



Clarified sludge (basic oxygen furnace sludge) – an adsorbent for removal of Pb(II) from aqueous solutions – kinetics, thermodynamics and desorption studies

Tarun Kumar Naiya, Ashim Kumar Bhattacharya, Sudip Kumar Das*

Department of Chemical Engineering, University of Calcutta, Kolkata, West Bengal 700 009, India

ARTICLE INFO

Article history:

Received 13 August 2008

Received in revised form 8 April 2009

Accepted 26 April 2009

Available online 3 May 2009

Keywords:

Clarified sludge

Adsorption

Pseudo second order

Mass transfer analysis

Freundlich adsorption isotherm

Desorption

ABSTRACT

The basic oxygen furnace waste generated in steel plant has been used as a low cost adsorbent for the removal of Pb(II) from aqueous solution. The effect of pH, adsorbent dosage, initial metal ion concentration, contact time and temperature on adsorption process was studied in batch experiments. Results of the equilibrium experiments showed that the solution pH was the key factor affecting the adsorption characteristics. Optimum pH for the adsorption was found to be 5 with corresponding adsorbent dosage level of 5 g/L. The equilibrium was achieved within 1 h of contact time. Kinetics data were best described by pseudo second order model. The effective particle diffusion coefficient of Pb(II) is the order of 10^{-10} m²/s. The maximum uptake was 92.5 mg/g. The adsorption data can be well fitted by Freundlich isotherm. The result of the equilibrium studies showed that the solution pH was the key factor affecting the adsorption. External mass transfer analysis was also carried out for the adsorption process. The thermodynamic studies indicated that the adsorption is spontaneous and endothermic. The sorption energy (10.1745 kJ/mol) calculated from Dubinin–Radushkevich isotherm indicated that the adsorption process is chemical in nature. Desorption studies were carried out using dilute mineral acids to elucidate the mechanism of adsorption. Application studies were carried out considering the economic viewpoint of wastewater treatment plant operations.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Environmentalists are primarily concerned with the presence of heavy metals due to their toxicity and impact on human health and environment. Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths [1,2]. Process industries, such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units generate large quantities of wastewater contaminated with lead. In drinking water lead contamination occurs due to the corrosion and leaching of lead pipes and Pb/Sn solder joints associated with copper service lines used in household plumbing [3]. The permissible level of lead in drinking water is 0.05 mg/L [4]. The permissible limit of lead in wastewater as set by Environment Protection Agency [5] and that of Bureau of Indian Standards (IS 10500) is 0.1 mg/L [6]. Keeping in view the

importance of the situation, specifically toxicity in children, it has diverted the global attention towards understanding its behavioral pattern in ecosystem and metabolism for adopting measures for its effective removal from such industrial and municipal waste effluents.

The safe and effective disposal of wastewater contaminated with Pb(II) is a challenging objective for industries because of cost effective treatment alternatives are not readily available. Common cleaning methods comprise chemical precipitation, co-precipitation, and formation of volatile compounds such as hydride and alkylate, ion exchange, electrolysis, membrane filtration, solvent extraction, fertilization and sorption to metal oxide, clay, activated carbon, organic sorbents. These methods differ with respect to cost, complexity and efficiency [7–17]. Among these technologies, adsorption is a user-friendly technique for the removal of heavy metal.

Efforts have been made to develop low-cost adsorbents, for the removal of heavy metal from aqueous solutions including natural water and industrial wastewater. These adsorbents are tea-industry waste, red mud, rice husk ash, waste slurry, kaolinitic clay, fly ash, paper mill sludge, pyrolyzed coffee residue and clay, phosphate, blast furnace sludge etc. [18–31].

In steel production in a basic oxygen furnace, for every ton of crude steel, about 100–150 kg of slag/sludge is generated in the form

* Corresponding author at: Department of Chemical Engineering, University of Calcutta, 92 A.P.C. Road, Kolkata, West Bengal 700 009, India.

Tel.: +91 33 2350 1397x247; fax: +91 33 351 9755.

E-mail address: drsudipkdas@vsnl.net (S.K. Das).

Nomenclature

A	Adsorbent in Eq. (6)
S	Adsobent in Eq. (6)
AS	Activated complex in Eq. (6)
b	Langmuir constant (Lmg^{-1})
C_{abs}	Concentration of metal ion on the adsorbent at equilibrium (mgL^{-1})
C_e	Concentration of metal ion in solution at equilibrium (mgL^{-1})
C_f	Final concentration of metal ion in solution (mgL^{-1})
C_0	Initial concentration of metal ion in solution, (mgL^{-1})
C_t	Concentration of metal ion in solution after time t (mgL^{-1})
$(C_0)_a$	Initial metal ion concentration in clarified sludge
V_a	Volume of adsorbent, L
V_s	Volume of the solution, L
$C_0(M)$	Concentration of metal ion in solution
k	Pseudo second order rate constant of adsorption [(mg/g) min]
K_{ad}	Lagergren rate constant (min^{-1})
K_A	Adsorption rate constant in Eq. (7)
K_S	Desorption rate constant in Eq. (7)
K_c	Thermodynamic equilibrium constant
K_d	Distribution coefficient, L/g
K_f	Measure of adsorption capacity, (mg/g)
K_{id}	Intraparticle diffusion rate constant, [(mg/g) $\text{min}^{1/2}$]
K_{bq}	Constant obtained by multiplying q_{max} and b
M^l	Mass of adsorbent, g
m	Amount of adsorbent added, g
n	Freundlich constants, intensity of adsorption
q	Amount adsorbed per gram of the adsorbent (mg/g)
q_e	Amount adsorbed per gram of the adsorbent at equilibrium (mg/g)
q_{max}	Maximum adsorption capacity, (mg/g)
q_t	Amount adsorbed per gram of adsorbent at time t min
r^2	Correlation coefficient
R_a	Radius of the adsorbent particle, m
R_L	Separation factor
S_s	External surface area of the adsorbent per unit volume (m^{-1})
Bt	Time dependent factor
D_e	Diffusion coefficient (m^2/s)
t	Time (min)
V	Volume of the solution (L)
F	Amount adsorbed per gram of adsorbent at time/amount adsorbed per gram of adsorbent at equilibrium
X_A	Fractional of adsorbate adsorbed on the adsorbent at any time, t
X_{Ae}	Fractional of adsorbate adsorbed on the adsorbent at equilibrium
X_m	Maximum adsorption capacity (mmol/g)
E	Mean sorption energy (kJmol^{-1})
ΔG^0	Gibbs free energy (kJmol^{-1})
ΔH^0	Heat of adsorption (kJmol^{-1})
ΔS^0	Entropy of adsorption ($\text{kJK}^{-1}\text{mol}^{-1}$)
<i>Greek letters</i>	
β	mass transfer coefficient (m/s)
λ	constant related to energy (mol^2/kJ^2)
ε	Polanyi potential (kJ^2/mol^2)

of waste depending upon the hot metal quality and steel making practice. The current capacity of crude steel production in India is 26 mtpa through basic oxygen furnace route and it generates about 3.9 million ton of sludge waste every year. The sludge initially in the dust form in the basic oxygen furnace arrested by hydro jetting and then by venture scrubbers and collected in clarifier for settling. In most steel plants this sludge is creating problems related to disposal. Presently it is only partially reprocessed and a significant proportion is either dumped or used for land filling [31].

The present study deals with a series of batch adsorption experiments to investigate and explore the feasibility of clarified sludge as low cost and readily available adsorbent for removal of heavy metals from aqueous solutions. Effect of different parameters such as initial pH, adsorbent dosage, initial metal ion concentration and contact time on the adsorption of Pb(II) have been investigated. The kinetics of the adsorption of Pb(II) onto clarified sludge have been studied using different adsorption techniques. Experimental data were fitted to various isotherm equations to determine the best isotherm to correlate the experimental data. Thermodynamics of adsorption process have been studied and the change in Gibbs free energy, enthalpy and entropy of adsorption has also been determined. The sorption energy of adsorption process has also been calculated. Desorption of loaded clarified sludge were also studied using dilute HCl and HNO₃ solution.

2. Materials and methods

The clarified sludge was collected from the sludge thickener of basic oxygen furnace of Rourkela Steel Plant, Rourkela, Orissa, India. The sludge initially in the dust form in the basic oxygen furnace was arrested by hydro jetting followed by venturi scrubbers and then collected in clarifier for settling. The sample was subjected to characterization by a variety of methods such as X-ray diffraction (XRD), chemical analysis, thermo gravimetric analysis (TGA), particle size, BET surface area, and scanning electron microscope (SEM). Clarified sludge, after collection it was ground, homogenized and dried at $105 \pm 5^\circ\text{C}$ for 3 h and cooled to ambient temperature in a desiccators. The details of the characteristics of the clarified sludge are given in our earlier paper [32] and Table 1.

All the necessary chemicals used in the study were of analytical grade. Lead nitrate [$\text{Pb}(\text{NO}_3)_2$] was obtained from E. Merck India Limited, Mumbai, India. Stock solution of Pb(II) was made by dissolving exact amount of $\text{Pb}(\text{NO}_3)_2$. The range of concentration of the metal components prepared from stock solution varied between 3 mg/L and 300 mg/L. The test solutions were prepared by diluting 1 g/L of stock metal solution with double distilled water.

The necessary amount of clarified sludge was taken in a 250 mL stopper conical flask containing 100 mL of desired concentration of the test solution for the batch adsorption studies at the desired pH value. Different initial concentration of metal solutions was prepared by proper dilution from stock 1 g/L metal standard. 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 solutions as per required pH value. Necessary amount of clarified sludge was then added and contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 120–130 rpm at 303 K. The time required for reaching the 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 SpectraAA 55, USA) as per procedure laid down in APHA, AWWA standard methods for examination of water and wastewater, 1998 edition [33].

Table 1
Characteristics of clarified sludge.

Particle size range μm	Effective particle diameter μm	Surface area m^2/g	Bulk density $\text{g}/\text{c.c.}$	Point of zero charge
250–350	302.298	78.54	1.98	9.80

3. Results and discussion

3.1. Effect of pH

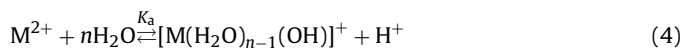
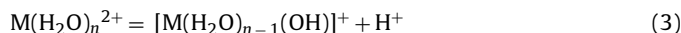
The experiments concerning the effect of pH was carried out in the range of pH that was not influenced by the metal precipitation mainly as metal hydroxide. The calculation from the solubility product equilibrium constant, K_{sp} [34] demonstrated that the suitable range for the Pb(II) adsorption is 3–7. In general, adsorption of cations is favored at $\text{pH} > \text{pH}_{\text{pzc}}$. The oxides of iron, calcium and silica present in clarified sludge develop charge on the adsorbent surface in contact with water. Except silica other metal oxides process for the pH range of interest because of zero point charge (pH_{zpc}) of SiO_2 , Fe_2O_3 and CaO are 2.2, 6.7 and 11.0, respectively [35]. A positive charge develops in the surface of oxides of clarified sludge in an acidic medium due to the aqua complex formation of the oxide present as follows:



The effects of initial pH on removal of Pb(II) are shown in Fig. 1. The sorption at the low pH range usually takes place with low removal efficiency. This is due to high concentration of proton in solution that competes with metal ion forming a bond with the active sites. These bonded active sites become saturated and was inaccessible to other cations. In addition, when pH increases from 3 to 5, 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 clarified sludge, favoring adsorption. The same trend has also been reported in the removal of Pb(II) ions by other vegetable materials such as spent grain [36], *Pinus sylvestris* [37], and crop milling waste [38].

The metal ions in the aqueous solution may undergo solvation and hydrolysis. The process involved for metal adsorption is as fol-

lows [39],



The pK_a value for Pb(II) is 7.7. Perusal of the literature on metal speciation shows that the dominant species is $\text{M}(\text{OH})_2$ at $\text{pH} > 6.0$ and M^{2+} and $\text{M}(\text{OH})^+$ at $\text{pH} < 6.0$. Maximum removal of metal was observed at pH 5 for adsorption. On further increase of pH adsorption decreases probably due to the formation of hydroxide of lead because of chemical precipitation [12,30,40]. So to ensure no interference from the metal precipitation, subsequent experiments were carried out at pH 5.

3.2. Effect of adsorbent dosage

The effect of adsorbent dosage in terms of distribution coefficient on the removal of Pb(II) ion at $C_0 = 10 \text{ mg/L}$ 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 5 g/L. The removed metal ion almost remained unchanged after adsorbent dosage 5 g/L. Increase in adsorption with increase in adsorbent dosage attributed to the availability of larger surface area and more adsorption sites. At low adsorbent dosage, $m < 1 \text{ g/L}$, the adsorbent surface become saturated with the metal ions and the residual metal ion concentration in the solution is large. With an increase in adsorbent dosage, the metal ion removal increased to higher metal ion uptake by the increased amount of adsorbent. For adsorbent dosage of 5 g/L, the incremental metal ion removal becomes very low as the surface metal ion concentration and the solution metal ion concentration comes to equilibrium with each other. For higher adsorbent dosage of 5.0 g/L, the removal efficiency becomes almost constant for the removal of Pb(II) ions onto clarified sludge.

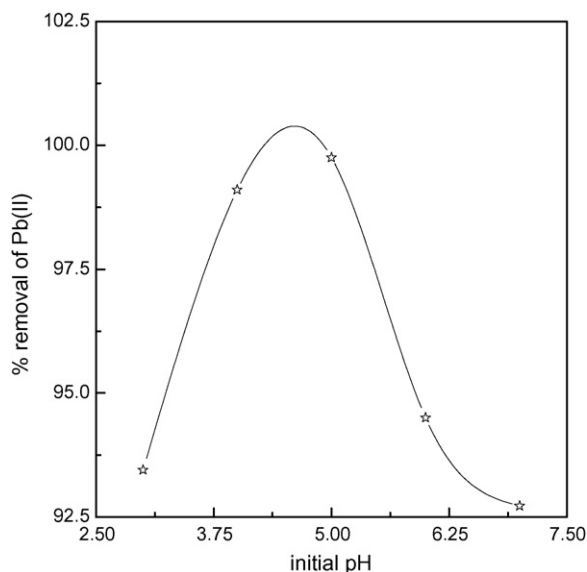


Fig. 1. Effect of pH on the adsorption of Pb(II) initial conc. 10 mg/L, adsorbent dosage 5 g/L, contact time 1 h.

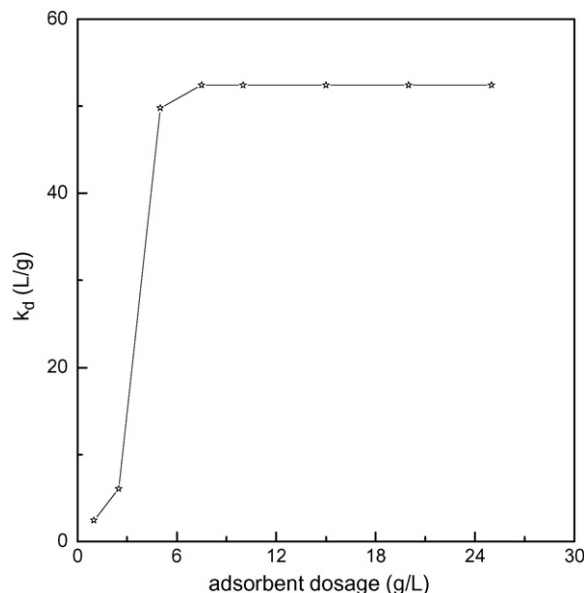


Fig. 2. Effect of adsorbent dosage on adsorption of Pb(II) pH 5, initial conc. 10 mg/L, contact time 1 h.

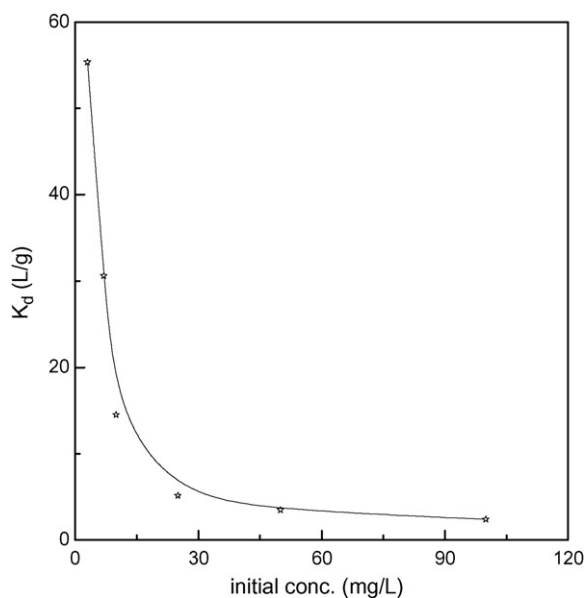


Fig. 3. Effect of initial concentration on the adsorption of Pb(II) pH 5, adsorbent dosage 5 g/L, contact time 1 h.

3.3. Effect of initial metal ion concentration

With increase in initial Pb(II) concentrations, more Pb(II) ions are left un-adsorbed in the solution due to the saturation of the binding sites. This indicates that energetically less favorable sites become involved with increasing ion concentration in aqueous solution. The Pb(II) ion adsorption is attributed to the different mechanisms of ion exchange as well as to the adsorption process. During the ion exchange process, the Pb(II) ion had to be moved not only through the pores of the adsorbent mass, but also through the channels of the lattice, they have to be replaced exchangeable cations. Diffusion was faster through pores and was retarded when the ion moves through the smaller diameter channels.

Here, the Pb(II) ion adsorption mainly be attributed to ion-exchange reactions in the micro pores of the adsorbents. Fig. 3 represents K_d as a function of Pb(II) ion concentration.

$$K_d = \frac{(C_0 - C_e)}{C_e} X \left(\frac{V}{M} \right) \quad (5)$$

The K_d values increased with the decreasing concentration of Pb(II) ion. In other words K_d values increased as the dilution of Pb(II) ion proceeds. This effect can be explained as at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the percentage removal of metal ion [41].

3.4. Effect of contact time

The experimental runs measuring the effect of contact time on the batch adsorption of metal solution containing 10 mg/L of Pb(II) at 303 K and initial pH value 5 is shown in Fig. 4. During the experiment contact time was varied from 0 min to 3 h. The initial rapid adsorption gives away a very slow approach to equilibrium. In present studies, for Pb(II) equilibrium was achieved by 1 h of contact time.

3.5. Adsorption kinetics study

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of metal ion

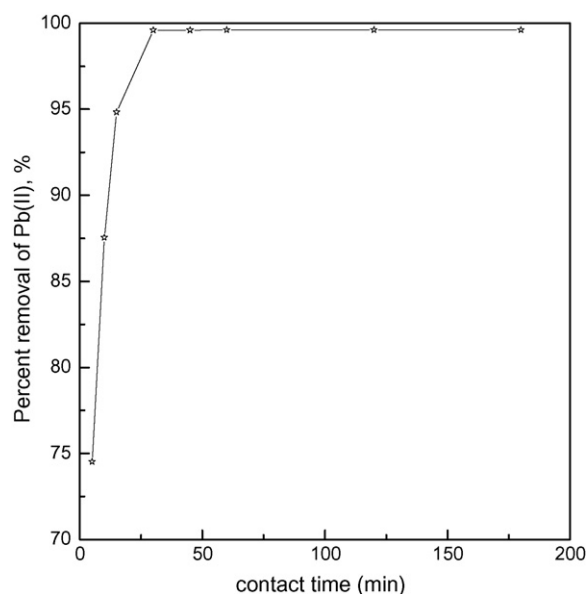


Fig. 4. Effect of contact time on the adsorption of Pb(II) initial conc. 10 mg/L, adsorbent dosage 5 g/L, pH 5.

uptake at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process [42]. The results obtained from the experiments were used to study the kinetics of metal ion adsorption. The rate kinetics of Pb(II) adsorption on clarified sludge was analyzed using pseudo first order [43], pseudo second order [44], and intraparticle diffusion models [45]. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (r^2).

3.5.1. Pseudo first order model

The adsorption of Pb(II) from a liquid phase to solid phase can be considered as a reversible process with equilibrium being established between the solution and solid phase. Adsorption phenomenon can be described as the diffusion control process, assuming a non-dissociation molecular adsorption of Pb(II) on clarified sludge particles as follows:



If initially no adsorbate present the adsorbent (i.e., $C_A S_0 = 0$ at $t = 0$), then assuming the first order rate kinetics the fractional uptake on the adsorbate by the adsorbent can be expressed as,

$$\frac{q}{q_e} = 1 - \exp\left[-\left(K_A C_S + \frac{K_A}{K_S}\right)t\right] \quad (7)$$

Equation can be transformed as:

$$\log(q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \quad (8)$$

where,

$$K_{ad} = \left[\left(K_A C_S + \frac{K_A}{K_S} \right) \right] t \quad (9)$$

and

$$q = X_A$$

and

$$q_e = X_{Ae}$$

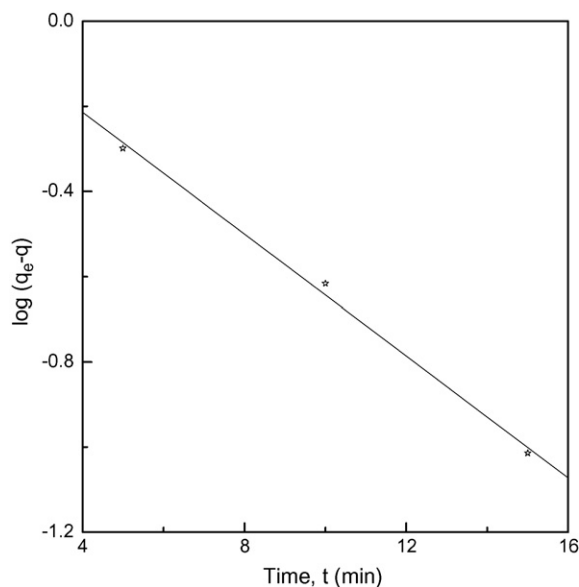


Fig. 5. Lagergren plot for the adsorption of Pb(II) by clarified sludge pH 5, initial conc. 10 mg/L, adsorbent dosage 5 g/L.

This equation is the so-called Lagergren equation [46]. The results are depicted in Fig. 5.

3.5.2. Pseudo second order model

The pseudo second order model [43] is based on the assumption of chemisorption of the adsorbate on the adsorbent. The kinetic rate model can be represented as:

$$\frac{dq_t}{dt} = k(q - q_t)^2 \quad (10)$$

Separating the variables in equation and integrating the boundary conditions, $q_t = 0$ at $t = 0$ and q_t at time t , the following equation is obtained

$$\frac{t}{q_t} = \frac{1}{k \cdot q^2} + \frac{1}{q} \cdot t \quad (11)$$

This is a linear form equation for a pseudo second order reaction. The constant (k and q) can be experimentally determined by plotting $(1/q_t) \cdot t$ against t from Fig. 6.

3.5.3. Intraparticle diffusion model

The possibility of intraparticle diffusion was explored by using the Weber–Morris intraparticle diffusion model [44].

$$q_t = K_{id} t^{0.5} \quad (12)$$

If the Weber–Morris plot of q_t vs $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the adsorption processes. The mathematical dependence of fractional uptake of the adsorbate on $t^{0.5}$ is obtained if the adsorption process is considered to be influenced by diffusion in the cylindrical and convective diffusion in the adsorbate solution. It is assumed that the external resistance to mass transfer surrounding the particles is significant only in the early stage of the adsorption. The first steeper portion represents this. The second linear portion is the gradual adsorption stage with intraparticle diffusion dominating.

In Fig. 7 the data points are related by two straight lines—first straight portion depicting the macropore diffusion and second representing the micropore diffusion. These show only the pore diffusion data. Extrapolation of the linear portion of the plots to the

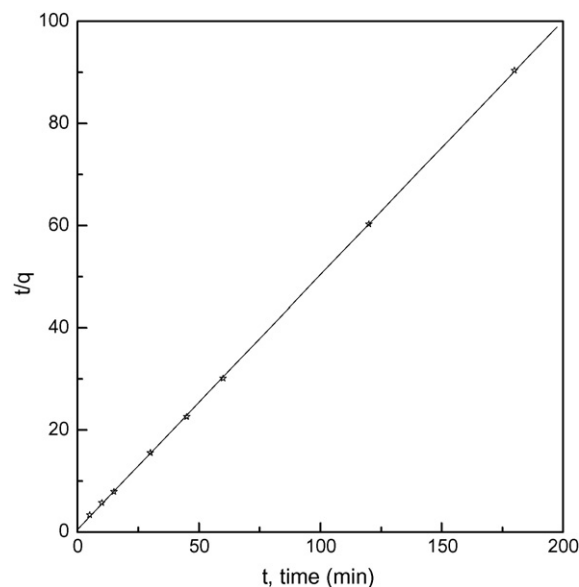


Fig. 6. Pseudo second order plot for the adsorption Pb(II) by selected adsorbents pH 5, initial conc. 10 mg/L, adsorbent dosage 5 g/L.

Y-axis gives the intercepts, which provide the boundary layer thickness. The deviation of straight lines from the origin (figure) 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 adsorption data for q vs $t^{0.5}$ for the initial period show curvature usually attributed to boundary layer diffusion effects or external mass transfer effects [45]. These indicate the mechanism of Pb(II) adsorption by clarified sludge is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step.

In order to quantify the applicability of each model, the correlation coefficient, r^2 , was calculated from these plots. The linearity of these plots indicates the applicability of the three models. The values of rate constants and correlation coefficients for each model are shown in Table 2. However, the correlation coefficient, r^2 , showed

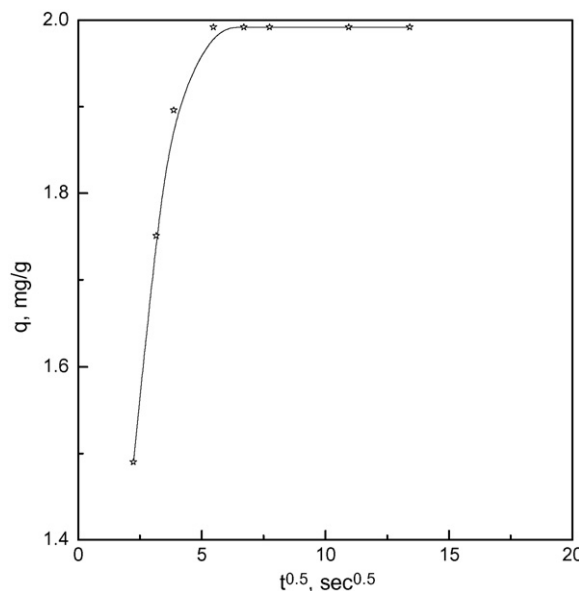


Fig. 7. Weber and Morris plot for the adsorption Pb(II) by selected adsorbents pH 5, initial conc. 10 mg/L, adsorbent dosage 5 g/L.

Table 2
Rate kinetics for adsorption.

Lagergren first order			Pseudo second order			Weber and Morris			Bangham		
$K_{ad} \times 10^{-2} \text{ min}^{-1}$	r^2	χ^2	$K_2 \text{ g mg}^{-1} \text{ min}^{-1}$	r^2	χ^2	$K_{id} \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$	r^2	χ^2	$k_0 \times 10^3 \text{ Lg}^{-1}$	α	r^2
16.47	0.958	8.389	0.467	0.999	0.0197	14.89	0.869	0.847	7.28	0.788	0.897

that the pseudo second order model, an indication of chemisorptions mechanism, fits better with the experimental data than the pseudo first order model. In addition, the Chi-square test was also done to support the best fit adsorption model. The equation for evaluating the best fit model is to be written as:

$$\chi_t^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \quad (13)$$

It has been found that χ^2 values are much less in pseudo second order model than that of pseudo first order and intraparticle diffusion model (Table 2). Thus, based on the high correlation coefficient and low χ_t^2 value, it can be said that adsorption of Pb(II) onto clarified sludge follow pseudo second order model than that of intraparticle diffusion model.

3.5.4. Mass transfer analysis

Mass transfer analysis for the removal of Pb(II) from aqueous solutions by clarified sludge were carried out using the following equation as proposed by McKay et al. [46]

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + MK_{bq}} \right) = \ln \left(\frac{MK_{bq}}{1 + MK_{bq}} \right) - \left(\frac{1 + MK_{bq}}{MK_{bq}} \right) \beta S_s t \quad (14)$$

The plot of $\ln \left((C_t/C_0) - (1/1 + MK_{bq}) \right)$ vs t results a straight line of slope $\left[\left((1 + MK_{bq}/MK_{bq}) \right) \beta S_s \right]$ and the values of mass transfer coefficients (β) calculated from the slopes of the plots was $2.20 \times 10^{-5} \text{ cm/s}$ with a high value (0.9987) of correlation coefficient. 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.

3.5.5. Determination of diffusivity

Kinetic data could be treated by the models given by Boyd et al. [47] which is valid for the experimental conditions used. Diffusion

found to be rate controlling in the adsorption of Pb(II) onto the particles of spherical shape. As the volume of the solution is much higher compared to the volume of the clarified sludge particle and if the concentration of metal ions is assumed constant from the surface to the centre of the adsorbent particle, then the fraction of metal ion bound at time t can be expressed as:

$$F(t) = 1 - \frac{6}{i^2 \pi^2} \sum_{i=1}^{\alpha} \exp \left(-\frac{D_e t \pi^2 i^2}{R_a^2} \right) \quad (15)$$

Applicability of Vermeulen's approximation is limited and highly depends on the ratio of the initial metal ion concentration in clarified sludge $(C_0)_a$ and in the solution C_0 and of the volume of adsorbent (V_a) and the volume of the solution (V_s) . For the criterion of 'infinite solution volume' that is given by the ratio $(C_0)_a V_a << C_0(M) V_s$, where the concentration of metal ion in the solution remains negligible throughout the process, and for the range $0 \leq F(t) \leq 1$ in the solution of divalent exchangeable ions, Eq. (15) can be simplified [48] as:

$$\ln \left[\frac{1}{1 - F^2(t)} \right] = \frac{\pi^2}{R_a^2} D_e t \quad (16)$$

where plot of $\ln[1/(1 - F^2(t))]$ vs t provides a line from those slope $\pi^2 D_e / R_a^2$ the diffusion coefficient, D_e can be calculated. The value of diffusion coefficient as calculated from the equation was found to be $3.56 \times 10^{-10} \text{ m}^2/\text{s}$ for the adsorption of Pb(II) onto clarified sludge.

The pores of clarified sludge have different sizes along its length and adsorbent has a wide pore size distribution. The adsorbent–adsorbate and adsorbent–adsorbent interactions have their impact on the diffusion process and affect the value of D_e . The properties of the adsorbents – pore size along the length of pore, orientation, electronic field and the interaction of the adsorbate–van der Waals attractive forces, surface diffusion characteristics and

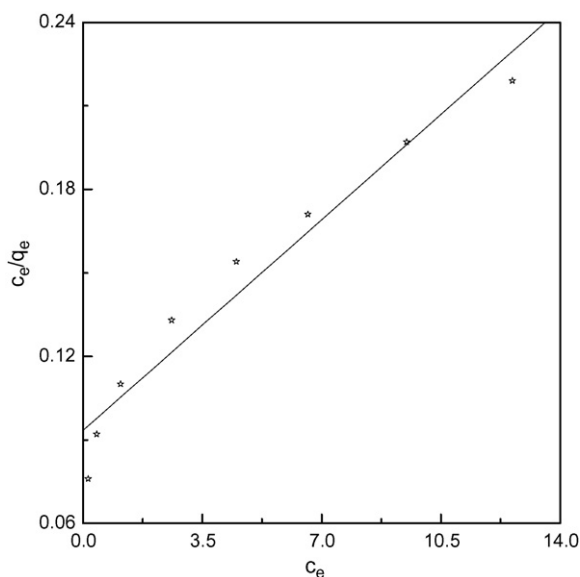


Fig. 8. Langmuir plot for the adsorption of Pb(II) by selected adsorbents pH 5, adsorbent dosage 5 g/L, contact time 1 h.

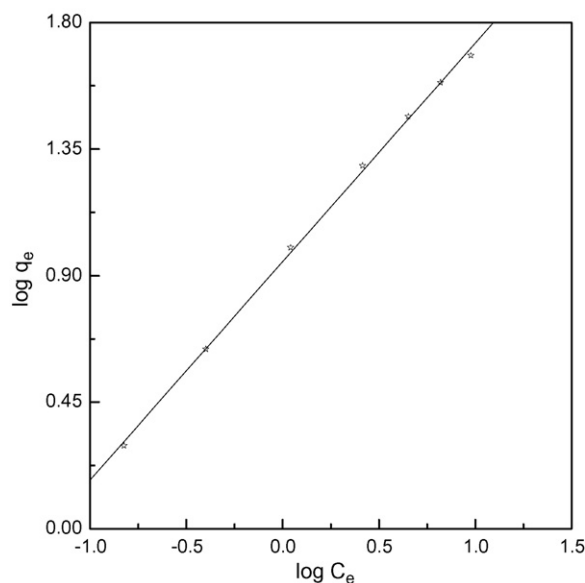


Fig. 9. Freundlich plot for the adsorption of Pb(II) by selected adsorbents pH 5, adsorbent dosage 5 g/L, contact time 1 h.

Table 3
Langmuir and Freundlich adsorption isotherm constants.

Langmuir constants					Freundlich constants				
q_{\max} mg g ⁻¹	b L mg ⁻¹	r^2	χ^2	SD	K_f ((mg/g)/(mg/L) ^{1/n})	n	r^2	χ^2	SD
92.51	0.115	0.952	0.639	0.012	8.914	1.287	0.999	0.247	0.019

adsorption mechanism – all affect the diffusion. Mesopores are found to occupy most of the pore length of clarified sludge. The diffusion within the pores of wider path and weaker retarding forces of electrostatic interaction accounts for the greater D_e and one within the pore of narrower mesh widths and stronger retarding forces accounts for lower D_e . For the present system, the value of D_e , fall well within the values reported in literature, especially for chemisorption system (10^{-9} – 10^{-17} m²/s) [49].

3.5.6. Reichenberg model

The rate of sorption is determined by applying well-known equation for the diffusion and mass transfer phenomena. For the fast reaction, the sorption may be due to film diffusion [50] and occur within the microspores of the adsorbent. In that case Reichenberg equation is applied, i.e.,

$$F(t) = \left(1 - \frac{6}{\pi^2}\right) e^{-Bt} \quad (17)$$

Above equation may be written as:

$$Bt = -0.4977 \ln(1 - F(t)) \quad (18)$$

The plot of Bt vs time is linear with a correlation factor of 0.9904 thereby indicating that sorption was controlled by film diffusion.

3.5.7. Bangham's equation

Whether pore diffusion is the only rate controlling step or not in the adsorption system is to be checked for kinetic data using Bangham's equation [51],

$$\log \log \left(\frac{C_0}{C_0 - q_{tm}} \right) = \log \left(\frac{k_0 m}{2.303V} \right) + \alpha \log(t) \quad (19)$$

where α (<1) and k_0 are constants. If the experimental data are represented by Eq. (19), then it is an indication that the adsorption kinetics is limited by pore diffusion. However, the above equation

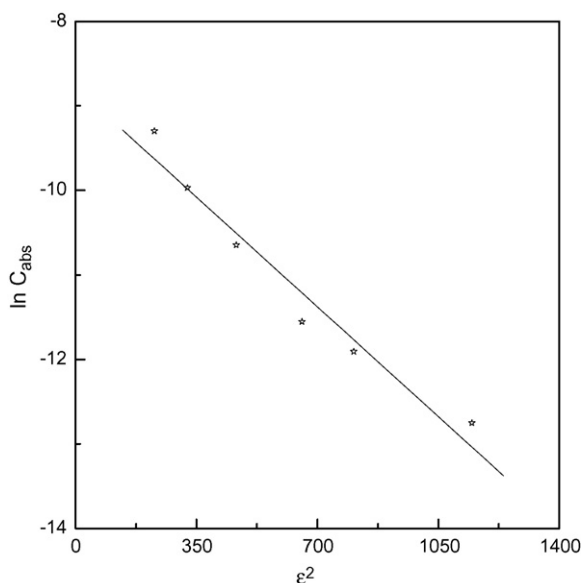


Fig. 10. Dubinin–Radushkevich isotherm of Pb(II) onto selected adsorbents pH 5, adsorbent dosage 5 g/L, contact time 1 h., temperature 303 ± 2 K.

does not give a good fit of the experimental data, indicating thereby that the diffusion of adsorbate into the pores of the adsorbent is not solely a rate-limiting step [52]. With increase in contact time, the effect of diffusion process on overall adsorption could be ignored. Values of Bangham parameters, correlation coefficient and error function values are given in Table 2.

3.6. 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) 303 K. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e .

3.6.1. Langmuir adsorption isotherm

The data obtained were then fitted to the Langmuir adsorption isotherm [53] applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented as follows,

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (20)$$

Linear plots of C_e/q_e vs C_e (Fig. 8) were employed to determine the value of q_{\max} (mg/g) and b (L/mg). The data obtained with the correlation coefficients (r^2) were listed in Table 3.

Weber and Chakraborti [54] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (21)$$

The R_L value indicates the shape of the isotherm as follows:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

According to McKay et al. [55], R_L values between 0 and 1 indicate favorable adsorption. The R_L value for the adsorption on clarified sludge at initial concentration of 10 mg/L (lowest concentration studied) and 300 mg/L (highest concentration studied) are 0.480 and 0.028, respectively. The data obtained represent a favorable adsorption.

Table 4
Effect of temperature on the removal efficiency. Experimental condition: pH 5, adsorbent conc. 5 g/L, and contact time 1 h.

Temperature (K)	Percentage removal of Pb(II) %		
	10 mg/L	25 mg/L	50 mg/L
303	99.2	98.32	99.63
313	99.45	99.1	99.26
323	97.87	97.32	98.02

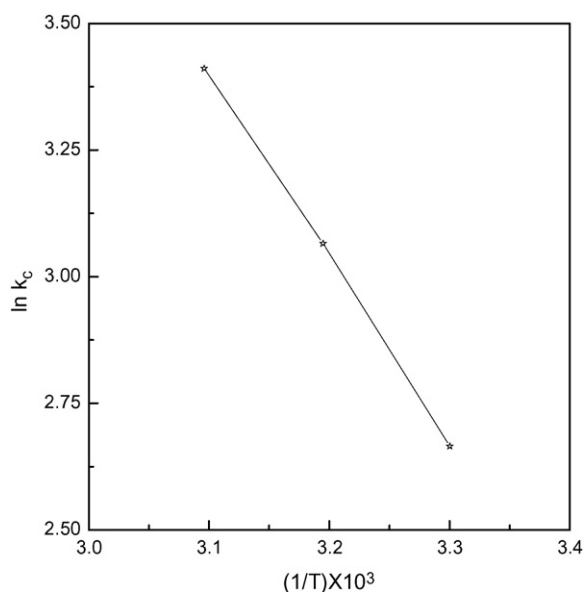


Fig. 11. Determination of thermodynamic parameter for the adsorption of Pb(II) on clarified sludge.

3.6.2. Freundlich adsorption isotherm

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [56], which is the earliest relationship known describing the adsorption equilibrium and is expressed by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (22)$$

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. (22) and Freundlich plots (Fig. 9). The amount of adsorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values for Freundlich constants and correlation coefficients (r^2) for the adsorption process are also presented in Table 3. The values of n between 1 and 10 (i.e. $1/n$ less than 1) represent a favorable adsorption. The values of n , which reflects the intensity of adsorption, also reflected the same trend. The n values obtained for the adsorption process represented a beneficial adsorption.

$$\chi_e^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad (23)$$

From the Table 3, it is seen that experimental data are better fitted to Freundlich ($r^2 = 0.999$) than Langmuir ($r^2 = 0.952$) adsorption isotherm. Moreover, Chi-square test was also done using Eq. (23) to select the better fit adsorption isotherm model. From the experimental data, χ^2 value of Freundlich (0.247) is lower than the Langmuir (0.639) adsorption isotherm model. Therefore, uptake of Pb(II) ion preferably follows the heterolayer adsorption process.

Table 5
Changes in thermodynamic parameters.

ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol)	T (K)	$-\Delta G^0$ (kJ/mol)	r^2
30.35	0.122	303	6.714	0.999
		313	7.976	
		323	9.159	

Table 6

Desorption of Pb(II) from loaded clarified sludge.

Strength of HNO ₃ (M)	Desorption (%)
0.1	68.90
0.25	87.8
0.5	98.42
0.75	98.43
1	98.42

3.6.3. Dubinin–Radushkevich (D–R) isotherm

The D–R isotherm [57] was employed in the following linear form:

$$\ln C_{\text{abs}} = \ln X_m - \lambda \varepsilon^2 \quad (24)$$

The Polanyi potential [58], ε , can be expressed as,

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (25)$$

A plot of $\ln C_{\text{abs}}$ vs ε^2 in Fig. 10 gave a straight line from which values of λ and X_m for Pb(II) was evaluated. Using the calculated value of λ , it was possible to evaluate the mean sorption energy, E , from

$$E = \frac{1}{\sqrt{-2\lambda}} \quad (26)$$

Although the Freundlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the adsorbent by the adsorbate. Hence, infinite surface coverage could be predicted mathematically. In contrast, D–R isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the sorption surface is chosen and assumed to be approximately by the Langmuir isotherm, the quantity $\sqrt{\lambda}$ can be related to the mean sorption energy, E , which is the free energy for the transfer of 1 mole of metal ions from the infinity to the surface of the adsorbent. The estimated value of E was 10.1745 kJ/mol, which is the range expected for chemisorptions (8–16 kJ/mol).

3.7. Adsorption thermodynamics

3.7.1. Effect of temperature on adsorption of Pb(II)

Adsorption experiments to study the effect of temperature were carried out at 303, 313 and 323 K at optimum pH value of 5 and adsorbent dosage level of 5 g/L. The equilibrium contact time for adsorption was maintained at 1 h. The percentage of adsorption decreases with rise of temperature from 303 to 323 K. The results were shown in Table 4 and it revealed the endothermic nature of the adsorption process which later utilized for determination of changes in Gibbs free energy (ΔG^0), heat of adsorption (ΔH^0) and entropy (ΔS^0) of the adsorption of Pb(II) from aqueous solutions. The increase in adsorption with rise in temperature may be due to the strengthening of adsorptive forces between the active sites of the adsorbents and adsorbate species and between the adjacent molecules of the adsorbed phase.

Table 7

Performance of fresh and recycled clarified sludge.

Adsorbent	Conc. of Pb(II) solution mg/L		Percent removal %
	Initial	Final	
Fresh	10	0.048	99.52
First recycle	10	0.716	92.84
Second recycle	10	1.276	87.24
Third recycle	10	2.643	73.57

Table 8
Results of removal of Pb(II) from industrial effluent using clarified sludge.

Test parameter	Untreated effluent	Treated effluent	Remarks
PH	2.7	5	–
Conductivity ($\mu\text{mhos/cm}$)	1737	1682	–
Pb(II) (mg/L)	2.84	0.043	Successfully meet the IS 10500 norms of discharge water of Pb(II) [6]
Fe (mg/L)	1.2	0.9	–
Ca (mg/L)	214	186	–
Mg (mg/L)	64	59	–
Chloride (mg/L)	18	14	–
TSS (mg/L)	26	23	–

3.7.2. Effect of temperature on thermodynamics parameter on adsorption of Pb(II)

The variation in the extent of adsorption with respect to temperature has been explained based on thermodynamic parameters viz. changes in standard free energy, enthalpy and entropy. The dependence on temperature of adsorption of Pb(II) on the clarified sludge were evaluated using equations:

$$\ln K_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (27)$$

and

$$\Delta G^0 = -RT \ln K_c \quad (28)$$

From the slope and intercept of the plot (Fig. 11), the values of ΔH and ΔS had been computed, while ΔG was calculated using Eq. (28). The values of these parameters thus calculated are recorded in Table 5. It may be concluded from the positive values of ΔH^0 that the sorption process is endothermic while the positive value of ΔS^0 is an indicative of increased randomness at the adsorbent–adsorbate interface during the adsorption. The negative value of ΔG^0 confirms the feasibility of the process and spontaneous nature of the adsorption process.

3.8. Desorption studies

The Pb(II) loaded clarified sludge creates disposal problem as it is hazardous in nature. This problem may be overcome to some extent by using desorption methods. It allows recovery of the Pb(II) ion from the metal loaded adsorbent and the adsorbent regeneration process.

Batch desorption experiments were carried out to further elucidate the mechanism of adsorption. Attempts were made to desorb Pb(II) ions from clarified sludge using 0.1 M solutions of dilute HCl and HNO₃ solution having good potential to dissolve metal ions under study by batch desorption technique maintaining the same conditions similar to batch adsorption studies. Initially to

Table 9
Comparison of adsorption capacities of the adsorbents for the removal of Pb(II) with those other adsorbents.

Sl No.	Adsorbents	Adsorption capacities of Pb(II) mg/g	Reference
1.	Kaolinite clay	4.76–6.76	[22]
2.	Blast furnace slag	40.0	[25]
3.	Pyrolyzed coffee residue and clay	47.00	[29]
4.	Celtek clay	18.8	[59]
5.	Activated slag	41.48	[60]
6.	Bentonite clay	20	[61]
7.	Clinoptilolite	166	[62]
8.	Phosphatic clay	28.7	[63]
9.	Baggase fly ash	2.50	[64]
10.	Fly ash	18.0	[65]
11.	Harro river sand	47	[66]
12.	Clarified sludge	92.51	Present work

observed the desorption capability of individual acids, the desorption experiments conducted for 1 h time. The results on batch desorption from adsorbate rich-adsorbent showed that HCl and HNO₃ could desorb 24% and 26% of the adsorbed Pb(II), respectively within 1-h time. Based on above findings, desorption studies with different concentrations of HNO₃ were carried out to desorb maximum amount of adsorbed Pb(II) from the adsorbent. The results of desorption experiments with various concentrations of HNO₃ (0.1–1 M) are shown in Table 6. It was evident that maximum desorption efficiency was obtained with 0.5 M HNO₃. The maximum percent recovery was 98.4% with 0.5 M HNO₃ solutions.

The regenerated adsorbent may be recycled for reuse and ultimately the adsorbents must be incinerated. Table 7 shows the performance of the regenerated adsorbent. Adsorption/desorption cycle of the clarified sludge decreases as the number of cycle increases. More than 90% metal ion removal is possible using two cycles for Pb(II).

3.9. Application studies using industrial effluents

Application studies for Pb(II) were carried out using a wastewater sample having following characteristics. pH, 2.7; Pb(II), 2.84 mg/L; conductivity, 1737 $\mu\text{mhos/cm}$; Ca, 214 mg/L; Fe, 1.2 mg/L; Mg, 64 mg/L; chloride, 18 mg/L and TSS, 26 mg/L.

In the above wastewater matrix, batch operation was carried out under optimum condition as obtained from batch adsorption studies. The results are shown in Table 8. Removal efficiency of 98.5% for Pb(II) was achieved and thereby meeting the CPCB limits (0.1 mg/L) of Pb(II) for discharge to inland surface water. Pb(II) concentration in the treated effluent was 0.043 mg/L.

3.10. Comparison of adsorption capacity with different adsorbents reported in literature

The adsorption capacities of the various adsorbents of similar types for the removal of Pb(II) have been reported in Table 9. The values reported in the form of monolayer adsorption capacity. The experimental data of the present investigations are comparable with the reported values.

4. Conclusions

In this study, batch adsorption experiments for the removal of Pb(II) from aqueous solutions have been carried out using clarified sludge as low cost, readily available adsorbent. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and adsorbent dosages. The obtained results can be summarized as follows,

- (1) The pH experiments showed that the governing factors affecting the adsorption characteristics. Optimum 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 dose of 5 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 30 min of contact time.
 - (4) The experimental data were better described by pseudo second order model as evident from correlation coefficient (r^2) and χ^2 values.
 - (5) The effective diffusivity calculated using Vermeulen's approximation was found to be $3.56 \times 10^{-10} \text{ m}^2/\text{s}$ which also indicated that the interaction between Pb(II) and clarified sludge is chemical in nature.
 - (6) Freundlich adsorption isotherm models were better fitted than Langmuir adsorption isotherm model. The monolayer adsorption capacity was obtained 92.51 mg/g for clarified sludge.
 - (7) Sorption energy for adsorption process were found to be 10.1745 kJ/mol, indicative of chemical adsorption phenomena responsible for the removal of Pb(II) from wastewater.
 - (8) The value of ΔH^0 and ΔS^0 were found to be 30.35 kJ/mol and 0.122 kJ/(mol K), respectively. The positive value of ΔH^0 indicate the endothermic nature of the process while a positive value of ΔS^0 suggested an increase randomness at the solid–solution interface during the adsorption of Pb(II) onto clarified sludge.
 - (9) Dilute HNO_3 solution have good potential to desorb Pb(II) under study by batch desorption technique maintaining the same conditions similar to batch adsorption studies.
 - (10) Studies on industrial wastewater from electroplating unit show the percentage removal was 98%.
- ## References
- [1] O.S. Amuda, A.A. Giwa, I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, *Biochem. Eng. J.* 36 (2007) 174–181.
 - [2] S. Manahan, *Environmental Chemistry*, Brooks/Cole, CA, USA, 1984.
 - [3] R.A. Goyer, I.J. Chisolm, Lead: In *Metallic Contamination and Human Health*, Academic press, New York/London, 1972.
 - [4] Guidelines for drinking water quality, World Health Organization, Geneva, Switzerland, 1984, vol. 1 and 2.
 - [5] EPA (Environmental Protection Agency), *Environmental Pollution Control Alternatives*, EPA/625/5-90/025, EPA/625/4-89/023, Cincinnati, US, 1990.
 - [6] IS 10500 Water specification (reaffirmed 1993), 1992, available—<http://www.hppcb.nic.in/EIAsorang/Spec.pdf>, date 8.9.2007.
 - [7] O.D. Uluzozlu, A. Sari, M. Tuzen, M. Soylok, Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina Tiliaceae*) biomass, *Biores. Technol.* 99 (2008) 2972–2980.
 - [8] Y.A. Bankovsky, M.V. Vircavs, O.E. Veveris, A.R. Pelne, D.K. Vircava, Preconcentration of microamounts of elements in natural waters with 8-Mercapto-quinoline and bis(8-Quinolyl)disulphide for their atomic adsorption determination, *Talanta* 34 (1987) 179–182.
 - [9] C. Frigge, E. Jackwerth, Systematic investigation of multi-element preconcentration from copper alloys by carbamate precipitation before atomic adsorption spectroscopic analysis, *Anal. Chim. Acta* 271 (1993) 299–304.
 - [10] J. Li, Y. Liu, T. Lin, Determination of lead by hydride generation atomic absorption spectrometry. I. A new medium for generating hydride, *Anal. Chim. Acta* 231 (1990) 151–155.
 - [11] R.E. Sturgeon, S.N. Willie, S.S. Berman, Atomic absorption determination of lead at picogram per gram levels by ethylation with in situ concentration in a graphite furnace, *Anal. Chem.* 61 (1989) 1867–1869.
 - [12] N. Khalid, S.A. Chaudhri, M.M. Saeed, J. Ahmed, Separation and preconcentration of lead and cadmium with 4-(4-chlorophenyl)-2-phenyl-5-thiazo-leacetic acid and its application in soil and seawater, *Sep. Sci. Technol.* 31 (2) (1996) 229–239.
 - [13] E. Carasek, J.W. Tonjes, M. Scharf, A new method of microvolume back extraction procedure for enrichment of lead and cadmium and determination by flame atomic absorption spectrometry, *Talanta* 56 (2002) 185–191.
 - [14] S. Hirata, K. Honda, T. Kumamru, Trace metal enrichment by automated on-line column preconcentration for flow-injection atomic absorption spectrometry, *Anal. Chim. Acta* 221 (1989) 65–76.
 - [15] S.S. Mandaoker, D.M. Dharmadhikari, S.S. Dara, Retrieval of heavy metal ions from solution by ferritization, *Environ. Pollut.* 83 (1994) 277–282.
 - [16] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn(II) from aqueous solution by using different adsorbents, *Chem. Eng. J.* 123 (2006) 43–51.
 - [17] R. Han, W. Zou, Z. Zhang, J. Shi, J. Yang, Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand I. Characterization and kinetic study, *J. Haz. Mater.* B137 (2006) 384–395.
 - [18] S. Çay, A. Uyanik, A. Özasiç, Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste, *Sep. Purif. Technol.* 38 (2004) 273–280.
 - [19] V.K. Gupta, M. Gupta, S. Sharma, Process Development for the removal of lead and chromium from aqueous solutions using red mud—an aluminium industry waste, *Water Res.* 35 (5) (2001) 1125–1134.
 - [20] V.C. Srivastava, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, *J. Haz. Mater.* B134 (2006) 257–267.
 - [21] S.K. Srivastava, R. Tyagi, N. Pant, Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants, *Water Res.* 23 (1989) 1161–1165.
 - [22] F.O. Orumwense, Removal of lead from water by adsorption on a Kaolinitic Clay, *J. Chem. Tech. Biotechnol.* 65 (1996) 363–369.
 - [23] S.A. Rajasekhar, N.S. Pandian, Effect of time and concentration of cations on the cation retention capacity of fly ash, in: *International Seminar on Environmental Planning and Management*, VRCE, Nagpur, India, 1996, pp. 211–214.
 - [24] A.L. Degodo, C. Perez, F.A. Copez, Sorption of heavy metals on blast furnace sludge, *Ind. J. Chem. Technol.* 32 (1998) 1989–1996.
 - [25] S.K. Srivastava, V.K. Gupta, D. Mohan, Removal of lead and chromium by activated sludge—a blast-furnace waste, *J. Environ. Eng.* 123 (1997) 461–468.
 - [26] N. Calace, D.A. Muro, E. Nardi, M.B. Petronio, M. Pietroletti, Adsorption isotherms for describing heavy metal retention in paper mill sludges, *Ind. Eng. Chem. Res.* 41 (2002) 5491–5497.
 - [27] A.S. Reddy, R.K. Pradhan, S. Chandra, Utilization of basic oxygen furnace (BOF) slag in the production of a hydraulic cement binder, *Int. J. Miner. Process* 79 (2006) 98–105.
 - [28] E. Lopez, B. Soto, M. Arias, A. Nunez, Arubans, M. Barnal, Adsorption properties of red mud and its use for wastewater treatment, *Water Res.* 32 (4) (1998) 1314–1322.
 - [29] V. Boonamnuayvitaya, C. Chaiya, W. Tanthapanichakoon, S. Jarudilokkul, Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay, *Sep. Purif. Technol.* 35 (2004) 11–22.
 - [30] A. Akil, M. Mouflih, S. Sebti, Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent, *J. Haz. Mater.* A112 (2004) 183–190.
 - [31] A.S. Reddy, R.K. Pradhan, S. Chandra, Utilization of basic oxygen furnace (BOF) slag in the production of a hydraulic cement binder, *Int. J. Miner. Proc.* 79 (2006) 98–105.
 - [32] A.K. Bhattecharya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies using different low-cost adsorbents, *Chem. Eng. J.* 137 (2008) 529–541.
 - [33] *Standard Methods for Examination of Water and Wastewater*, 20th ed., APHA, AWWA, Washington D.C., New York, 2008, pp. 529–541.
 - [34] P. Pavasant, R. Apiratikul, V. Sunkhum, P. Suthiparinyanont, S. Wattanachira, T.F. Marhaba, Biosorption of Cu^{2+} , Cd^{2+} , Pb^{2+} , and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*, *Biores. Technol.* 97 (2006) 2312–2329.
 - [35] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modeling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, *Chem. Eng. J.* 117 (2006) 79–91.
 - [36] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, *Process Biochem.* 36 (2000) 1–5.
 - [37] V.C. Tudy-Costades, H. Fauduest, C. Porte, A. Delacroix, Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto saw dust of *Pinus sylvestris*, *J. Haz. Mater.* B 105 (2003) 121–142.
 - [38] A. Saeed, M. Iqbal, M.W. Akhtar, Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram musk), *J. Haz. Mater.* B 117 (2005) 65–73.
 - [39] G. Wulfsberg, *Principles of Descriptive Chemistry*, Brookes/Cole Publishing, Monterey CA, 1987, p. 25.
 - [40] S. Schiewer, B. Volesky, Modelling of proton–metal ion exchange in biosorption, *Environ. Sci. Technol.* 29 (1995) 3049–3058.
 - [41] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of lead(II) from aqueous solution by adsorption on carbon aerogel using a response surface methodological approach, *Ind. Eng. Chem. Res.* 44 (7) (2005) 1987–1994.
 - [42] Eddy Metcalf, Inc., *Wastewater Engineering, Treatment and Reuse*, Fourth ed., Tata McGraw-Hill Publishing Company Limited, New Delhi, 2003.
 - [43] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe. *Kungliga Svenska Vetenskapsakademien, Handlingar* 24 (7) (1898) 1–3.
 - [44] Y.S. Ho, G. McKay, D.J. Wase, C.F. Foster, Study of the sorption of divalent metal ions on peat, *Ads. Sci. Tech.* 18 (2000) 639–650.
 - [45] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89 (1963) 31–60.
 - [46] G. McKay, M.S. Oterburn, A.C. Sweeney, Surface mass transfer processes during color removal from effluent using silica, *Water Res.* 15 (1981) 327–331.
 - [47] G.E. Boyd, A.W. Adamson, L.S. Mayers, The exchange adsorption of ions from aqueous solutions on organic fly ash, *Kinetic II*, *J. Am. Chem. Soc.* 69 (1947) 2836–2848.
 - [48] F. Helfferich, *Ion Exchange*, Dover Publications Inc, New York, 1995.
 - [49] V.C. Srivastava, I.D. Mall, I.M. Mishra, Adsorption of toxic metal ions onto activated carbon study of adsorption behavior through characterization and kinetics, *Chem. Eng. Proc.* (2007), Online April 2007.

- [50] D. Reicherberg, Properties of Ion-exchange resins in relation to their structure, III, Kinetics of exchange, *J. Am. Chem. Soc.* 75 (1953) 589.
- [51] C. Aharoni, S. Sideman, E. Hoffer, *J. Chem. Technol. Biotechnol.* 29 (1979) 404.
- [52] V.C. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by baggase fly ash and activated carbon: equilibrium, kinetics and thermodynamics, *Col. Surf. A: Physiochem. Eng. Aspects* 272 (2006) 89–104.
- [53] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica, and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1368.
- [54] T.W. Weber, R.K. Chakraborti, Pore and Solid diffusion models for fixed bed adsorbents, *J. Am. Inst. Chem. Eng.* 20 (1974) 228–238.
- [55] G. McKay, H.S. Blair, J.R. Gardener, Adsorption of dyes on chitin I. Equilibrium studies, *J. App. Polymer Sci.* 27 (1982) 3043–3057.
- [56] H. Freundlich, Adsorption in solution, *Phy. Chem. Soc.* 40 (1906) 1361–1368.
- [57] M.M. Dubilin, L.V. Radushkevich, *Proc. Acad. Sci. USSR, Phys. Chem. Sec* 55 (1947) 331.
- [58] M. Polanyi, Theories of the adsorption of gases. A general survey and some additional remarks, *Trans. Faraday Soc.* 28 (1932) 316.
- [59] A. Sari, M. Tuzen, M. Soylak, Adsorption of Pb(II) and Cr(III) from aqueous solution on celtek clay, *J. Haz. Mat.* 144 (2007) 41–46.
- [60] M. Kılıç, M.E. Keskin, S. Mazlum, N. Mazlum, Effect of conditioning for Pb(II) and Hg(II) biosorption on waste activated sludge, *Chem. Eng. Proc.* 47 (2008) 31–40.
- [61] R. Naseem, S.S. Tahir, Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent, *Water Res.* 35 (2001) 3982–3986.
- [62] N. Bekta, S. Kara, Removal of lead from aqueous solutions by natural clinoptilolite: equilibrium and kinetic studies, *Sep. Purifn. Technol.* 39 (2004) 189–200.
- [63] S.P. Singh, L.Q. Mab, M.J. Hendry, Characterization of aqueous lead removal by phosphatic clay: equilibrium and kinetic studies, *J. Haz. Mat.* 136 (2006) 654–662.
- [64] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste, *J. Col. Int. Sci.* 271 (2004) 321–328.
- [65] S. Wang, T. Terdkiatburana, M.O. Tadie, Single and co-adsorption of heavy metals and humic acid on fly ash, *Sep. Purif. Technol.* 58 (2008) 353–358.
- [66] R. Ahmed, T. Yamin, M.S. Ansari, S.M. Hasany, Sorption behaviour of lead(II) ions from aqueous solution onto Haro river sand, *Ads. Sci. Technol.* 24 (6) (2006).