Geotechnical Engineering Journal of the SEAGS & AGSSEA Vol. 46 No.4 December 2015 ISSN 0046-5828

Study on Factors Affecting Heavy Metal Sorption Characteristics of Two Geomaterials

K. M. Nithya[1], D. N. Arnepalli[2] and S. R. Gandhi[3]
[1]Former research scholar, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India
[2]Assistant Professor, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India
[3] Professor, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India
E-mail: kmnithya@gmail.com

ABSTRACT: This study investigates effect of liquid to solid ratio, initial concentration of heavy metals, pH and composite heavy metal solution and nature of sorbent on sorption capacity of two different geomaterials such as clayey soil and moorum. The batch sorption experiments were carried out with the selected geomaterials using different heavy metal solutions such as Copper, Manganese, Zinc, Lead and Chromium. Based on the experimental results, the following conclusions are drawn i) increasing liquid to solid ratio decreases the removal rate of heavy metal, however heavy metal sorbed on unit mass of the sorbent increased at equilibrium ii) increase in pH and the initial heavy metal concentration leads to an increase in the heavy metal uptake by the geomaterials iii) nature of the clay mineral present in the geomaterials plays significant role in controlling the sorption characteristics of the geomaterials compared to amount of clay content present in the geomaterials iv) observed order of selectivity of heavy metals is Cr >Pb >Cu >Mn ~Zn.

KEYWORDS: Heavy metal, Geomaterials, Sorption capacity, Landfills, Clay liner

1. INTRODUCTION

The increasing problem of mobility of heavy metals into the environment as a result of mining, industrial and agricultural activities reveal that the removal of heavy metal ions from the waste solutions is essential due to its toxic nature (Gulec et al. 2001). The most common heavy metals in leachate solution are copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn). The concentration of these heavy metals varies from 0 to 100 ppm in municipal solid waste leachate and 100 to 10000 ppm in mining wastes, sewage sludge and various industrial wastes (Yong and Diperno, 1991).

Clay liners have been conventionally used as barriers in landfills to prevent contamination of groundwater and subsoil by leachate. Among the various available natural liner materials, compacted clay liners are popularly used because of their low cost with reasonable low hydraulic conductivity, high sorption capacity and resistance to damage and puncture (Daniel and Benson, 1990; Guney et al. 2008; Kang and Shackelford, 2010; Cossu, 2013). If natural clay or clayey soils are not abundantly available, locally available geomaterial which satisfies liner requirements can be used to construct the landfill liners (Kaya and Durukan, 2004; Lakshmikantha and Sivapulliah, 2006). The primary function of a liner system is to prevent movement of leachate into the subsoil and ground water. Thus, the sorption characteristics of geomaterial play a significant role in evaluating their potential use as landfill liner material (Wagner, 2013).

Batch sorption experiments are commonly employed to assess sorption characteristics of geomaterials (McBride, 1994; ASTM D 4646-04, 2008; Arnepalli et al. 2010). Batch test results from the literature studies showed that the solution composition, liquid to solid ratio, initial concentration of the heavy metal solution, pH of solution and the soil nature (e.g., soil constituent) had considerable effect on sorption of heavy metals on clays (Roy et al. 1991; Chang and Wang, 2002; Arnepalli et al. 2010; Allen et al. 1995; Kumar et al. 2006; Degryse et al. 2009; Liu and Lu, 2011). However, no study has been reported on effect of these variables on the sorption characteristics of clayey soil and moorum for heavy metals such as Copper, Manganese, Zinc, Lead and Chromium.

With this in view, the main objective of the present study is to evaluate the effect of these parameters on sorption of selected heavy metals on locally available soils such as clayey soil and moorum. The objective was achieved by conducting batch sorption experiments with varying liquid to solid ratios (*L/S*), initial concentration of heavy metal solution, pH of solution and composite heavy metal solution. The effect of composite heavy metal on sorption capacity was assessed under fixed environmental conditions such as initial concentration, pH and liquid to solid ratio.

2. MATERIALS CHARACTERIZATION

2.1 Materials

Samples of clayey soil and moorum were chosen in this study. The geomaterials were processed by removing the gravel size particles; further the processed samples were tested for their physical, geotechnical, chemical and mineralogical, and sorption characteristics and the details are presented in the following section. Heavy metals such as copper, Cu^{2+}, in its sulphate form; zinc, Zn^{2+}, and lead, Pb^{2+}, in their nitrate form and manganese, Mn^{2+}, and chromium, Cr^{3+} in their chloride form were used as model contaminants. The heavy metals were chosen to simulate landfill leachate collected from hazardous waste disposal facility, i.e., engineered landfill, developed and operated by M/S Ramkey, at Hyderabad, Andhra Pradesh, India The concentration of the heavy metals presents in the solution is determined using an Atomic Absorption Spectrometer, AAS (Perkin Elmer, USA).

2.2 Physical and Geotechnical characteristics

The specific gravity of the geomaterials was obtained using a water pycnometer, by following the guidelines presented in ASTM D854-06. The particle size distribution of the geomaterials were assessed as per ASTM D422-94. The consistency limits such as liquid limit, LL, plastic limit, PL and shrinkage limit, SL, along with differential free swell index, FSI were determined by following the guidelines presented in ASTM D4318-94 and ASTM D427-94 respectively, and the results obtained are presented in Table 1. Based on the particle size distribution and consistency limits, the geomaterials were classified according to Unified Soil Classification System, USCS (ASTM D2487-94), as depicted in Table 1. The compaction characteristics of the geomaterial such as maximum dry density, γ_{dmax} and optimum moisture content, OMC, were determined as per the guidelines presented in ASTM D698-04 and results are presented in Table 1. The coefficient of permeability, *k*, of the selected geomaterials is evaluated using the flexible wall permeameter, and by following the guidelines presented in ASTM D5084 (2010) and results obtained are illustrated in Table 1.

2.3 Chemical and Mineralogical characteristics

As depicted in Table 2, the chemical characteristics of the geomaterials such as cation exchange capacity, CEC, as per IS 2720 Part XXIV-76, carbonates (Hesse et al 1972), organic matter (ASTM D2974-07) and pH (ASTM D4972-01) were determined. The specific surface area, SSA, of these samples was obtained by employing the nitrogen gas adsorption technique with the help of BET surface area analyser.

Table 1 Physical and geotechnical characteristics of the geomaterials

Property	Value	
	CS	MO
G	2.7	2.71
Particle size distribution characteristics		
Size	*Percent fraction (%)*	
Gravel	0	2.7
Sand	24	59.2
Silt	42	21.5
Clay	34	16.6
Consistency limits (%)		
Liquid limit	49	49
Plastic limit	20	21
Shrinkage limit	13	14
Plasticity Index	29	28
USCS* Classification	CL	SC
Geotechnical characteristics		
γ_{dmax} (g/cc)	1.7	1.4
OMC (%)	18	24
FSI (%)	40	30
k ($\times 10^{-10}$ m/s)	0.71	4.8

*Unified soil classification system (ASTM D2487, 1994)

Table 2 Chemical and mineralogical characteristics of the geomaterial

Property	Materials	
	CS	MO
Chemical characteristics		
pH	6.5	8.9
CEC (meq./100g)	18.1	24.2
SSA (m2/g)	53.7	65.9
Carbonates (%)	9	9.3
Organic matter (%)	8.6	9.8
Major Oxides (%)		
SiO_2	44.2	44.2
Al_2O_3	13.2	13.2
Fe_2O_3	31.6	31.6
TiO_2	5.9	5.9
SO_3	---	---
CaO	2.3	2.3
K_2O	0.5	0.5
MgO	0.4	0.4
P_2O_5	0.8	0.8
MnO	0.7	0.7
Cl	---	0.1
Mineral present		
Mineral Name	Kaolinite, Illite, Quartz, Feldspar	Chlorite, Illite, Illite-Montmorillonite, Hematite, Muscovite

-- less than detectable limit of the instrument (0.001%)

Further the chemical compositions of the geomaterials were obtained using an X-ray Fluorescence setup, XRF (Phillips 1410, Holland). Four grams of finely ground sample, 1 g of microcrystalline cellulose and isopropyl alcohol were mixed thoroughly, using mortar and pestle and the mixture was kept below an infrared lamp for slow drying. A small aluminum dish of inner diameter 33 mm and height of 12 mm was taken and two third of this dish was filled with mixture of 70 percent methylcellulose and 30 percent paraffin wax, followed by filling up the container by the dried sample. In order to make a sample pellet, the filled aluminum dish was compressed with the help of a hydraulic jack by applying a load of approximately 15 tons. Further the chemical composition of the geomaterial was determined by mounting the compressed sample pellet in the sample holder of the XRF test setup, and the obtained results are presented in Table 2 in their major oxide form.

In addition to this the mineralogical characteristics of the material was determined with the help of an X-ray Diffraction Spectrometer, XRD, (Phillips 2400, Holland), using a graphite monochromator and Cu-Kα radiation. Minerals present in these samples were identified by using the database "Joint Committee on Powder Diffraction Standards" (JCPDS-94) search files, and the results are presented in Table 2.

2.4 Sorption characteristics

The processed material, i.e., the material passing through 2 mm sieve was employed to perform batch sorption experiments (Grolimund et al. 1995). Two grams of sample was mixed with 100 ml of the corresponding heavy metal solution with different initial concentration in the air tight polypropylene sample bottles. The sample bottles were kept on a mechanical shaker and shaken for an equilibration sorption period of 24 hours (ASTM D4646-04). Later these bottles were removed from the shaker and their contents were centrifuged, which helps in separating solid particles from the solution. The clear solution was transferred from these bottles and was filtered using a 45 μm filter paper. The filtrate was analyzed for various heavy metals using AAS.

Furthermore, blank tests i.e., sampling bottles filled with a certain concentration of heavy metal without the geomaterial and control experiments i.e., sampling bottles filled with the geomaterials and the distilled water were performed to establish the sorption capacity of the sample bottle and the trace level concentrations of the concerned heavy metal residual present in the geomaterial (Grolimud et al. 1995; Gao et al. 1997; ASTM D4646-04). The obtained sorption capacity of the sample bottle and trace level residual concentrations present in the geomaterial were used to compute the corrected initial concentration of the solution, C_i and equilibrium solution concentration, C_e , i.e., the concentration of heavy metal present in the solution after equilibration time. Later, the normalized mass of the heavy metal sorbed on the geomaterial, C_s, was computed using Eq. (1).

$$c_s = (c_i - c_e) \times (L/S) \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1 Effect of liquid to solid ratio (*L/S*)

To demonstrate the effect of liquid to solid ratio on mass of the contaminant removed by the geomaterial, C_s, the variation of C_s with *L/S* was developed as shown in Figures 1 and 2. Furthermore, the percent removal of concentration from 100 ml solution, *PR*, of various heavy metals over a wide range of concentration values and *L/S* were obtained using Eq. (2). The obtained results are presented in Tables 3 to 4.

$$PR = \frac{(c_i - c_e)}{c_i} \times 100 \qquad (2)$$

It can be observed from the Figures 1 and 2 that, the amount of heavy metal sorbed by the geomaterial varies nonlinearly with *L/S* and its variation becomes insignificant at high *L/S* values. This may be due to the mass of the contaminant present in the solution is significantly high at large *L/S* values, as compared to the affinity of the potential sorption sites available (Vengris et al. 2001; Bordas and Bourg, 2001; Arnepalli et al. 2010). In addition, at high *L/S* values dispersion of particles increases available sorption sites between the particles, whereas at low *L/S* values aggregation and flocculation decreases available sorption sites.

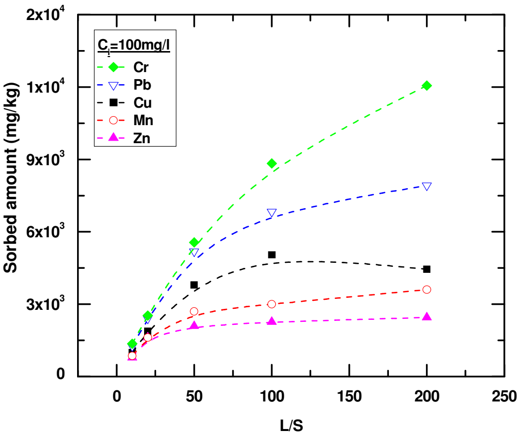


Figure 1 Variation of mass of the heavy metals sorbed by the clayey soil with liquid to solid ratio

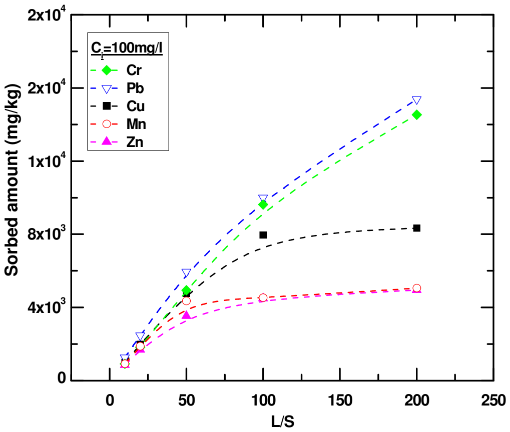


Figure 2 Variation of mass of the heavy metals sorbed by the moorum with liquid to solid ratio

It can also be observed from the data presented in Tables 3 and 4 that, percent removal of heavy metal present in a 100 ml solution, *PR*, decreases as *L/S* value increases, this is mainly because, at high *L/S* values the mass of the geomaterial available for removal of heavy metal from the constant volume of the solution, is quite low. On the other hand for low *L/S* values, the number of sorption sites available is significantly high when compared to the mass of the contaminant present in the solution, which in turn increases the sorption of heavy metals. Though the available sorption sites for removal of heavy metals is high at a low *L/S* value, this scenario may impose significant competition between the heavy metals and desorbed cations such as $Mg^{2+}$and Ca^{2+} (Bittel and Miller, 1974). This demonstrates the fact that, the efficiency of the geomaterial to retain heavy metal increases with the increase of *L/S*, for a given concentration value. It can also be noticed that, the rate of increase in sorption due to increase in *L/S* value, is almost constant for all the initial concentration of the different heavy metals considered in this study. In view of the above mentioned facts, it is essential to consider the effect of *L/S* while assessing the long term performance of landfill liners.

Table 3 Percent removal of various heavy metals by clayey soil over wide range of liquid to solid ratio

Heavy Metal	***L/S***	**Initial Concentration (mg/l)**			
		≤ 100	**≤ 200**	**≤ 300**	**≤ 600**
Cu	10	99	96.5	87.5	73
	20	94	89.5	79	64
	50	76	68.5	56	45
	100	59	51.5	35	22.5
	200	22	19.5	16	13.5
Mn	10	92	86.6	75.5	64
	20	83	75.5	62	48
	50	58	47	30.5	20.5
	100	25	20.5	14.5	11.5
	200	19	15	9.5	6
Zn	10	96	85.5	71	58.5
	20	90	76.5	53.5	36
	50	47	37	23	15
	100	25	19.5	12	8
	200	14	11	6.5	5-3
Pb	10	98	97.5	96	94.5
	20	95	94	91.5	88.5
	50	87	85	80.5	72.5
	100	52	45.5	35	25.5
	200	33	30.5	25	20
Cr	10	99.5	98.8	97.5	96.5
	20	99	98.5	97	93.5
	50	98	94.5	87	75
	100	96	83	62	44.5
	200	65	52	34	23

Table 4 Percent removal of various heavy metals by moorum over wide range of liquid to solid ratio

Heavy Metal	***L/S***	**Initial Concentration (mg/l)**			
		≤ 100	**≤ 200**	**≤ 300**	**≤ 600**
Cu	10	99	98.5	97.5	96.5
	20	99	98.0	95.0	87.5
	50	94	88.0	78.0	66.5
	100	80	70.0	55.0	42.5
	200	41	34.5	26.0	20.0
Mn	10	99	98.0	95.5	85.0
	20	97	90.5	78.5	57.5
	50	90	73.0	49.0	31.5
	100	46	37.5	25.5	18.0
	200	26	22.0	15.5	10.5
Zn	10	99	98.5	97.0	88.5
	20	97	92.0	81.5	63.5
	50	86	73.0	52.5	35.5
	100	52	41.0	25.5	17.5
	200	28	22.0	13.5	9.0
Pb	10	99	98.5	97.5	97.0
	20	98	97.0	95.5	94.5
	50	92	90.0	85.5	76.5
	100	82	74.5	62.0	50.5
	200	58	51.5	41.5	33.0
Cr	10	100	99.0	98.5	98.0
	20	99	98.5	98.0	97.5
	50	99	97.0	92.5	80.5
	100	98	89.0	73.0	55.5
	200	75	64.5	49.0	39.0

3.2 Effect of Initial Concentration

In order to evaluate the effect of initial concentration of heavy metal ions present in the solution on sorption characteristics of the geomaterials, batch sorption experiments were carried out with different initial metal ion concentrations. The obtained results are graphically represented in the form of "variation of mass of heavy metal sorbed by the geomaterial, C_s, with initial concentration, C_i" and "variation of percent removal, *PR*, of heavy metals with initial concentration C_i," for a *L/S* of 50 for the geomaterials and heavy metals considered in this study, as depicted in Figures 3 and 4. It can be observed from Figures 3 and 4 that the increase in initial concentration of heavy metal results in an increase and decrease of the amount of heavy metal uptake per unit weight of the sorbent and percent removal rate of heavy metal, respectively. This may be because at the high initial concentrations, the ratio of number of moles of heavy metal to the available sorption sites is high as compared to that of low initial concentration.

Furthermore, it can be observed from Figures 3 and 4 that the removal of heavy metal chromium and lead are greater than 70 percent over a range of initial concentration (100-600 mg/l). In case of copper there is slight drop in the removal rate at higher initial concentrations, whereas for the manganese and zinc the removal rate was reduced significantly as the initial concentration increases. The difference in percent removal rate of different heavy metal ions at the same initial concentration may be attributed due to the difference in their chemical affinity and cation exchange capacity. In view of the above facts, it can be concluded that the influence of initial concentration of heavy metals on removal rate is highly depends on the nature of the geomaterial and heavy metals (Ayala et al. 2008; Shu-li et al. 2009).

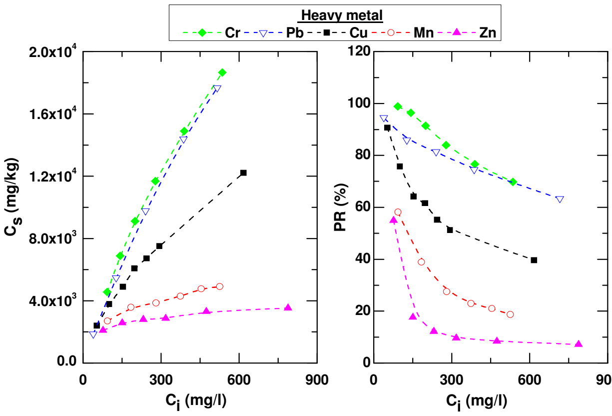


Figure 3 Effect of initial concentration on mass of heavy metal sorbed and percent removal by the clayey soil

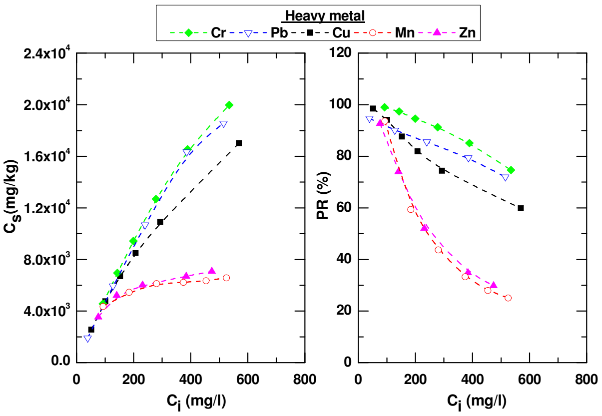


Figure 4 Effect of initial concentration on mass of heavy metal sorbed and percent removal by the moorum

3.3 Effect of Sorbent

To demonstrate the influence of the sorbent/geomaterial nature on sorption behaviour of heavy metals, the variation of mass of heavy metals sorbed by geomaterials with initial concentration were obtained. For the sake of briefness, the results corresponding to copper is only presented in the form of Figure 5.

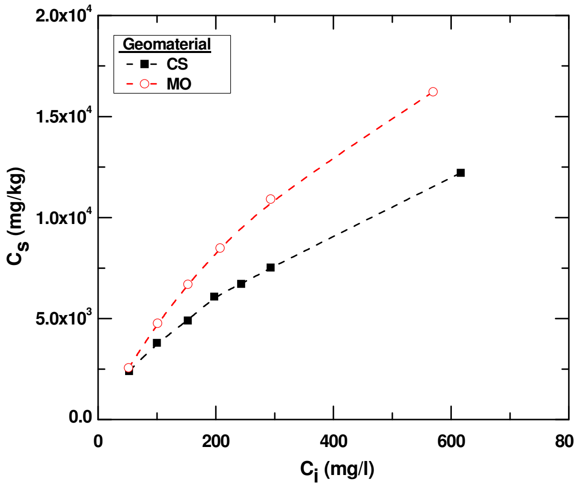


Figure 5 Effect of sorbent on sorption behaviour of copper

It can be noticed from Figure 5 that moorum exhibited a higher sorption affinity towards all heavy metals compared to that of the clayey soil. Though the clayey soil contains a reasonably high clay content as compared to that of moorum, still it exhibits a low retention capacity for all the heavy metals considered in this study. This may be attributed to the relatively low pH of the clayey soil and presence of less reactive clay minerals in it (Kookana and Naidu, 1998; Ouhadi et al. 2001). On the other hand moorum exhibited high retention capacity, as its specific surface area and pH is high and it also contains clay minerals such as illite and montmorillonite in it**.**

3.3 Effect of pH

The solution pH plays a predominant role in determining the sorption behaviour of heavy metals as the solubility of the heavy metal, carbonates and phosphates depends on the pH of the solution (Bruemmer et al. 1986). The pH of the solution also affects metal hydrolysis; ion pair formation; organic matter solubility and surface charge of iron and aluminum oxides and organic matter (Bruemmer et al. 1986; McBride, 1994; Sauve et al. 1988).

In view of the above facts the present study attempts to evaluate the influence of pH of the solution on the sorption behaviour of various heavy metals on the selected geomaterials corresponding to the *L/S* value of 50. It can be noticed that, the majority of the heavy metals considered in this study may get precipitated at pH value 6 and above, hence pH of the model contaminant is maintained less than 6 by adding 0.1M HNO_3 and NaOH. The batch sorption experiments were conducted by varying the solution pH from 2 to 5. The results obtained for clayey soil and moorum are presented in Figure 6 to 10.

It can be observed from Figures 6 to 10 that sorption of heavy metal increases with increase in the pore solution pH of heavy metal solution. It is conceivable that at low solution pH values, the higher number of protons H^+ available in the solution and competes with the positively charged heavy metal ions to get sorbed more on the geomaterial. Further, as the pH increases and the balance between protons, H^+, and hydroxide ions, OH^-, is predominant and only positively charged metal ions get sorbed on the geomaterials (Forbes et al. 1974; Farrah and Pickering, 1977) which results in an increase in sorption capacity of the geomaterial.

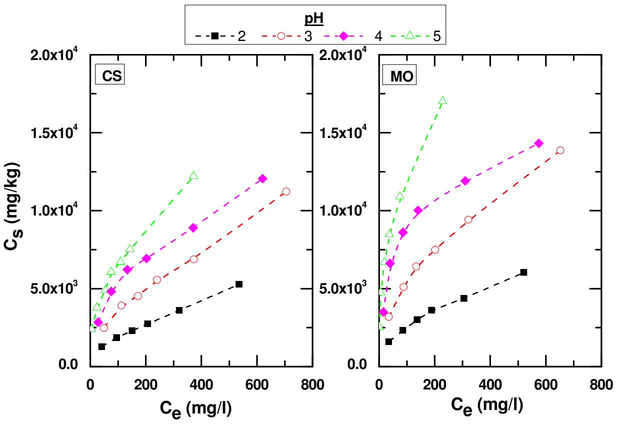


Figure 6 Effect of solution pH on the sorption capacity of clayey soil and moorum for heavy metal copper

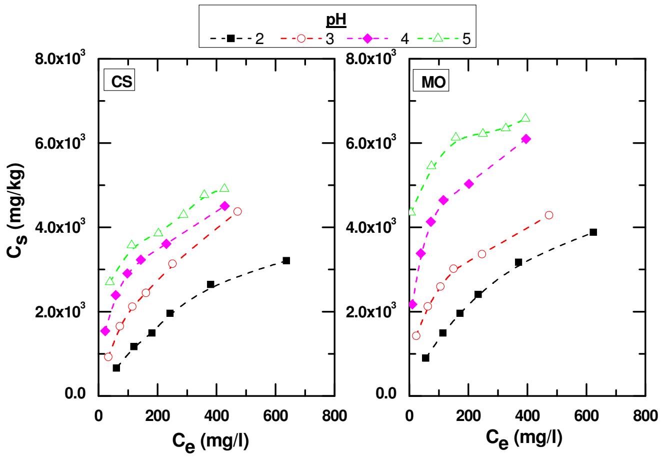


Figure 7 Effect of solution pH on the sorption capacity of clayey soil and moorum for heavy metal manganese

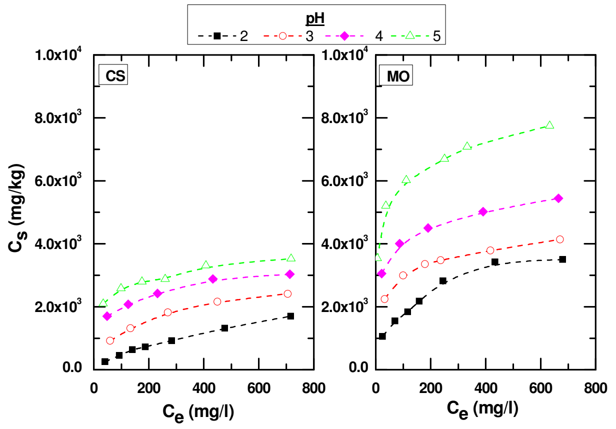


Figure 8 Effect of solution pH on the sorption capacity of clayey soil and moorum for heavy metal zinc

Furthermore it has been noticed that the solution pH effect is strongly evident for copper and lead when compared to other heavy metals considered in this study. The reason for this behaviour is that the surface complexation reactions associated with the lead and copper are influenced by the electrostatic attraction between the surface charge and the dissolved ions. Since the hydrated lead ion have greater ionic radius (1.2 Å), it has lower charge density and therefore, are more affected by the protonation of the surface groups that limits the number of sorption sites on geomaterial. In addition to this, the reduction in sorption affinity of heavy metal copper as result of decrease in pH is probably due to the formation of ion structure upon aquation (Farrah and Pickering, 1977). That is $[\mathrm{Cu}\ (\mathrm{H_2O})_6]^{2+}$ has tetragonal distortion due to the Jahn-Teller effect in which the octahedral structure has been contracted along the x and y axes (Nicholls, 1974). This contraction along the x and y axis results in a structure having four shorter bonds and two longer bonds which lowers the energy of the ion structure and this hinders the binding of the heavy metal copper with surface groups of the geomaterial and this effect is more prominent when these groups are more protonated (Charlet et al. 1993; Wanner et al. 1994).

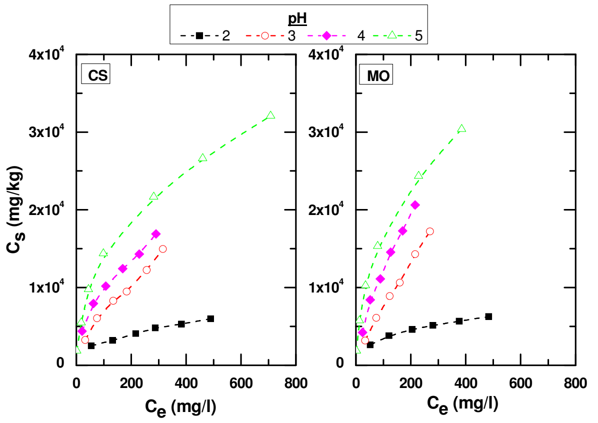


Figure 9 Effect of solution pH on the sorption capacity of clayey soil and moorum for heavy metal lead

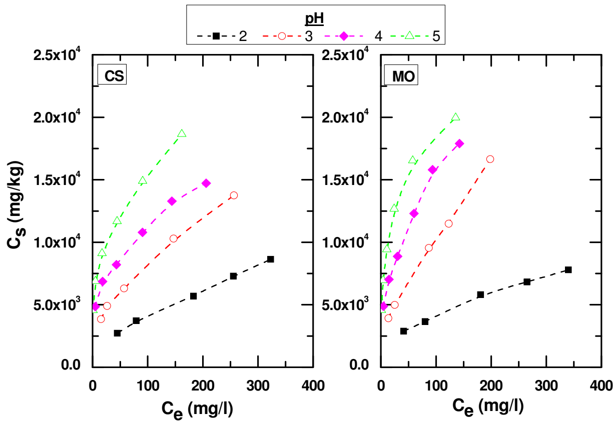


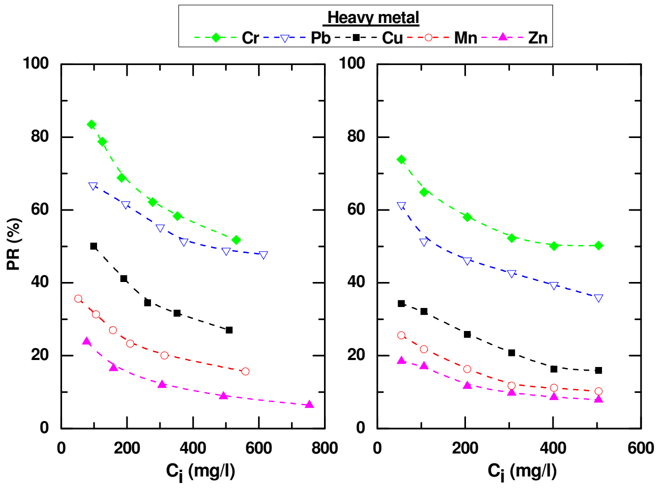
Figure 10 Effect of solution pH on the sorption capacity of clayey soil and moorum for heavy metal chromium

3.4 Competition and Selectivity Order of the Heavy Metals

To study the influence of solution composition on the sorption characteristics of the geomaterials, batch sorption experiments were conducted corresponding to *L/S* of 50 with single and composite heavy metal solutions which contain different heavy metals such as chromium, lead, copper, zinc and manganese. The results pertaining to both single and composite heavy metal solutions are presented in Figures 11 and 12.

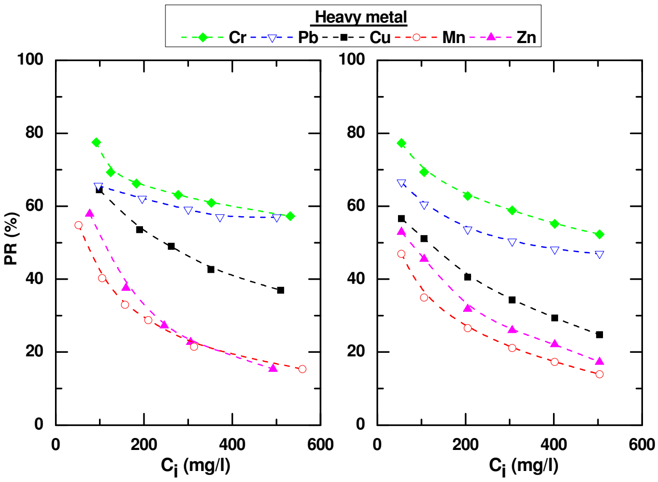
It can be noted from Figures 11 and 12 that the percent removal of heavy metal by the geomaterial corresponding to composite solution is lower when compared to that of the single heavy metal solution. This may be attributed to the competition among the heavy metals not only for the potential sorption sites but also for precipitation onto the geomaterial surface (Elliott et al. 1986).

When the single heavy metal solution is allowed to interact with the geomaterial, only that particular heavy metal is involved with the formation of the metal complex with the available hydroxyl group. However if the metal solution contains more than one heavy metal, there is a possibility of competition among the heavy metals present in the solution to form metal complexes with that available hydroxyl group, which leads to reduction of the sorption affinity of the geomaterials towards the composite heavy metal solution.



(a) single heavy metal (b) composite heavy metals

Figure 11 Percent removal of heavy metal by clayey soil



(a) single heavy metal (b) composite heavy metals

Figure 12 Percent removal of heavy metal by morum

It can be noticed from Figures 11 and 12 that selectivity order of heavy metals for both single and composite solutions seems to be same and the observed order of selectivity is Cr >Pb >Cu >Mn ~Zn. This order of selectivity of heavy metals can be substantiated by considering chemical characteristics of heavy metals which are adopted from the literature as presented in Table 5 (Wiklander and Nilsson, 1954; Evans, 1966; Hsu, 1989; Schwertmann and Taylor, 1989; Sposito, 1986).

It can be noted that the selected geomaterials have shown higher affinity towards the heavy metal chromium even its electro negativity value is smaller than copper and lead, as depicted Table 5. This anomaly may be due to the higher valence of the heavy metal chromium (Smith and McGrath, 1990). It is also observed that lead is the second most preferentially sorbed heavy metal by both clayey soil and moorum geomaterials when compared to the heavy metal copper. This finding may be substantiated by considering the misono softness parameter of heavy metals which determines the relative tendency of the metal to form covalent bonds based on the ionic radius and the ionization potential (Sposito, 1989). Furthermore, the heavy metal zinc is preferentially sorbed over manganese for the geomaterial moorum whereas in the case of clayey soil, manganese is preferentially sorbed over zinc. Based on the above facts it is concluded that, the selectivity of heavy metals of similar valence can be determined approximately by considering the misono softness parameter of heavy metals.

Table 5 Chemical characteristics of the heavy metals considered in this study (Sposito, 1986)

Heavy metal	Valence	Electro negativity	Misono softness parameter (nm)
Chromium	3	1.66	0.226
Lead	2	1.8	0.393
Copper	2	1.9	0.284
Zinc	2	1.6	0.240
Manganese	2	1.55	0.273

4. CONCLUSION

This study presents an investigation on the effects of the liquid to solid ratio, initial concentration of heavy metals, nature of sorbent, pH of solution and solution composition on the sorption of heavy metals onto two types of geomaterials. Based on this study, the following conclusions can be drawn.

- With the increase of liquid to solid ratio results decrease of removal rate of heavy metal, however sorbed heavy metal on unit mass (C_s) of the sorbent increased at equilibrium for both the geomaterials. Further, increasing the initial heavy metal ion concentration leads to an increase in the heavy metal uptake in the geomaterials.
- The nature of clay mineral present in the geomaterials plays significant role in controlling the sorption characteristics of the geomaterials compared to that of amount of clay content present in the geomaterials.
- A unit change in the soil solution pH results in a significant change in its retention capacity and hence the sorption mechanism of heavy metals in the soils. The decrease of solution acidity increases the amount of sorbed ion on the sorbent.
- Both the geomaterials sorbed larger amounts of heavy metals under the single component condition, indicating the influence of solution composition on geomaterial sorption performance.
- The higher valence heavy metals are preferentially sorbed by geomaterials when compared to the lower valence heavy metals.
- The selectivity of heavy metals of the same valence can be approximately determined by considering the misono softness parameter of heavy metals

The sorption capacity of geomaterials is significantly affected by various parameters which should be considered while assessing the long term performance of a landfill liner.

5. REFERENCES

Allen, H.E., Chen, Y.T., Li, Y. and Huang, C.P. (1995) "Soil partition coefficients for Cd by column desorption and comparison to batch adsorption measurements". Environmental Science and Technology, 29, pp1887-1891.

Arnepalli, D.N., Rao, B.H., Shanthakumar, S. and Singh, D.N. (2010) "Determination of Distribution Coefficient of Geomaterials and Immobilizing Agents". Canadian Geotechnical Journal, 47, pp1139-1148.

ASTM Standard D422 (1994) Standard test method for particle size analysis of soils, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D427 (1994) Standard test method for shrinkage factors of soils by mercury method, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D4318 (1994) Standard test method for liquid limit, plastic limit and plasticity index of soils, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D2487 (1994) Standard classification of soils for engineering purposes (Unified Soil Classification System), Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D4972 (2001) Standard test method pH of soils, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, *USA*.

ASTM Standard D4646 (2004) Standard test method for 24-h batch-type measurement of contaminant sorption by soils and sediments, Annual Book of ASTM Standards, 04.11, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D854 (2006) Standard test methods for specific gravity of soil solids by water pycnometer method, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D698 (2007) Standard test method for laboratory compaction characteristics of soils using light effort, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM Standard D2974 (2007) Standard test methods for moisture, ash, and organic matter of peat and other organic soils, Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

ASTM D5084 (2010). Standard test methods for measurement of hydraulic conductivity of saturated porous materials using a flexible wall permeameter. Annual Book of ASTM Standards, 04.08, ASTM International, West Conshohocken, PA, USA.

Ayala, A., Vega, J.L., Alvarez, R and Loredo, J. (2008) "Retention of heavy metal ions in bentonites from Grau Region". Environmental Geology, 53, pp1323-1330.

Bittel, J.E. and Miller, R.J. (1974) "Lead, cadmium and calcium selectivity coefficients on montmorillonite, illite and kaolinite". Journal of Environmental Quality, 3, Issue 3, pp 250-253.

Bordas, F.and Bourg, A. (2001) "Effect of solid–liquid ratio on the mobilization of cu, Pb, Cd and Zn from polluted river sediment, Water Air Soil Pollution, pp128, 391–400.

Bruemmer, G.W., Gerth, J. and Herms, U. (1986) "Heavy metal species, mobility and availability in soils" Journal of Plant Nutrition and soil Science, 149, pp382-398.

Cossu, R (2013) "Groundwater contamination from landfill leachate: when appearances are deceiving!". Waste Management, 33, pp1793–1794.

Chang, T. W. and Wang, M. K. (2002) "Assessment of sorbent/water ratio effect on adsorption using dimensional analysis and batch experiments". Chemosphere, 48, pp 419-426.

Charlet, L., Schindler, P.W., Spadini, L., Furrer, G., and Zysset, M. (1993) "Cation adsorption on oxides and clays: the aluminum case". Aquatic Science, 55, Issue 4, pp1015–1621.

Daniel, D.E., and Benson, C.H. (1990) "Water content-density criteria for compacted soil liners". Journal of Geotechnical Engineering, 119, Issues 2, pp. 223–237.

Degryse, F., Smolders, E. and Parker, D. R. (2009) "Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications - a review", European Journal of Soil Science, 60, pp590-612.

Elliott, H.A., Linerati, M.R. and Huang, C.P. (1986) "Competitive adsorption of heavy metals by soils". Journal of Environmental Quality, 15, pp214-219

Evans, R.C.(1966) An introduction to crystal chemistry. Cambridge University Press, London.

Farrah, H. and Pickering, W.F. (1977) "The sorption of Lead and Cadmium species by clay minerals". Australian Journal of Chemistry, 30, pp1417-1422.

Forbes, E.A., Posner, A.M. and Quirk, J.P. (1974) "The specific adsorption of inorganic Hg (II) species and Co (III) complex ions on goethite". Journal of Colloid and Interface Science, 49, pp403-409.

Gao, S., Walker, W.j., Dahlgren, R., and Bold, J. (1997) "Simultaneous sorption of Cd, Cu, Ni, Pb and Cr on soil treatment with sewage sludge supernatant". Water, Air and Soil Pollution, 93, pp331-345.

Grolimund, D., Bokkovec, M., Federer, P., and Sticher, H. (1995) "Batch experiments for sorption capacity of porous media". Environmental Science and Technology, 29, pp2317-2321.

Guney,Y., Koparal, S., and Aydilek, A.H., (2008) "Sepiolite as an alternative liner material in municipal solid waste landfills". Journal of Geotechnical and Geoenvironmental Engineering, 134, Issues 8, pp1166–1180.

Gulec,N., Gunal, B.C., and Erler, A. (2001) "Assessment of soil and water contamination around an ash-disposal site: a case study from the seyitomer coal-fired power plant in Western Turkey". Environmental Geology, 40, pp331–344

Hesse, P.R. (1972) A textbook of soil chemical analysis, Chemical Publishing, New York.

Hsu, P.H.(1989) Aluminium oxides and oxyhydroxides. In J.B. Dixon and S.B. Weed (eds.), Minerals in soil environments, ASA and SSSA, Madison, WI, pp379-438.

IS 2720, Part XXIV (1976) Methods of test for soils: Determination of cation exchange capacity, Indian Standards Institute, New Delhi, India, pp3-10.

JCPDS, (1994) Powder diffraction file, 44, 7354-CD ROM (PDF 1-44), International Centre for Diffraction Data, Pennsylvania, USA.

Kang, J., and Shackelford, C. (2010) "Membrane Behavior of Compacted Clay Liners". Journal of Geotechnical and Geoenvironmental Engineering, 136, Issues 10, pp1368–1382.

Kaya, A., and Durukan, S. (2004) "Utilization of bentonite-embedded zeolite as clay liner". Applied Clay Science, 25, pp83-91.

Kumar, M. and Philip, L. (2006) "Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils". Chemosphere, 62, pp1064- 586.

Kookana, R. S., and Naidu, R. (1998) "Effect of soil solution composition on cadmium transport through variable charge soils". Geoderma, 84, pp235-248.

Lakshmikantha, H. and Sivapulliah, P.V. (2006) "Relative performance of lime stabilized amended clay liners in diffeent pore fluids". Applied Clay Science, 24, pp1425-1448

Liu, X. and Lu, X. (2011) "Correlation between Bentonite's Cation Exchange Capacity 594 (CEC) activated clay quality indexes and activation strength". Applied Mechanics and Materials, 99-100, pp1031-1034.

Mcbride, M.B. (1994) Environmental Chemistry of Soils. Oxford University, Newyork.

Nicholls, D. (1974) Complexes, first row transition elements, London: Basingstoke, Macmillan.

Ouhadi V.R., and Yong, R.N., (2001) "The Role and Influence of Clay Fraction of Marly Soils on their Geotechnical and Geo-environmental Performance". Proceedings of the 3rd BGS Geo-environmental Engineering Conference, pp216 - 223.

Roy, W.R., Krapac,I.G., Chou, S.F.G., and Griffith, R.A. (1991) "Batch type procedures for estimating soil adsorption of chemicals". EPA/530/SW-87/006-F, USEPA, Washington, DC.

Sauve, S., McBride, M. and Hendersnot, W.H. (1988) "Soil solution speciation of lead (II): Effects of organic matter and pH". Soil Science Society of America Journal, 62, pp618-621.

Schwertmann, U. and Taylor, R.M. (1989) Iron oxides. In J.B. Dixon and S.B. Weed (eds.), Minerals in soil environments, ASA and SSSA, Madison, WI.

Shu-li, D., Yu-Zhuang, S., Cui-na, Y., and Bo-hui, X. (2009) "Removal of copper from aqueous solution by bentonites and the factors affecting it". Mining Science and Technology, 19, 489-492.

Smith, S., and McGrath, S.P. (1990) Chromium and nickel. In Alloway, B.J. (eds.) Heavy metals in soil. Glasgow, Academic & Professional, London, pp. 125-150.

Sposito, G. (1986). Distribution of potentially hazardous trace metals. Metal Ions Biological Systems, 18, pp1-20.

Sposito, G. (1989) The chemistry of soils, Oxford University Press, New York.

Vengris, T., Binkiene, R and Sveikauskite, A. (2001) "Nickel, copper and zinc removal from waste water by a modified clay sorbent". Applied Clay Science, 18, pp183-190.

Wagner, J.F. (2013) "Developments in clay Science". Chapter 5.3, Handbook of clay science, 5, pp663-676.

Wanner, H., Albinson, Y., Karnland, O., Wieland, E., Wersin, P., and Charlet, L. (1994) "The acid/base chemistry of montmorillonite". Radiochimica Acta, 66–67, pp157–162.

Wiklander, L., and Nilsson, E. (1954) "Ion release as influenced by the mode of exchange". Journal of Colloid Science, 9, pp223-232.

Yong, R.N., and Di Perno, N. (1991) "Sources and characteristics of waste: with specific reference to Canada". McGill University, Geotechnical Research Center, Geoenvironmetal Series.