Egypt. J. Soil Sci. **43**, No.4, pp. 529-545 (2003)

Polymerized Bitumen Emulsions in Remediation of Heavy Metal Contaminated Soils

O.A. El-Hady*, N.F. Ghaly and A.M. Zaghloul***

**National Research Center, Dokki and **Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.*

TREATING contaminated soils with bitumen emulsions or/and some water soluble and emulsified polymers may offer the possibility to reduce the mobility of heavy metals and control their release to the soil solution.

Two soils contaminated with heavy metals were chosen. The first is a sandy loam soil from El-Cabal El-Asfar farm that is irrigated with sewage effluent since 1911. The second is a clay loam soil very near to Mustorod industrial zone and irrigated with water contaminated with industrial wastes. Soils were treated with bitumen emulsion 50% active material w/w (Bit.) polyvinylacetate butylacrylate emulsion 50% active material w/w (PVAc BuA) and mixtures of both at the ratios of 1:1, 2:1, 3:1, 4:1 and 5:1. Examined application rates were 0.5 and 1% active material w/w. Levels of the various extractable fractions of heavy metals (Cu, Pb, Cd, Ni and Co) were determined. These are: exchangeable + soluble ($CaCl_2$ extractable), adsorbed (acetic acid extractable), organically complexed (Na-pyrophosphate extractable) and occluded (acid oxalate extractable). The difference between the sum of extracted metal content and the total content was designed as the residual fraction, *i.e.* heavy metals held in primary minerals.

Extractable heavy metals from untreated soils are very high indicating their contamination with studied minerals. Applying the examined emulsions reduces the concentration of different extractable forms of heavy metals by varying degrees being lower with increasing their application rate. Such decrease in released heavy metals ranged between 20 and 25%; 35 and 45% and 25 and 40% from the sandy loam soil and between 15 and 25%, 25 and 45% and 20 and 40% from clay loam soil treated with Bit., PVAc BuA and their mixtures at the rate of 0.5% (active material w/w), respectively. By doubling the application rate of examined emulsions to be 1% (active material w/w), more decrease in released heavy metals to be 30-40%, 45-60% and 35-55% for the 1^{st} soil and 25-35%; 40-55% and 35-50% for the second one was obtained using the three types of emulsions mentioned above, in sequence. Noteworthy that, higher ratios of PVAc BuA in bitumen-polymer mixtures yield lower amounts of extractable heavy metals.

Taking into consideration that the preparation costs of one ton of bitumen emulsion, PVAcBuA emulsion and mixtures of both (50% active material w/w for each) are about 500, 3000 and 920 to 1750 L.E., in sequence, Bit. (even if its application rate is doubled) or the lower application rate of bitumen-polymer mixture at the ratio of 5 or 4:1 seem to be preferable and more economic than using PVAc BuA, separately. Preparation of more effective and cheaper polymers to be used as modifiers for bitumen emulsions are of great importance.

Keywords: Remediation, Contaminated soils, Heavy metals, Bitumen emulsions and polymerized bitumen emulsions

The scarcity of fresh water for agriculture in the arid zone areas is considered to be the most limiting factor for food production. Countries, including Egypt, have looked to municipal and industrial wastewater reuse in order to cover the shortage of high quality waters. Because of the chemical, physical and biological nature of that water, there are potential problems associated with its reuse in agriculture. Some of the major concerns are health hazards, salinity build up and toxicity hazards (El-Sokkary and Sharaf, 1996). High content of heavy metals in such effluents (*e.g.* Fe. Mn, Zn, Cu, Pb, Cd, Ni, Co and Cr) may accumulate in soils to levels either causing phytotoxic conditions or bio-accumulate in plants at levels which adversely affect the health of the consumers (Header, 1987). There is also concern that the sludge born metals may be leached below plant rooting zones and contaminate ground water supplies (Abdel Sabour *et al.*, 1996 and El-Sokkary, 1996).

Previous studies (Ghaly, 1998; El-Hady & Abd El-Hady, 1999 and El-Hady *et al.*, 1997 and 2000 a and b) referred to the importance of using emulsified asphalt (Bit.) or polymers-especially those having hydrophobic characters-as means for reducing the extractability of heavy metals from contaminated soils and lowering their mobility for plants uptake or ground water supplies. Polyvinyl acetate butyl acrelate emulsion (PVAc BuA) showed superiority over other examined polymers and latex emulsions. Modifying Bit with such polymer may be more efficient than applying bitumen emulsion (Bit.) solely.

Preparing effective and at the same time low priced remediators for soils contaminated with heavy metals using Bit. modified with (PVAc BuA) is the aim of the present work, taking into consideration that the preparing costs of Bit. and PVAc BuA (both are 50% active material w/w) are ≃ 500 and ≃ 3000 L.E / ton, respectively (Prices of 2002).

Material and methods

Materials

Soils

Two contaminated soils with heavy metals were examined namely:

1- Sandy loam soil of El-Gabal El-Asfar farm which is located in the Eastern Desert 25 km east of Cairo. Sewage effluent of Cairo city has been used to irrigate the growing crops in this area since 1911.

2- Clay loam soil of Mustorod industrial zone, it is situated in greater Cairo, very near to the Ismailia canal. Many factories representing different industrial sectors are found in this area. Most of the soils near to such factories are contaminated with different heavy metals. Besides, the contaminated irrigation water which adversely affect the agricultural potentiality.

The general properties of the soils are given in Table 1. The high clay and organic matter content of sandy soil was the result of the sewage sludge applied to the soil before putting it under cultivation and of the repeated irrigation with Cairo sewage effluent for more than 80 years.

Examined remediators

Bitumen emulsion (50% active material w/w) (Bit.)

a- Used bitumen: Bitumen of penetration 60/70 a product of El-Nassr Petroleum Company, Suez was used. Physical properties and constituents of the used bitumen are illustrated in Table 2.

b- Emulsifier: The used emulsifier was the cationic slow-set emulsifier (Impact CP2), a product of Westvaco Chemicals Company, Germany. Its physical properties are illustrated in Table 3.

c- Method of preparation: Water was warmed up to 70°C. The emulsifier (2% by weight) was added while stirring, followed by hot bitumen (135°C). Stirring was continued until the emulsion became completely homogeneous.

TABLE 1. Analytical data of contaminated Soils under study.

Components	Soil 1 El-Gabal El-Asfar soil	Soil 2 Mustorod soil
1 . Mechanical analysis:		
- Coarse sand (2-0.2 mm)	23.4	6.5
- Fine sand (0.2- 0.02 mm)	48.9	22.5
- Silt (0.02.0.002 mm)	8.7	32.5
- Clay (less than 0.002 mm)	19.0	38.5
- Texture class	Sandy loam	Clay loam
2. Chemical analysis		
- Organic material %	7.1	1.65
- $CaCO_3$ %	0.01	3.8
- pH (1:25)	6.5	7.4
- EC dS m^{-1}	1.6	4.2
3. Heavy metals content (ppm)		
- Cu (total)	146.6	148.2
- DTPA extractable	19.6	16.7
- Pb (total)	470.0	176.2
-DTPA extractable	15.0	8.5
- Cd (total)	5.2	7.5
- DTPA extractable	0.8	0.3
- Co (total)	65.0	42.5
- DTPA extractable	4.6	2.7
- Ni (total)	125.0	48.5
- DTPA extractable	6.2	1.8

TABLE 2. Physical properties and chemical constituents of the used bitumen.

Properties	Values
Physical Properties:	
- Penetration at 25 ^{0}C 100 g, 5 sec.	64
- Kinematic viscosity at 135^{0}C, C.st.	390
- Absolute viscosity at 60^{0}C, poise	2342
- Flash point, ^{0}C (Cleveland open cup).	+250
- Ductility at 25^{0}C, 5cm/min.	+100
- Softening point ^{0}C (Ring &Ball).	51
- Solubility in trichloroethylene, %.	99.7
Chemical Constituents, wt%:	
- Oils	26.3
- Resins	52.9
- Asphaltenes	20.8

TABLE 3. Properties of the used emulsifier.

Properties	Values
- Trade name	Impact CP2
- Structure	Lignin/tall oil amine
- Physical form	Liquid
- Boiling point ^{0}C	>100
- Specific gravity, g/ml, 25^{0}C	1.101
- Density (ips / ga), 25 ^{0}C	9.173
- Viscosity, cps, 25 ^{0}C	14.500
- Solid %	60
- pH @ 15% solids	10.11

Polyvinyl acetate butyl acrylate emulsion (50% active material w/w) (PVAc BuA)

Polyvinyl acetate butyl acrylate emulsion (PVAc BuA) 50% active material w/w was prepared in the Polymers and Pigments Dept., NRC by emulsion polymerization of vinyl acetate and butyl acrelate. Polymerization conditions were: a) polymerization was carried out under nitrogen atmosphere, *i.e.* in the absence of air, b) initiator used was the redox pair initiator system, *i.e.* sodium bisulphite ($NaHSO_3$) and potassium persulphite ($K_2S_2O_8$) at the ratio of 1: 2.5. Initiator: monomer (w/w) was 0.5%c) emulsifying agent was 0.5% polyvinyl alcohol having boiling point of 120°C and Mol. wt. 700000 and d) temperature used and time of polymerization were 60°C and 8 hr with continuous stirring, respectively (El-Hady and Abd El-Hady, 1999).

3. Modified Bit. with PVAc BuA (50% active material w/w)

Five different polymerized bitumen emulsions were prepared as follows: The emulsified polymer PVAc BuA emulsion (50% active material) was added to the emulsified bitumen (Bit. 50% active material) just after the emulsification of bitumen, taking into consideration that bitumen polymer ratios were 5:1, 4:1, 3:1, 2:1 and 1:1. Stirring was continued until the emulsions became completely homogeneous (Sitz *et al.*, 1991).

Soil treatments

Soils were brought to an initial water content of 3-5% for the sandy loam soil and of 5 to 10% for the clay loam soil and then left two hours to reach equilibrium. Two application rates of examined emulsions were chosen. *i.e.* 0.5% and 1.0% active material (w/w). Water diluted emulsions were sprayed on the moistened soil with a commercial paint sprayer and mixed with a small rake. The final water content in treated soils was 6 to 8% and 15 to 20% for sandy loam soil and clay loam soil, respectively. Treated soils were allowed to be air-dried before being passed through a 8 mm sieve (El-Hady, 1979 and El-Hady &Tayel, 1981).

Extraction of heavy metals

Sequential fractionation of Cu, Pb, Cd, Co and Ni in the soils was carried out according to the method proposed by Mclaren and Crawford (1973), taking into consideration the modifications made by other workers (El-Sokkary, 1979 and Aboulroos *et al*.,1991). The method consists of successive extraction of the soil with different extractants. The reagents, extraction times and solution: solids ratios were as follows: a) 0.05 M $CaCl_2$, 24 hr and 10 :1 to remove soluble plus exchangeable heavy metals; b) 2.5 percent acetic acid (HAc), 24 hr and 10:1 to remove heavy metals weakly adsorbed on inorganic sites; c) 0.1 M sodium pyrophosphate ($Na_4P_2O_7$), pH 10,16 hr. 100:1 to remove heavy metals complexed with organic matter, and d) acid oxalate solution (0.1 M oxalic acid and 0.175 M ammonium oxalate, pH 3.25), 2.5 hr 50:1 to remove occluded heavy metals with secondary minerals.

Determination of heavy metals

The extracted heavy metals (Cu, Pb , Cd, Co and Ni) were determined using an Atomic Absorption Spectro-photometer IL-157 (Cottenie *et al.*, 1982).

Results and Discussion

Data presented in Table 4 shows that the concentration of extractable heavy metals in untreated soils is very high, indicating contamination. For the El-Gabal El-Asfar sandy loam soil, the sum of the four fractions amounted to 118.2 ppm for cupper, 169.6 ppm for lead, 2.14 ppm for cadmium, 38.8 ppm for nickel and 22.3 ppm for cobalt. Relevant values for the Mustorod clay loam contaminated soil were 52.4, 55.6, 2.08, 13.23 and 15.45 ppm for the aforementioned heavy metals, respectively. The data show also that the water soluble + exchangeable fraction ($CaCl_2$ extractable) in both soils represents only a small percentage of the total content being traces for Cu, Pb and Cd and in the range of 2 to 15% of the sum of the four fractions for the other metals. These low percentages indicate that heavy metals applied to the soils from either sewage sludge or industrial wastes were strongly sorbed in non-exchangeable form. In most cases, the relative abundance of the various fractions of heavy metals followed the order:

a) Sandy loam soil + sewage effluent for 80 years: organically complexed > occluded > adsorbed > exchangeable +soluble.

b) Clay loam soil + water contaminated with industrial wastes: adsorbed> occluded > organically complexed > exchangeable + soluble. This may be due to the high content of organic matter (7.1%) accumulated year by year in the sandy loam soil and of clay content (38.5%) in the clay loam soil.

TABLE 4. Levels of the various extractable fractions of heavy metals in untreated contaminated soils.

Metal	Sandy loam soil Extractable fraction (ppm)				Clay loam soil Extractable fraction (ppm)			
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Cu	0.5	22.4	66.7	28.6	n.d.	30.6	4.2	17.6
Pb	n.d.	25.0	118.0	26.6	n.d.	36.8	8.6	10.2
Cd	o.1	0.66	0.90	0.48	0.12	0.70	0.72	0.54
Ni	3.o	6.8	12.4	16.6	2.05	5.33	2.70	3.15
Co	0.4	1.0	18.0	2.9	2.25	6.35	3.20	3.65

Fractions	Extractant	Solution:solid ratio	Extraction time
(1) Soluble+ exchangeable	$CaCl_2$ 0.05M	10 : 1	24h
(2) Weakly adsorbed	Acitic acid 2.5%	10: 1	24h
(3) Organically bound	Na pyrophosphate 0.1M($Na_4P_2O_7$) pH 10	100:1	16h
(4) Occluded	NH_4 oxalate 0.175M +oxalic acid 0.1M pH 3.25	50:1	2.5h

Application of bitumen (Bit.) reduced the concentration of different extractable forms of heavy metals and firther decreased it with increasing its application rates (Table 5 and Fig. 1-5). In this respect, such decrease in released heavy metals from El-Gabal El-Asfar sandy loam soil treated with Bit. ranged between 19.7 and 24.2% with an average of 22.2 ± 1.95% for the lower application rate *i.e.* 0.5% (active material w/w) and between 29.3 and 42.5% with an average of 33.8 ± 5.5% for the higher ones (1% active material w/w). Relevant values for Mustorod clay loam soil were between 12.2 and 25.9 % with an average of 18.8 ± 5.8 and between 22.9 and 42.1% with an average of 35.0±8.1 %, respectively.

TABLE 5. Reduction in extracted heavy metals (%) from contaminated soils treated with bitumen emulsion; PVAcBUA emulsion and bitumen emulsions modified with the polymer at different ratios of bitumen: polymer.

Soil type	Treatment No.	Examined material Bit.:PVAcBuA	Cu		Pb		Cd		Co		Ni		Average	
			Application rate (active material %w/w)											
			0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%
Sandy loam soil	T1	1:0	20.7	29.3	22.6	29.3	23.8	42.5	19.7	32.3	24.2	35.8	22.2±1.95	33.84±5.53
	T2	5:1	25.3	33.2	26.1	32.5	26.6	43.9	22.9	35.4	25.8	36.6	25.34±1.44	36.32±4.55
	T3	4:1	30.0	37.1	28.5	35.8	29.9	47.7	26.9	39.5	28.1	39.7	28.68±1.30	39.96±4.63
	T4	3:1	34.4	40.1	32.4	39.2	31.3	50.5	30.0	42.6	32.5	43.6	32.12±1.63	43.2±4.46
	T5	2:1	37.9	43.1	34.4	41.4	33.2	52.8	30.9	45.7	35.1	48.2	34.3±2.57	46.24±4.48
	T6	1:1	40.7	45.5	36.7	43.9	36.4	55.6	33.2	48.9	39.4	51.8	37.28±2.91	49.14±4.73
	T7	0:1	43.4	48.3	37.9	45.7	38.3	58.9	34.5	50.7	43.3	55.9	39.48±3.83	51.9±5.43
Clay loam soil	T1	1:0	12.2	22.9	22.7	38.5	18.3	40.9	25.9	42.1	13.6	30.6	18.54±5.83	35.0±8.11
	T2	5:1	14.6	25.2	29.1	41.2	24.0	44.2	28.0	44.0	17.1	34.5	22.56±6.47	37.82±8.07
	T3	4:1	17.6	26.5	32.2	43.7	26.9	47.1	30.7	46.1	20.1	37.9	25.5±6.43	40.26±8.48
	T4	3:1	20.2	28.1	34.2	46.6	29.8	47.1	33.3	48.8	20.7	40.5	27.64±6.77	42.22±8.49
	T5	2:1	22.5	30.2	35.6	47.8	33.7	51.9	36.6	51.8	25.9	42.5	30.86±6.28	44.84±9.04
	T6	1:1	24.4	33.2	36.2	49.1	38.5	54.8	40.3	53.7	29.0	44.1	33.68±6.73	46.98±8.79
	T7	0:1	26.9	37.4	37.1	51.6	42.3	57.7	43.6	54.6	32.6	46.4	36.5±6.92	49.54±7.96

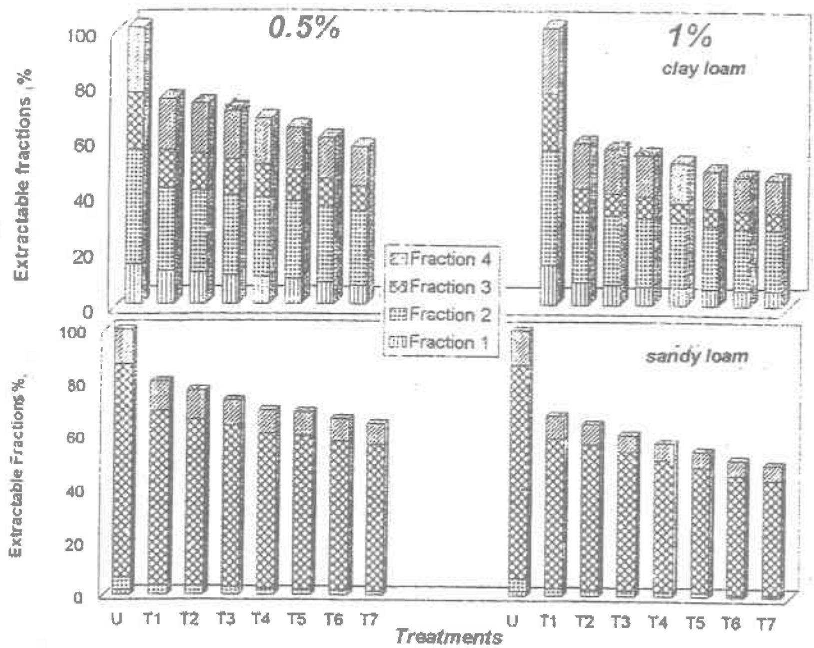

Fig. 1. Extractable fractions of Cobalt (Co) in ammended contaminated soils in relation to untreated soil.

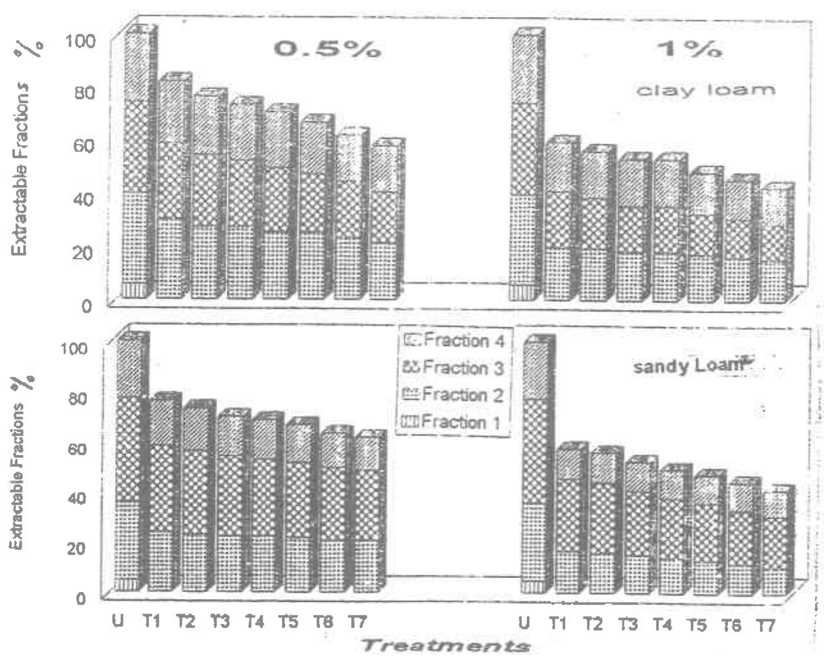

Fig. 2. Extractable fractions of Cadmium (Cd) in ammended contaminated soils in relation to untreated soil.

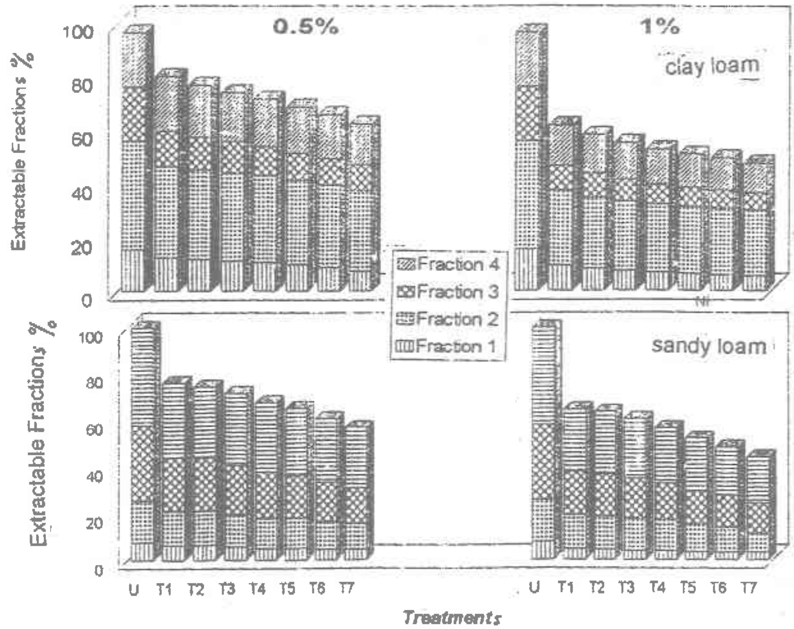

Fig. 3. Extractable fractions of Nickel (Ni) from ammended contaminated soils in relation to untreated soil.

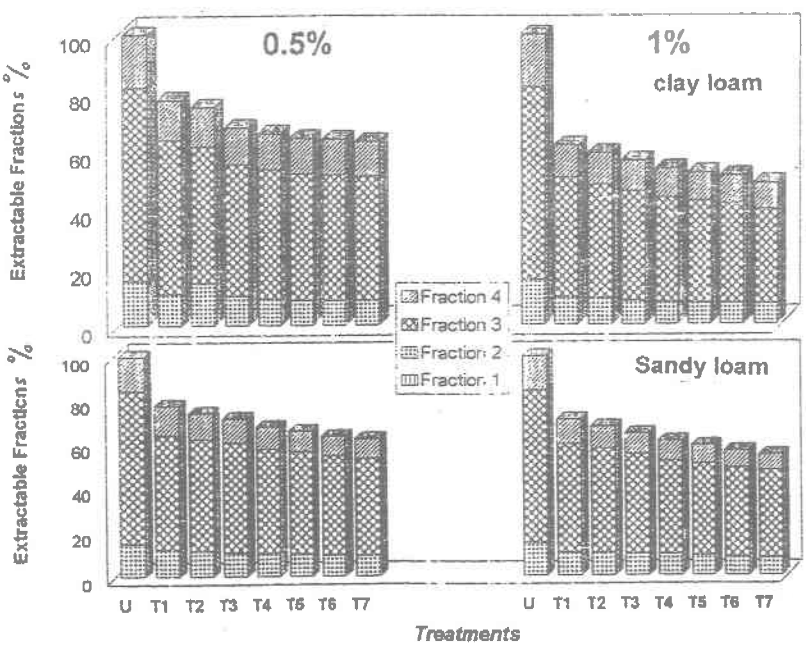

Fig. 4. Extractable fractions of Lead (Pb) from ammended contaminated soils in relation to untreated soil.

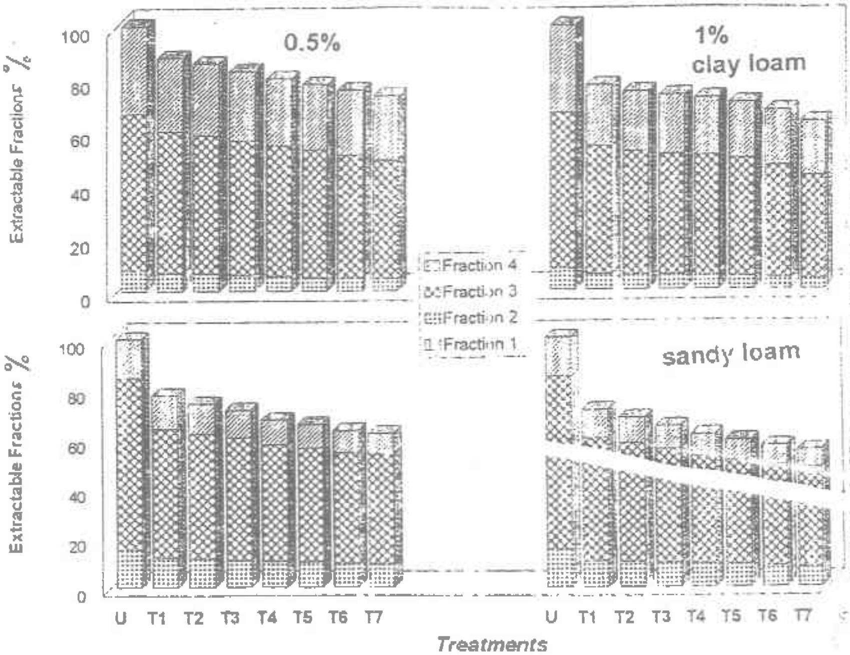

Fig. 5. Extractable fractions of Copper (Cu) from ammended contaminated soils in relation to untreated soil.

On the other hand, PVAc BuA emulsion was more efficient in reducing the release of heavy metals from contaminated soils than that of Bit. having similar concentrations. Decrease in released heavy metals ranged between 34.5 and 43.4% or between 45.7 and 58.9% with an average of 39.5 ± 3.8 or 51.9 ± 5.4% by treating the sandy loam soil with the two examined rates 0.5% or 1% (active material w/w). Corresponding averages of reduction in extractable heavy metals for the clay loam soil were 36.5 ± 6.9% or 49.5 ± 8.0%.

Treating the soils with polymerized bitumen emulsions (T2; T3; T4; T5 & T6 treatments) gradually decreased the release of the studied heavy metals being lower with emulsions having higher percentages of the polymer. More decrease in the amount of extractable heavy metals were obtained when doubling the application rate of the emulsion to be 1% (active material w/w) (Table 5 and Fig.1-5).

The multiple regression analysis (Snedecor and Cochran, 1980) was used to describe the relation between the components of prepared emulsions, *i.e.* percentage of PVAcBuA in the Bit.-PVAc BuA emulsion (Xl) and the application rate of the emulsion (X2) and percent of reduction in extracted heavy metals from contaminated soil treated with examined emulsions (Y). The regression equations and the multiple correlation coefficients are given in Table 6. It is worthy to mention that all the interactions are highly significant.

TABLE 6. Multiple correlation coefficients and regression equations for the relations between the components of examined emulsions and their application rates and the reduction in extracted heavy metals from treated soils.

Soil type	Heavy metal	Regression equation	Multiple correlation coefficient
Al-Gabal Al-Asfar Sandy loam soil	Cu	Y =19.86 + 0.21 X1+ 12.63 X2	0.889**
	Pb	Y =18.80 + 0.15 X1+ 14.09 X2	0.900**
	Cd	Y =7.03 + 0.16 X1+ 37.83 X2	0.980**
	Co	Y = 8.84 + 0.16 X1+ 27.71 X2	0.938**
	Ni	Y =13.41 + 0.21 X1+ 23.77 X2	0.954**
	Sum	Y =11.43 + 0.18 X1+ 25.09 X2	0.837**
Mustorod Clay loam soil	Cu	Y = 5.36 + 0.15 X1+ 18.60 X2	0.959**
	Pb	Y =15.16 + 0.12 X1+ 26.11 X2	0.943**
	Cd	Y = 4.85 + 0.20 X1+ 37.20 X2	0.964**
	Co	Y =13.92 + 0.16 X1+ 29.37 X2	0.959**
	Ni	Y = 0.01 + 0.17 X1+ 33.57 X2	0.964**
	Sum	Y = 7.86 + 0.15 X1+ 28.97 X2	0.775**

X1: Percentage of PVAcBuA in the prepared emulsion.

X2: Application rate of the emulsion.

Y : Percentage of reduction in extracted heavy metal from treated soil

** : Significant at 1% level.

Reduction in the extractability of heavy metals from contaminated soils treated with bitumen emulsions and /or polymers could be discussed on the basis of the action of these materials as binding agents. Besides, the possible mechanisms to form stable structural units and, under the conditions of our study, the low extractability of elements obtained after treating contaminated soils with bitumen emulsions, may vary due to one or more of the following reasons: a) the adhesive properties of the used emulsion and its distribution on or into soil structural units. This differs by the type of the emulsion, its viscosity, and the type and the amount of the used modifier (polymer), and the application rate of the emulsion from one side and the content of the other binding materials in the soil, *i.e.*, fine soil fractions such as clay, organic matter, amorphous inorganic materials and $CaCO_3$, polyvalent cations including heavy metals themselves etc. from the other side, and b) the coating effect of applied hydrophobic bitumen emulsions (coating thickness and hardness) which captures the different forms of heavy metals (soluble, exchangeable, chelated or precipitated) inside the structural units and at the same time gives the structural units water repellent characteristics (El-Hady, 1979 and El-Hady & Tayel, 1981). This in turn affects the contact between heavy metals in the soil and water (or other extractants) or the diffusion of water through soil structural units (El-Hady *et al.*, 1984). There can be other effects which still be examined, such as the activation of sand neutral surfaces due to the precipitation of heavy metals on the quartz grain surfaces, thereby improving their electrostatic interaction with used polymers (El-Hady *et al.*, 1990).

Taking into consideration that the preparation costs of one ton of Bit. emulsion, PVAcBuA emulsion and modified Bit. emulsion with different ratios of the polymer (50% active material for each) are about 500, 3000 and 920 to 1750 L.E, in sequence (prices of 2002). Bitumen emulsion (even if its application rate is doubled) or the lower application rate of bitumen modified polymer at the ratios of 5:1 or 4:1 seem to be preferable and more economic than using PVAcBuA, separately. Preparation of more effective and cheaper polymers to be used as modifiers for bitumen emulsions are of great importance.

References

Abdel-Sabour, M.F., Ismail, A.S. and Aboul Naga, H. (1996) Environmental impact of Cairo sewage effluent on Ll-Gabal El-Asfar farm . *Egypt. J. Soil Sci.* **36** (1-4), 329.

Aboulros, S.A., Holah, Sh. Sh., El-Kherbawy, M.I. and Badawy,E.H. (1991) Fractions of some heavy metals in soils irrigated with sewage effluent for different years. *Egypt. J. Soil Sci.* **31** (1), 43.

Cottenie, A , Verloo, M., Kiekens, L.,Velghe, G., G. and Camergynck, R. (1982) "*Chemical Analysis of Plants and Soils*" Lab. Anal Agroch., Fac. Agric ., State Univ. Gent, Belgium.

El-Hady, O.A. (1979) Effect of soil conditioners on physical properties and nutritional status of soils. *Ph.D. Thesis*, Fac. Agric ., Al-Azhar Univ., Cairo, Egypt.

El-Hady, O.A. and Abd El- Hady, B.M. (1999) Effect of some coating materials on the pattern of heavy metals released from contaminated soils. 5th *Arab.Int. Conf. On "Polymer Science and Technology"*, Egypt, Soc. Polymer Sci. and Techn.(ESPST) Luxor, Aswan, Sep.18-22,1999.

El-Hady, O.A., Ghaly, N.F. and Zaghloul, A.M. (2000a) Polymers versus bitumen emulsions for reducing the extractability of heavy metals from contaminated soils. *Egypt. Soil Sci. Soc. Golden Jubilee Congress*, Oct. 23-25, 2000 Cairo, Egypt.

El-Hady, O.A., Lotfy, A.A. and Abd El-Hady, B.M. (1990) The interaction between polyacrylamide as a conditioner for sandy soils and some plant nutrients. II: Effect on the extractability of nutrients. *Egypt. J. Soil Sci.* **30**(4) 545.

El-Hady, O.A., Moustafa, A.B., Lotfy, A.A. and Abd El-Hady, B.M. (1984) The interaction between polyacrylamide and some nutrients in sandy soils.*12th Egyptian Chemical Conference, Cairo 7-10 April*, 1984.

El-Hady, O.A., Saleh, A.L. and Ghaly, N.F. (1997) Pollution control of environment using some locally prepared bitumen emulsions. II. Minimizing the hazardous effects of heavy metals in contaminated soils." *Int. Conf. Petroleum & Environment EPRI,V.E.A & J.A.A. 16-18 Dec.1997*, Cairo, Egypt.

El-Hady, O.A., Saleh, A.L. and Ghaly, N.F. (2000b) Minimizing the hazardous effects of heavy metals in contaminated soils using some locally prepared bitumen emulsions. *Egypt. J. Soil Sci.* **40** (1-2), 223.

El-Hady, O.A. and Tayel, M.Y. (1981) Optimizing process of soil conditioning. *Egypt J. Soil Sci. Special Issue "Soil Conditioners"*, 89.

El-Sokkary I.H. (1979) The chemical fractionation of soil zinc and its specific and total adsorption by Egyptian soils. *Plant & Soils*, **53**, 117.

El–Sokkary, I.H. (1996) "Synopsis on contamination of the agricultural ecosystem by trace elements: An emerging environmental problem. *Egypt. J. Soil Sci.* **36** (1-4), 1.

El-Sokkary, I.H. and Sharaf, A.I. (1996) "Enrichment of soils and plants irrigated by wastewater by zinc and cadmium". *Egypt. J. Soil Sci.* **36** (1-4), 219.

Ghaly, N.F. (1998) Studies on: Pollution control of environment using some petroleum compounds. *Ph D. Thesis*, Environmental Studies and Research Inst.. Ain Shams Univ., Cairo, Egypt.

Header, F.I.E. (1987) Toxicity hazard of some heavy metals to plants grown in polluted soils. *Ph. D. Thesis*, Fac. Agric., Ain Shams Univ., Cairo, Egypt.

Mclaren, R.G. and Crawford, D.V. (1973) Studies on soil copper. 1. The fractionation of copper in soils. *J. Soil Sci.* **24**, 172.

Sitz, G.E., Marysville, Roger, K. Chatterjee, Columbus (1991) Process for the production of polymer modified asphalts and asphalt emulsions. *M.S. Patent*, P. No. 5, 109, 610.

Snedecor, G.W and Cochran, W.G. (1980) *"Statistical Methods"*, 7^{th} ed. Iowa State Univ. Press., Ames., Iowa., USA.

(*Received* 12/2001)

مستحلبات بتيومينية معدلة بالبوليمرات لعلاج الأراضي الملوثة بالمعادن الثقيلة

عمر عبد العزيز الهادي* ، نجوى فهيم غالي** وعلاء الدين محمد زغلول*
*المركز القومي للبحوث بالدقي **ومعهد بحوث البترول بمدينة نصر -القاهرة – مصر.

يمكن معاملة الأراضي الملوثة بالمعادن الثقيلة بمستحلبات البتيومين أو بالبوليمرات الذائبة في الماء أو المستحلبة فيه من خفض انسياب هذه المعادن إلى محلول التربة ومنه إلى النباتات المنزرعة.

اختير لهذه الدراسة نوعان من الأراضي الملوثة بالفلزات الثقيلة الأولى أرض رملية طميية من مزرعة الجبل الأصفر والتي أضيف إليها مخلفات الصرف الصحي عند بداية زراعتها وتروى بمياه الصرف الصحي منذ عام ١٩١١. أما الثانية فهي أرض طينية طميية قريبة من المنطقة الصناعية بمسطرد والملوثة بمخلفات الصناعات الكيماوية بالإضافة إلى مياه الري الملوثة والتي تؤثر تأثيراً عكسيا على الإنتاج الزراعي هذه المناطق.

عوملت الأراضي بمعدلين ٠.٥ و١٪ (مادة فعالة وزنا) من أي من:
١- مستحلب بتيوميني (٥٠٪ مادة فعالة وزنا).
٢-مستحلب البولي فينيل أسيتات بيوتيل أكريلات (٥٠٪ مادة فعالة وزنا).
٣- مخاليط كلا من المستحلبين سالفي الذكر بنسب ١:١، ١:٢، ١:٣، ١:٤، ١:٥ على الترتيب.
٤- قدرت الصور التي توجد عليها الفلزات الثقيلة (النحاس الرصاص-الكالسيوم -الكوبالت -النيكل) في الأرض غير المعاملة والمعاملة باستخدام طريقة الاستخلاص المتتابع كالتالي:

الجزء المستخلص	المادة المستخلصة وتركيزها	زمن الاستخلاص	نسبة المادة المستخلصة للتربة
١-الجزء الذائب المتبادل	كلوريد الكالسيوم ٠.٥ مولر	٢٤ ساعة	١:١٠
٢-الجزء المدمص على مواقع التبادل غير العضوية	حمض الخليك ٢.٥٪	٢٤ ساعة	١:١٠
٣- الجزء المرتبط في معقدات عضوية	بيرو فوسفات الصوديوم ٠.١ مولر	١٦ ساعة	١:١٠٠
٤- الجزء المغطى بالأكاسيد الحرة	حمض اكساليك ٠.١ مولر + اكسالات أمونيوم ٠.١٧٥ مولر (PH= ٣.٢٥)	٢.٥ ساعة	١:٥٠

مع الأخذ فى الاعتبار أن الفرق بين مجموع الصور المستخلصة والمحتوى الكلى للفلزات الثقيلة هو الجزء من هذه الفلزات المرتبط بالمعادن الأولية فى التربة.

تشير النتائج المتحصل عليها إلى الآتى:

١- يلاحظ ارتفاع تركيز الفلزات الثقيلة المستخلصة من كلا النوعين من الأراضى دليل تلوثها.

٢- أدت معاملة كلا من النوعين من الأراضى بالمستحلبات المختبرة إلى انخفاض تركيز الفلزات الثقيلة المستخلصة بصورها المختلفة ويزداد هذا الانخفاض بزيادة معدل إضافة المستحلب.

٣- تراوح الانخفاض فى تركيز الفلزات الثقيلة المستخلصة بين ٢٠-٢٥٪، ٣٥-٤٥٪، ٢٥-٤٠٪ فى حالة الأرض الرملية الطميية وبين ١٥-٢٥٪، ٢٥-٤٠٪، ٢٠-٤٠٪ من الأرض الطينية الطميية بمعاملة التربة بمعدل إضافة ٠.٥٪ بأى من المستحلب البتيومين أو مستحلب البوليمر أو مخاليطهما على التوالى. وقد ازداد هذا الانخفاض ليصبح ٣٠-٤٠٪، ٤٥-٦٠٪، ٣٥-٥٥٪ بالنسبة للتربة الأولى و٢٥-٣٥٪، ٤٠-٥٥٪، ٣٥-٥٠٪ بالنسبة للتربة الثانية عند معاملة التربة بالثلاثة أنواع من المستحلبات سالفة الذكر على الترتيب بمعدل إضافة ١٪ آخذين فى الاعتبار أنه كلما زادت نسبة مستحلب البولى فينايل أسيتات فى الخليط كلما قلت نسبة الفلزات الثقيلة المستخلصة.

آخذين فى الاعتبار أن تكلفة تحضير الطن (٥٠٪ مادة فعالة وزنا) من مستحلبات البتيومين والبولى فينيل اسيتات ومخاليطها هى ٥٠٠، ٣٠٠٠، ٩٢٠-١٧٥٠ جنيها مصريا على التوالى، لذا فان استخدام المستحلب البتيومينى حتى لو ضوعفت معدل إضافته أو معدل الإضافة المنخفض من المستحلب البتيومين المحسن بالبوليمر بنسبة ٥ أو ٤ بتيومين: ١ بوليمر يبدو مناسبا وأقل تكلفة من استخدام مستحلب البوليمر بمفرده.

تحضير بوليمرات أكثر فاعلية وأقل سعرا لاستخدامها كمحسنات لخواص المستحلبات البتيومينية يعد من الأهمية.