ADSORPTION EFFICACY OF ADMIXTURES ON LEAD CONTAMINATED POROUS MEDIA

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Abstract: Adsorption of lead (II) ions on to the low cost admixtures such as fly ash, charcoal and shredded tyre pieces was investigated to assess the possible uses of these adsorbents. The influences of various proportions of adsorbents, adsorbent dosage, initial concentration and pH were investigated. The maximum % lead removal was achieved at 5% of charcoal (i.e., 94.84 % at pH of 4.8) and 15% of shredded tyre (i.e., 93.74% at pH of 9) admixed soil correspondingly. The distribution coefficient values are increased up to 10% of charcoal. For both fly ash and shredded tyre pieces, the convex shape of curve was observed. The optimum levels of additives for improving sorption capacity of soil are found to be 10% of charcoal, 15% of fly ash and 15% of shredded tyres blended soil. At the end, out of all admixtures charcoal showed good adsorption capacity compared to other additives and available locally at low cost.

Keywords: *Pb (II), retardation factor, distribution coefficient, sorption, batch equilibrium test*

1.0   Introduction

In recent decades, there has been significant sources of metal pollutants in soils rapidly expanding due to industrial activities like mine tailings, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, coal combustion residues and disposal of heavy metal wastes. These activities pose great impact on the ground and possibly deteriorate the environment. The rapid tempo of industrialization has led to severe problem of water pollution. Awareness encouragement of pollutant toxicity has forced industries and municipal authorities to treat wastewater before discharging to the natural water bodies (Anuradha, 2003). According to WHO, the maximum permissible limit (MPL) of lead in drinking water is 0.1 mg/L (WHO Guideline, 1984). Hence, the appropriate treatment of industrial wastewater which releases lead into the aquatic and terrestrial systems is very important. Major sources of lead contamination are exhaust gases from petrol engines which account for nearly 80%

of the total lead in the air (Sherene, 2010). Adsorbent materials such as activated carbon and naturally occurring zeolites (clinoptilolite and chabazite) can show good sorption effect in porous media to control the contamination. Ionic competition reduced lead ion removal by the zeolites, but enhanced activated carbon performance (Kelly *et al.*, 2004).The adsorption capacities of activated carbons increased with the initial lead concentration with the process of sorption followed a pseudo first order kinetics and parameters such as activation energy (E_a) and pseudo rate constant (k_0). The thermodynamic parameters such as change in enthalpy (ΔH), change in entropy (ΔS) and change in Gibbs free energy (ΔG) have shown the adsorption endothermic and non spontaneous (Gueu*et al.*, 2007). Sorption kinetics of lead ions are described by a pseudo-second-order model modified with a new parameter, t_0, included to account for an initial resistance due to the film boundary layer. The pseudo-second-order rate constant, initial sorption rate, and sorption capacity, together with time constant, t_0, also have been determined and correlated as a function of the system variables (Ho *et al.*, 2001). Pb(II) ions can be predominantly adsorbed onto ferrihydrite through inner sphere complexation, not retaining their primary hydration shell upon sorption (Paras *et al.*, 2003). Similarly, bromine pretreatment alters porosity and specific surface area of chitosan by means of physicochemical interaction with cationic sites of chitosan skeleton, besides imparting anionic alteration at amino linkages of chitosan, to remove lead (II) by chemical interactions on superfluous active sites as characterized by Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM), Differential Thermal Analysis (DTA) and elemental analysis (Rajendra *et al*., 2012).

Feasibility of employing calcareous soil to remove lead (II) ions from its aqueous solutions was investigated under batch mode (Das and Mondal, 2011). The lead adsorption was favored with maximum adsorption at pH 6.0. Sorption equilibrium time was observed in 60 min and the equilibrium adsorption data were analyzed by the Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin adsorption isotherm models. Finally it was concluded that the calcareous soil has potential application as an effective adsorbent for removal of lead ions from aqueous solution. The adsorption of Pb(II) onto GMZ bentonite in the absence and presence of soil humic acid (HA)/fulvic acid (FA) using a batch technique was done by Suowei *et al.* (2009). The influences of pH from 2 to 12, ionic strengths from 0.004 M to 0.05 M NaNO, soil HA/FA concentrations from 1.6 mg/L to 20 mg/L, foreign cations (Li+, Na+, K+), anions (Cl-, NO_3^-), and addition sequences on the adsorption of Pb (II) onto GMZ bentonite were tested. The results demonstrated that the adsorption of Pb (II) onto GMZ bentonite increased with increasing pH from 2 to 6. HA was shown to enhance Pb (II) adsorption at low pH, but to reduce Pb (II) adsorption at high pH, whereas FA was shown to decrease Pb (II) adsorption at pH from 2 to 11. The results also demonstrated that the adsorption was strongly dependent on ionic strength and slightly dependent on the concentration of HA/FA. The kinetics analysis revealed that the overall adsorption process was successfully fitted with the pseudo-second-order kinetic model using Alginate-SBA-15 (ALG-SBA-15) which was synthesized by encapsulation of the

nanoporous SBA15 in the biopolymeric matrix of calcium alginate (Cheragali, 2012). Increase in K with the increase in temperature indicated positive effect of temperature on Pb sorption. High absolute values of G, and positive values of ΔH and ΔS suggested that the sorption reaction was spontaneous and endothermic (Sudarshan and Dhanwinder, 2010). Low Molecular Weight Organic Acids (LMWO) can solubilize Pb in soil by decreasing soil pH or increasing soil organic contents, but have little effect on its translocation. Due to heterogeneous structure, humic substances (HS) role is complex (Shahid *et al.*, 2012).

There are numerous technologies to remove heavy metals from the contaminated wastewater such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation methods and electro-remediation methods (Horsfall and Abia, 2003 & Amrit *et al.*, 1999). However, most of these methods might not efficient in removing heavy metal at very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment. Hence, the simple, effective, low cost and eco-friendly techniques are required for the fine tuning of effluent wastewater treatment. The search for low cost, and easily available adsorbents has led to the investigation of materials of agricultural and biological origin, alongside those of industrial by-products as adsorbents for removal of heavy metals (Alemayehu *et al.*, 2008). From the aforementioned review of literatures, it is understand that there is a quantum of work has been carried out on the adsorption of Pb (II) contaminated soil by various means. In the present study an experimental work has been carried out towards understanding the adsorption efficacy of lead using different admixtures such as fly ash (FH), charcoal (CC) and shredded tyre pieces (ST).

2.0   Experimental Investigation

2.1   Materials

2.1.1   Soil

In the present investigation soil was collected from Shabad, Hyderabad in India. The site is open land and free from unwanted debris. While collecting samples, an attempt was made to choose only intrinsic soil belonging to category CH which has major percentage of fine fractions. The properties of soil used in the study are reported in Table 1. Soil has fine fractions (< 0.075mm) of 86% and coarse fraction (> 0.075 mm) of 14%. The soil collected from the field was air dried and stored in airtight containers in the laboratory.

Table 1: Properties of soil

S. No	Soil property	Values	Code
1	Grain size distribution		
	Gravel (%)	14	
	Silt (%)	35	IS: 2720 (Part - 4)
	Clay (%)	51	
2	Atterberg's limits		
	Liquid Limit, LL (%)	56	
	Plastic Limit, PL (%)	18	IS: 2720 (Part – 5)
	Plasticity Index, PI (%)	38	
	Shrinkage Limit, SL (%)	14	IS: 2720 (Part – 6)
3	IS classification	CH	
4	Specific gravity, G	2.72	IS: 2720 (Part -3/Section -2)
5	OMC (%)	13.8	IS: 2720 (Part – 7)
	MDD (kN/m^3)	17.8	
6	Differential Free Swell Index, DFSI (%)	76	IS: 2720 (Part - 40)
7	UCC (kPa)	112	IS: 2720 (Part – 10)

Note: IS - Indian Standard Code of Practice

2.1.2 *Admixtures Used in the study*

Admixtures such as fly ash (FA), charcoal (CC) and shredded tyre pieces (ST) were used along with soil to study their efficacy in removal of Pb (II).

2.1.2.1 *Fly ash (FA)*

Fly ash was collected from the Vijayawada Thermal Power Station (VTPS), Vijayawada in Andhra Pradesh (AP) state, India. Fly ash physical and chemical composition is presented in Table 2.

Table 2: Physical and chemical properties of fly ash

Property	Values	Property	Value
Specific gravity	1.97	Chemical Composition	
Grain Size Distribution		% SiO_2	60.5
% Gravel	0	% Al_2O_3	30.8
% Coarse Sand	0	% Fe_2O_3	3.6
% Medium Sand	0	% CaO	1.4
% Fine Sand	97.5	% MgO	0.91
% Silt & Clay	2.5	% SO_3	0.14
Effective Diameter, D_{10} (mm)	0.085	% $K_2O + Na_2O$	1.1
Coefficient of Uniformity, C_u	2.2		
Coefficient of Curvature, C_c	1.2		

The fly ash collected was stored in airtight containers in the laboratory and it was used with the soil under controlled conditions maintained in the laboratory. The fly ash used in the present study contains majority of fine sand fraction and it is around 97%. Remaining fraction is about 2.5% is of silt range. Figure 1, presents the photograph of fly ash used in the study.

Figure 1: Fly ash

2.1.2.2 Charcoal (CC)

Charcoal was collected from locally available market and after properly air dried stored in air tight container. It is in a light, black color consisting of carbon and any remaining ash, obtained by removing water and other volatile constituents from animal and vegetation substances. Figure 2 presents photography of charcoal used in the study.

Figure 2: Charcoal

2.1.2.3 Shredded Tyre Pieces (ST)

The shredded tyre pieces were prepared from the locally available tyre scrap and have basic geometrical shape and size between 1 to 12 mm. Care has been taken that the shredded tyre chips are free from steel wire. Figure 3 shows the photograph of shredded tyre pieces used in the present investigation.

Figure 3: Shredded tyre pieces

2.2   Methodology - Batch Equilibrium Test

Batch equilibrium tests were conducted on aqueous solution added to soil samples, which was air dried and stored in the laboratory under controlled conditions. The stock solution of Pb (II) ions was prepared by dissolving an accurate quantity of lead nitrate (Pb (NO3)2) in de-ionized water and other Pb (II) solutions were prepared from stock solution by dilution and pH was adjusted by 0.1 M HNO and/or 0.1 M NaOH solutions. The fresh dilutions were made for each adsorption experiment and concentrations of contaminant in the form of aqueous solutions were prepared to cover broad range of concentration such as 10, 100, 500, 1000 mg/L. These are the concentrations which constitute the designed solution phase to evaluate the capability of suspended soil particles to absorb all the contaminants. Also at these concentrations, the behavior of contaminants with the aid of interaction characteristics dictated by surface properties of soil solids. For proper dispersion of contaminant solution in soil media, it is a common practice to use a soil to contaminant solution (weight to the volume ration) of 1:10, and also proper agitation point of view, the constant temperature about 27°C can be maintained (Bedient *et al.*, 1994). The contaminant and soil mixtures were prepared in a conical flask and subjected to centrifugation at 250 rpm for about 15 minutes. These solutions were separated from soil solids by extraction using Whattman filter paper and the solution concentrations were measuredby Atomic Absorption Spectrophotometer (AAS). From this, mass adsorbed (S) to the soil (mg/kg) was recorded and tabulated. Also, the equilibrium concentrations (C) of the contaminant solutions were estimated.

The adsorption mass ratio, S in mg/kg can be computed from the expression (Eq. 1) given below.

$$S = \frac{(C_o - C)\,V}{M} \tag{1}$$

Where, S = adsorption mass ratio in mg/kg, V = volume of liquid in conical flask (40 ml), C_o = initial contaminant concentration, C = equilibrium concentration and M = mass of soil in the flask (4g).

The percentage of Pb (II) ions removal is given by the following equation:

$$\% \text{ Removal} = \frac{(C_i - C_f)}{C_f} \times 100 \tag{2}$$

where, C_i = initial concentration of the metal ion, C_f = final concentration of the metal ion in thesolution.

The obtained batch equilibrium test results are plotted and discussed in the following sections.

3.0   Results and Discussion

Adsorption of Pb (II) ions by various admixtures has been studied. The graphical representations of the mass of contaminant adsorbed per unit dry mass of soil or organic matter (S) versus concentration of the contaminant (C) are called Isotherms. In order to use isotherms, the mass adsorbed an instantaneous equilibrium must be reached between the sorbent and the sorbate.

3.1   Adsorption Isotherm

The amount sorbed phase concentrations to solution phase concentration at equilibrium are called as distribution coefficient (K_d). The distribution coefficient (K_d) can be defined as the ratio between sorbed phase concentrations to the solution phase concentration at equilibrium. In the present investigation, soil following linear isotherm and are presented in Figure 4. The obtained results from batch equilibrium test are presented in Table 3. It can be seen that as the initial concentration of the contaminant increases, the mass adsorbed to the soil is increasing linearly irrespective of the percentage fine fraction prevailing in the system. This can be attributed that an increased contact surface of adsorbent particles increased with fine content.
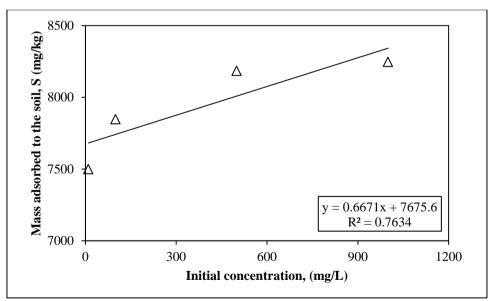

Figure 4. Isotherm for soil

Table 3: Batch equilibrium test results for soil

S. No	Initial concentration, C_o (mg/L)	Final Concentration, C (mg/L)	Sorption, S (mg/kg)	Distribution coefficient, K_d (L/kg)
1	10	759.89	7498.9	
2	100	884.68	7846.8	0.66
3	500	1318.42	8184.2	
4	1000	1824.66	8246.6	

The isotherm fitted for soil lead to the linear fitting and the respective equations are presented in Eq. 3.

For soil linear isotherm equation is,

$$S = 0.667 \, C_o + 7675 \tag{3}$$

and R^2 value is 0.763

3.2 Influence of Initial Lead Concentration

Influence of initial lead concentration on various proportions of admixtures has been presented in Figures 5 to 7. During the analysis the temperature of 27°C, agitation speed of 250 rpm and maximum contact time equal to 24 Hrs was used. From these figures, it can be noticed that, as the initial lead concentration increases the amount of mass adsorbed to the soil – admixtures also varied linearly. This may be due to the increased contact surface area of adsorbent particles with the increased fines content. For the case of charcoal, as the percentage of charcoal increases amount of adsorption increased up to 10% and later the values showing lesser than the previous. Similarly for fly ash and shredded tyre, adsorption of lead increased with the percentage of admixture added to soil. At the beginning, faster rate of lead adsorbed to the soil was observed due to the large number of available sorption sites and slower adsorption rate at the end is probably due to saturation of active sites and attainment of equilibrium.
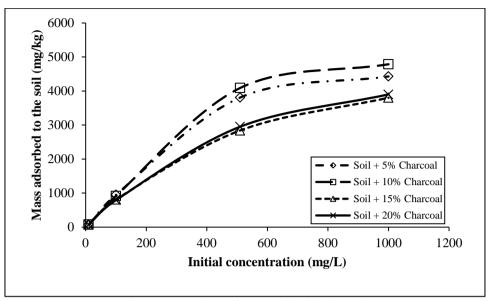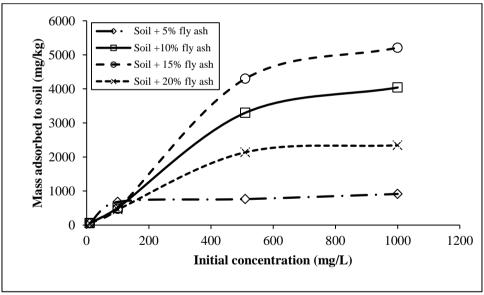
Figure 5. Sorption effect on soil with charcoal
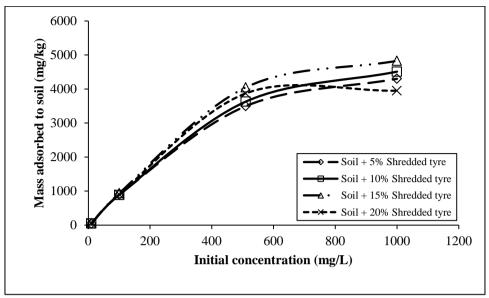

Figure 6. Sorption effect on soil with fly ash

Figure 7. Sorption effect on soil with shredded tyre

3.3   Influence of pH

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH, which influences both the adsorbent surface metal binding sites. The pH of added solution was examined from solution a different pH levels. Variation of Pb^{2+} removal onto the various proportions of soil –mixtures with pH is presented in Figure 8. At pH < 2.5, H^+ ions compete with Pb (II) ions for the surface of the adsorbent which would hinder Pb(II) ions from reaching the binding sites of the sorbet caused by the repulsive forces. At pH > 6.0,the Pb(II) gets precipitated due to hydroxide anions forming a lead hydroxide precipitate. The maximum efficiency was observed 94.84% at pH of 4.8 for 100 mg/L with 5% Charcoal and 93.74 % at pH of 9.0 for 100 mg/L was attained using 15% of Shredded tyre. Likewise, optimum amount of removal was noticed 84.27% at pH of 6 for 15% of fly ash.
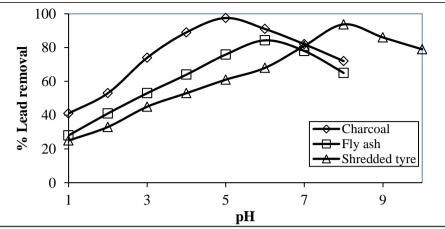
Figure 8. Effect of pH on % lead removal

3.4.   *Admixture Effect on the Percentage of Removal of Lead*

Figures. 9 and 11 present the effect of initial concentration on percentage lead removal with charcoal and shredded tyre admixed soil respectively. In both the figures, the fittings are following similar trend. The maximum % lead removal was achieved at 5% of charcoal (i.e., 94.84 % at pH of 4.8) and 15% of shredded tyre(i.e., 93.74% at pH of 9) admixed soil correspondingly. Figure 10 shows shuffled variation of % lead removal with initial concentration admixed with fly ash. The maximum percentage of lead removal was achieved at 5% of charcoal (i.e., 94.84 % at pH of 4.8) and 15% of shredded tyre (i.e., 93.74% at pH of 9) admixed soil, respectively.
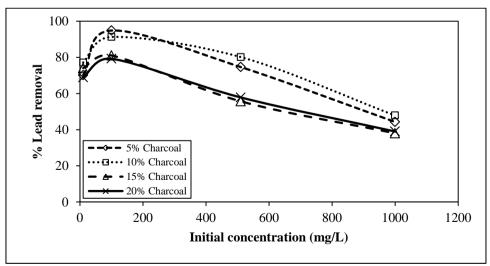

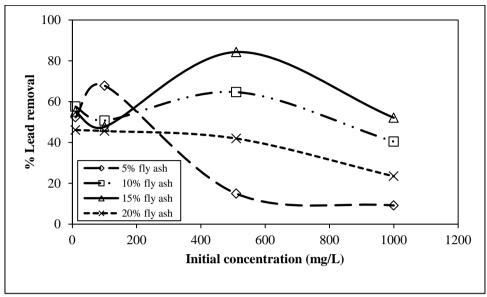
Figure 9. Influence of charcoal on % lead removal

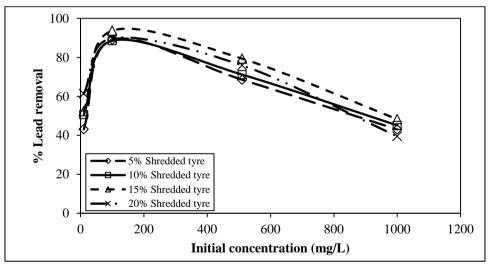Figure 10. Influence of fly ash on % lead removal

Figure 11. Influence of shredded tyre on % lead removal

3.3 Influence of Admixtures on Distribution Coefficient (K_d)

The variation of distribution coefficient (K_d) with % admixtures added to soil is presented in Figure 12. It can be seen that up to 10% of charcoal there is an increment in K_d and subsequently normalized values were observed. For both fly ash and shredded

tyre pieces, the convex shape of curve is observed. The K_d values are linearly increased up to certain extent and after that the values are normalized. This can be evidently attributed that the increased contact surface of adsorbent particles with the increased fine content.
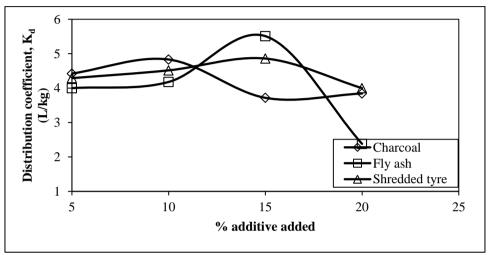

Figure 12.Influence of additives on distribution coefficients

4.0   Conclusions

The removal of Pb (II) ions by using low cost adsorbents was studied in the batch experimental systems. Based on the results and discussions, the following conclusions can be drawn. Equilibrium metal adsorption increase with increase in the initial concentration of Pb (II) ions. The adsorption of Pb (II) followed a linear variation. The maximum % lead removal was achieved at 5% of charcoal (i.e., 94.84 % at pH of 4.8) and 15% of shredded tyre (i.e., 93.74% at pH of 9) admixed soil correspondingly. The distribution coefficient values are increased up to 10% of charcoal. For both fly ash and shredded tyre pieces, the convex shape of curve was observed. The distribution coefficient values linearly increased up to certain extent and after that the values were normalized. The optimum levels of additives for improving sorption capacity of soil are found to be 10% of charcoal, 15% of fly ash and 15% of shredded tyres blended soil. Furthermore efficient reuse of low cost adsorbents was found to be possible and the method is very simple, cost effective and environmental friendly.

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