

Removal of Pb(II) from aqueous solutions by adsorption onto clayey soil of Indian origin: Equilibrium, kinetic and thermodynamic profile

Papita Das Saha*, Shamik Chowdhury*[†], Siddhartha Datta**, and Shyamal K Sanyal**

*Department of Biotechnology, National Institute of Technology, Mahatma Gandhi Avenue, Durgapur (WB) 713209, India

**Chemical Engineering Department, Jadavpur University, 188, Raja Subodh Chandra Mullick Road, Jadavpur, Kolkata (WB) 700032, India

(Received 24 August 2011 • accepted 18 December 2011)

Abstract—The feasibility of applying natural, untreated clayey soil as low-cost alternative adsorbent for Pb(II) removal from aqueous solutions was investigated with a batch experimental set-up. Experiments were carried out as a function of initial solution pH (1-8), contact time (10-360 min), initial Pb(II) concentration (20-100 mg L⁻¹), adsorbent dose (0.5-5 g) and temperature (303-333 K). Adsorption equilibrium data were well described by the Langmuir isotherm with maximum adsorption capacity of 121.86 mg g⁻¹ at 303 K. Adsorption of Pb(II) followed pseudo-second-order kinetics. Gibbs free energy (ΔG^0) was spontaneous for all interactions, and the adsorption process exhibited exothermic enthalpy values. The adsorbent was easily regenerated by using 0.1 M HNO₃ solution and was reused for five sorption-desorption cycles without any considerable loss in adsorption capacity. It could be concluded that clayey soil may be used as an inexpensive and effective adsorbent without any treatment or any other modification for the removal of Pb(II) ions from aqueous solutions.

Key words: Adsorption, Clayey Soil, Pb(II), Equilibrium, Kinetics, Thermodynamics

INTRODUCTION

Over the past several decades, the intensification of industrial activities has led to increased amounts of heavy metals being dumped into the environment [1-4]. The rate at which these metallic substances are discharged into the environment, especially water bodies, is increasing at an alarming rate. Heavy metal ions are of great concern because of their toxic nature, bioaccumulating tendency, detrimental effects on human life and public health, and negative impacts on the environment [5]. According to the United States Environmental Protection Agency (EPA), the metals of most immediate concern are arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, mercury, tin and zinc [6].

Lead (Pb) is a hazardous heavy metal used in a wide variety of industrial applications, including storage battery manufacturing, printing, pigments, fuels, metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass manufacturing, and preparation of photography material [7-10]. It is also used in insecticides, water pipes, ointments, medicinal concoctions, matches and explosives [9]. These industries often discharge lead into the aquatic environment without adequate treatment. The presence of lead in the environment can threaten human life due to its toxicity, accumulation in food chains and persistence in nature. Lead is a potent neurotoxic metal if inhaled or swallowed. It disperses throughout the body immediately and causes harmful effects wherever it lands. The major biochemical effects of Pb(II) are its interference with heme synthesis, plumbism, change in brain wave (EEG) patterns,

protoporphyrin elevation in RBCs, interference with neurotransmission, impairment of vitamin D activity, blue lead line in gums, bone marrow damage, paralysis of wrist joints, encephalopathy conditions, disturbance in cerebral function, dyspepsia, vertigo and kidney damage [8,11-15]. Severe lead poisoning can also cause sterility, stillbirths, abortion and neonatal deaths [16,17]. The maximum allowable level of Pb(II) in wastewater as set by the Environmental Protection Agency (EPA) is 0.05 mg L⁻¹ and that of Bureau of Indian Standards (BIS) is 0.1 mg L⁻¹ [15]. WHO and United States Public Health Services have set a limit of 0.01 mg L⁻¹ as an acceptable limit of Pb(II) for drinking water. The elimination of Pb(II) from wastewaters is therefore a priority concern.

The removal of Pb(II) from wastewaters by traditional processes includes its precipitation with lime or alkali hydroxide, coagulation, electrolytic deposition, reverse osmosis and ion-exchange [17]. However, these methods are expensive and have significant disadvantages such as generation of metal-bearing sludge or wastes, incomplete metal removal and the disposal of secondary waste. This situation has in recent years led to extensive investigations for the development of a method that is highly selective, more efficient, easy to operate and hence cost effective. Adsorption, often referred to as passive uptake and physico-chemical binding of chemical species or ions to a solid surface, has been suggested as a potential alternative to the existing physical/chemical methods for the removal of heavy metals from industrial effluents [18]. A number of investigations have been conducted using natural materials or the wastes/by-products of industries for the removal of Pb(II) from aqueous systems [19]. However, the adsorption capacities of most of the reported adsorbents are still limited. New economical, easily available and highly effective adsorbents are still under development.

[†]To whom correspondence should be addressed.
E-mail: chowdhuryshamik@gmail.com

Hence attempts are made in this study to develop an inexpensive adsorbent for wastewater treatment using clayey soil.

Clayey soil is defined as soil that is composed of clay particles. Clays are distinguished from other particles present in soil such as silt by differences in size and mineralogy. Clay particles are characterized by their small size (particle size less than 0.002×10^{-3} m), flake or layered shape, high affinity for water, low porosity and slow diffusive transport [20]. Clay exhibits plasticity when mixed with water in certain proportions, and becomes hard and firm when dried and converted into permanent rock like mass on firing [21]. Clay particles are negatively charged and hence they attract and pick up negatively charged particles [21]. With a view to find an alternative novel adsorbent for effluent and wastewater treatment, the present work on removal of Pb(II) from aqueous solution using clayey soil was taken up. This study reports for the first time, on the feasibility of applying clayey soil as low-cost alternative adsorbent for removal of Pb(II) from aqueous solutions. The adsorption characteristics of Pb(II) on clayey soil was investigated with respect to well-established operational parameters, including the effect of pH, initial metal ion concentration, adsorbent dosage, contact time and temperature. The adsorption kinetics, isotherm and thermodynamics were also investigated and reported.

MATERIALS AND METHODS

1. Adsorbent Collection and Preparation

Clayey soil used in this study was collected from the banks of river Matla owing to its high clay content and low permeability. The Matla river forms a wide estuary in and around the Sundarbans in South 24 Parganas district in the Indian state of West Bengal. The clayey soil sample was not purified prior to usage. It was initially sun-dried for seven days followed by drying in hot air oven at 383 ± 1 K for two days. The dried soil was crushed and sieved to give a

fraction of 100 mesh screen and then stored in sterile, closed glass bottles and used as an adsorbent. The characterization of the adsorbent has been reported elsewhere [20,21].

2. Preparation of Adsorbate Solutions

All the chemicals used in the experiments were of analytical grade. Stock Pb(II) solution ($1,000 \text{ mg L}^{-1}$) was prepared by dissolving 1.5984 g of $\text{Pb}(\text{NO}_3)_2$ in 100 mL double distilled water and making the final volume quantitatively to 1,000 mL using double distilled water. Experimental Pb(II) solutions were prepared by diluting the stock solution with suitable volume of double distilled water. The initial solution pH was adjusted with 1 N HNO_3 or 1 N NaOH solution using a digital pH meter (LI 127, ELICO, India) calibrated with standard buffer solutions.

3. Experimental Procedure

3-1. Batch Experiments

The batch tests were carried out in 250 mL glass-stoppered, Erlenmeyer flasks with 100 mL of working volume, with a concentration of 50 mg L^{-1} . A weighed amount (0.2 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 6 h in an incubator shaker (Innova 42, New Brunswick Scientific, Canada) at 303 ± 1 K. The influence of pH (1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0), contact time (10, 20, 30, 40, 60, 90, 120, 180, 240 and 360 min), initial Pb(II) concentration (20, 40, 50, 80, 100 mg L^{-1}), adsorbent dose (0.5, 1, 2, 3, 4, 5 g L^{-1}) and temperature (303, 313, 323, 333 K) was evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual concentration of Pb(II) in the solution. The residual amount of Pb(II) in each flask was measured with an atomic absorption spectrophotometer (AAnalyst 200, Perkin Elmer, USA) at a wavelength of 217.0 nm.

3-2. Calculations

The amount of Pb(II) adsorbed at equilibrium q_e (mg g^{-1}) was calculated according to a mass balance on the metal ion concentra-

Table 1. Isotherm and kinetic models used in this study

Model	Equation	Parameters	Reference
Isotherm models			
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$	q_e (mg g^{-1}): equilibrium adsorption capacity q_m (mg g^{-1}): maximum adsorption capacity K_L (L mg^{-1}): Langmuir constant C_e (mg L^{-1}) equilibrium adsorbate concentration in solution	[22]
Freundlich	$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$	K_F (mg g^{-1}) (L g^{-1}) ^{1/n} : Freundlich constant n: Heterogeneity factor	[22]
Dubinin-Radushkevich (D-R)	$\ln q_e = \ln q_m - \beta \varepsilon^2$ $\varepsilon = RT \ln \left(1 + \frac{1}{C}\right)$ $E = \frac{1}{\sqrt{2\beta}}$	β (mmol^2/J^2): D-R constant ε (J mmol^{-1}): Polanyi potential E ($\text{kJ} \cdot \text{mol}^{-1}$): mean sorption energy R: universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$) T (K): temperature	[22]
Kinetic models			
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	q_t (mg g^{-1}): amount of adsorbate adsorbed at time t k_1 (min^{-1}): pseudo-first-order rate constant	[22]
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$): pseudo-second-order rate constant	[22]
Intraparticle-diffusion	$q_t = k_i t^{0.5}$	k_i ($\text{mg g}^{-1} \text{min}^{-0.5}$): intraparticle diffusion rate constant	[22]

tion using Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i is the initial Pb(II) concentration (mg L^{-1}), C_e is the equilibrium Pb(II) concentration in solution (mg L^{-1}), V is the volume of the solution (L), and m is the mass of the adsorbent used (g).

The percent removal (%) of Pb(II) was calculated using Eq. (2):

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

To ensure the accuracy, reliability, and reproducibility of the collected data, all adsorption experiments were performed in triplicate, and the mean values were used in data analysis.

In an adsorption study, it is necessary to fit the equilibrium adsorption data using different adsorption isotherm models and kinetic equations in order to analyze and design an adsorption process. Therefore, different theoretical models (Table 1) were applied to the experimental data in order to find a model which adequately predicts kinetic and isotherm data.

RESULTS AND DISCUSSION

1. Effect of pH

The solution pH is one of the most important parameters governing the uptake of heavy metal ions from aqueous solutions [9]. Therefore, the effect of pH on the adsorption capacity of clayey soil for Pb(II) was investigated in the pH range 1-8 and the results are presented in Fig. 1. The % Pb(II) removal was positively correlated with pH of up to 5.0 and then remained practically constant. Maximum Pb(II) removal was observed at pH 5.0 (95.56%). Therefore, pH 5.0 was considered as the optimum pH for adsorption of Pb(II) by clayey soil. Similar values of optimum pH for adsorption of Pb(II) are reported in the literature using maple sawdust [23], activated sawdust [24] and lateritic nickel ores [25]. At pH higher than 7, precipitation of lead occurred and removal due to adsorption was re-

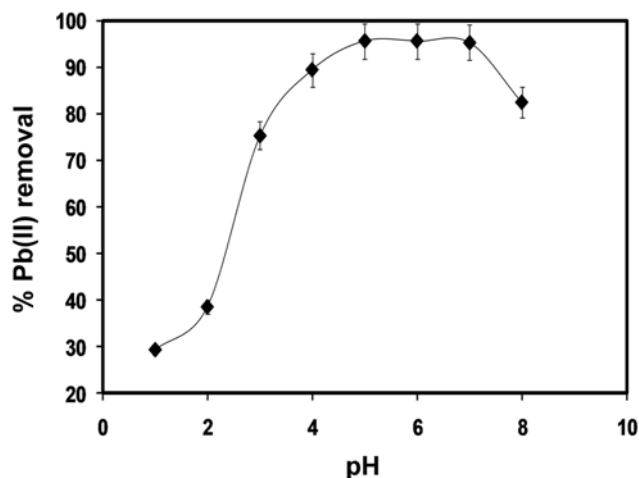


Fig. 1. Effect of pH on Pb(II) removal by clayey soil (experimental conditions: initial conc. 50 mg L^{-1} , adsorbent dose: $0.2 \text{ g}/0.1 \text{ L}$, temp. 303 K , agitation speed 150 rpm , contact time 6 h).

duced. The relatively low % Pb(II) removal by clayey soil at very low pH values can be attributed to the competition faced by Pb(II) ions with H^+ ions to get adsorbed on the binding sites of the adsorbent which are responsible for metal adsorption [26]. However, with increasing pH, this competition weakens and metal cations replace H^+ ions bound to the adsorbent surface resulting in increased metal ion uptake.

2. Effect of Adsorbent Dose

Fig. 2 shows the adsorption profile of Pb(II) versus different clayey soil concentration in the range of 0.5 to 5.0 g. It was observed that the percentage Pb(II) removal increased with increase of adsorbent dose, reaching a maximum (95.63%) at around 2.0 g. The positive correlation between adsorbent dose and Pb(II) removal can be related to increase in adsorbent surface area and availability of more adsorption sites [27]. Further increase in adsorbent dose did not significantly change the adsorption yield. This is due to the binding of

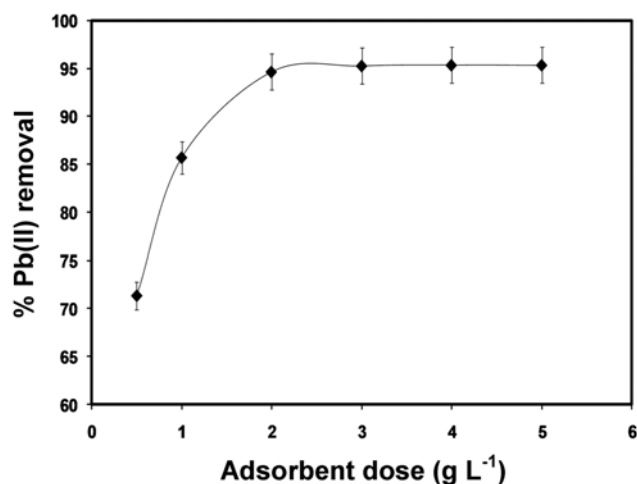


Fig. 2. Effect of adsorbent dose on adsorption of Pb(II) by clayey soil (experimental conditions: initial conc. 50 mg L^{-1} , temp. 303 K , pH 5, agitation speed 150 rpm , contact time 6 h).

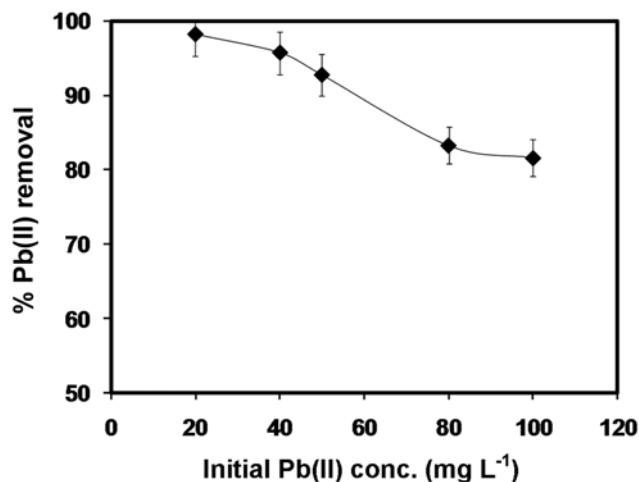


Fig. 3. Effect of initial Pb(II) concentration on adsorption of Pb(II) using clayey soil (experimental conditions: adsorbent dose: $0.2 \text{ g}/0.1 \text{ L}$, temp. 303 K , pH 5, agitation speed 150 rpm , contact time: 6 h).

almost all metal ions to the adsorbent surface and establishment of equilibrium between the Pb(II) ions on the adsorbent and in the solution [21]. Therefore, the optimum adsorbent dose was taken as 2.0 g for the successive experiments.

3. Effect of Initial Metal Concentration

In batch adsorption processes, the rate of adsorption is a function of the initial concentration of metal ions, which makes it an important factor for effective adsorption. The percentage metal removal at different initial Pb(II) concentration using clayey soil is presented in Fig. 3. The percentage removal of metal ion decreased with increase in initial Pb(II) concentration and showed little decrease at higher concentrations. This can be explained by the fact that the adsorbent has a limited number of active sites that become saturated at a certain concentration [28]. Although the percentage removal of metal ion decreased, the equilibrium adsorption capacity of the clayey soil increased with increasing Pb(II) ions concentration. The initial metal ion concentration provides an important driving force to overcome all the mass transfer resistance between the solution and solid phases, hence a higher initial concentration of metal ion may increase the adsorption capacity [14]. A similar trend was observed for the adsorption of Pb(II) by bamboo charcoal [14].

4. Effect of Contact Time

The adsorption capacity of clayey soil towards Pb(II) as a function of contact time is shown in Fig. 4. The adsorption of Pb(II) increased with rise in contact time up to 70 min, and a further increase in contact time did not enhance the adsorption. The adsorption process attained equilibrium after 120 min. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurs and is normally controlled by the diffusion process from the bulk to the surface. In the later stage, the availability of active sites decreases, thus slowing down the transfer of metal ion from solution to adsorbent surface and the sorption is likely an attachment-controlled process. Similar results have been reported in literature for adsorption of Pb(II) on *Strychnos potatorum* seed powder [16] and pine bark [13].

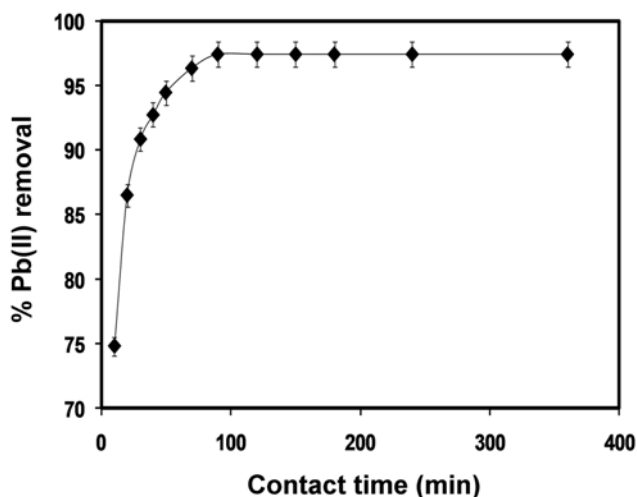


Fig. 4. Effect of contact time on Pb(II) removal by clayey soil (experimental conditions: initial conc. 50 mg L^{-1} , adsorbent dose: $0.2 \text{ g}/0.1 \text{ L}$, temp. 303 K , pH 5, agitation speed 150 rpm).

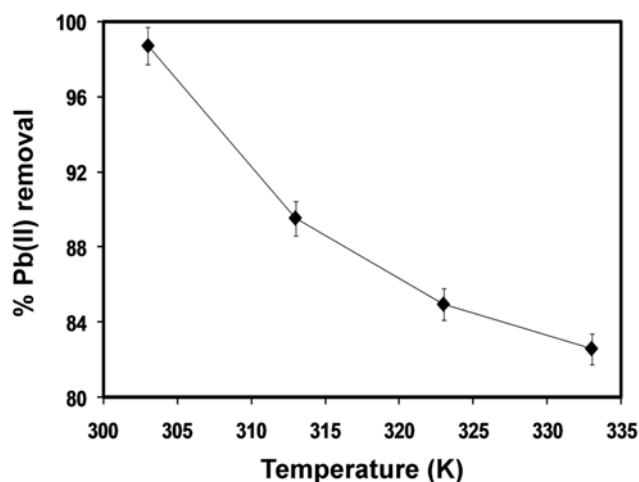


Fig. 5. Effect of temperature on adsorption of Pb(II) by clayey soil (experimental conditions: initial conc. 50 mg L^{-1} , adsorbent dose: $0.2 \text{ g}/0.1 \text{ L}$, temp. 303 K , pH 5, agitation speed 150 rpm , contact time 6 h).

5. Effect of Temperature

Temperature is a highly significant parameter governing the adsorption processes. Fig. 5 displays the effect of temperature on the adsorption of Pb(II) using clayey soil. As seen, the percent removal of Pb(II) decreased with increasing temperature. The decrease in metal ion removal efficiency with increasing in temperature could be due to weakening of the bonds between the metal ions and the active site of the adsorbent. Also, with the increase of temperature, the solubility of Pb(II) increased. Consequently, the interaction forces between the solute and solvent were stronger than those between solute and adsorbent [22]. The solute was thus more difficult to adsorb. The observed trend in decreased metal ion removal capacity with increasing temperature suggests that the adsorption of Pb(II) by clayey soil is kinetically controlled by an exothermic process.

6. Adsorption Isotherms

In this investigation, the Freundlich, the Langmuir, and the Dubinin-Radushkevich (D-R) models (Table 1) were used to describe the equilibrium data of Pb(II) onto clayey soil acquired at different temperatures. The results are shown in Table 2 and the modelled isotherms are plotted in Fig. 6.

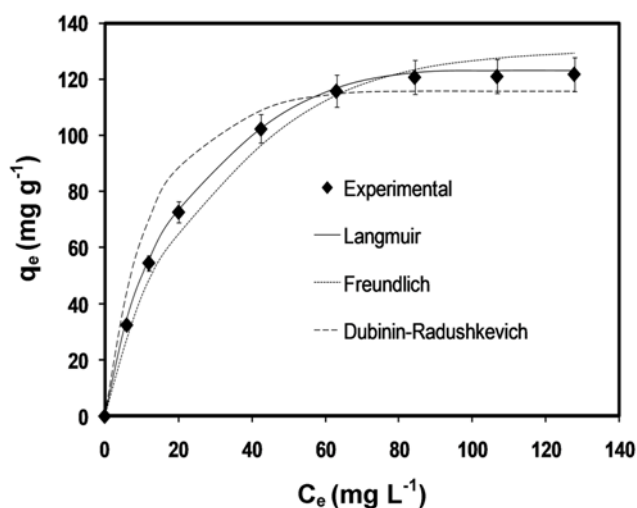
The Langmuir isotherm constants K_L and q_m were calculated from the slope and intercept of the plot between C_e/q_e and C_e . The maximum Pb(II) sorption capacity of clayey soil was found to be 121.86 mg g^{-1} at 303 K and pH 5.0. The values of K_L decreased with the increase in temperature, which accounts for the exothermic nature of the adsorption process.

The Freundlich constants K_F and $1/n$ were calculated from the intercept and slope of the straight line plot of $\log q_e$ versus $\log C_e$. As it can be seen in Table 2, the sorption capacity (K_F) decreased with increase in temperature, which implied that the sorption process was exothermic in nature. The magnitude of n gives a measure of favorability of adsorption. The value of n between 1 and 10 (i.e., $1/n$ less than 1) represents a favorable sorption. For the present study the value of n also presented the same trend representing a beneficial sorption.

In order to distinguish between physical or chemical nature of

Table 2. Adsorption isotherm constants for adsorption of Pb(II) onto clayey soil at different temperatures

T (K)	Langmuir isotherm parameters			Freundlich isotherm parameters			D-R isotherm parameters			
	q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	n	R^2	q_m (mg g ⁻¹)	β (mmol ² J ⁻²)	E (kJ mol ⁻¹)	R^2
303	121.86	6.353	1.0000	33.05	3.734	0.9859	114.89	3.80×10^{-9}	11.47	0.9486
313	118.29	4.913	0.9999	32.58	3.312	0.9782	107.42	4.38×10^{-9}	10.68	0.9421
323	112.61	3.658	0.9999	31.49	2.603	0.9819	102.38	5.73×10^{-9}	9.34	0.9452
333	109.43	1.804	0.9999	29.32	2.183	0.9842	96.67	6.23×10^{-9}	8.95	0.9426

**Fig. 6. Comparison between the measured and modelled isotherm profiles for adsorption of Pb(II) by clayey soil (experimental conditions: initial conc. 50 mg L⁻¹, adsorbent dose: 0.2 g/0.1 L, temp. 303 K, pH 5, agitation speed 150 rpm, contact time 6 h).**

the adsorption process, the equilibrium data were tested with the D-R isotherm model. The plots between $\ln q_e$ and e^2 gave straight lines at all temperatures; the values of constants q_m and β thus obtained are given in Table 2. The mean free energy (E), calculated using the D-R isotherm constant β , gives information about the adsorption mechanism as physical or chemical. If the magnitude of E is between 8 and 16 kJ·mol⁻¹, the sorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ·mol⁻¹, the sorption process is of physical nature [22]. The estimated values of E for the present study were found in the range expected for chemical adsorption (Table 2). Thus the sorption of Pb(II) onto clayey soil was chemical in nature.

In comparing the linear correlation coefficients of the three isotherms listed in Table 2, it could be concluded that the adsorption of Pb(II) onto clayey soil best fitted to the Langmuir isotherm equation under the temperature range studied. The excellent fit of the Langmuir isotherm to the experimental data at all temperatures studied confirms that the adsorption is monolayer. The adsorbed Pb(II) ions did not interact or compete with each other and that they were adsorbed by forming a monolayer. It also implies that the binding energy on the whole surface of the adsorbent was uniform and that sorbate-sorbate interaction was negligible. Table 3 summarizes the comparison of the maximum Pb(II) adsorption capacity of various sorbents including clayey soil. The comparison shows that clayey soil

Table 3. Comparison of maximum Pb(II) adsorption capacity of clayey soil with other reported low-cost adsorbents

Sorbent	q_{max} (mg g ⁻¹)	Reference
Ficus religiosa leaves	37.45	[12]
Prosopis juliflora seed powder	40.32	[28]
Pseudomonas aeruginosa	68.40	[29]
Grape stalks	49.70	[30]
Mustard husk	30.48	[31]
Fly ash	15.08	[32]
Bael leaves	104.0	[33]
Saw dust	21.05	[34]
Modified peanut husk	29.14	[34]
Aspergillus niger	32.60	[35]
Ulmus tree leaves	201.00	[36]
Caulerpa lentillifera	29.00	[37]
Sago waste	46.60	[38]
Cicer arietinum	50.20	[39]
Papaya wood	17.40	[40]
Groundnut shells	12.20	[41]
Coir	18.90	[42]
Strychnos potatorum seed powder	16.42	[16]
Pine bark	76.80	[13]
Snowberry	62.16	[43]
Barley straws	23.20	[44]
Rice husk	58.10	[45]
Pinus silvestris sawdust	22.22	[46]
Clayey soil	121.86	Present study

has higher adsorption capacity of Pb(II) than many of the other reported adsorbents.

7. Adsorption Kinetics

In the present study, three kinetic models (pseudo-first-order, pseudo-second-order and intraparticle diffusion model (Table 1)) were applied to investigate the reaction pathways and potential rate limiting steps of the adsorption of Pb(II) onto clayey soil.

The pseudo-first-order model did not provide an accurate fit to the experimental data. The plots of $\log(q_e - q_t)$ versus t for the pseudo-first-order model at studied temperatures did not show good linearity (figure not shown). The first-order rate constant, k_1 , the correlation coefficient, R^2 and the theoretical and experimental equilibrium adsorption capacity q_e are given in Table 4. From Table 4, the R^2 values were reasonably low at the studied temperatures. Moreover, experimental q_e values were not in good agreement with the calculated theoretical q_e values. Therefore, it can be concluded that the

Table 4. Kinetic parameters for adsorption Pb(II) onto clayey soil

T (K)	$q_{e,exp}$ (mg g ⁻¹)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
		$q_{e,cal}$ (mg g ⁻¹)	k_1 (min ⁻¹)	R ²	$q_{e,cal}$ (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	h (mg g ⁻¹ min ⁻¹)	R ²
303	84.68	59.45	0.02947	0.9037	85.13	0.00926	67.10	0.9999
313	81.23	55.72	0.02420	0.8946	81.98	0.00894	60.08	1.0000
323	77.51	51.38	0.01732	0.9163	78.32	0.00812	49.80	0.9998
333	75.33	47.92	0.01462	0.9082	76.05	0.00726	41.98	0.9999

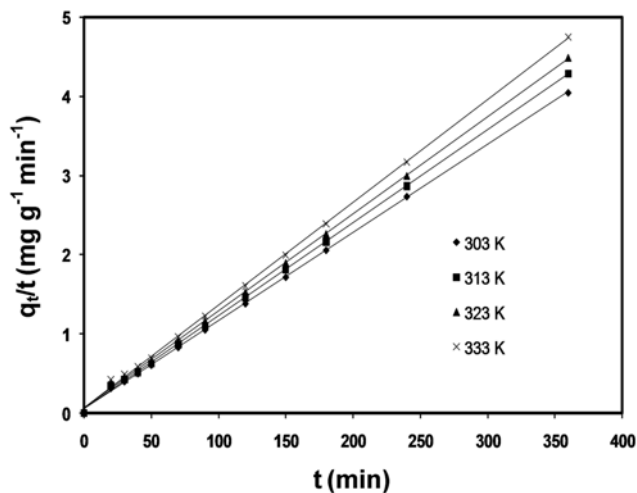


Fig. 7. Pseudo-second-order kinetic plots for adsorption of Pb(II) onto clayey soil at different temperatures (experimental conditions: initial conc. 50 mg L⁻¹, adsorbent dose: 0.2 g/0.1 L, pH 5, agitation speed 150 rpm, contact time 6 h).

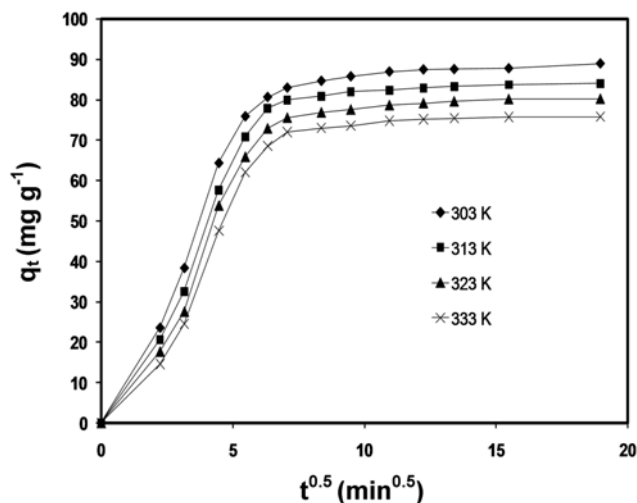


Fig. 8. Weber and Morris plots for adsorption of Pb(II) onto clayey soil at different temperatures (experimental conditions: initial conc. 50 mg L⁻¹, adsorbent dose: 0.2 g/0.1 L, pH 5, agitation speed 150 rpm, contact time 6 h).

pseudo-first-order model was not suitable for modelling the adsorption kinetics of Pb(II) onto clayey soil.

Further, the kinetic data was fitted to the pseudo-second-order equation. The plot of t/q_t against t at different temperatures is shown in Fig. 7. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.99$) over the temperature range of 303–333 K. The data obtained for the pseudo-second-order kinetic model at the four different temperatures is listed in Table 4.

An analysis of the data in Table 4 suggests that the kinetics of adsorption of Pb(II) on clayey soil can be explained more accurately by the pseudo-second-order kinetic model. The calculated q_e values were found to be quite close to the experimental q_e values at all the temperatures studied (303–333 K). So, it was inferred that adsorption of Pb(II) onto clayey soil followed pseudo-second-order kinetics. This suggests that the rate-limiting step of this sorption system may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate. A similar phenomenon was observed in adsorption of Pb(II) on lateritic nickel ores [25], seed powder of *Prosopis juliflora* [28], bael leaves (*Aegle marmelos*) [33], *Acacia leucocephala* bark powder [47], and seed husk of *Calophyllum inophyllum* [48]. The initial adsorption rate, h , as well as the rate constant, k_2 , decreased with increase in temperature indicating exothermic nature of the adsorption process.

In many adsorption processes, the adsorbate species are most probably transported from the bulk of the solution into the solid phase through intraparticle diffusion/transport. So the intraparticle diffusion is another kinetic model which was used to study the rate of Pb(II) adsorption onto clayey soil. According to this model, if the plot of q_t versus $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion, while, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process [45]. The Weber Morris plot for adsorption of Pb(II) onto clayey soil at different temperatures is given in Fig. 8.

The plots in the figure are multimodal with three distinct regions. The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step, and final plateau region indicates equilibrium uptake. Based on these results it might be concluded that intraparticle diffusion was involved in Pb(II) adsorption onto clayey soil, but it was not the sole rate determining step and that some other mechanisms also play an important role. A similar multi-linearity was observed for adsorption of Pb(II) on *Acacia leucocephala* bark powder [47] and pecan nutshell [50].

8. Adsorption Thermodynamics

The activation energy E_a for Pb(II) adsorption onto clayey soil was calculated by the Arrhenius equation [22]:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (3)$$

where k is the rate constant, A is the Arrhenius constant, E_a is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), R is the gas constant ($8.314\text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$) and T is the temperature (K).

By plotting $\ln k_2$ versus $1/T$ (figure not shown), E_a was calculated from the slope of the linear plot and was found to be around $61.45\text{ kJ}\cdot\text{mol}^{-1}$. According to literature, an E_a value of $61.45\text{ kJ}\cdot\text{mol}^{-1}$ suggests that adsorption of Pb(II) onto clayey soil is a chemisorption process [51]. The finding is in accordance with the observations of Baysal et al. on adsorption of Pb(II) onto *Candida albicans* biomass [52].

Thermodynamic behavior of adsorption of Pb(II) on clayey soil was evaluated by the thermodynamic parameters - Gibbs free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0). These parameters were calculated by using the following equations [22]:

$$\Delta G^0 = -RT \ln K_c \quad (4)$$

$$K_c = \frac{C_a}{C_e} \quad (5)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

where K_c is the distribution coefficient for adsorption, C_a is the equilibrium adsorbate concentration on the adsorbent ($\text{mg}\cdot\text{L}^{-1}$) and C_e is the equilibrium adsorbate concentration in solution ($\text{mg}\cdot\text{L}^{-1}$). ΔG^0 for adsorption of Pb(II) onto clayey soil at all temperatures was calculated by using Eq. (4) and was found to be -16.94 , -15.13 , -11.83 and $-9.52\text{ kJ}\cdot\text{mol}^{-1}$ at $T=303$, 313 , 323 and 333 K , respectively. The negative value of ΔG^0 at all temperatures confirms the spontaneous nature and feasibility of Pb(II) adsorption onto clayey soil.

The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of ΔG^0 versus T . The value of ΔH^0 was estimated as $-94.66\text{ kJ}\cdot\text{mol}^{-1}$, and $-255.05\text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ for ΔS^0 . The negative value of ΔH^0 implies that the adsorption phenomenon is exothermic. The negative entropy (ΔS^0) value suggests a decrease in the randomness at the solid/solution interface during the adsorption process. The distribution of lead ions in solution was obviously more disordered compared to lead ions bound to the adsorbent surface and this resulted in net decrease in entropy.

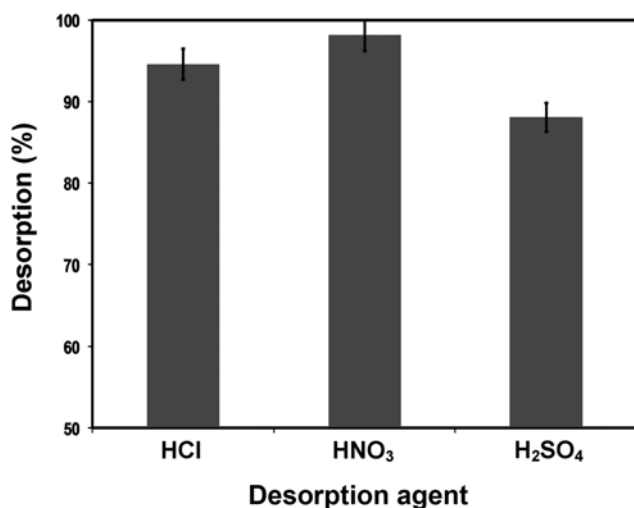


Fig. 9. Effect of the type of desorption agent on the desorption of Pb(II) ions from clayey soil.

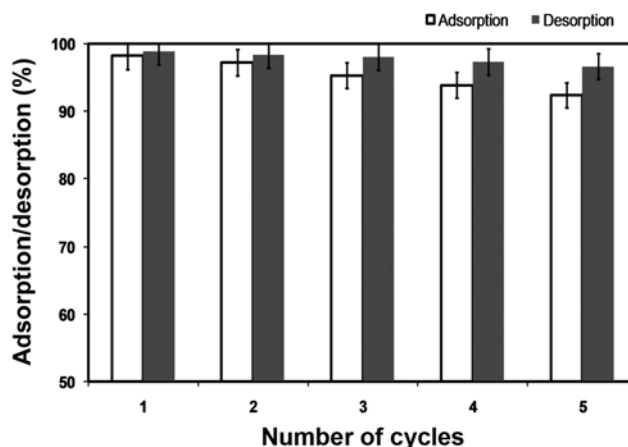


Fig. 10. Adsorption-desorption cycles for Pb(II) ions by clayey soil.

9. Desorption and Reuse

The regeneration of the adsorbent is one of the key factors in estimating its potential and feasibility for commercial application. The reuse of the adsorbent is also vital, if the adsorbent is to be employed for treatment of industrial wastewater. Three different desorption agents, HCl (0.1 M), HNO₃ (0.1 M) and H₂SO₄ (0.1 M) were used to recover the adsorbed Pb(II) ions from the adsorbent and the results are shown in Fig. 9.

The maximum desorption was achieved with 0.1 M HNO₃ solution, and hence it was selected as the desorption agent for Pb(II) ions. About 99% of the metal was recovered. The reusability of the adsorbent was tested in five consecutive adsorption-desorption cycles in batch mode (Fig. 10). The results suggest that the clayey soil has potential to be used repeatedly in Pb(II) adsorption studies without much significant loss in the total adsorption capacity.

CONCLUSION

The adsorption properties of clayey soil for Pb(II) were investigated. The operational parameters such as pH, initial metal ion concentration, adsorbent dose, contact time, and temperature, were found to have an effect on the adsorption efficiency of clayey soil. Pb(II) was optimally adsorbed at pH 5. Equilibrium was attained after 120 min. Afterwards, there was no significant increase in Pb(II) adsorption. High temperature did not favor the adsorption of the metal ion, and the optimal removal was observed at 303 K. Maximum Pb(II) adsorption at pH 5, temperature 303 K, initial Pb(II) concentration $50\text{ mg}\cdot\text{L}^{-1}$ was $121.86\text{ mg}\cdot\text{g}^{-1}$. The adsorption kinetics followed pseudo-second-order model, indicating towards chemisorption. Intraparticle diffusion was not the sole rate-controlling step. The study of equilibrium sorption revealed that the Langmuir isotherm model gave the best fit to experimental data. The nature of adsorption of Pb(II) on clayey soil was chemical adsorption as inferred from the Dubinin-Radushkevich (D-R) isotherm model. The calculated thermodynamic parameters showed the exothermic and spontaneous nature of the adsorption of Pb(II) onto clayey soil. The adsorbent was easily regenerated by using 0.1 M HNO₃ solution and was reused for five sorption-desorption cycles without any considerable loss in adsorption capacity. From these results, it can be concluded that clayey soil can be efficiently used for the removal of Pb(II) from

aqueous solutions.

REFERENCES

- H. S. Lee and J. H. Suh, *Korean J. Chem. Eng.*, **17**, 477 (2000).
- T.-Y. Kim, S.-K. Park, S.-Y. Cho, H.-B. Kim, Y. Kang, S.-D. Kim and S.-J. Kim, *Korean J. Chem. Eng.*, **22**, 91 (2005).
- H. N. Bhatti, I. I. Bajwa, M. A. Hanif and I. H. Bukhari, *Korean J. Chem. Eng.*, **27**, 218 (2010).
- M. Kazmi, N. Feroze, S. Naveed and S. H. Javed, *Korean J. Chem. Eng.*, **28**, 2033 (2011).
- M. S. Rahman and M. R. Islam, *Chem. Eng. J.*, **149**, 273 (2009).
- L. Velasquez and J. Dussan, *J. Hazard. Mater.*, **167**, 713 (2009).
- R. Nadeem, M. H. Nasir and M. S. Hanif, *Chem. Eng. J.*, **150**, 40 (2009).
- A. Ornek, M. Ozacar and I. A. Sengil, *J. Hazard. Mater.*, **37**, 192 (2007).
- S. Qaiser, A. R. Saleemi and M. Umar, *J. Hazard. Mater.*, **166**, 998 (2009).
- R. Jalali, Y. Ghafourian, Y. Asef, S. J. Davarpanah and S. Sepehr, *J. Hazard. Mater.*, **92**, 253 (2002).
- V. K. Gupta and A. Rastogi, *J. Hazard. Mater.*, **152**, 407 (2008).
- T. K. Naiyaa, A. K. Bhattacharya, S. Mandal and S. K. Das, *J. Hazard. Mater.*, **163**, 1254 (2009).
- A. Gundogdu, D. Ozdes, C. Duran, V. N. Bulut, M. Soylak and H. B. Senturk, *Chem. Eng. J.*, **153**, 62 (2009).
- H. Lalhruiatluanga, K. Jayaram, M. N. V. Prasad and K. K. Kumar, *J. Hazard. Mater.*, **175**, 311 (2010).
- J. Goel, K. Kadirvelu, C. Rajagopal and V. K. Garg, *J. Hazard. Mater.*, **B125**, 211 (2005).
- K. Jayaram, I. Y. L. N. Murthy, H. Lalhruiatluanga and M. N. V. Prasad, *Colloids Surf. B.*, **71**, 248 (2009).
- M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *J. Hazard. Mater.*, **170**, 969 (2009).
- Z.-Y. Yao, J.-H. Qi and L.-H. Wang, *J. Hazard. Mater.*, **174**, 137 (2010).
- D. Sud, G. Mahajan and M. P. Kaur, *Bioresour. Technol.*, **99**, 6017 (2008).
- P. Saha and S. K. Sanyal, *Desalination*, **259**, 131 (2010).
- P. Saha, S. Chowdhury, S. Gupta and I. Kumar, *Chem. Eng. J.*, **167**, 874 (2010).
- S. Chowdhury and P. Saha, *Chem. Eng. J.*, **164**, 168 (2010).
- B. Yu, Y. Zhang, S. S. Shukla and K. L. Dorris, *J. Hazard. Mater.*, **84**, 83 (2001).
- R. Ayyappan, A. C. Sophia, K. Swaminathan and S. Sandhya, *Process Biochem.*, **40**, 1293 (2005).
- M. Mohapatra, S. Khatun and S. Anand, *Chem. Eng. J.*, **155**, 184 (2009).
- M. H. Nasir, R. Nadeem, K. Akhtar, M. A. Hanif and A. M. Khalid, *J. Hazard. Mater.*, **147**, 1006 (2007).
- M. E. Argun, S. Dursun, C. Ozdemir and M. Karatas, *J. Hazard. Mater.*, **141**, 77 (2007).
- K. Jayaram and M. N. V. Prasad, *J. Hazard. Mater.*, **169**, 991 (2009).
- J. Chang, R. Law and C. Chang, *Water Res.*, **31**, 1651 (1997).
- M. Martýnez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa and J. Poch, *J. Hazard. Mater.*, **133**, 203 (2006).
- A. K. Meena, K. Kadirvelu, G. K. Mishra, C. Rajagopal and P. N. Nagar, *J. Hazard. Mater.*, **150**, 619 (2008).
- H. Cho, D. Oh and K. Kim, *J. Hazard. Mater.*, **127**, 187 (2005).
- S. Chakravarty, A. Mohanty, T. N. Sudha, A. K. Upadhyay, J. Konar, J. K. Sircar, A. Madhukar and K. K. Gupta, *J. Hazard. Mater.*, **173**, 502 (2010).
- Q. Li, J. Zhai, W. Zhang, M. Wang and J. Zhou, *J. Hazard. Mater.*, **141**, 163 (2007).
- Y. D. Arzu, *Biochem. Eng. J.*, **28**, 187 (2006).
- M. R. Sangi, A. Shahmoradi, J. Zolgharnein, G. H. Azimi and M. Ghorbandoost, *J. Hazard. Mater.*, **155**, 513 (2008).
- R. Apiratikul and P. Pavasant, *Bioresour. Technol.*, **99**, 1266 (2008).
- S. Y. Quek, D. A. Wase and C. F. Forster, *Water SA*, **24**, 251 (1998).
- A. Saeed, M. Iqbal and M. W. Akhtar, *J. Hazard. Mater.*, **117**, 65 (2005).
- Saeed, M. W. Akhtar and M. Iqbal, *Sep. Purif. Technol.*, **45**, 25 (2005).
- S. R. Shukla and R. S. Pai, *J. Chem. Technol. Biot.*, **80**, 176 (2005).
- K. Conrad and H. C. B. Hansen, *Bioresour. Technol.*, **98**, 89 (2007).
- S. T. Akara, A. Gorgulu, B. Anilan, Z. Kaynak and T. Akara, *J. Hazard. Mater.*, **165**, 126 (2006).
- E. Pehlivan, T. Altun and S. Parlayýcý, *J. Hazard. Mater.*, **164**, 982 (2009).
- K. K. Krishnani, X. Meng, C. Christodoulatos and V. M. Boddu, *J. Hazard. Mater.*, **153**, 1222 (2008).
- V. C. Taty-Costodes, H. Fauduet, C. Porte and A. Delacroix, *J. Hazard. Mater.*, **105**, 121 (2003).
- V. S. Munagapati, V. Yarramuthi, S. K. Nadavala, S. R. Alla and K. Abburi, *Chem. Eng. J.*, **157**, 357 (2010).
- O. S. Lawal, A. R. Sanni, I. A. Ajayi and O. O. Rabi, *J. Hazard. Mater.*, **177**, 829 (2010).
- S. G. Susmita and G. K. Bhattacharya, *J. Colloid Interface Sci.*, **21**, 21 (2006).
- J. C. P. Vagheti, E. C. Lima, B. Royer, B. M. da Cunha, N. F. Cardoso, J. L. Brasil and S. L. P. Dias, *J. Hazard. Mater.*, **162**, 270 (2009).
- C. Zhu, L. Wang and W. Chen, *J. Hazard. Mater.*, **168**, 739 (2009).
- Z. Baysal, E. Cinar, Y. Bulut, H. Alkan and M. Dogru, *J. Hazard. Mater.*, **161**, 62 (2009).