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REMOVAL OF LEAD FROM AQUEOUS SOLUTION USING LOW COST ABUNDANTLYAVAILABLE ADSORBENTS LIKE CHINA CLAY AND FLY ASH

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ABSTRACT

The removal of poisonous Pb (II) from wastewater by different low-cost abundant adsorbents was investigated. China clay and Fly ash were used as different adsorbent for the removal of heavy metal like Pb(II) ion. The influence of pH, contact time, metal concentration, adsorbent dosages on the selectivity and sensitivity of the removal process was investigated. The adsorption efficiencies were found to be pH dependent, increasing by increasing the solution pH in the range from 2.5 to 6.5. The equilibrium time was attained after 120 min and the maximum removal percentage was achieved at an adsorbent loading weight of 1.5 gm. The equilibrium adsorption capacity of adsorbents used for lead were measured and extrapolated using linear Freundlich, Langmuir and Temkin isotherms and the experimental data were found to fit the Temkin isotherm model.

KEYWORDS: Low-cost adsorbents (China clay and fly ash), lead, adsorption, wastewater, Adsorption Isotherms.

INTRODUCTION

The greater environmental awareness in both the public and regulatory sphere in recent years has necessitated greater treatment of industrial effluent. As such there has been a great deal of research into finding cost-effective methods for the removal of contaminants from wastewater. The permissible limit of Lead in drinking water was 0.01 mg/l reported in drinking water IS 10500:2012.Permissibe limit was also reported as 0.05 mg/l(BIS), 0.01mg/l (WHO), 0.015 mg/l (USEPA) and 0.01 mg/l (Eropean Commission) in drinking water.[1] In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly.[2] Some previous investigations on the removal of heavy metal ions with many agricultural byproducts have been reported.[3,4,5] The present study undertakes the adsorption efficiency of china clay and Fly ash for the removal of Pb(II) from aqueous systems.

MATERIALS AND METHODS

In each experiment, a 50 mL of the metal ion solution were mixed with a definite amount of the adsorbent. The mixture of the test solution and each of the adsorbents was shaken on a reciprocating shaker at 140 rpm. At the end of each experiment, adsorbents were separated from the solution and the remaining lead concentration was analyzed using a Perkin-Elmer Optima 2000 Inductively coupled plasma (ICP-OES). The adsorption experiments were carried out at room temperature. The pH ofthe suspension in the experiments was adjusted with NaOH and HCl.

1: Adsorbents and their Characterization

The physic-chemical nature of the adsorbate significantly affects the rate and extent of adsorption of pollutants from water and wastewaters by adsorption technique. The chemical constituents of various adsorbents vary from sample to sample depending upon the source of collection. Therefore, the characterization of adsorbents is quite essential in order tohave a better insight into the mechanism of the adsorption process. China clay is a mineral of kaolinite group. It does not swell with addition of water. The alumina content present in it does not form isomorphous series with any other metallic compounds. It is generally used in the manufacture of different types of ceramic goods. It has been used by several workers.[6-10] as an adsorbent for water and wastewater treatment by adsorption process. It was collected from Patharghatt village of Bhagalpur district, Bihar (India). It was used as such without any pretreatment just after sieving through 53µm pore size sieve. The different chemical constituents of adsorbents were determined using gravimetric, EDTA and colorimetric methods.[11-12] The chemical analysis and characterization of China clay is given in table :1.

Fly ash was obtained from Obera Thermal Power Plant, Mirzapur, UP (INDIA). They were used as such without any pretreatment just after sieving through 53µm pore size sieve (Table:2).

Table 1: Chemical analysis of China clay as Adsorbent.

Constituents	Percentage by weight
SiO_2	46.22
Al_2O_3	38.40
CaO	0.86
Fe_2O_3	0.68
MgO	0.37
Loss of ignition	13.47
Particle size	53µm
Mean Particle size diameter	$51x10^{-4}$ cm
Surface Area	13.52 m^2g^{-1}
Porosity	0.330
Density	2.692 gcm^{-3}

Table 2: Chemical analysis of Fly ash as Adsorbent.

Constituents	Percentage by weight
SiO_2	56.04
Al_2O_3	25.90
CaO	2.22
Fe_2O_3	1.26
MgO	0.94
Loss of ignition	13.64
Particle size	53µm
Mean Particle size diameter	$48x10^{-4}$ cm
Surface Area	5.77 m^2g^{-1}
Porosity	0.360
Density	3.420 gcm^{-3}

RESULTS

The main parameters influencing metal sorption were investigated: contact time, initial metal ion concentration, amount of adsorbent and pH value of solution. The results were expressed as the removal efficiency of the adsorbent towards metal ions or the Percentage removal, which was defined as:

Percentage Adsorption = $[(Co – Ce) / Co] x 100$

Where, Co and Ce are the initial and equilibrium concentration (ppm) of metal ions in solution, respectively.

1. Effect of contact time

The removal of Pb(II) from the synthetically prepared wastewater increases with increasing contact time and attains equilibrium at about 180 min(Table:1). The results for the effect of contact time on lead removal by China clay and Fly ash are presented in Figure 1. The plots represent the percentage removal of lead vs the contact time for the 25 ppm initial metal concentration. The plots reveal that maximum percent metal removal was attained after about 180 min. of contact time.

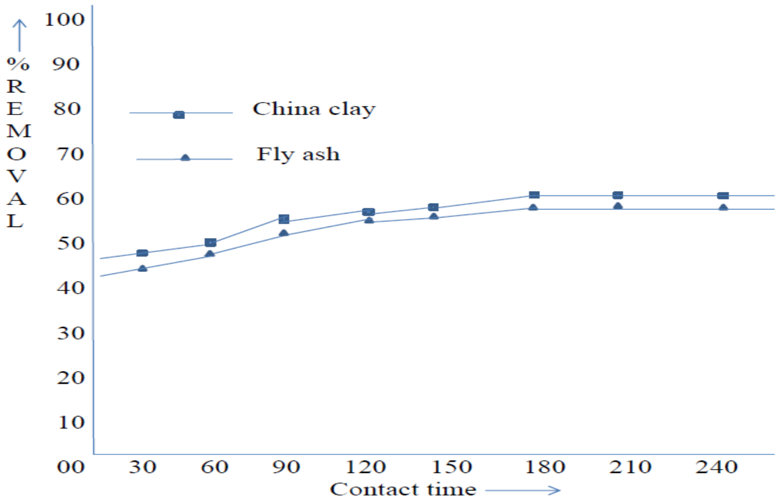

Figure 1: Percentage removal of Pb(II) (25ppm) on adsorbents.

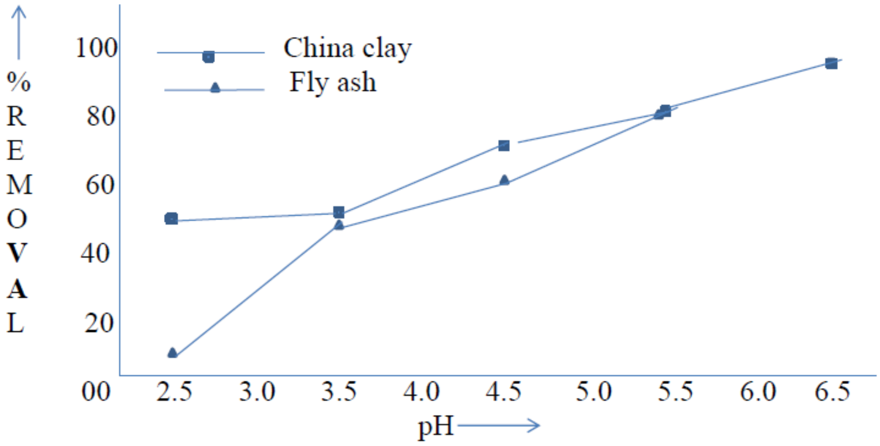

Figure 3: Effect of pH on lead removal (25 ppm solution) throughadsorption on adsorbents.

Table 1: Percentage adsorption of Pb(II) at different contact time on adsorbents, at concentration 5 ppm, Particle size 53 µm.

Contact time(minutes)	% Removal in case ofChina clay	% removal in case ofFly ash
30	48	44
60	50	46
90	54	50
120	56	52
150	58	54
180	59	55
210	59	55
240	59	55

Table 3: Percentage adsorption of Pb(II) at different pH on adsorbents, atconcentration 25 ppm, Particle size 53 µm,

pH of solution	% Removal in case of China clay	% removal in case of Fly ash
2.5	52	8
3.5	55	48
4.5	74	60
5.5	80	80
6.5	90	90

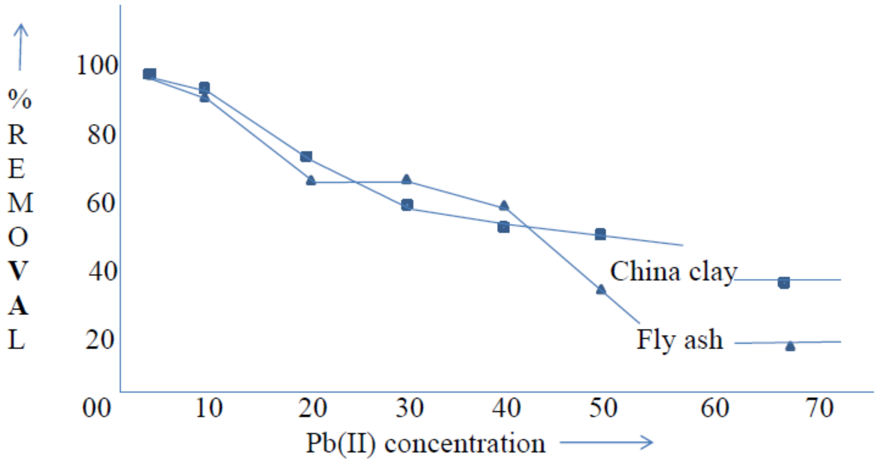

Figure 2: Effect of initial Pb(II) concentration on its removal by different adsorbents at 90 min of contact time, pH 4.5 and 1.0 gm adsorbents.

2: The effect of initial lead concentration

The effect of initial lead concentration is presented in Figure. 2. The increase in initial concentration of lead (II) from 5 to 50ppm decreased its percentages removal on the different adsorbents under investigation (Table:2).

Table 2: Effect of initial Pb(II) concentration on different adsorbents at 180 min of contact time, pH 4.5 and 1.0 gm adsorbents. At concentration25 ppm, Particle size 53 µm.

Concentrations(ppm)	% Removal in case of China clay	% removal in case of Fly ash
5	98	98
10	92	88
15	78	70
20	75	66
25	72	64
30	60	65
40	55	60
50	50	35

3. Effect of pH

The effect of pH is presented in Figure: 2.The effect of pH on adsorptionof lead was studied at room temperature by varying the pH of metal solution from 2.5 to 6.5. Lead removal recorded its minimum values at pH 2.5.This can be justified on the bases that at lower pH values, the H+ ions compete with the metal cation for the adsorption sites in the system,which in turn leads to partial releasing the later(Table:3). The heavy metal cations are completely released under extreme acidic conditions.[13] The adsorption percent increases in the pH range of 4.5-6.5, showing the maximum adsorption at pH 6.5. The greatest increase in the rate of adsorption of Pb(II) ions on China clay and Fly ash was observed in the pH range from 2.5 to 4.5. The effect of initial lead concentration is presented in Figure.3. The increase in initial concentration of lead (II) from 5 to 50ppm decreased its percentages removal on the different adsorbents under investigation.

4. Effect of adsorbent loading weight

The effect of adsorbent loading weight is presented in Fig. 4. The dependence of Pb(II) sorption on adsorbent dose was studied by varying the amount of adsorbents from 0.25 to 2.0 gm, while keeping other parameters (pH, concentration, and contact time) constant. It can be inferred that the percentage removal of lead increases with increasing adsorbents doses from 0.25 g to 1.5 g. It must be also noted that there was non-significant increases in removal percentages when adsorbents dose was increased from 1.5 g to 2.0 g. This suggests that after a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. The increase in Pb(II) removal percentage with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent.

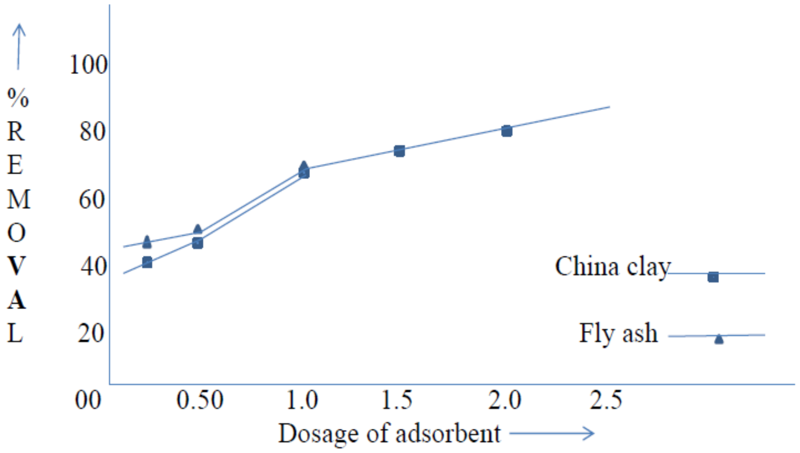

Figure 4: Effect of adsorbent dosage vs Pb(II) concentration at 180 min of contact time, pH 4.5 and 1.0 gm adsorbents.

Table 4: Effect of adsorbent dosage at 180 min of contact time, pH 4.5and 1.0 gm adsorbents. At concentration 25 ppm, Particle size 53 µm.

Adsorbent Dosage	% Removal in case ofChina clay	% removal in case ofFly ash
0.25	40	45
0.50	45	48
1.00	65	67
1.50	72	72
2.00	77	75

5. Isothermal studies

The experimental data for the uptake of lead metal ions by china clay and Fly ash over the studied concentration range were processed inaccordance with the three of the most widely used adsorption isotherms: Langmuir, Freundlich and Temkin isotherms. The data were found to fit on the Temkin isotherm model assuming chemical adsorption between Lead ions and the used adsorbents. The Temkin isotherm model is given by the following equation:

$X = a + b \ln C$

Where C = Concentration of adsorbate in solution at equilibrium (mg/l). X = Amount of metal adsorbed per unit weight of adsorbent (mg/gm), a and b are constants related to adsorption capacity and intensity of adsorption. Plots of ln C against X are given in Figures: (5 and 6) for the adsorption of lead onto China clay and Fly ash, respectively. The Temkin isotherm equation fits the present data because it takes into account the occupation of the more energetic adsorption sites at first. Fornatural unmodified materials such as the studied ones it is highly probable that their adsorption sites are energetically nonequivalent.[14] Examination of the data showed that the Temkin isotherm is an appropriate description of the data for lead ions sorption over the concentration ranges studied.

(i) Temkin adsorption isotherm equation of lead on China clay is,
$Y = 3.248\ X + 8.105$

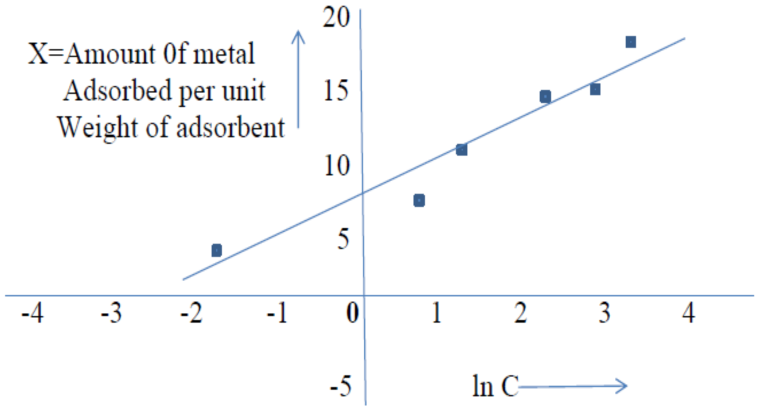

Figure 5: Temkin adsorption isotherm of lead on China clay.

(ii) Temkin adsorption isotherm equation of lead on Fly ash is,
$Y = 4.751\,X + 8.661$

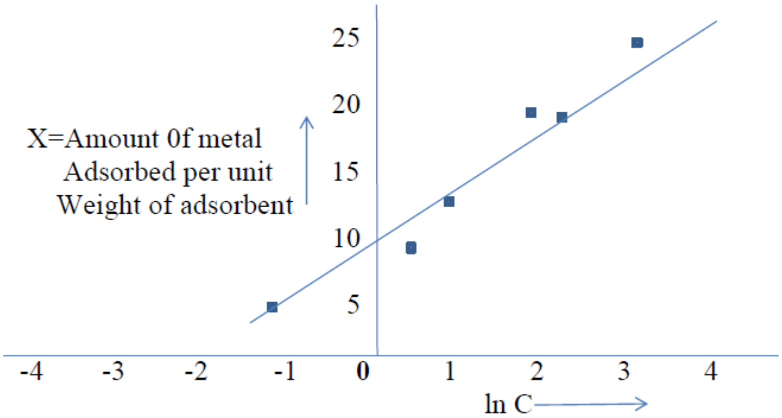

Figure 6: Temkin adsorption isotherm of lead on Fly ash.

DISCUSSION AND CONCLUSION

Removal of the poisonous lead ions from solutions was possible using China clay and Fly ash as adsorbents. China clay was the most effective,for which the removal reached 98% of Pb(II) at room temperature. The sorption process, nevertheless, proceeded in two distinct phases. The rates of adsorption were fast initially, and then the rate of metal removal declined appreciably as contact time increased before attaining equilibrium. The fast-phase sorption may be explained as the passive uptake through adsorption, or the bio-sorbent surface ion exchange.[15] Since the adsorption phenomenon characteristically tends to attain instantaneous equilibrium.[16] and many agricultural wastes act as natural ion exchange agents.[17] It is also relevant to point out that since active sorption sites in a system is a fixed number and each active site can adsorb only one ion in a monolayer,[18] the metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution. The rate of metal removal is of greatest significance for developing a natural adsorbent-based water-treatment technology. The optimum pH for removal was found to be in the range from 4.5-6.5, at which Pb(II) removal reaches 98% for the two investigated adsorbents. The effect of pH can be explained the availability of negatively charged groups at the bio-sorbent surface is necessary for the sorption of metals to proceed,[19] which at the highly acidic pH 2.0 is unlikely as there is a net positive charge in the system due to H+ and H_3O+. In such a system H+ compete with metal ions,[20] resulting in active sites to become protonated to the virtual exclusion of metal binding on the bio-sorbent surface.[21] This means that at higher H+ concentration, the adsorbent surface becomes more positively charged thus reducing the attraction between adsorbent and metal cations.[22] In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater metal uptake.[23] The optimum pH for lead removal was found to be 4.5. The percentage uptake was found to be highly dependent on the initial concentration of the adsorbate and adsorbent fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available adsorption sites are limited thereby adsorbing almost the same amount of adsorbate thus resulting in a decrease in percentage removal of the adsorbate corresponding to an increase initial adsorbate concentration.[24] Increases in the adsorbent loading weight, and contact time were found to increase the percentage removal of Pb(II).While the increase in the initial lead concentration resulted in a decrease in the removal efficiencies of the different adsorbents. The isothermal study of the Pb(II) adsorption on the different adsorbents was found to be best fitted to the Temkin isotherm model, which reflects chemical adsorption mechanism. This work showed that locally available materials such as China clay and fly ash can be used as efficient sorbents for lead ions removal, representing an effective and environmentally clean utilization of waste matter. More studies are needed to optimize the system from the regeneration point of view, to investigate the economic aspects and to confirm the applicability of this new sorbent under real conditions, such as in the industrial effluent treatment.

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