Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21095

81 (2017) 133–142
June

Removal of lead ions from aqueous solutions by low-rank Pakistani coal

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Received 22 December 2016; Accepted 1 July 2017

ABSTRACT

Low-rank Pakistani coal was studied as an adsorbent for the removal of lead ions (Pb^{2+}) from aqueous solutions. Adsorption efficiency was studied as a function of contact time, pH, amount of adsorbent, temperature, concentration of adsorbate and concentration of different acids using batch method and atomic absorption spectrometric technique. Maximum removal of lead ions was achieved at 5 pH, using 0.5 g of adsorbent for 10 mL of 4.826×10^{-5} mol L^{-1} lead concentration with equilibration time of 50 min. The adsorption of lead followed pseudo-second-order kinetics with rate constant "K_2" of 1.261 g mg^{-1} min^{-1}. The adsorption data obeyed the Freundlich, Langmuir and Dubinin–Radushkevich isotherms over the lead concentration range of 4.826×10^{-5} to 3.378×10^{-4} mol L^{-1}. The characteristic Freundlich constants, that is, $1/n = 0.609 \pm 0.016$ and $K = 2.164 \pm 0.063$ m mol g^{-1} have been computed for the adsorption system. Thermodynamic parameters for the adsorption process were determined and discussed. The adsorption of lead by the presence of high concentration of foreign ions has also been studied. The proposed method was successfully applied for the removal of lead from spiked tap water sample.

Keywords: Pakistani coal; Lead removal; Thermodynamics; Tap water

1. Introduction

Heavy metals are generally known to be a threat toward humans and ecosystems due to their high potential toxicity. They could not be biodegraded into harmless materials and, to make matters worse, were accumulated in the organisms [1]. Lead is one of the high potential toxic heavy metals when absorbed into the body. For the last few decades, the contamination of water due to indiscriminate disposal of lead has been creating universal threat. Lead is extensively used in lead storage batteries, refineries, pulp and paper, petrochemicals, ceramic, glass, paint, oil, printing, pigments, photographic materials, explosive manufacturing and electronic goods. It also enters the environment by the combustion of fossil fuel, automobile emissions, mining activity and sewage wastewater [2].

The presence of high levels of lead in the environment may cause long-term health risks to humans and ecosystems like nausea, weight loss, vomiting, constipation, chronic nephritis, impaired concentration, sleep disturbance, muscular aches and pains, brain damage and anemia [3]. It is therefore mandatory that their levels in drinking water, waste water and water used for agricultural and recreational purposes must be reduced to within the allowable concentrations recommended by national and international health authorities. Lead removal from the wastewater prior to discharge into environment is, therefore, necessary. Current Environmental Protection Act (EPA) drinking water standard for lead is 0.05 mg/L, but a level of 0.02 mg/L has been proposed and is under review [2]. These concentration values are considered as the thresholds not to exceed for the safety of public health and more worldwide for the maintenance of an ecological equilibrium [4].

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1944-3994/1944-3986

Increasingly stringent legislation on the purity of drinking water has created a growing interest in the development of the conventional treatment processes. Various methods have been used for the treatment of lead-containing wastewaters that include chemical precipitation or coagulation [5–7], diffusive gradients in thin films technique [7], electrochemical reduction [8], ultrafiltration [9,10], ion exchange [11,12], solvent extraction [13] and adsorption.

High operational costs, formation of by-products and incomplete removal, particularly at low concentrations, have been known as factors against the use of these conventional processes. Therefore, there is need to develop a cost-effective, simple, rapid and efficient procedure. The adsorption process under certain conditions has a definite edge over other methods due to its simplicity, high enrichment factor, high recovery, rapid phase separation, low maintenance cost and ability to couple with different detection techniques in on-line and off-line mode.

Different researchers used various adsorbents for the removal of lead from industrial wastewater. The adsorbents used are calcite [14], MnO_2-loaded resin [15], activated carbon [16], chitosan nanofibers [17], *Carpobrotus edulis* plant [18], clinoptilolite [19], low-grade manganese ore [20], alkali-treated tea residue [21], *Hydrilla verticillata* [22], Greek lignite [23], rice husk [24], peanut husk [25], banana stem [26], alfalfa biomass [27], *Azolla filiculoides* [28], sugarcane bagasse [29], nipah palm shoot biomass [30] and sulfur-functionalized silica [31].

The aim of the present work is to study the potential of low-rank Pakistani coal as an adsorbent for the removal of lead from wastewater. The material has been selected since it is abundantly available as a low-cost material even after its wide consumption as a fuel in power generation plants, brick kilns and different other mills. The inexpensive Pakistani coal has also been used as an adsorbent for the removal of strontium [32], chromium [33], and copper [34] from aqueous media. Moreover, no work has been reported so far regarding the adsorptive removal of lead ions using low-rank Pakistani coal.

2. Materials and methods

2.1. Equipment

The absorption measurements were made with a Hitachi model Z-2000 polarized Zeeman atomic absorption spectrophotometer. The instrument has a strong magnetic field across the burner, which provides a double-beam optical correction system. A water cooled, premix, fish-tail type burner, having a slot of 100 × 0.5 mm^2, was used for the air-acetylene flame. Hollow cathode lamp of lead from Hitachi was used as a radiation source. The instrumental parameters used for the quantification of lead were as follows: lamp current 7.5 mA, width of slit 1.3 nm, wavelength 283.3 nm, burner height 7.5, fuel (C_2H_2) flow 2.0 L min^{-1} and oxidant (air) flow 15.0 L min^{-1}.

2.2. Reagents

Low-rank Pakistani coal was collected from mines in the province of Punjab (Khushab, Makerwal). The sample was ground and sieved to a particle size of about 500 μm. The coal powder was initially activated at 300°C in a muffle furnace for 4 h. In order to remove the mineral contents, to improve the hydrophilicity of surface and to enhance the acidic behavior of the material, the sample was treated with 2M H_2SO_4 at room temperature for 2 h according to the modified procedure of Shen et al. [35], Wibowo et al. [36] and Zhang et al. [37]. After acid treatment, the coal was washed with deionized water to the neutral pH of the filtrate. The washed coal sample was dried at 60°C till constant weight and stored in a plastic container.

The surface area of low-rank Pakistani coal sample was measured according to Brunauer–Emmett–Teller method (BET) by nitrogen adsorption at 77 K using Quanta chrome S1 BET surface area analyzer. Before nitrogen adsorption, the sample was degased for 2 h at final pressure of 133.32×10^{-4} Pa. The determined value of surface area was found to be 4.8 m^2 g^{-1}. The bulk density, percent porosity, pH and pH_{zpc} of the adsorbent were determined by using the reported methods [38,39] and were found to be 2.0 g mL^{-1}, 53%, 5.1 and 3.1, respectively.

Stock solution of lead (1,000 mg L^{-1}) was prepared by dissolving 0.1 g of Specpure metal (Johnson Matthey, UK) in a minimum amount of distilled nitric acid. The resultant solution was diluted to 100 mL with water. Fresh working standard solutions in the range of 1.0–10.0 mg L^{-1} were prepared by appropriate dilution of this stock solution immediately before use. Buffer solutions of pH 1.0–9, with an ionic strength of 0.1 M, were prepared by using appropriate volumes of solutions of KCl and HCl (pH 1–3), CH_3COONa and CH_3COOH (pH 4–5), NH_4Cl and NH_4OH (pH 6–7.5), H_3BO_3, NaCl and NaOH (pH 8–9). All the reagents used were of Analytical Grade and used as such. Distilled and deionized water was used in all experiments.

2.3. Adsorption procedure

Adsorption measurements were performed using a batch technique at room temperature except where otherwise specified by shaking 0.50 g of coal sample in a 10 mL of an aqueous solution of known concentration of lead ions at pH 5.0 in 35 cm^3 culture tubes for a given time period. After filtration, the concentration of lead ions in filtrate was determined by atomic absorption spectrophotometer using optimized instrumental parameters.

The percentage sorption of lead ions from the solution was calculated using the following expression:

$$\% \text{ Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where C_i, initial concentration of lead ions in solution (mg L^{-1}); C_f, concentration of lead ions in solution after equilibrium (mg L^{-1}).

All the experiments were conducted at 298 ± 1 K and the reported values are the average of at least two independent measurements with an average relative standard deviation of ±3.9% unless otherwise specified.

3. Results and discussion

3.1. FTIR studies

The chemical modification of coal and its interactions with lead ions were followed by using *Fourier transform infrared*

(FTIR) spectroscopy. The FTIR spectra of coal, activated coal and Pb(II)-loaded activated coal are shown in Fig. 1.

The absorption band at 2,914, 1,736, 1,613, 1,439, 1,361, 1,217 and 1,027 cm^{-1} are attributed to the stretching of aliphatic C–H, carboxylic C=O, C=O, O–H bending of adsorbed H_2O, S=O, C–O and C–OH groups, respectively. Absorption bands at 430–470 cm^{-1} and 516 cm^{-1} are due to mineral components [40–42]. In the case of activated coal, the shifting of bands at 1,736, 1,364 and 1,217 cm^{-1} to 1,734, 1,361 and 1,216 cm^{-1} respectively, with enhanced intensity could be explained on the basis of increased number of carboxylic acid groups as a result of oxidation and incorporation of sulfate group on the surface of the coal.

Following the lead ion adsorption, the FTIR spectrum of coal exhibited changes in the peak position and relative intensities. The peaks at 1,734, 1,361 and 1,217 cm^{-1} were shifted to 1,730, 1,367 and 1,210 cm^{-1} respectively, with decreased intensity, which suggest the binding of lead ions with carboxylic acid and sulfonic group present on the surface of the activated Pakistani coal. Similar observations of minor shifts and decrease in the intensities of the FTIR peaks after the adsorption of metal ions on different adsorbents have been reported [40,43].

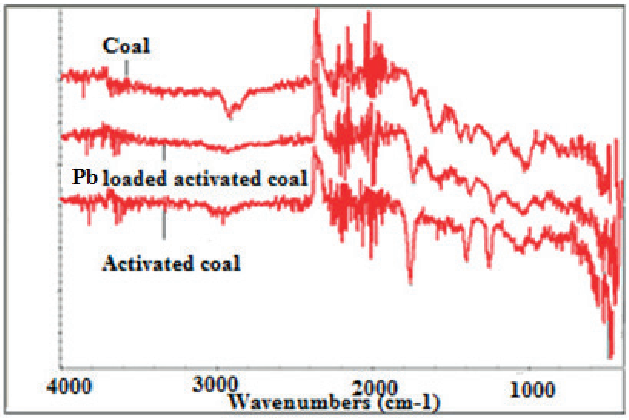

Fig. 1. FTIR spectra of coal, activated coal and Pb ions-loaded coal.

3.2. SEM studies

The scanning electron microscopy (SEM) images of low-rank Pakistani coal and lead-loaded coal were recorded at different magnifications from 100 to 20,000 and those at 20,000 have been shown as a representative in Fig. 2, which shows that before adsorption, the surface of the coal was rough and porous in nature, whereas the SEM of lead-loaded coal possess smooth surface indicating the lead adsorption.

3.3. Influence of acid concentration

The chemical contact of the adsorbent surfaces results in certain variations in adsorption characteristics. Therefore, the adsorption characteristics of lead (4.826 × 10^{-5} mol L^{-1}) was studied in mineral acid solutions (HNO_3, HCl, $HClO_4$) in the concentration range of 0.0001 to 1.0 mol L^{-1} using the arbitrarily selected 0.4 g of coal and shaking time of 10 min and the results are shown in Fig. 3, which depicts that the adsorption of lead ions decreases with an increase in acid concentration. This behavior could be explained on the basis of competition between the excess of H^+ ions in the medium and positively charged lead ions at higher acid concentration. All the acids used showed almost similar adsorption trend.

The maximum adsorption of metal at acid concentration of 0.0001 mol L^{-1} is in accordance with the concept of zero point charge (ZPC) which is 3.1 for sulfuric acid treated Pakistani coal. This indicates that the adsorption of lead ions occurs on the coal surface containing sulfate ions.

3.4. Effect of pH

The pH plays a significant role in the adsorption process by affecting the surface charge of an adsorbent, the extent of ionization and speciation of the adsorbate. Therefore, the effect of pH of the solutions on the adsorption efficiency of Pb(II) was investigated at different pH ranging from 2.0 to 9, using 10 cm^3 of 4.826 × 10^{-5} mol L^{-1} of lead solution, with 0.4 g of coal and shaking time of 10 min. The concentration of lead, dose of coal and shaking time were selected arbitrarily and the results are presented in Fig. 4.

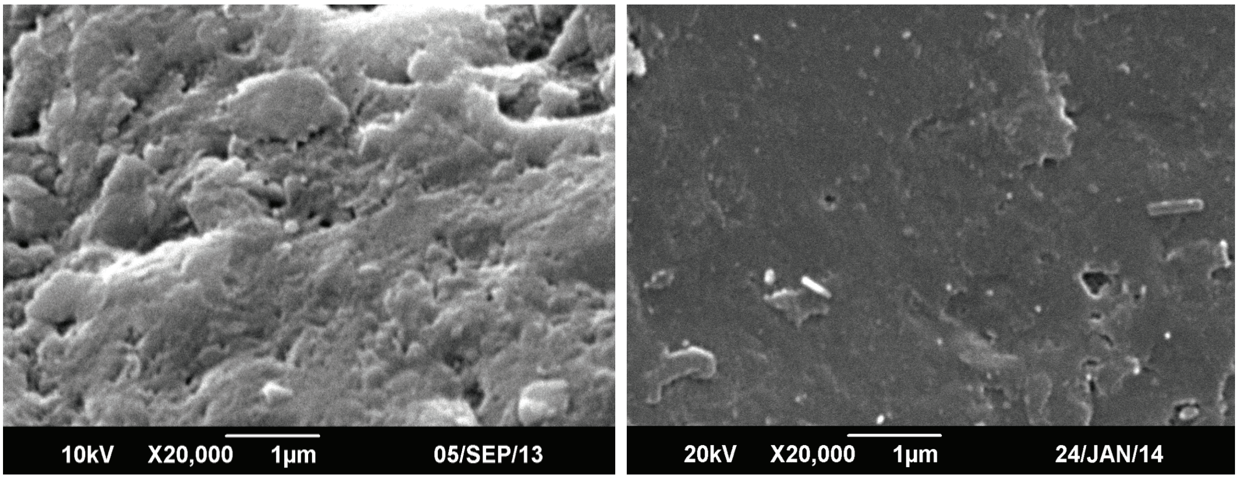

Fig. 2. SEM images of the coal before (A) and after (B) lead ions adsorption.

A sharp increase in the adsorption of lead was observed with the variation of solution pH from 2.0 to 5.0. With further increase in pH, the adsorption was rapidly decreased. From pH 6 to 9, the adsorption seems to increase. Maximum adsorption of lead has been reported on coal fly ash [44] and copper on Pakistani coal [34].

At low pH, the surface ligands were associated with the hydrogen ions compare with positively charged lead ions. With the increase in pH, more ligands such as carboxyl, sulfonic would be exposed, possessed negative charges with subsequent attraction of positively charged lead ions and more adsorption onto the coal surface. The increase in the adsorption of lead ions from pH 3 to 5 could be attributed to the point of zero charge of coal. Above pH_{zpc} coal surface would have a net negative charge. The ionic state of ligands will be such as to favor reaction with lead ions. This would lead to electrostatic attractions between positively charged lead ions and negatively charged binding sites; hence, the significant increase in binding efficiency. The decreased adsorption of lead ions beyond pH 5.0 could probably be due to the hydrolysis of lead ions such as $Pb(OH)^+$, which have less affinity for adsorption on the coal surface. Similar arguments have been reported for lower adsorption of lead ions from solution pH of 5–8 on different adsorbents [45–47]. Since maximum adsorption of lead ions occurred at pH 5.0, this optimum pH was selected for further experiments regarding the optimization of various parameters.

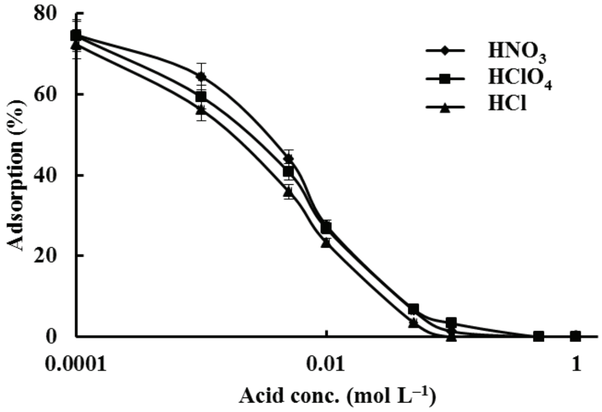

Fig. 3. Variation of percentage adsorption of lead ions on low-rank Pakistani coal as a function of acid concentration.

The adsorption of Pb(II) on coal surface may be explained via ion-exchange mechanism that is facilitated by the dissociation of acidic groups present on the coal surface. The cation-exchange mechanism can occur in the aqueous solution as follows:

$$m[\text{Coal–OH}] \rightleftharpoons m[\text{Coal–O}]^- + mH^+ \tag{2}$$

$$M^{n+} + m[\text{Coal–O}]^- \rightleftharpoons M[\text{Coal–}]_m^{(n-m)} \tag{3}$$

The overall reaction could be represented as follows:

$$m[\text{Coal–OH}] + M^{n+} \rightleftharpoons M[\text{Coal–}]_m^{(n-m)} + mH^+ \tag{4}$$

where [Coal–OH], activated coal surface; M^{n+}, metal ions with n + charge; mH^+, number of protons released.

Eq. (2) represents deprotonation of the activated coal while Eq. (3) the attachment of the lead ions on the coal surface. At low pH values, Eq. (2) dominates as a result of the adsorption surface being surrounded by H^+ ions that compete for binding sites on the coal surface and whose presence would result in the reduction of Pb(II) ions interaction with the binding sites due to the higher repulsive force that arises.

3.5. Effect of coal weight

Effect of the weight of low-rank Pakistani coal on the adsorption of lead ions was studied by varying the weight of coal from 0.1 to 0.75 g using 4.826×10^{-5} mol L^{-1} of lead solution at 5.0 pH for time interval of 30 min and the results are shown in Fig. 5, which is a plot of percentage adsorption of lead vs. adsorbent weight. Fig. 5 shows that the percentage adsorption increases with an increase in adsorbent weight up to 0.5 g beyond which almost constant adsorption was observed. Therefore, coal weight of 0.5 g was considered to be sufficient for the removal of lead and was selected for all further experiments.

The increase in the percent adsorption of lead ions with an increase in weight of the coal could be attributed to the availability of more active sites with the increase in the adsorbent dose.

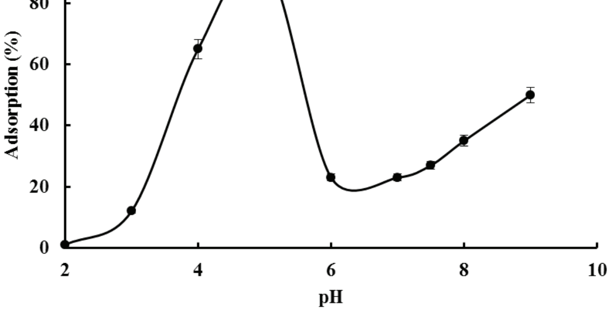

Fig. 4. Effect of pH on the adsorption of lead on low-rank Pakistani coal.

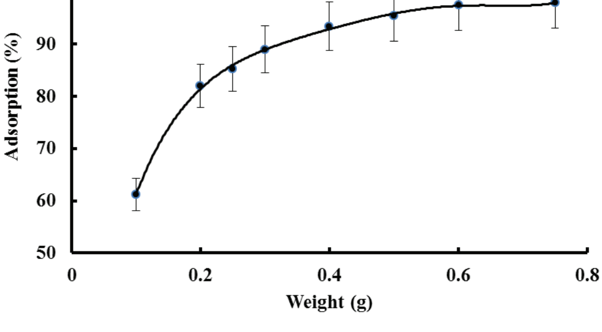

Fig. 5. Effect of amount of coal on the adsorption of lead on low-rank Pakistani coal.

3.6. Influence of shaking time

The influence of shaking time on the adsorption of lead ions was studied by varying the shaking time from 5 to 70 min using 4.826 × 10^{-5} mol L^{-1} of lead solution at 5.0 pH with 0.5 g of coal as illustrated in Fig. 6. The increase in percentage adsorption with increase in shaking time is due to more contact time for Pb(II) ions with low-rank Pakistani coal. After 50 min, no significant increase was observed; therefore, this time duration was selected for further experiments. The initial rapid adsorption of lead ions could probably be due to the availability of more vacant active sites on the surface of adsorbent; however, in the latter stage, the adsorption process became slow due to the availability of lower number of active sites for binding the lead ions on adsorbent surface.

3.6.1. Kinetic explanation

The time-dependent adsorption data were applied to the Morris–Weber [48] equation:

$$q_t = K_{\text{Int}} t^{0.5} \tag{5}$$

where q_t, the adsorbed concentration (mg g^{-1}) at time "t"; K_{Int}, intraparticle diffusion coefficient.

The plot of q_t vs. $t^{0.5}$ is shown in Fig. 7, which clearly shows that initially the adsorption was rapid up to 30 min, which then slowed down to 70 min, which were depicted from two distinct slopes of 0.023 and 0.003 for first 20 min and 30–70 min, respectively.

The nature of the adsorption either via film diffusion or intraparticle diffusion mechanism was verified using the Reichenberg [49] equation:

$$X = \left(1 - \frac{6}{\pi^2}\right) e^{-\beta_t} \tag{6}$$

where

$$\text{X} = \frac{Q_t}{Q_e} = \frac{\text{Amount of metal adsorbed at time "}t\text{"}}{\text{Amount of metal adsorbed at equilibrium}}$$

The value of β_t is a mathematical function of X that can be calculated for each value of X by using the following equation:

$$\beta_t = -0.4977 \ln(1 - X) \tag{7}$$

The plot of β_t vs. time is a straight line (Fig. 7) with a correlation factor of 0.997, which indicates that the sorption is controlled by film diffusion.

In order to evaluate kinetic adsorption parameters, the obtained kinetic adsorption data of lead ions on Pakistani coal was fitted to the first-order Lagergren (Eq. (8)) and pseudo-second-order (Eq. (9)) rate equations using the linearized forms as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where q_e, amount of lead ions adsorbed at equilibrium (mg g^{-1}); q_t, amount of lead ions adsorbed at time "t" (mg g^{-1}); t, time in min; k_1, rate constant of the first-order model (min^{-1}); k_2, rate constant of the pseudo-second-order model (g mg^{-1} min^{-1})

The straight lines were obtained by plotting $\log(q_e - q_t)$ vs. "t" and t/q_t vs. "t" with correlation coefficients (R^2) of 0.989 and 0.999, respectively (Fig. 8). The determined kinetic parameters for the first-order and pseudo-second-order models are given in Table 1. The higher R^2 value and good correspondence between the determined (0.206 mg Pb g^{-1}) and the experimental (0.195 mg Pb g^{-1}) values of adsorption capacity confirm that the experimental kinetic data are more in agreement with the pseudo-second order rate equation.

3.7. Effect of initial lead concentration

The effect of lead concentration on the efficiency of adsorption was investigated under the optimized conditions of contact time 50 min, adsorbent weight 0.5 g, and the pH 5.0. The initial concentration of lead was varied from 2.413 × 10^{-5} to 3.378 × 10^{-4} mol L^{-1}. It was observed that the

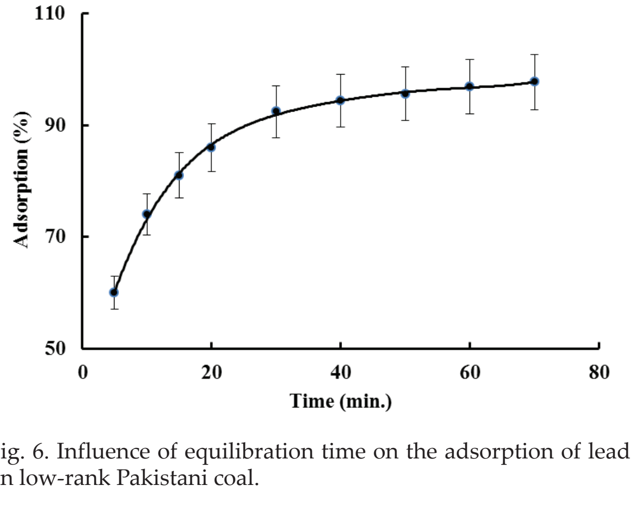

Fig. 6. Influence of equilibration time on the adsorption of lead on low-rank Pakistani coal.

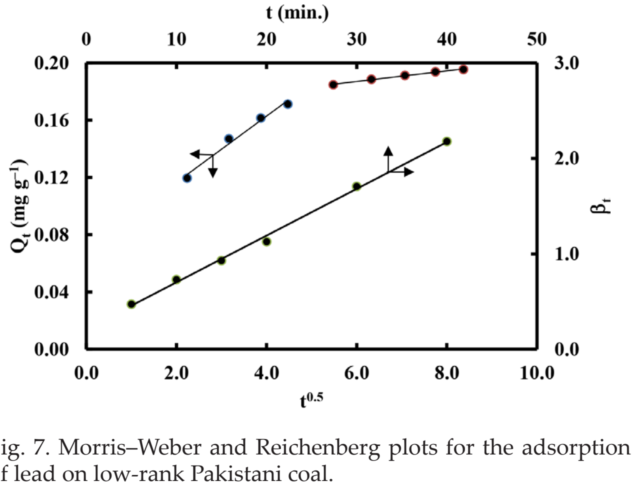

Fig. 7. Morris–Weber and Reichenberg plots for the adsorption of lead on low-rank Pakistani coal.

percentage adsorption decreases gradually with an increase in the concentration of lead. This could be explained based on the availability of relatively lesser number of active sites in a fixed amount of coal at higher concentrations of lead.

3.7.1. Adsorption isotherms

To optimize the design of an adsorption process, it is important to study the most appropriate expressions for equilibrium plots. Freundlich, Langmuir, and Dubinin–Radushkevich (DR) isotherm models were used to describe the adsorption equilibrium using the optimized parameters.

The Freundlich adsorption isotherm is the relationship between the concentration of the metal uptake per unit mass of an adsorbent (C_{Ad}) and the concentration of metal at equilibrium (C_E). Mathematically it is shown in Eq. (10):

$$C_{\mathrm{Ad}} = K_E^{\frac{1}{n}} \tag{10}$$

The logarithmic form of Eq. (10) can be written as follows:

$$\log C_{\mathrm{Ad}} = \log K + \frac{1}{n} \log C_E \tag{11}$$

where C_{Ad}, amount of lead adsorbed (mol g^{-1}); C_E, equilibrium concentration of lead in solution (mol L^{-1}); $1/n$ and K, Freundlich constants.

A plot of $\log C_{\mathrm{Ad}}$ vs. $\log C_E$ yields a straight line with a correlation coefficient "R^2" of 0.997. The linear plot (Fig. 9) supports the applicability of the Freundlich adsorption model in the present study. Similar results were reported for the adsorption of copper on low-rank Pakistani coal [34].

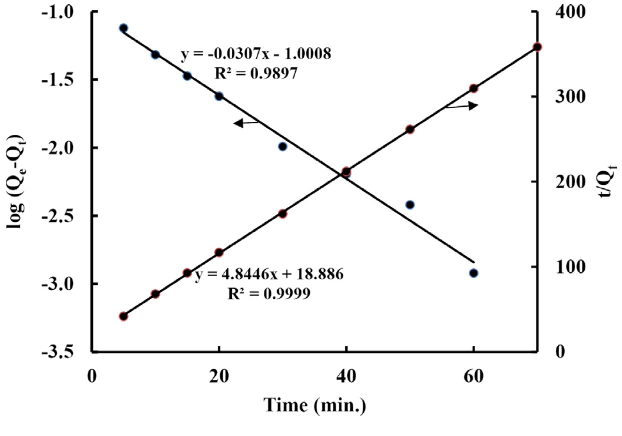

Fig. 8. Lagergren first-order- and pseudo-second-order plots of lead adsorption on low-rank Pakistani coal.

Table 1
Determined kinetic parameters for the adsorption of lead ions on coal

Pseudo-first order			Pseudo-second order		
q_e, mg g^{-1}	k_1, min^{-1}	R^2	q_e, mg g^{-1}	K_2, g mg^{-1} min^{-1}	R^2
0.100	0.069	0.989	0.206	1.261	0.998
			0.195^a		

^{a}Experimentally determined value.

The values of $1/n$ and K were determined from the slope and the intercept of the Freundlich plot and were found to be 0.609 ± 0.016 and 2.164 ± 0.063 m mol g^{-1}, respectively. The fractional value of the adsorption affinity ($1/n$) corresponds to a heterogeneous surface of the low-rank Pakistani coal.

Table 2 summarizes the comparison of lead adsorption capacities from aqueous solution with a variety of adsorbents which reveals that the Pakistani coal has higher adsorption capacity of 448.38 mg g^{-1} than different adsorbents (19.9–263 mg g^{-1}), indicating a promising future of low-rank Pakistani coal for removal of lead from aqueous solutions.

According to the Langmuir adsorption isotherm model, all adsorption sites have equal affinity for the metal ions. The linear form of Langmuir adsorption isotherm may be represented as follows:

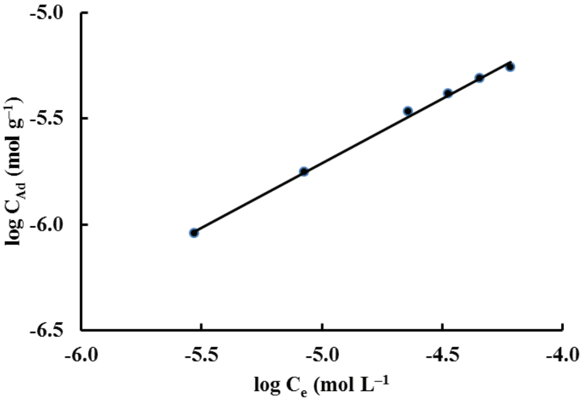

Fig. 9. Freundlich adsorption isotherm of lead ions on low-rank Pakistani coal.

Table 2
Adsorption capacities of lead for different adsorbents

S. No.	Adsorbent	$Q_{\mathrm{max,}}$ mg g^{-1}	Source
1	Calcite	19.92	[14]
2	MnO_2-loaded resin	80.64	[15]
3	Activated carbon	184.0	[16]
4	Chitosan nanofibers	263.15	[17]
5	*Carpobrotus edulis* plant	175.0	[18]
6	Clinoptilolite	27.7	[19]
7	Low-grade manganese ore	142.85	[20]
8	Alkali-treated tea residue	64.10	[21]
9	*Hydrilla verticillata*	104.2	[22]
10	Greek lignite	150.1	[23]
11	Rice husk	120.48	[24]
12	Peanut husk	29.14	[25]
13	Banana stem	91.74	[26]
14	Alfalfa biomass	89.2	[27]
15	*Azolla filiculoides*	228	[28]
16	Sugarcane bagasse	196	[29]
17	Nipah palm shoot biomass	52.86	[30]
18	Sulfur-functionalized silica	46.3	[31]
19	Low-rank Pakistani coal	448.38	Present study

$$\frac{C_E}{C_{\text{Ad}}} = \frac{1}{Qb} + \frac{C_E}{Q} \tag{12}$$

where C_{Ad}, concentration of lead adsorbed at equilibrium (mol g^{-1}); C_E, equilibrium concentration of lead in solution (mol L^{-1}); Q and b, Langmuir isotherm constants.

A plot of C_E/C_{Ad} vs. C_E yields a straight line (Fig. 10), with a correlation coefficient "R^2" of 0.983, indicating the applicability of the Langmuir model in the present work. Similar results have been reported for the adsorption of copper on Nigerian brown coal [50].

The values of Langmuir constants "Q" and "b" were determined from the slope and intercept of the plot and were found to be (7.797 ± 0.511) × 10^{-2} m mol g^{-1} and (3.71 ± 0.318) × 10^{3} dm^{3} mol^{-1}, respectively. The higher value of sorption capacity (K_f) calculated from Freundlich isotherm compared with the Langmuir isotherm model may be attributed to the multilayer and mono-layer adsorption of the lead ions, respectively.

In order to classify the physical or chemical adsorption, the DR isotherm was also checked using Eq. (13):

$$C_{\text{Ad}} = C_m \exp(-\beta\varepsilon^2) \tag{13}$$

where C_{Ad} is the amount of lead adsorbed on low-rank Pakistani coal, C_m is the maximum amount of lead that can be adsorbed on coal using the optimized experimental conditions, β is a constant with a dimension of energy, and ε is Polanyi potential.

$$\varepsilon = \text{RT}\ln\left(1 + \frac{1}{C_E}\right) \tag{14}$$

where R, ideal gas constant; T, absolute temperature; C_E, equilibrium concentration of lead in solution.

The linear form of D–R isotherm can be represented as follows:

$$\ln C_{\text{Ad}} = \ln C_m - \beta\varepsilon^2 \tag{15}$$

A straight line was obtained when lnC_{Ad} was plotted against ε^2 with R^2 = 0.997 (Fig. 11), indicating that lead ions adsorption on low-ranked Pakistani coal also obeys the D–R equation. From the linear plot value of "β" determined was –4.64 × 10^{-3} k J^{2} mol^{-2}. By substituting the value of "β", the mean adsorption energy (E_{Ad}) was calculated using Eq. (16):

$$E_{\text{Ad}} = \frac{1}{(-2\beta)^{1/2}} \tag{16}$$

The values of sorption free energy (E_{Ad}) for physical adsorption are in the range of 1–8 kJ mol^{-1}, and greater than 8 kJ mol^{-1} for chemical adsorption. The determined value of "E_{Ad}" from Eq. (16) was 10.381 ± 0.169 kJ mol^{-1}, indicating chemisorption or ion-exchange process [51].

On the basis of maximum "R^2" value of 0.998, the Freundlich adsorption isotherm seems to be more appropriate isotherm for the experimental data of lead sorption on low-rank Pakistani coal.

3.8. Effect of temperature

The adsorption of 2.413 × 10^{-4} mol L^{-1} of lead ions on low-rank Pakistani coal was carried out using optimized conditions at different temperatures (283–333 K) and the results are shown in Table 3, which showed that the lead ions adsorption increases with the rise in temperature. Van't Hoff plot, that is, lnK_c vs. 1/T was a straight line (Fig. 12) and was used to determine ΔH and ΔS from the slope and intercept, respectively, by using the following equation:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{17}$$

where K_c, ΔS, ΔH, R and T are equilibrium constant, change in entropy, enthalpy change, gas constant and absolute temperature, respectively, for the adsorption process.

The equilibrium constant (K_c) was calculated by using the equation:

$$K_C = \frac{C_{\text{Eq}.S}}{C_{\text{Eq}.L}} \tag{18}$$

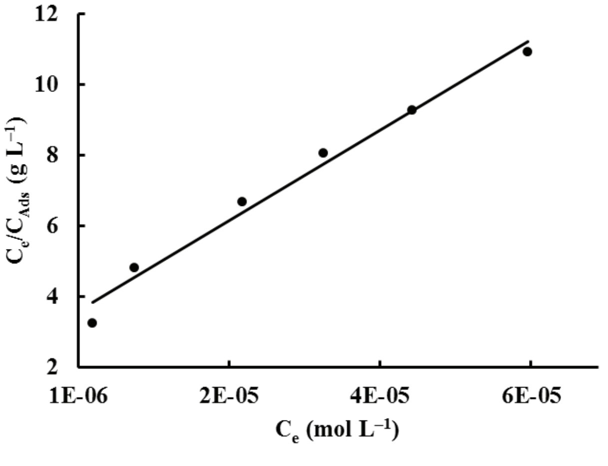

Fig. 10. Langmuir adsorption isotherm of lead ions on low-rank Pakistani coal.

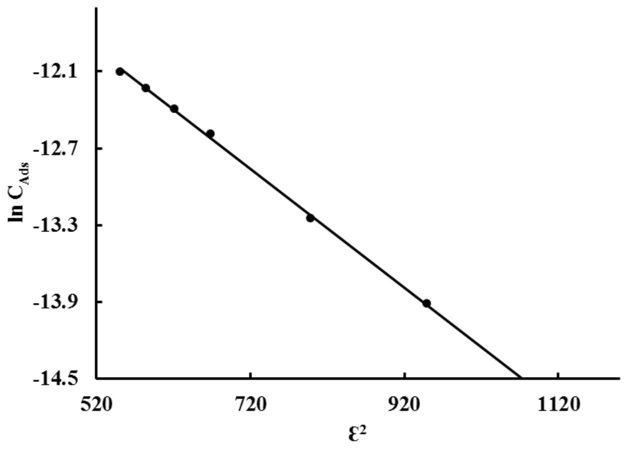

Fig. 11. Dubinin–Radushkevich adsorption isotherm of lead ions on low-rank Pakistani coal.

Table 3
Effect of temperature and thermodynamic parameters for the adsorption of lead ions on low-rank Pakistani coal

Temp. (K)	$1/T$ (K^{-1}) 10^{-3}	Concentration adsorbed (mol L^{-1}) × 10^{-4}	Concentration in bulk (mol L^{-1}) × 10^{-5}	K_c	$\ln K_c$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
283	3.534	1.875	5.381	3.484	1.248	–2.936		180.314
288	3.472	2.041	3.716	5.493	1.704	–4.080		181.035
293	3.413	2.122	2.910	7.291	1.987	–4.840		180.300
303	3.300	2.268	1.448	15.666	2.751	–6.930	47.991	180.498
313	3.195	2.328	0.854	27.247	3.305	–8.601		179.038
323	3.096	2.362	0.512	46.167	3.832	–10.291		177.470
333	3.003	2.382	0.314	75.919	4.330	–11.988		175.781

Note: Low-rank Pakistani coal, 500 mg; shaking time, 50 min; volume equilibrated, 10 cm^3; pH, 5.0; lead ion concentration, 2.413×10^{-4} mol L^{-1}.

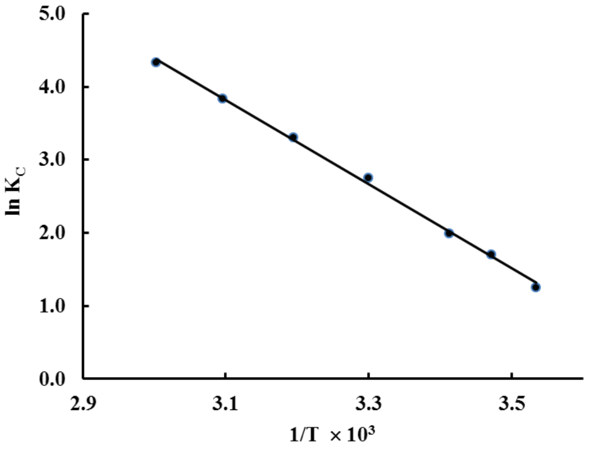

Fig. 12. Van't Hoff plot for the adsorption of lead ions on low-rank Pakistani coal.

where $C_{Eq.S}$ is the concentration of lead adsorbed at equilibrium (mg L^{-1}) and $C_{Eq.L}$ is the concentration of lead in solution at equilibrium (mg L^{-1}). The ΔG and ΔS for the specific adsorption process have also been calculated using the equations as follows:

$$\Delta G = -RT\ln K_c \tag{19}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{20}$$

The calculated values of ΔH, ΔG and ΔS have been summarized in Table 3. The negative values of ΔG represent that the adsorption of lead on Pakistani coal is a spontaneous process. The increase in the numerical value of $-\Delta G$ with the rise in temperature indicates that the adsorption process of lead ions on coal is more favorable at higher temperatures. The positive values of enthalpy change indicate the endothermic nature of the adsorption process, whereas the positive value of ΔS represents increase in the randomness during the adsorption process.

3.9. Interference of foreign ions

The presence of other cations and anions in the adsorptive medium may affect the environment and solution chemistry of the particular metal, which influences the adsorption efficiency of an adsorbent. Therefore, using the optimized conditions, the adsorption of 4.826×10^{-5} mol L^{-1} of lead ions on coal was also examined in the presence of high concentration (50 mg L^{-1}) of various cations and anions. The anions used were as their sodium salts, while for cations the nitrate salts were used. The results are summarized in Table 4.

The results show that adsorption efficiency of lead on coal was decreased in the presence of Ca^{2+}, Al^{3+} and Cu^{2+} up to 22%. While the adsorption of lead on coal was almost constant in the presence of all the anions studied, except EDTA which decreased the adsorption significantly. This decrease in the adsorption efficiency of lead may be due to the competitive action of cations or the formation of stable compounds/complexes with anions under the experimental conditions.

3.10. Applicability of the proposed method

In order to determine the efficiency and applicability of the developed procedure, it was applied for the removal of the spiked lead (4.826×10^{-5} mol L^{-1}) in tap water sample containing 1 mL of buffer solution of pH 5. The spiked tap water (10 mL) was whirled with 0.5 g of Pakistani low-rank coal for 50 min. Quantitative removal of lead (99.98%) was observed indicating that the developed procedure may be used for the removal of lead from such matrices.

3.11. Desorption

To make useful of lead ion recycling processes, adsorbed lead ions should be easily desorbed under suitable conditions. Desorption experiments were carried out by using 1.0 M HNO_3 as the desorption medium. The low-rank Pakistani coal adsorbed with the maximum concentration of lead ions was placed within the desorption medium and shaken for 30 min. It was observed that at least 87% of the adsorbed lead was desorbed. This clearly indicates that the low-rank Pakistani coal can be reused for the removal of lead ions from aqueous solutions.

4. Conclusions

The present study revealed that abundantly available cheaper low-rank Pakistani coal has greater potential for the removal of lead from aqueous solutions. The adsorption of

Table 4
Influence of cations and anions on the adsorption of 4.826×10^{-5} mol L^{-1} of lead ions on Pakistani coal

Cations			Anions		
Ions	Concentration, mol L^{-1}	% Adsorption	Ions	Concentration, mol L^{-1}	% Adsorption
No cation	–	96.55	No anion	–	96.55
Na^+	2.176×10^{-3}	96.85	F^-	2.632×10^{-3}	97.70
K^+	1.282×10^{-3}	94.65	Cl^-	1.410×10^{-3}	96.75
Mg^{2+}	2.085×10^{-3}	94.45	Br^-	6.258×10^{-4}	96.75
Ca^{2+}	1.250×10^{-3}	78.15	I^-	3.94×10^{-4}	95.70
Al^{3+}	1.853×10^{-3}	86.75	$C_2O_4^{2-}$	5.682×10^{-4}	98.15
Cr^{3+}	9.616×10^{-4}	90.50	PO_4^{3-}	5.265×10^{-4}	100.00
Se^{2+}	6.332×10^{-4}	95.95	NO_2^-	1.087×10^{-3}	96.65
Fe^{3+}	8.954×10^{-4}	95.40	S^{2-}	1.560×10^{-3}	96.45
Sb^{3+}	5.706×10^{-4}	96.05	CN^-	1.923×10^{-3}	96.60
Co^{2+}	6.888×10^{-4}	93.90	HCO_3^-	8.197×10^{-4}	96.70
Zn^{2+}	4.107×10^{-4}	91.60	ClO_4^-	5.028×10^{-4}	96.40
Ni^{2+}	8.516×10^{-4}	93.45	BO_3^-	8.502×10^{-4}	95.85
Mn^{2+}	9.102×10^{-4}	93.45	CO_3^{2-}	8.333×10^{-4}	96.20
Cu^{2+}	7.868×10^{-4}	80.50	EDTA	1.344×10^{-4}	36.15
B^{3+}	4.625×10^{-3}	91.90	NO_3^-	8.065×10^{-4}	96.60

lead on coal followed the pseudo-second-order rate equation ($R^2 = 0.999$) with intraparticle diffusion process. The adsorption data followed the Freundlich, Langmuir and DR isotherms over the lead concentration range studied. The adsorption mean free energy from the DR isotherm is 11.180 kJ mol^{-1} indicating ion-exchange mechanism of chemisorption. The thermodynamic quantities, that is, ΔG and ΔH represent spontaneity and endothermicity of lead ion adsorption on low-rank Pakistani coal. On the basis of this study, it was concluded that the abundantly available, efficient, inexpensive and eco-friendly low-rank Pakistani coal has great lead removal potential from contaminated environmental aqueous media.

Acknowledgments

Tariq Javed would like to acknowledge Higher Education Commission, Islamabad, Pakistan, for awarding an indigenous PhD fellowship and Pakistan Institute of Nuclear Science and Technology, Islamabad, Pakistan, for providing research facilities for the present work.

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