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Removal of Pb (II) from Aqueous Solutions using Fuller's Earth

Tarun Kumar Naiya, Biswajit Singha, Ashim Kumar Bhattacharya, Sudip Kumar Das

***Abstract*—**Fuller's earth is a fine-grained, naturally occurring substance that has a substantial ability to adsorb impurities. In the present study Fuller's earth has been characterized and used for the removal of Pb(II) from aqueous solution. The effect of various physicochemical parameters such as pH, adsorbent dosage and shaking time on adsorption were studied. The result of the equilibrium studies showed that the solution pH was the key factor affecting the adsorption. The optimum pH for adsorption was 5. Kinetics data for the adsorption of Pb(II) was best described by pseudo-second order model. The effective diffusion co-efficient for Pb(II) adsorption was of the order of 10^{-8} m^2/s. The adsorption data for metal adsorption can be well described by Langmuir adsorption isotherm. The maximum uptake of metal was 103.3 mg/g of adsorbent. Mass transfer analysis was also carried out for the adsorption process. The values of mass transfer coefficients (β) obtained from the study indicate that the velocity of the adsorbate transport from bulk to the solid phase was quite fast. The mean sorption energy calculated from Dubinin-Radushkevich isotherm indicated that the metal adsorption process was chemical in nature.

***Keywords*—**Fuller's earth, Pseudo second order, Mass Transfer co-efficient, Langmuir

I. Introduction

LEAD is one of the toxic environmental pollutants which is found in nature and found as introduced contaminant into the environment. Pb(II) poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain. Process industries, such as battery manufacturing, printing and pigment, metal plating and finishing, soldering material, ceramic and glass industries generate large quantities of wastewater contaminated with lead. Drinking water is polluted due to the corrosion and leaching of lead pipes and Pb/Sn solder joints associated with copper service lines used in household plumbing [1]. The permissible limit of lead in wastewater as set by Environment Protection Agency [2] and that of Bureau of Indian Standards (IS 10500) is 0.1 mg/L [3].

Tarun Kumar Naiya is Assistant Professor at Petroleum Engineering Department, Indian school of Mines, Dhanbad, Jharkhand, India-826004.(Phone: +91-326-2235879; fax: +91-326-2296632; E-mail: trn2711@yahoo.com.)

Biswajit Singha and Ashim Kumar Bhattacharya are Senior Research Fellow at Chemical Engineering Department in University of Calcutta, Kolkata, India-700009.

Sudip Kumar Das is Professor at at Chemical Engineering Department in University of Calcutta, Kolkata, India-700009. e-mail : drsudipkdas@vsnl.net

There are various methods of Pb(II) from waste water. Methods include chemical precipitation, ion exchange, electrolysis, membrane filtration, solvent extraction, fertilization and sorption to metal oxide, clay, activated carbon, organic sorbents. These technologies suffer badly due to cost ineffectiveness especially when metal concentration is very low. Adsorption process seems to be most effective method for removal of heavy metal if combined with appropriate regeneration steps.

This process solves the problem of sludge disposal and renders the system more viable. In the last few years, several approaches using activated carbon have been studied in this area. The high cost of activated carbon has motivated scientists into the search for new low cost abundantly available adsorbents. Industrial by-products are almost zero-cost materials and in the same time their utilization could contribute to the solution of their management problem improving the material efficiency within several industrial activities. Several researchers [4–6] use a number of potential low cost adsorbents such as, tannin rich materials, clays, zeolites, red mud, fly ash, agricultural siliceous waste, etc for removal of heavy metals.

II. Experimental Section

A. Materials

Fuller's earth as synthetic adsorbents, was procured from Loba Chemie Pvt. Ltd., Mumbai, India. All the necessary chemicals used in the study were of analytical grade.

Lead nitrate [$Pb(NO_3)_2$] was obtained from E. Merck India Limited, Mumbai, India. Stock solution of Pb(II) was made by dissolving exact amount of respective metal salt. The range of concentration of the metal components prepared from stock solution was varied between 3 mg/L to 300 mg/L. The test solutions were prepared by diluting 1 g/L of stock metal solution with double distilled water.

B. Experimental Procedures

100 ml of test solution for the batch adsorption studies was taken in 250 ml stopper conical flask at the desired pH value and concentration. pH of the solution was monitored in a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions by adding 0.1 M HCl and 0.1 M NaOH solution as per required pH value. Necessary amount of Fuller's earth was then added and contents in the flask were shaken for the desired contact time in an electrically thermo stated reciprocating shaker @ 120-130 strokes/min at 30^0C. The time required for reaching equilibrium condition estimated by drawing samples at regular intervals of time till equilibrium was reached.

The contents of the flask were filtered through filter paper and the filtrate was analyzed for remaining metal concentration in the sample using Atomic Absorption Spectrophotometer (VARIAN SPETRA AA 55, USA) as per procedure laid down in APHA, AWWA standard methods for examination of water and wastewater, 1998 edition [7].

III. Results And Discussion

A. Effect of pH

The effect of pH on adsorption was studied in the range of pH that was not influenced by the metal precipitation mainly as metal hydroxide. Solubility product equilibrium constant, K_{sp} [8] denote that the suitable range for the Pb(II) adsorption is 3-7. In general, adsorption of cations is favored at $pH>PH_{pzc}$. The oxides of iron, silica present in Fuller's earth develop charge on the adsorbent surface in contact with water. A positive charge develops in the surface of oxides of Fuller's earth in an acidic medium due to the aqua complex formation of the oxide present as follows:

$$-MO + HOH \xrightarrow{H^+} M - OH^{2+} + OH^- \quad (1)$$

Adsorption of Pb(II) with the variation of pH is shown in Fig. 1. The sorption at the low pH range usually takes place with low removal efficiency. This is due to competition between high concentration of proton and metal ion expected to form a bond with the active sites. These bonded active sites become saturated and was inaccessible to other cations. In addition when pH increases, there is a decrease in positive surface charge (since the deprotonation of the sorbent functional groups could be occurs), which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of Fuller's earth, favoring adsorption. To ensure no interference from the metal precipitation, subsequent experiments were carried out at pH is equal to 5.

B. Effect of adsorbent concentration

The effect of adsorbent dosage on the removal of Pb(II) ion was studied and results are represented in Fig. 2 . The removal of metal ion was found to increase with an increase in adsorbent dosage from 1 to 7.5 g/L. The metal ion removed almost remain unchanged after adsorbent dosage 5.0 g/L. Increase in adsorption with increase in adsorbent dosage attributed to the availability of larger surface area and more adsorption sites. Adsorbent dosage of 5.0 g/L is taken to be the optimum adsorbent dosage value for further study.

C. Effect of contact time and adsorption rate kinetics mechanism

Effect of contact time on the adsorption of metal solution at initial pH value 5 is shown in Fig. 3. During the experiment contact time was varied from 0 min. to 5 h. The initial rapid adsorption gives away a very slow approach to equilibrium. In present studies, for Pb(II) equilibrium was achieved by 2 hr of contact time.

D. Adsorption kinetics study

The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The rate kinetics of metal ion adsorption on Fuller's earth was analyzed using pseudo first-order [9], pseudo-second order [10], and intraparticle diffusion models [11]. The conformity between experimental data and the model predicted values was expressed by correlation coefficients (r^2).

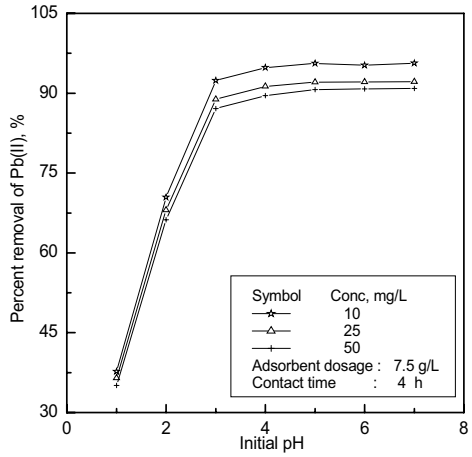

Fig. 1 Effect of pH on adsorption

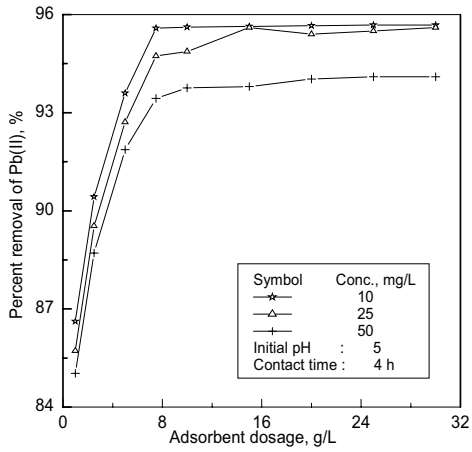

Fig. 2 Effect of adsorbent dosage on adsorption

1. Lagergren model

The integral form of the Lagergren [13] model generally expressed as follows,

$$\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \quad (2)$$

The values of log ($q_e - q_t$) are linearly correlated with t. The plot of log ($q_e - q_t$) versus t (Fig.) give a linear relationship from which K_{ad} and q_e can be determined. The values of rate constants, r^2 and χ^2 are shown in Table I.

2. Pseudo second order model

The kinetics of adsorption process may also be analyzed by pseudo second order rate equation [10]. The linearized form of pseudo second order model, is expressed as

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Fig. 4 show pseudo second order plot. The values of pseudo second order rate constants along with correlation coefficients, r^2 and chi square, χ^2 are shown in Table I.

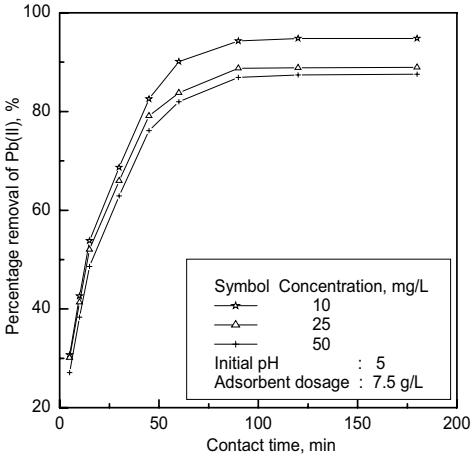

Fig. 3 Effect of contact time on adsorption

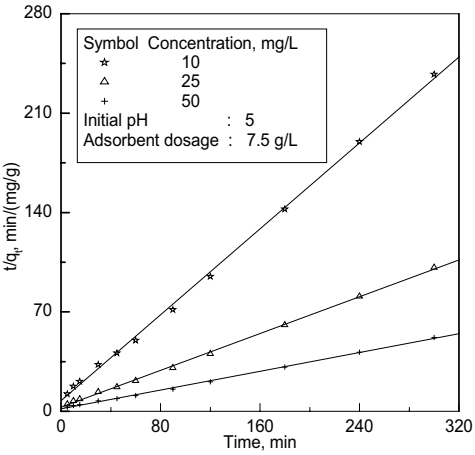

Fig. 4 Pseudo second order plot for adsorption

3. Intraparticle diffusion model

The intraparticle diffusion model is based on the theory proposed by Weber and Morris [11] According to this theory the model Equation (4) can be expressed as

$$q = K_{id} t^{0.5} + C \quad (4)$$

Data points in Weber Morris plot are related by two straight lines - first straight portion depicting the macropore diffusion and second representing the micropore diffusion.

The deviation of straight lines from the origin may be due to difference in rate of mass transfer in the initial and final stage of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not sole rate-controlling step. The values of rate constants and correlation coefficients for each model are shown in Table I.

TABLE I
KINETIC PARAMETERS FOR ADSORPTION OF PB (II) ON FULLER'S EARTH

Pseudo first order model				
C_0 mg/L	$K_{ad} \times 10^2$ min^{-1}	r^2		χ^2
10	4.5645	0.9839		3.1112
25	4.4195	0.9944		4.1767
50	4.2606	0.9936		6.6483
Pseudo second order model				
C_0 mg/L	$k_2 \times 10^2$ g/mg min	h_2 mg/g min	r^2	χ^2
10	7.705	0.135	0.9991	0.0455
25	3.553	0.339	0.9992	0.0957
50	1.553	0.569	0.9991	0.1958
Intraparticle diffusion model				
C_0 mg/L	C mm	K_{id} $mg/g.min^{0.5}$	r^2	χ^2
10	0.1195	0.1437	0.9914	3.0311
25	0.3565	0.3289	0.9847	6.8528
50	0.7827	0.5743	0.9595	8.6349

4.Mass Transfer Analysis

External mass transfer coefficient can be obtained from the plot $\ln\left(\frac{C_t}{C_o} - \frac{1}{1+M'K_{bq}}\right)$ vs. t by using the Equation (5). Table II show the value of mass transfer coefficient at different initial metal ion concentration. It indicates that the velocity of the adsorbet transport from bulk to the solid phase is quite fast. Values of mass transfer coefficient are not proportionately related to initial metal ion concentration. So, external mass transfer is not solely rate limiting step [12].

$$\ln\left(\frac{C_t}{C_o} - \frac{1}{1+M'Y_S}\right) = \ln\left(\frac{M'Y_S}{1+M'Y_S}\right) - \left(\frac{1+M'Y_S}{M'Y_S}\right)\beta S_s t \quad (5)$$

5. Determination of effective diffusion coefficient

Adsorption data obtained from kinetic study could be described well by the models given by Boyd et al. [13]. Effective diffusion co-efficient for the solution of divalent exchangeable ion can be determined using the equation (Equation 6)

$$\ln\left[\frac{1}{1-F^2(t)}\right] = \frac{\pi^2}{R_a^2} D_e t \quad (6)$$

Where plot of $\ln[1/(1-F^2(t))]$ versus t provide a line from whose slope $\pi^2 D_e / r^2$ the diffusion coefficient, D_e can be calculated. The value of diffusion co-efficient as calculated from the equation is tabulated in Table II. The value of D_e, do not fall well within the values reported in literature, especially

for chemisorptions system (10^{-9} - 10^{-17} m^2/s) [14]. So adsorption of Pb(II) on Fuller's earth is physical in nature.

TABLE II
MASS TRANSFER ANALYSIS DATA FOR ADSORPTION OF Pb (II)

	Mass transfer co-efficient		Effective diffusion co-efficient	
C_0 mg/L	$\beta \times 10^5$ cm/s	r^2	$D_e \times 10^{10}$ m^2/s	r^2
10	1.45712	0.9978	708.3331	0.9934
25	1.36543	0.9978	710.7513	0.9954
50	1.2346	0.9992	850.1807	0.9999

E. Adsorption isotherms

The adsorption isotherm for the removal of metal ion was studied using initial concentration of between 10 and 300 mg/L at an adsorbent dosage level of 5.0 g/L for Pb(II) 30°C.

1. Langmuir isotherm

Equilibrium adsorption of Pb(II) assuming monolayer adsorption onto a surface with a finite number of indentical sites is represented by Langmuir adsorption isotherm model [15]

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{7}$$

2. Freuindlich isotherm

Friundlich adsorption model [16] assumed heterolayer adsorption onto adsorbent surface and linear form can be described by Equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

From the Table III, it is seen that experimental data for Pb(II) adsorption are better fitted to Langmuir than Freundlich adsorption isotherm. Therefore uptake of Pb(II) ion preferably follows the monolayer adsorption process.

TABLE III
ISOTHERM PARAMETERS FOR PB (II) ADSORPTION

Langmuir	q_{max} mg g^{-1}	b L mg^{-1}	r^2	χ^2
	103.31	0.021	0.992	0.036
Freundlich	K_f $(mg/g)/(mg/L)^{1/n}$	n	r^2	χ^2
	1.216	1.549	0.996	0.432

3. Dubinin-Radushkevich (D-R) isotherm

The D-R isotherm [17] was employed in the following linear form:

$$\ln C_{abs} = \ln X_m - \lambda \varepsilon^2 \tag{9}$$

The Polanyi potential [31], ε, can be expressed as,

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{10}$$

A plot of ln C_{abs} vs ε^2 in Fig. 6 gave a straight line from which values of λ was evaluated. Using the calculated value of λ, it was possible to evaluate the mean sorption energy, E, from

$$E = \frac{1}{\sqrt{-2\lambda}} \tag{11}$$

The value of E for the adsorption, 8.8319 kJ/mol is in the range of 9-16 kJ/mol which indicate that adsorption of Pb(II) on Fuller's earth is to be physical in nature [18].

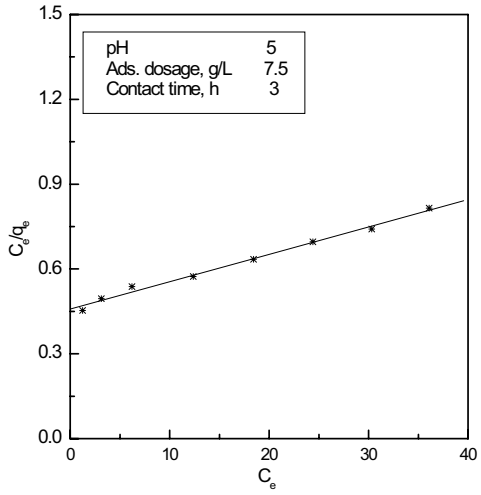

Fig. 5 Langmuir adsorption plot for adsorption

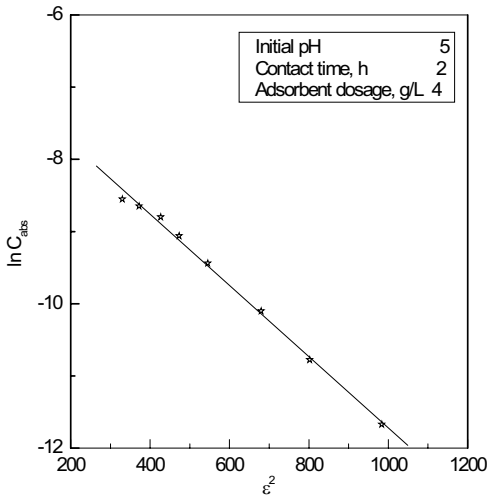

Fig. 6 Dubinin Radushkevich plot for adsorption

IV. CONCLUSIONS

The obtained results can be summarized as follows,

1. Maximum adsorption at pH 5-and at higher pH precipitation of hydroxyl species onto the adsorbents (pH 3-7).
2. Maximum uptake was obtained at adsorbent dosage of 5.0 g/L, which may be considered as optimum adsorbent dosage level at the specified conditions.
3. The equilibrium time for adsorption of Pb(II) from aqueous solutions was achieved within 2 hr of contact time.
4. The experimental data were better described by pseudo 2nd order model as evident from correlation co-efficient (r^2) and χ^2 values.

5. Langmuir adsorption isotherm models were better fitted than Langmuir adsorption isotherm model. The monolayer adsorption capacity was obtained 103.31 mg/g for Fuller's earth.
6. Sorption energy calculated from Dubinin-Raduskevich (D-R) isotherm indicated that the adsorption processes are chemical in nature.

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