Y = specific adsorption or amount adsorbed by adsorbent material (μ g/gm)

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Table (2): Effect of cement kiln dust (CKD) concentrations on heavy metals removals from aqueous solution.

 $CB =$ Concentration of zinc and manganese in water.

 $Ce =$ Concentration of zinc and manganese in water with cement kiln dust.

 $Y =$ specific adsorption.

Ym = Maximum adsorption.

 $K =$ Equilibrium constant.

Table (3): Specific adsorption of cyanophos by certain adsorbent materials.

 $CB =$ Concentration of cyanophos in water (μ g/ml)

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 $Ce =$ concentration of cyanophos in water with adsorbent material ($\mu g/ml$)

 $Y =$ specific adsorption by amount adsorbed by adsorbent material (µg/mg)

Adsorbent materials		Cyanophos		Lead			
	From langmuir isotherm From experimental data			From langmuir isotherm		From experimental data	
	Ym	K	(Highest specific adsorption $(\mu g/g)$	Ym	ĸ	(Highest specific adsorption $(\mu g/g)$	
Waterlens	125.00	62500.0	109.1	76.92	2564.0	80.8	
Spirogyra	100.00	3571.0	107.14	5.88	13.67	19.2	
Peat-moss	270.27	90090.0	267.8	23.26	310.13	27.6	
Rice husk ash	909.09	113636.4	370.0	109.89	9990.0	120.0 \mathcal{A}	
Kaolinite	76.92	2564.1	67.3	16.67	222.3	32.0	
Cement-kiln-dust	100.00	50000.0	129.6	625.0	125000	520.0	

Table (4): Comparison of specific adsorption between experimental measurement and langmuir calculation.

 $Ym =$ Maximum adsorption and $K =$ Equilibrium constant related to the affinity of the binding site.

Table (5): Percent losses of cyanophos in water as affected by the algal spirogyra.

Days after treatment	Water				Water containing spirogyra			
	PPM	% loss	Rate of degradation	DT_{50}	PPM	% loss	Rate of degradation	DT_{30}
2 _h	4.68	6.4	7.55×10^{-6} sec ⁻¹	7.6	4.53	9.4	2.66×10^{-5} sec ⁻¹	2.8
4 ክ	4.52	9.6			4.03	19.4		
	4.18	16.4			3.62	27.6		
$\overline{2}$	4.07	18.6			2.89	42.2		
3	3.45	31.0			1.77	64.6		
4	2.68	46.4			0.65	87.0		

 DT_{50} = Median degradation time (days).

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إزالة بعض المعلان الثقيلة ومبيد السيانوفس من الماء بواسطة مواد المصلص مختلفة أحمد على على رميح* عبد الغلي عبد الحكيم عبد الغلي**

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مختلفة ، كما درس إدمصاص الزنك والمنجنيز بواسطة مخلفات صناعة الأسمنت وقسيد تسم در اسة سعة الإدمصاص القصوى وكذلك قوة الإرتباط لهذه العواد. كما درس تحطـــــم مبيـــد السيانوفوس في الماء بواسطة الطحلب سبير وجير إ. وقد أوضحت النتائج أن سعة الإدمصاص القصر ي و قو ة الإر تباط لمخلفات صناعة الأسمنت عالية جداً قد تغير (في التخلص من المعادن الثقيلة وقد كانت سعة الإيمصياص القصوى لمخلفات صناعة الأسعنت هسي ٦٢٥ ، ٥٨٨,٢ ، ٧٦، ميكروجم / جم للرصاص والزنك والعنجنيز على للقوالي. اتضح أن نائج حرق ســـوس خ الأرز على ٤٥٠ °م ذات قدرة عالية في إدمصاص الرصاص وكذلك مبيد السيانوفوس حيث كانت سبعة الإدمصياص القصيوي ١٠٩,٨٩ ، ٩٠٩,٠٩ ميكر وجسم / جسم للرصياص والسيانوفوس بينما كانت قوة الارتباط ٩٩٩٠ ، ١١٣٦٣٦,٤ اللرصاص ومبيد الســـيانوفوس على التوالي قدرت متبقيات السيانوفس في المياه غير المحتوية علـــي طحلــب ســبير وجير ا بالقيمة ٢٨,٤ جزء في المليون بينما في المياه المحتوية على سبير وجير ابـ ٤,٥٣ جزء فــي المليون بعد ساعتين من المعاملة. تتاقصت كمية السيانوفس في المياه غير المحتويـــــــة علـــــى سبير وجيرا إلى ٢,٦٨ جزء في العليون بعد ٩٦ ساعة معللة نسبة فقد ٤٦،٤% بينمــا فـــ , المياه المحتوية على طحلب سبير وجير ا وصلت إلى ١,٦٥ جزء في المليون ممثلة نسبة فقــد مقدار ها ٨٧%. كانت فترة تحطم النصف TD50 للسيانوفس في المياه ٧,٦ يوم بينما في المياه المحتوية على طحلب سبير وجيرا ٢,٨ يوم.