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Heavy Metal Retention Of Cochin Marine Clay

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Abstract:- The retention of heavy metals in soils depends on several factors like temperature, chemical composition of the soils, pH, ion activity and particle size (Fetter, 1990). So, in the present study, effects of some of these factors on retention are included**.**

I. INTRODUCTION

Compacted soils are being used extensively for construction of liners and barriers at many waste disposal sites. The function of pollution control liners is to minimize pollutant migration by convection and /or diffusion (Brandl, 1992). For soils to efficiently perform as a liner, it should posses high adsorption capacity (Sivapullaiah et al., 1997). Lead and zinc, commonly found in most of the landfills (Barnhart, 1978) are toxic in nature. Hence, these two metals along with other heavy metals like cadmium, copper and iron were selected for the retention studies on marine clays.

II. MATERIALS USED

A. Cochin Marine Clay

Marine clay was collected from Greater Cochin area on the Western coast of India. The earlier investigation reports show that in almost all locations thick uniform layers of marine clays could be obtained after 3 to 9 meters. Hence, bulk samples of the clay were collected by bore holes advanced by shell and augur method. Bore holes were taken to the clay layers for collection of samples. The boring operations were carried out as per the direction given in IS: 1892 – 1979 – code of practice for surface investigation for foundations. Care was taken not to include bentonite slurry during the boring operations as it might contaminate the soil samples. Samples collected from different locations. Studies by Jose et al. (1989) show that drying significantly influences the index properties of Cochin marine clay. Therefore, the clay samples at two different initial conditions viz. moist and sundried were prepared for the laboratory investigations. For uniformity among the samples collected different boreholes, representative samples collected from same depth but different bore holes at various locations of the same site were pooled together and mixed thoroughly into a uniform mass and preserved in polythene bags. This is designated as the 'moist' sample of Cochin marine clay (MMC).The approximate composition of the clay is given in Table 2. The properties of the marine clay are given in Table1.

Table 1 Property of Soils Used.

Serial No.	Property		Marine clay
1	Specific Gravity		2.67
2	Liquid Limit	(%)	126
3	Plastic Limit	(%)	43.5
4	Plasticity Index	(%)	82.5
5	Shrinkage Limit	(%)	17.8
6	Volume Change	(%)	67.01
7	Linear Shrinkage	(%)	23.02
8	Activity		2
9	Free Swell Index	(cc/g)	5.4
10	Cation Exchange Capacity(meq / 100g)		31.4
11	Surface Area(m^2 /g)		32
12	PH		7.56
13	Conductivity(μs /cm^2)		9860
14	Organic Matter	(%)	13.7
15	Grain Size Distribution:		
	Coarse Sand (2.0 – 4.75 mm)	(%)	0
	Medium sand (0.425-2.0mm)	(%)	3

	Fine Sand (0.075– 0.425mm)	(%)	14.5
	Silt size,(0.002 - 0.075mm)	(%)	41
	Clay Size, (<0.002mm)	(%)	41.5

Table 2 Compositions of the Soils Used

Compound	Marine Clay
Al_2O_3	**7**
SiO_2	**78.14**
MgO	**0.2**
CaO	**1**
Fe_2O_3	**2**
Loss on Ignition	**4.92**

B. Fine chemicals

In many of the industrial wastes, the heavy metal contaminant cations generally encountered are zinc (Zn^{++}), lead (Pb^{++}), iron (Fe^{2+}&Fe^{3+}), cadmium (Cd^{++}), copper (Cu^{++}) and alkali metals such as sodium (Na^{+}). Since most of the heavy metal industries may contain the metals in their sulfate forms $ZnSO_4$, FeSO4, $CdSO_4$ and $CuSO_4$ of AR grade were used. But, the solubility of lead sulfate is very low. Hence, the soluble form of lead (lead nitrate) was used. The sodium used was in its chloride form. The details of the chemicals used are given in table 3.4.

Table 3 Chemical and Physical Data of Chemicals Used (*)

Sl. No	Chemicals	Molecular weight	Specific Gravity	Solubility in 100 parts (cold water)
1	$FeSO_4.7H_2O$	278.03	1.899	32.8
2	$PbSO_4$	303.28	6.20	0.0028
3	$Pb (NO_3)_2$	331.23	4.53	38.8
4	$ZnSO_4.7H_2O$	287.56	1.9661	115.2
5	$CdSO_4. H_2O$	226.49	3.786	Soluble
6	$CuSO_4.5H_2O$	159.61	3.606	14.3
7	NaCl	58.45	2.164	35.7

*** Lange, N.A (1980)**

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III TEST PROCEDURE

A. Atomic Absorption Spectrum

In the retention study, the amount of ions retained by the different soils are analysed using AAS. The principle of atomic absorption spectroscopy depends on the fact that the amount of light passing through the flame containing the sample vapor is a function of the concentration of the element in the vapor. For the present study, the ions retained by the material was estimated using a Perkin – Elmer 2380 model atomic absorption spectrophotometer (AAS)

IV RESULTS AND DISCUSSION

The capacity of the marine clay to retain the metal ions depends on many factors relating to the clay characteristics (ie, chemical composition, specific surface area, cation exchange capacity etc.), the cation characteristics (concentration of the ion, pH of the solution etc.) and other factors like temperature and reaction time. The composition of the wastes deposited in the landfill affects the leachate properties like concentration of the ion and pH of the leachate which will affect the retention characteristics of the marine clay and hence the effect of the above parameters on the capacity of marine clay to retain metal ion is studied.

Fig. 1(a) represents the amount of lead retained as function of the initial concentration of the lead. It can be observed from the figure that the amount of lead retained by the marine clay increases to a maximum and remains constant for further increase in the initial concentration of lead. The shape of the curve suggests that the variation of retention of lead by marine clay is similar to Langmuir's adsorption isotherm.

The Langmuir adsorption isotherm equation is given by (Fetter, 1990)

$$\frac{C}{C^*} = \frac{1}{ab} + \frac{C}{b}$$

Where, C - is the equilibrium concentration of the ion (mg/l)
C* - is the amount adsorbed per unit weight of marine clay (mg/g)
a - is an adsorption constant related to the binding energy
b - is the maximum adsorption for the marine clay.

When the adsorption isotherm is plotted according to the Langmuir's adsorption equation (i.e, C/C* versus C), it gives a straight line with a slope 0.0089 (fig. 1(b)). The inverse of the slope of the isotherm (112.36) is the parameter 'b' which gives the maximum retention of lead by marine clay. Corresponding to this maximum retention of 112.36 mg/g, the minimum initial concentration can be seen to be 3175 mg/l. (Fig. 1a)

Similarly Figs. 2 (a) to 4 (b) present the variation of the amount of different metals of zinc, cadmium, copper respectively retained by marine clay as a function of the initial concentration of the respective metal ions. The maximum retention of the different metals by marine clay and the corresponding values for the minimum initial concentration are shown in Table 3

Fig 6 shows the heavy metal retention by marine clay from the respective individual salt solutions of different initial concentrations. For initial concentrations below 1500mg/l, the lead retention is more compared to other metals. But, the retention of zinc metal is at a higher range of 70%. The selectivity order of retention is Zn > Pb > Cu > Cd. The figure shows the quantity of metal retained and percentage retained against initial concentration of solutions of respective individual salts. The figure shows that for 55% retention, the quantity of zinc retained is 277.8 mg/g. Whereas the lead, copper, cadmium retention is 112.3mg/g, 35mg/g and 15.5mg/g respectively corresponding to 55% retention.

Table 3 Maximum Retention Capacity of Marine Clay

Metal	Maximum retention		Minimum initial concentration	
	(mg/g)	(meq)	(mg/l)	(meq)
Lead	112.36	0.68	1975	11.93
Zinc	277.8	2.18	3950	27.6
Cadmium	18.69	0.165	3175	28
Copper	65.36	0.528	4250	34

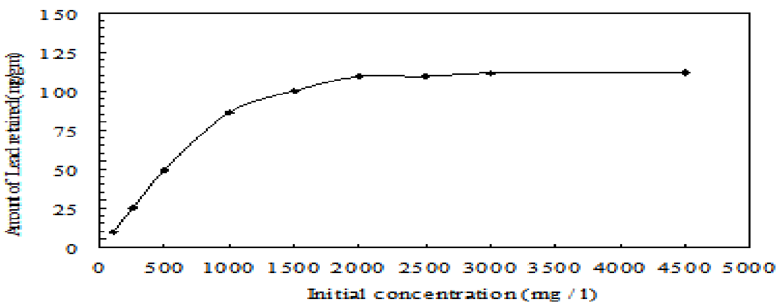

Figure 2 (a) Retention of Lead by Marine Clay against Initial concentration

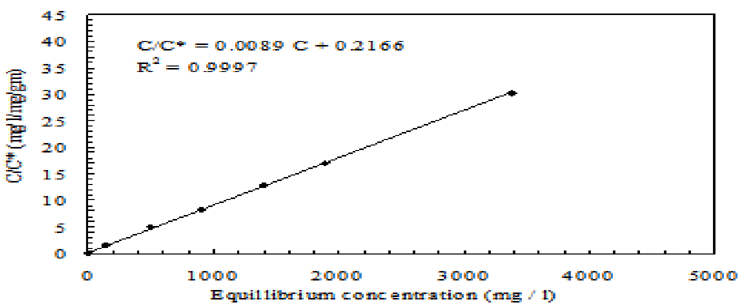

Fig. 2 (b) Langmuir Adsorption Isotherm for Lead adsorbed by Marine Clay

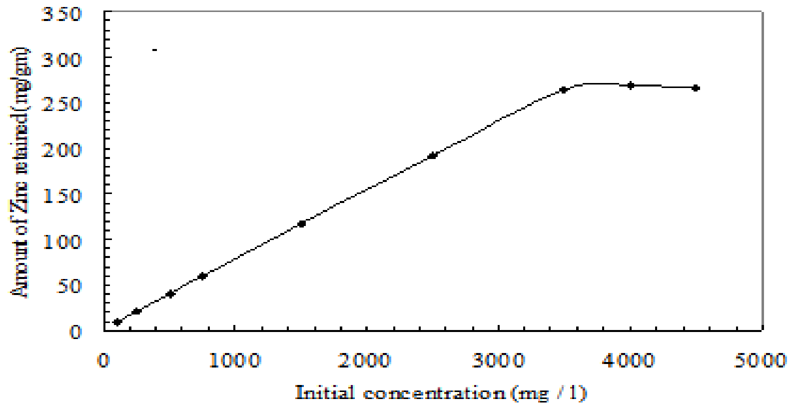

Figure 3(a) Retention of Zinc by Marine Clay against Initial Concentration

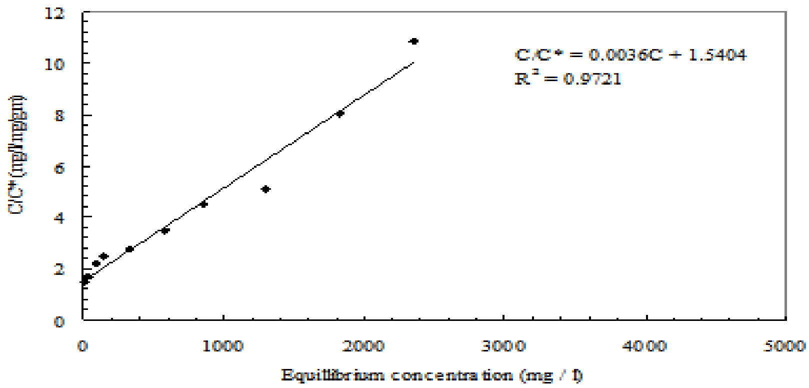

Fig. 3 (b) Langmuir Adsorption Isotherm for Zinc adsorbed by Marine Clay

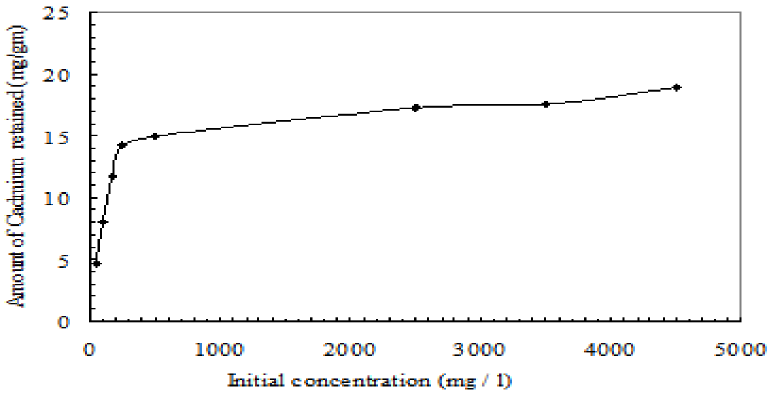

Fig. 4(a) Retention of Cadmium by Marine Clay against Initial Concentration

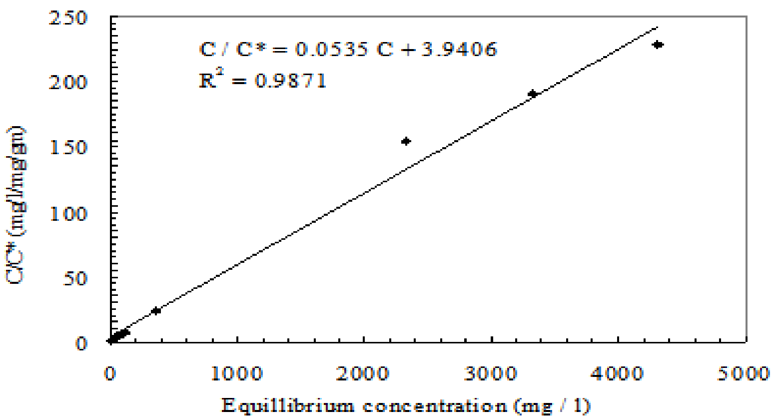

Fig. 4(b) Langmuir Adsorption Isotherm for Cadmium retained by Marine Clay

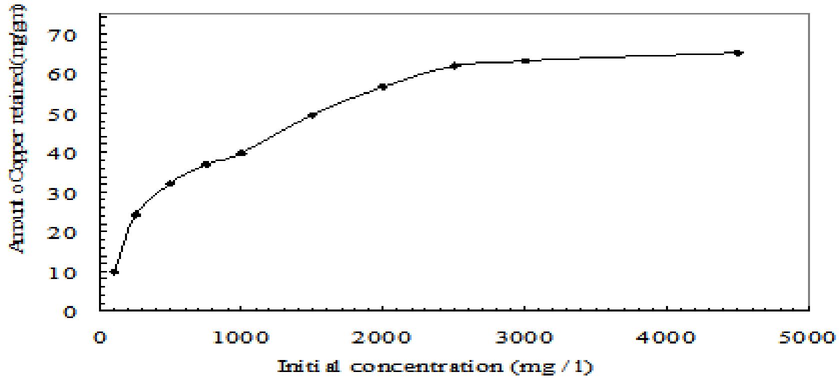

Fig. 5 (a) Retention of Copper by Marine Clay against Initial concentration

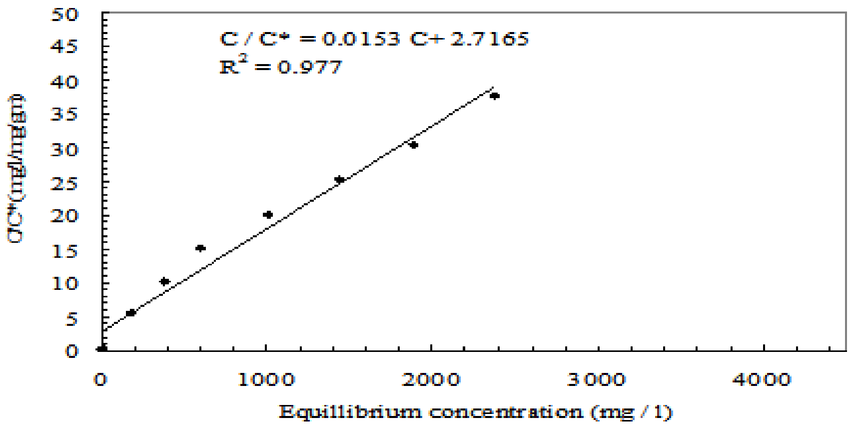

Fig. 5(b) Langmuir Adsorption Isotherm for Copper retained by Marine Clay

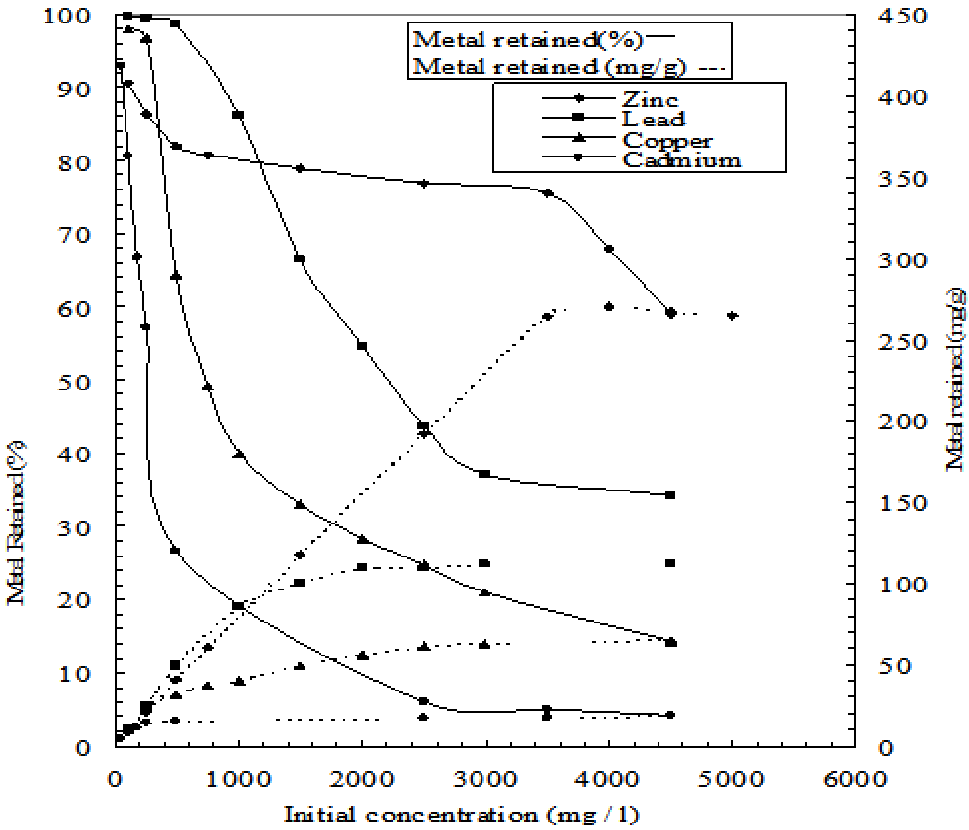

Fig. 6 Retention of Heavy Metals by Marine Clay against Initial Concentration of Pure Salt Solutions

In the case of 90 % retention, the zinc retained is only 5mg/g. This is almost same as that for cadmium. But, the copper and lead retained is 32 mg/g and 94 mg/g respectively. The figure shows that as the initial concentration of ions increases the ions retained per unit weight of adsorbent increases and comes to a steady value. The figure also shows that the retention is more for zinc compared to other metals. Fig. 6 compares the percentage retention of different heavy metals ions by marine clay from different pure salt solutions The percentage lead retention is decreasing and becoming steady at 62 % But, the trend is decreasing, for both zinc and cadmium. The percentage retention is decreasing as the initial concentration of the solution is increasing. The figure shows that the selectivity order of retention is Cu > Pb > Zn > Cd.

V CONCLUSIONS

The retention studies on marine clays led to the following conclusions:

Marine clay can retain effectively different heavy metals like zinc, lead, iron, cadmium and copper. As that for bentonite the retention increases as the concentration of the ions increase up to a particular limit and after that the retention increases marginally or decreases. The maximum retention capacity of the marine clay varies with different cations. The maximum retention capacity is 112.4 mg/g for lead, 312.2 mg/g for zinc, 18.7 mg/g for cadmium and 65.4 mg/ g for copper. The preferential order of retention is Zn > Pb> Cu> Cd.

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