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SORPTION AND DESORPTION STUDIES OF METALLIC ZINC ON AN ALLUVIAL SOIL

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ABSTRACT

The sorption of metallic zinc from the pH-adjusted aqueous solution at varying initial concentrations onto a clay soil through batch equilibrium experiments has been studied. The pH of the initial concentrations ranging between 50 mg/L to 250 mg/L has been varied from 3 to 7. The sorption data fitted very well with both Langmuir and Freundlich isotherm models and Freundlich model gave higher correlation coefficients. The maximum sorption of metallic zinc occurred at pH=6. The pseudo-second order kinetics model was most agreeable with the experimental sorption data, whereas the pseudo-first order model was found to be insufficient. A nonionic surfactant was tested for its desorption potential and was found to be fairly effective at 2% concentration with removal of more than 60% sorbed Zinc.

Key words: Sorption, isotherms, desorption, zinc

INTRODUCTION

Background concentrations of heavy metals in soils, which depend on the local geology, may be supplemented to different degrees by anthropogenic inputs. Many industrial processes and operations generate stack emissions, solid wastes and sludges that contain heavy metals, which enter atmosphere and also find their way into aquatic and terrestrial ecosystems. Being non-biodegradable, heavy metals are environmentally persistent and may have long-term effects on the crop, animals, human health, soil properties, and quality of the whole environment. Sorption of metals from aqueous solution onto solid particles is an important process that influences their accumulation and transport in the environment. In the past, interaction of heavy metals with soil inorganic particles has been extensively studied employing macroscopic, kinetic or equilibrium approaches, and many attempts have been made to model adsorption of metals on mineral surfaces. These studies have revealed that various factors such as presence or absence of other ions, pH, temperature, and residence time can affect the sorption/desorption of heavy metals from soils, soil clay fractions, and other soil components (Eick *et al.*, 1999; Martinez *et al.*, 1999; Atanassova and Okazaki, 1997; Atanassova, 1995; Backes *et al.*, 1995; Harter, 1992).The effective remediation of contaminated soils needs a basic and thorough understanding of the mechanism(s) of heavy metal interaction with soil media particles, and factors that affect their retention and/or release from these particles.

Zinc is one of the most abundantly occurring elements in the earth's crust and an essential micronutrient for all living things. Zn usually occurs in +2 oxidation state and forms complexes with inorganic and organic ligands, which affect its adsorption reactions with soil surface. Zn is readily adsorbed by clay minerals, carbonates, or hydrous oxides. A large fraction of the total Zn in polluted soils and sediments becomes associated with Fe and Mn oxides (Hickey and Kittrick, 1984; Kuo *et al.*, 1983). Precipitation is not a major mechanism of retention of Zn in soils as Zn compounds are highly soluble and therefore very mobile in aquatic systems. Zn adsorption on soils

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mobile in aquatic systems. Zn adsorption on soils increases with pH, as is the case with all other cationic metals. Zn has many commercial and industrial uses. The primary industrial use of Zn is as a corrosion resistant coating for Fe and steel. It is used in dry cell batteries, mixed with other metals to form alloys and in the manufacture of paints, ceramics, rubber, wood preservatives, dyes and fertilisers, dietary foods, drugs and other medicinal preparations. Exposure of Zn in large amounts is extremely toxic to living organisms. In humans, it can cause a range of serious ailments including anemia, damage to pancreas, lungs, metal fume fever, decreased immune functions, growth retardation, birth defects and cancer on sustained exposure.

Surfactant washing is an ex-situ process in which the contaminated soil is first excavated, placed as heaps on plastic liners and treated with washing solutions such as a surfactant; batch washing and/or continuous flow washing techniques are also employed. In-situ flushing, on the other hand, involves the delivery of washing solution to the contaminated medium by irrigation and/or injection wells; the contaminant-laden wash solution is simultaneously pumped up for treatment by recovery wells. Surface-active agents, or surfactants, are the chemical compounds that have the potential to alter the properties of fluid interfaces. Surfactants work as a remediation tool by lowering the contaminant-water interfacial tension and thereby causing a degree of contaminant mobility, and enhanced contaminant solubility in water. The surfactant when added in sufficient quantity to an aqueous solution forms micelles. The threshold concentration at which micelles begin to form is known as critical micelle concentration (CMC). The phenomenon known as micellar solubilisation (Abriola *et al*., 1995) is responsible for increasing the solubility of hydrophobic compounds up to 100-1000 times.

The objective of the present work was to study the sorption of Zn by a clay soil under varying pH conditions at different initial concentrations through batch equilibrium process. Various analytical techniques, including Langmuir and Freundlich sorption isotherms were used to evaluate the sorption data. The pseudo-first and second-order models were tested to investigate the sorption kinetics. The potential of an anionic surfactant (sodiumlauryl sulphate (SDS) to desorb Zn from the contaminated matrix was also investigated.

MATERIALS AND METHODS

The soil sample for the experimental work was collected from non-vegetation depth through an open excavation. Standard stock solutions of Zn metal (analytical reagent-grade) in deionised water were prepared from which 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L concentrations were used for sorption experiments. The sorption experiments were performed in a rotary shaker at 15-20 rpm using 300 mL stop-corked bottles containing 250 mL of a Zn solution and 10 g/L of soil for different time intervals ranging from 15 minutes to 16 hours. The initial pH of the sorbate (Zn solution) was adjusted for each set of experiment by adding 0.1M HCL or 0.1M NaOH. The partly desorbed sorbate corresponding to each time interval was centrifuged for at least 5 minutes at 500 rpm and then vacuum-filtered to separate out the soil particles. The filtrate was used to determine the residual Zn using atomic absorption spectrophotometer (Perkin Elmer 3100).

For desorption experiments, the contaminated soil samples corresponding to sorbate concentration of 100 mg/L and pH=6 were used. The surfactant concentrations of 1%, 2%, and 3% were employed, using the same procedure as for the sorption experiments. The amount of metal sorbed and desorbed by the soil was calculated from the initial metal concentration of the solution and metal content of the supernatant after the specified period of shaking using the following equation:

$$Q=(C_o-C_e)*\frac{V}{M} \qquad (1)$$

Where Q, is the metal uptake or sorption/desorption (mg/g) for the specified period, C_o and C_e are the initial and equilibrium metal concentrations in the solution (mg/L), respectively. V and M, respectively are the volume of solution (250 mL) and mass of sorbent (10 g/L).

The soil mineralogical composition was determined from X-ray diffraction (XRD) patterns measured in a Rigaku DMAX 2000/JADE 6.0 X-ray diffractometer. The surface morphology of the soil samples were investigated by scanning electron microscopy (SEM) using a JOEL Microscope.

RESULTS

Fig. 1 and Fig. 2 represent the SEM and XRD of virgin soil. The soil properties are presented in Table 1. Tables 2 and 3 respectively present the summaries of batch adsorption test results to establish Langmuir and Freundlich adsorption isotherms. Langmuir and Freundlich constants at different sorbate pH are given in Table 4, whereas in Table 5 kinetic parameters for different initial sorbate concentrations are presented. Table 6 shows desorption data corresponding to contaminated soil samples at initial sorbate concentration of 100 mg/L and at pH=6.

The experimental results of sorption of Zn at various initial concentrations and for pH=6.0 are shown in Fig. 3.

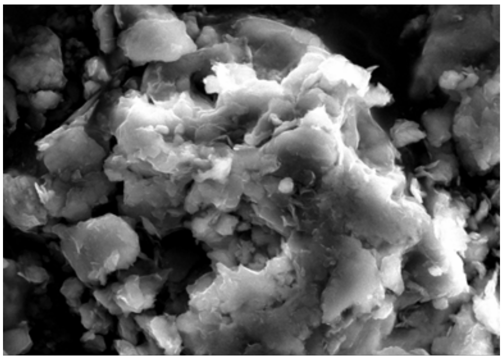

Fig. 1: Scanning electron microscope image of virgin Soil

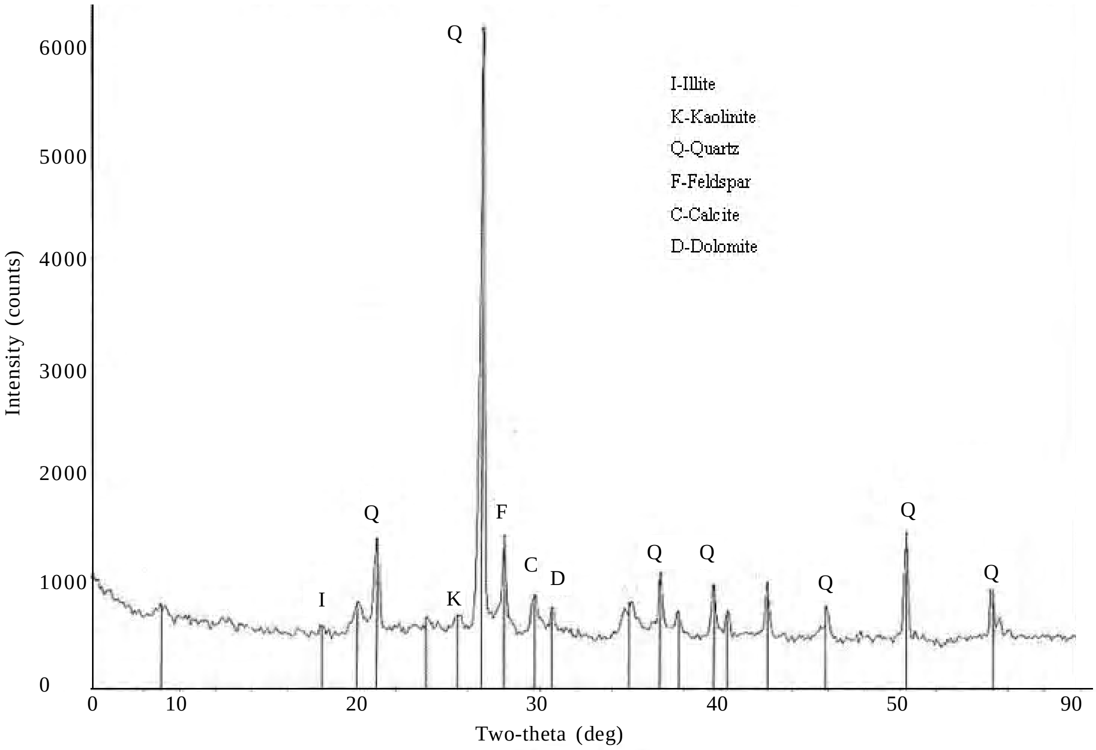

Fig. 2: X-ray Diffractogram of a virgin soil

Table 1: Composition and properties of soil used (As per IS 2720)

Property	Value
Particle Size Distribution	
Sand (%)	3.3
Silt (%)	70.0
Clay (%)	26.7
Atterberg Limits	
Liquid Limit (%)	60.5
Plastic Limit (%)	27.4
Shrinkage Limit (%)	11.8
Plasticity Index (%)	33.1
Specific gravity	2.64
Maximum Dry Unit Weight (kN/m^3)	14.7
Optimum Moisture Content (%)	20.5
Hydraulic Conductivity (m/sec)	4.46×10^{-8}
Specific Surface Area (m^2/g)	0.18
Cat ion exchange capacity (USEPA) (meq/100 g)	17.38
pH	7.80
Organic Content (%)	2.25
Soil classification	CH
Compression Index (C_c)	0.325
Coefficient of Consolidation, C_v (m^2/s)	1.443×10^{-8}
Unconfined Compressive Strength (kPa)	137.0

Table 2: Langmuir parameters at different pH conditions

System pH	Parameters	Initial sorbate concentration (mg/L)				
		50	100	150	200	250
3	*C_e	14.32	36.21	58.00	86.91	128.45
	**Q_e	3.57	6.38	9.20	11.31	12.16
	C_e/Q_e	4.00	5.67	6.30	7.68	10.56
4	*C_e	8.52	25.30	42.90	68.38	89.15
	**Q_e	4.15	7.47	10.71	13.16	16.08
	C_e/Q_e	2.05	3.39	4.00	5.20	5.54
5	*C_e	4.93	17.73	29.47	46.53	64.66
	**Q_e	4.51	8.23	12.05	15.35	18.53
	C_e/Q_e	1.09	2.15	2.44	3.03	3.49
6	C_e	4.74	17.06	28.37	44.78	62.24
	Q_e	4.53	8.29	12.16	15.52	18.78
	C_e/Q_e	1.05	2.06	2.33	2.88	3.31
7	*C_e	4.97	17.91	29.79	47.05	65.34
	**Q_e	4.50	8.21	12.02	15.30	18.47
	C_e/Q_e	1.10	2.18	2.45	3.07	3.54

* mg/L ** mg/g

Table 3: Freundlich parameters at different pH conditions

System pH	Parameters	Initial sorbate concentration				
		50 (mg/L)	100 (mg/L)	150 (mg/L)	200 (mg/L)	250 (mg/L)
3.0	ln C_e	2.66	3.59	4.06	.46	4.85
	ln Q_e	1.27	1.85	2.22	2.42	2.50
4.0	ln C_e	2.14	3.23	3.76	4.22	4.49
	ln Q_e	1.42	2.01	2.37	2.58	2.78
5.0	ln C_e	1.59	2.87	3.38	3.84	4.17
	ln Q_e	1.51	2.11	2.49	2.73	2.92
6.0	ln C_e	1.56	2.84	3.34	3.80	4.13
	ln Q_e	1.51	2.11	2.50	2.74	2.93
7.0	ln C_e	1.60	2.88	3.39	3.85	4.18
	ln Q_e	1.50	2.10	2.49	2.73	2.92

Table 4: Langmuir and Freundlich constants at different sorbate-pH

pH	Langmuir parameters			Freundlich parameters		
	X_m (mg/g)	K	R^2	n	K_f	R^2
3.0	18.24	0.01665	0.98422	1.70	0.77	0.97897
4.0	23.49	0.02085	0.95414	1.74	1.20	0.99770
5.0	26.55	0.03113	0.93726	1.81	1.82	0.99397
6.0	27.20	0.03142	0.94012	1.79	1.83	0.99289
7.0	26.40	0.03111	0.93848	1.79	1.78	0.99333

Table 5: Kinetic parameters for the effect of initial sorbate concentration

Initial conc. (mg/L)	First order kinetics			Second order kinetics			
	K_1	Q_e	R^2	K_2	Q_e	h	R^2
50	0.01711	2.08	0.89114	0.02630	4.61	0.56	0.99990
100	0.01580	3.14	0.77373	0.01756	8.38	1.23	0.99986
150	0.01359	4.79	0.79176	0.01201	12.14	1.77	0.99988
200	0.01594	6.11	0.81173	0.00888	15.70	2.19	0.99978
250	0.01571	7.94	0.81503	0.00619	19.60	2.38	0.99976

Table 6: Desorption data at initial sorbate concentration 100 mg/L and pH=6

Surfactant Concentration	Agitation Time (min)						
	15	30	60	120	240	480	600
1%	14.78	18.41	25.72	36.59	39.22	40.29	40.31
2%	18.25	29.67	39.18	45.44	47.74	49.65	49.89
3%	20.56	35.42	42.08	46.16	49.13	50.69	51.37

DISCUSSION

Effect of initial sorbate concentration

Increasing the initial Zn concentration from 50 mg/L to 100 mg/L (Fig. 3) led to the amount sorbed by 83%; from 100 mg/L to 150 mg/L, the increase was 47%; from 150 mg/L to 200 mg/L an increase of 28% was seen; whereas from 200 mg/L to 250 mg/L, an increase of 21% was recorded. Thus with increasing metal concentration in solution a decreasing percent of sorption increase was observed. At lower concentrations, the ratio of amount of sorbate available and that of number of sorption sites was low; hence comparatively, a higher percent of adsorption resulted. With subsequently higher initial concentrations this ratio progressively increased due to number of sorption sites becoming fewer compared to the amount of sorbate available, and therefore a decreasing trend in percent sorption from a lower to a higher concentration was seen. Obviously the fractional sorption becomes progressively initial concentration dependent as the initial concentration is increased.

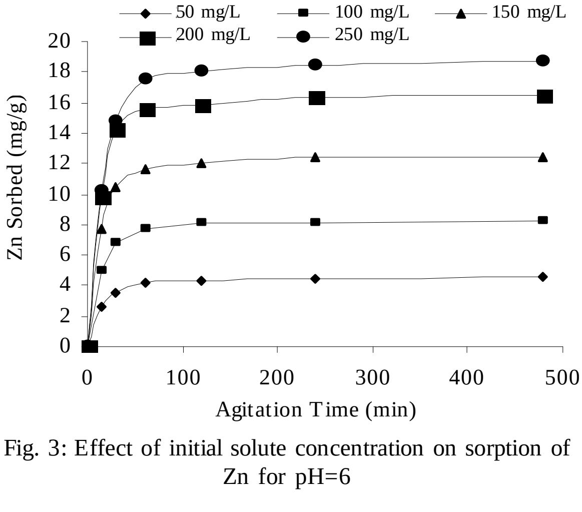

Fig. 3: Effect of initial solute concentration on sorption of Zn for pH=6

Effect of pH

The initial pH of the solution is a very important factor for metal sorption on soils. The pH, either directly or indirectly, affects several mechanisms of metal retention by soils. An important aspect of the effect of pH on metal mobility is the buffering capacity of soils for acidity. Many researchers have acknowledged that the adsorption of metals is directly proportional to the soil pH. The effect of pH on the sorption of Zn on soil is given in Fig. 4.

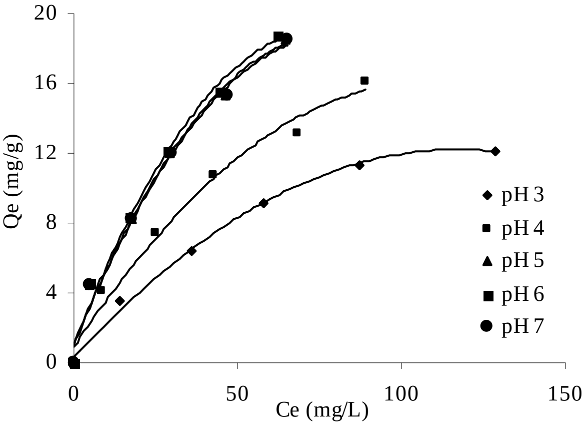

Fig. 4: Effect of pH on sorptive capacity of clay for Zn

The results show that the metal sorption for initial concentration of 250 mg/L increased from 27% at initial experimental pH of 3 to approximately 54% at the pH 6, however, it slightly decreased at higher pH of 7. Lesser metal uptake at low pH values indicates that the excess of protons compete for the same binding sites on the soil particle surfaces. Studies of Harter, 1983; McBride, 1977 and 1982; Cavallaro, 1980; Davis and Leckie, 1978; Farrah and Pickering, 1976a, b; McLaren and Crawford, 1973; James and Healey, 1972 etc. reveal that the pH dependence of adsorption reactions of cationic metals is attributed partly to the preferential adsorption of hydrolysed metal species to the free metal ion. The proportion of hydrolised metal species increases with pH. Work by McBride and Blasiak, 1979 showed increased retention of Zn with increasing pH. However, the solution retention of Zn increased at pH above 7. This phenomenon has also been observed in other studies (Kuo and Baker, 1980) and has been attributed to the solubilisation of organic complexing ligands, which effectively compete with the soil surfaces for the metal cation.

Langmuir and Freundlich models

The Langmuir sorption model was chosen for the estimation of maximum sorption by the sorbent. The Langmuir adsorption isotherm can be expressed as (Casey, 1997):

$$Q_e = \frac{X_m K C_e}{(1 + K C_e)} \qquad (2)$$

Where, Q_e is amount of metal sorbed at equilibrium per unit weight of the sorbent (mg/g), X_m, is the maximum sorption or metal uptake from solution (mg/g) and K, is the Langmuir equilibrium constant (L/mg). For fitting the experimental data the Langmuir equation can be linearised as follows:

$$\frac{C_e}{Q_e} = \frac{1}{X_m K} + \frac{C_e}{X_m} \qquad (3)$$

The Freundlich model is represented by the following equation (Casey, 1997):

$$Q = K_f C_e^{1/n} \qquad (4)$$

Where K_f (l/g) and n, are Freundlich constants. For fitting the experimental data, the Freundlich model can be linearised as follows:

$$\ln Q = \ln K_f + 1/n \ln C_e \qquad (5)$$

The Langmuir and Freundlich parameters were found through linearisation of experimental data, and are presented in Table 4. The linearised plots of Langmuir and Freundlich models are shown in Figs 5 and 6. The results reveal that the model parameters are largely dependent on the initial sorbate concentration values. Langmuir sorption model served to estimate the maximum metal adsorption values where they could not be reached in batch equilibrium experiments. Both the maximum metal adsorption, X_m and the Langmuir equilibrium constant, K increased with increasing pH values from 3 to 6 and slightly decreased at pH=7. The constant, K, represents the affinity between the sorbate and the sorbent, and indicates that the binding capacity peaks at pH value of 6. The Freundlich equilibrium constant, K_f, which also indicates the binding affinity between the sorbate and the sorbent, increased constantly with pH value up to 6.0 and was in agreement with the Langmuir constant, K. The Freundlich constant, n, was greater than unity for all pH values, indicating good adsorption of Zn at increasing pH values and initial sorbate concentrations. The regression coefficients, R^2, which were close to unity for both the Langmuir and Freundlich models (Freundlich model gave higher coefficients for all pH values) together with other parameters, confirmed that the adsorption of Zn follows Langmuir and Freundlich adsorption models.

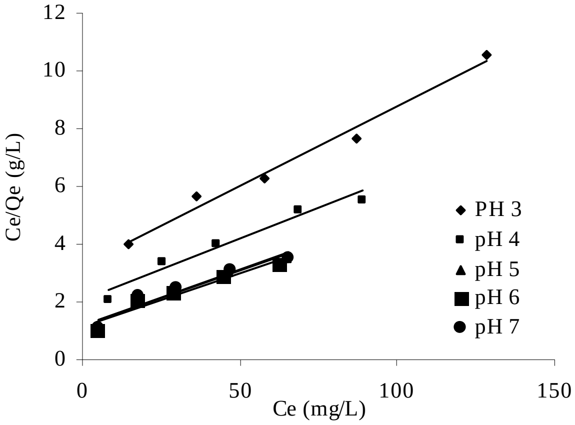

Fig. 5: Linearised Langmuir isotherms at different solution pH values

Kinetic models

The batch sorption data was analysed using pseudo-first and second kinetics models.

Pseudo-first-order model

The linearised form of pseudo-first-order equation is given by the following expression: (Ho and McKay, 1998).

$$\log(Q_e - Q_t) = \log Q_e - K_1 t / 2.303 \qquad (6)$$

Where Q_t, is the amount of metal sorbed at any time t (mg/g) and K_1, is the rate constant (1/min). In order to obtain the rate constants, the plots of log (Q_e-Q_t) against t, were made at different initial metal concentrations and are shown in Fig. 7. The kinetic constants and equilibrium adsorption Q_e values from the linearised plots are given in Table 5.

The calculated Q_e values from the intercept of the plots were much less than the experimental, Q_e values, showing the insufficiency of first-order kinetics to fit the experimental data. Moreover, the first-order equation did not fit well for the range of contact time used in the experimental work and was valid only over the initial 30 minutes to an hour of the sorption process. The correlation coefficients R^2 were also found to be rather smaller suggesting the inadequacy of the first-order kinetics.

The expression for linearised form of pseudo-second-order kinetics is given as: (Ho and McKay, 1998):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^{2}} + \frac{1}{Q_e} t \qquad (7)$$

Where, K_2 is the equilibrium rate constant (g/mg/min). The plots of second-order kinetics drawn for t/Q_t against t are shown in Fig. 8, whereas in the Table 5 the rate constants and the initial and equilibrium adsorption values are given. Good fits were obtained for all the initial concentrations. The equilibrium adsorption Q_e values obtained from the plots are close to the experimental values. The correlation coefficients are very near to one, the highest value being equal to 0.99990. All the facts suggest that the experimental sorption data approximate the second-order kinetic model.

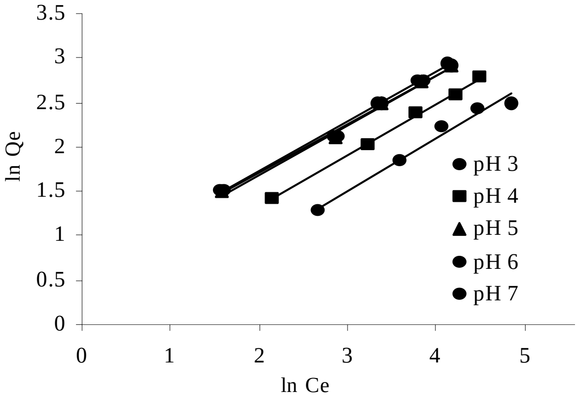

Fig. 6: Linearised Freundlich Isotherms at different solution pH values

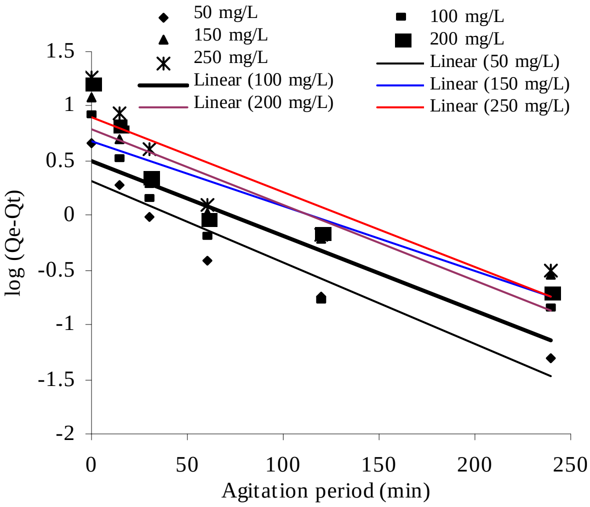

Fig. 7: Pseduo-First-Order kinetics plots at different initial solute concentrations and for pH=6

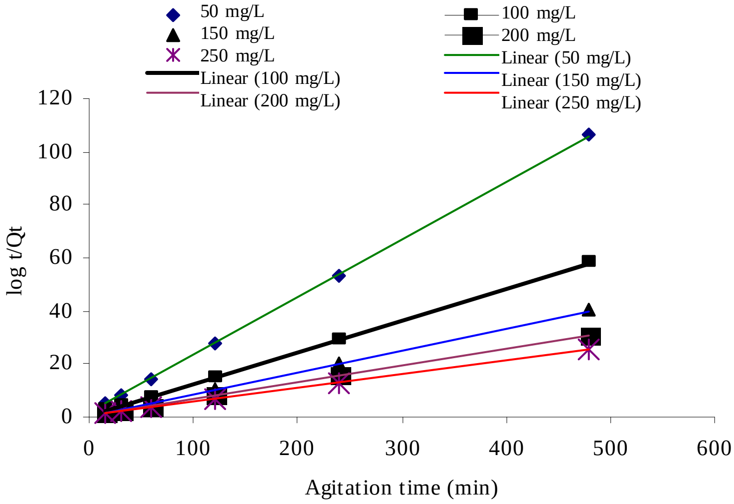

Fig. 8: Pseduo-second-order kinetics plots at different initial solute concentrations for pH=6

Desorption experiments

The desorption experiments were conducted with aqueous solutions of SDS, an anionic surfactant at concentrations of 1%, 2%, and 3% on zinc-sorbed soil corresponding to initial sorbate concentration of 100 mg/L and pH=6.

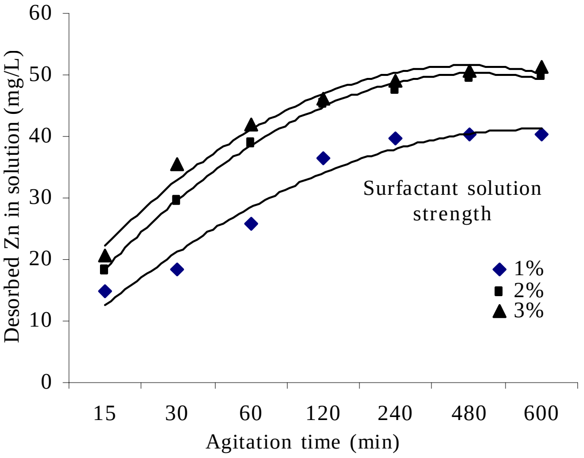

Fig. 9: Removal of sorbed Zn by surfactant solution
Initial Zn concentration: 100 mg/L at pH=6

The comparative results given in Table 6 and shown in Fig. 9 present that the degree of desorption of Zn from soil into the surfactant solution was 49% for 1% concentration; 61% for 2% concentration and 63% for 3% concentration. The 2% surfactant concentration gave the best results as there was only a nominal increase in desorption at the concentration of 3%. The used surfactant solution is therefore fairly effective in desorption of Zn from the contaminated soil.

REFERENCES

Abriola, L. M., Pennell, K. D., Pope, G. A., Dekker, T. J., Luning-Prak, D., (1995). Impact of Surfactant Flushing on the Solubilization and Mobilization of Dense Nonaqueous-Phase Liquids. Chapter 2 In: Surfactant-Enhanced Subsurface Remediation. ACS Symposium Series 594, American. Chem. Soc., Washington.

Aharoni, C., Sparks, D. L., (1991). Kinetics of Soil Chemical Reactions – A Theoretical Treatment, In: Rate of Soil Chemical Processes. Soil Society of America, Madison, WI.

Attanasova, I. D., (1995). Adsorption andDesorption of Cu at High Equilibrium Concentrations by Soil and Clay Samples from Bulgaria. Environ. Pollut., **87**: 17-21.

Attanasova, I.D., and OkazakiM. (1997). Adsorption-Desorption Characteristics of High Levels of Copper in Clay Fractions. Water. Air. Soil. Pollut., **98**: 213-228.

Backes, C. A., McLaren, R. G., Rate, A. W., Swift, R. S., (1995). Kinetics of Cadmium and Cobalt Desorption from Iron and Manganese Oxides. Soil. Sci. Soc. Am. J., **59**: 778-785.

Casey, T. J., (1997). Unit Treatment Processes in water and Wastewater Engineering. John Wiley and Sons Ltd. England. pp: 113-114.

Cavallaro, N., McBride M. B., (1980). Activities of Cu^{2+} and Cd^{2+} in Soil Solutions as Affected by pH. Soil. Sci. Soc. Am. J., **44**: 729-732.

Davis, J. A., Leckie, J. O., (1978). Effect of Adsorbed Complexing Ligands on Trace Metal Uptake by Hydrous Oxides. Environ. Sci. Technol., **12**: 1309-1315.

Eick, M. J., Peak, J. D., Brady, P. V., Pesek, J. D., (1999). Kinetics of Adsorption/Desorption on Geothite: Residence Time Effects. Soil. Sci., **164**: 28-39.

Farrah, H., Pickering, W. J., (1976a). The Adsorption of Copper Species by Clays: I. Kaolinite. Aust. J. Chem., **29**: 1167-1176.

Farrah, H. Pickering, W. J., (1976b). The Adsorption of Copper Species by Clays: II. Illite and Montmorillonite. Aust. J. Chem., **29**: 1649-1656.

Harter, R. D., (1992). Competitive Sorption of Co, Cu, and Ni Ions by Calcium Saturated Soil. Soil. Sci. Soc. Am. J., **56**: 444-449.

Harter, R. D., (1983). Effect of Soil pH on Adsorption of Lead, Copper, Nickel, and Zinc. Soil Sci. Soc. Am. J., **47**: 47-51.

Hickey, M. G., Kittrick, J. A., (1984). Chemical Partitioning of Cadmium, Copper, Nickel, and Zinc in Soils and Sediments Containing High Levels of Heavy Metals. J. Environ. Qual., **13**: 372-376.

Ho, Y. S., McKay, G., (1998). Sorption of Dye from Aqueous Solution by Peat. Chem.l Eng. J., **70** (2): 115-124.

IS 1498: (1970). Classification and Identification of Soils for General Engineering Purposes (Amendement-2). Bureau of Indian Standards, New Delhi.

IS 2720. Methods of Tests for Soils.Bureau of Indian Standards, New Delhi.James, R. O., Healy, T. W., (1972). Adsorption of Hydrolysable Metal Ions at the Oxide-Water Interface: III. Thermodynamic Model of Adsorption. J. Colloid Interface Sci., **40**: 65-81.

Kuo S., Baker, A. S., (1980). Sorption of Copper, Zinc, and Cadmium by Some Acid Soils. Soil Sci. Soc. Am. J., **44**: 968-974.

Kuo, S., Heilman, P. E., Baker, A. S., (1983). Distribution and Forms of Copper, Zinc, Cadmium, Iron and Manganese in Soils Near a Copper Smelter. Soil. Sci., **135**: 101-109.

Martinez, C. E., Sebastein, S., Jacobson, A., Mcbride, M. B., (1999). Thermally Induced Release of Adsorbed Pb upon aging Ferrihydrite and Soil Oxides. Enviro. Sci. Technol., **33**: 2016-2020.

McBride, M. B., (1977). Copper (II) Interaction with Kaolinite Factors Controlling Adsorption. Clays. Clay. Miner., **26**: 101-106.

McBride, M. B., (1982). Hydrolysis and Dehydration Reactions of Exchangeable Cu^{2+} on Hectorite. Clays. Clay. Miner., **30**: 202-206.

McBride M. B., Blasiak J. J., (1979). Zinc and Copper Solubility as a function of pH in an Acidic Soil. Soil Sci. Soc. Am. J., **43**: 866-870.

McLaren, R. G., Crawford, D. V., (1973). Studies on Soil Copper: II. The Specific Adsorption of Copper by Soils. J. Soil Sci., **24**: 443-452.

U.S. EPA., (1996b). Report: Recent Developments for In situ Treatment of Metals-contaminated Soils. U.S. EPA, Office of Solid Waste and Emergency Response, Draft.