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Adsorption characteristics of copper ions on low-rank Pakistani coal

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ABSTRACT

The adsorption behavior of copper ions on low-rank Pakistani coal has been studied as a function of contact time, nature of electrolytes (HNO_3, HCl, H_2SO_4 and $HClO_4$), amount of adsorbent, concentration of adsorbate and temperature, using batch method. The quantification of copper was made by atomic absorption spectrometric technique. Maximum adsorption was observed at pH 5.0, using 70 g L^{-1} of adsorbent for 10 mL of 5 mg L^{-1} copper concentration with equilibration time of 70 min. The adsorption of copper was decreased with the increase in the concentrations of all the acids used. The kinetic data showed an intraparticle diffusion process with sorption being pseudo-second-order. The calculated rate constant k_2 was 15.625 g mg^{-1} min^{-1}. The adsorption data obeyed the Freundlich, Langmuir and Dubinin–Radushkevich isotherms over the copper concentration range of 5–70 mg L^{-1}. The characteristic Freundlich constants, that is, $1/n = 0.447$ and $K = 10.422$ mg g^{-1} whereas the Langmuir constants $Q = 4.242$ mg g^{-1} and $b = 0.014$ L mg^{-1} have been computed for the sorption system. The sorption mean free energy from the Dubinin–Radushkevich isotherm is 11.236 kJ mol^{-1} indicating ion-exchange mechanism of chemisorption. The uptake of copper was increased with the rise in temperature (283-333 K). Thermodynamic quantities, that is, $\Delta G°$, $\Delta S°$ and $\Delta H°$ have also been calculated and discussed for the system. Adsorbent was characterized by using fourier transform infrared spectroscopy (FTIR) and scanning electron microscope before and after the adsorption of copper. Influence of other cations and anions on the adsorption of copper has also been studied.

Keywords: Pakistani coal; Copper adsorption; Kinetics; Sorption isotherms; Thermodynamics

1. Introduction

Environmental pollution by heavy metals is a critical and complicated problem that has been, and still is, a focus of attention all over the world. Heavy metals are among the primary pollutants of surface and groundwater. Industrial and municipal wastewater often contains metal ions that can be harmful to aquatic life and human health [1]. Copper is the most common toxic and harmful metal which is extensively used material in jewelry, paints, pharmaceutical products, wood preservatives, pigments, metal works, petroleum refinery, motor vehicle, and aircraft plating and finishing. Another important risk concerning contamination is the accumulation of copper in the soil for a long time. Also, copper may be found as a pollutant in food, especially shellfish, liver, mushroom, nuts and chocolate. In addition, any processing method or container using copper material may pollute the product, such as food, water or drink [2,3]. Copper, which is a heavy metal, has extensive application and is capable of causing haemolysis, liver and kidney damage, gastrointestinal disorder, diarrhea and respiratory problems. The concentration of Cu(II) ions from industrial processes is estimated to be about 100 to 200 mg L^{-1}. According to water quality standards, this value is very high and should be reduced to a value of 1.0 to 1.5 mg L^{-1} [4]

Conventional methods for copper ion removal that have been used include ion exchange [5–7], reverse osmosis [8], electrodialysis [9], coagulation and flocculation [10,11],

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flotation [12], precipitation [13] and evaporative recovery and adsorption [14].

High operational costs, formation of by-products and incomplete metal removal, particularly at low concentrations, have been identified as factors against the use of these conventional processes [15]. 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 decontamination of copper from industrial wastewater. The adsorbents used are Kolubara lignite [16], granular active carbon [17], coconut husk [18], palm fiber [19], sawdust [20], fly ash [21], aspergillus oryzae [22], low-rank Turkish coals [23], sawdust [24], jute fibers [25], sugar beet pulp [26], lignite and humic substances [27], pomegranate peel [28], Nigerian brown coal [4] and so on. An economical adsorbent can reduce the cost of adsorption process that has always been searched. The low cost adsorbent can be defined as one which is abundantly available in nature, or waste material, or is a by-product from another industry [29].

The aim of the present work is to check the potential of low-rank Pakistani coal as a sorbent for the removal of copper from wastewater. The selected material is abundantly available as a low-cost material even after its wide consumption as a fuel in power generation plants, brick kilns and various other mills. The Pakistani coal possesses a granular structure, high surface area, highly oxygenated with many carboxyl and phenolic hydroxyl functional groups which are capable to adsorb the copper ions via ion exchange process. Due to the presence of such properties, the coal is a good candidate for adsorption of copper ions.

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, fishtail type burner, having a slot of 100 × 0.5 mm^2, was used for the air-acetylene flame. Hollow cathode lamp of copper from Hitachi was used as a radiation source.

2.2. Reagents

Low-rank Pakistani coal was collected from mines in the provinces of Punjab (Khushab, Makerwal). The samples were ground and sieved to a particle size of about 500 µm. The coal powder was activated at 300°C for 4 h then treated with 2 M H_2SO_4 at room temperature for 2 h. After treatment, the coal decanted and washed with deionized water until the neutral pH of the filtrate. The washed coal sample was dried at 60°C till constant weight and stored in plastic container. The coal sample was characterized for a variety of parameters using different techniques, and the results are presented in Table 1.

Stock solution of copper (1,000 mg L^{-1}) was prepared by dissolving 0.1 g of specpure metal (Johnson and Matthey, UK) in a minimum amount of distilled nitric acid. The resultant solution was diluted to 100 mL with water. Standard solutions were prepared by proper dilution of this stock solution. Fresh working standards were made immediately before use. Distilled and deionized water was used throughout.

Buffer solutions of 1–13 pH, 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 8–10), and Na_2HPO_4 and NaOH (pH 11–13). All the reagents used were of Analytical Grade and were used as such.

2.3. Adsorption measurements

Adsorption measurements were performed via a batch technique at room temperature (297 ± 1 K) except where otherwise specified by shaking 70 g L^{-1} of coal powder in 10 ml of an aqueous solution of known concentration of copper ions at 5.0 pH in 30 cm^3 culture tubes for a given time period. After filtration with filter paper, the concentration of copper ions in filtrate was determined by atomic absorption spectrophotometer using optimized instrumental parameters (Table 2). The value of copper ions adsorbed in each analysis is the average of at least two measurements.

Table 1
Characteristics of low-rank Pakistani coal

Parameter	Value
Bulk density (g mL^{-1})	2.0
Particle size (µm)	500
BET surface area (m^2 g^{-1})	4.8
Porosity (%)	53
Ash content (%)	18.39
Organic content	81.61
pH_{zpc}	3.1
pH	5.10

Table 2
Optimized atomic absorption spectrophotometer parameters used for the determination of copper ions

Parameters	Values
Lamp current (mA)	7.5
Resonance absorption line (nm)	324.8
Width of slit (nm)	1.3
Photo multiplier tube voltage (v)	330
Burner type	Standard*
Burner height (mm)	7.5
Fuel (C_2H_2) flow (L min^{-1})	2.0
Oxidant (air) flow (L min^{-1})	15.0

*See experimental.

The percentage adsorption of copper ions from the solution was determined using the following expression:

$$\%\,\text{age adsorption} = \frac{C_i \quad C_f}{C_i} \times 100 \tag{1}$$

where C_i (mg L^{-1}) is the initial concentration of copper ions in the solution, and C_f (mg L^{-1}) is the concentration of copper ions in solution after equilibrium.

3. Results and discussion

3.1. FTIR test

The chemical modification of coal and Cu(II)-loaded coal interactions was followed using FTIR spectroscopy. The FTIR spectra of coal, activated coal and Cu(II)-loaded activated coal were shown in Fig. 1.

An adsorption band at 2,914 cm^{-1} in coal attributed to C–H aliphatic alkane. A band at 1,736 cm^{-1} is due to C=O stretching of carboxylic group. A peak at 1,613 cm^{-1} assigned to either aromatic C=C or C=O stretching. The peak at 1,439 cm^{-1} is due to C–H stretching. The peak at 1,361 cm^{-1} is due to S=O stretching of sulfonic group. The band at 1,210 cm^{-1} is attributed to C–O stretching vibrations. The band at 1,027 cm^{-1} originates from the C–O stretching vibration of –C–O–H group. Absorption bands at 430–470 cm^{-1} and 516 cm^{-1} are due to mineral components. In case of activated coal, the band at 2,914, 1,613, 1,439, 1,027 and 908 cm^{-1} disappeared. 1,736, 1,364 and 1,217 cm^{-1} peaks shifted to 1,734, 1,364 and 1,217 cm^{-1}, respectively, with more intensity. Some peaks in activated coal after adsorption show lower intensities and also show small differences in frequencies indicating the participation of these functional groups in the adsorption of Cu(II) by activated coal. The major changes are the band at 1,734 cm^{-1} shifted to 1,730 cm^{-1} with lower intensity. The bands at 1,367 and 1,210 cm^{-1} were shifted to lower frequency region with reduction in intensity.

This represents that the sulfonate and carboxylate functional groups present on activated low-rank Pakistani coal were mainly active sites for Cu(II) adsorption.

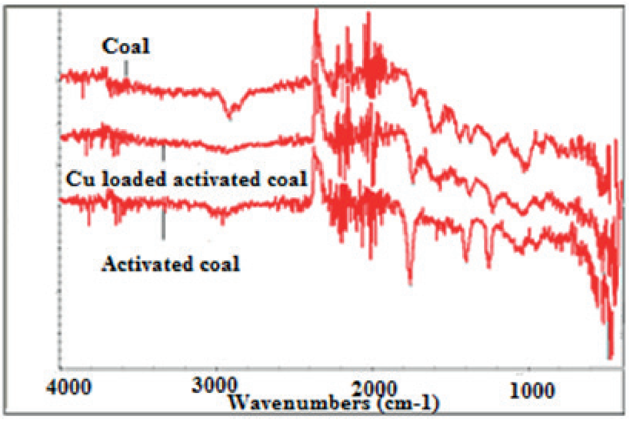

Fig. 1. FTIR spectra of coal, activated coal and copper ions-loaded activated coal.

3.2. Effect of pH

The adsorption of copper from aqueous solution is strongly dependent on the pH of the solution. This affects the surface charge of the absorbent, the extent of ionization and the speciation of the adsorbate species. The adsorption of the copper was studied from aqueous solution by varying the pH from 1 to 10, using 10 mg L^{-1} of copper with 50 g L^{-1} of low-rank Pakistani coal. The concentration of copper and dose of 50 g L^{-1} of coal was selected arbitrarily, and the results are presented in Fig. 2. The Fig. 2 shows that the percentage adsorption of copper increased significantly with pH values up to 5.0, and after 5.0, it is decreased. A sharp increase in the percentage adsorption was observed at pH 10. This can be explained by precipitating Cu(II) ions in solution. At pH 10, insoluble copper hydroxide starts precipitating from the solution which makes true sorption studies impossible [29]. At low pH values, the percentage adsorption is very low. The low adsorption percentage at low pH could probably be due to the presence of higher concentration of H^{+} ions in the solution which compete with the Cu(II) ions for the adsorption sites of activated coal [28]. When pH is increased, H^{+} concentration in the solution decreases but Cu(II) ion concentration remains constant resulting to increased percentage adsorption.

On considering the pH$_{zpc}$ of low-rank Pakistani coal, another possibility for Cu(II) adsorption can be provided. At pH below 5.0 (pH$_{zpc}$), the activated coal surface is positively charged due to the protonation of active sites, and this protonation effect will be significant at low pH values due to the presence of high conc. of H^{+} ions in the solution. The pH value of solution decreased during adsorption, and this is due to the release of H^{+} ions from the surface of coal. This data represents the fact that below pH$_{pzc}$, the adsorption of Cu(II) occurs through ion exchange process as follows:

$$2\text{H} - \text{coal suface} + \text{Cu}^{2+} \rightarrow (\text{coal suface})_2\,\text{Cu} + 2\text{H}^{+} \tag{2}$$

Above pH$_{pzc}$, the low-rank Pakistani coal surface bearing negative charge and the positively charged copper ions

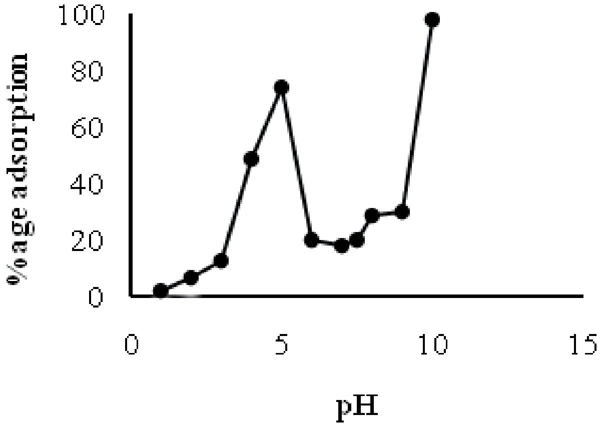

Fig. 2. Effect of pH on the adsorption of copper ions on low-rank Pakistani coal (C_i = 10 mg L^{-1}, coal dosage = 50 g L^{-1}, t = 50 min, T = 297 K).

adsorbed through electrostatic interaction. Since maximum percentage adsorption occurred at pH 5.0, this optimum pH for Cu(II) adsorption was selected for further experiments.

3.3. Effect of acid concentration

The chemical interaction of the adsorbent surfaces results in certain variation in adsorption properties. Therefore, the adsorption characteristics of copper (10 mg L^{-1}) was studied in mineral acid solutions (HNO_3, HCl, $HClO_4$ and H_2SO_4) varying a concentration range from 0.0001 to 1.0 mol L^{-1} using optimized parameters. Fig. 3 shows that adsorption of copper ions decreases with an increase in acid concentration. This is due to the competition between the excess of H^+ ions in the medium and positively charged copper ions. Almost all the acids show same adsorption trend.

3.4. Effect of adsorbent weight

Effect of the low-rank Pakistani coal weight on Cu(II) adsorption was studied by varying the adsorbent weight from 10 to 80 g L^{-1} using 5 mg L^{-1} copper solution in 0.0001 M HNO_3 for time interval of 30 min. It is clear from Fig. 4, which is a plot of percentage adsorption of copper vs. adsorbent weight that percentage adsorption increases with an increase in adsorbent weight. This is because by increasing the adsorbent weight, the number of active sites available for adsorbent-adsorbate interaction is increased as well. Just 70 g L^{-1} of coal is sufficient for the quantitative adsorption of copper ions used beyond which percentage adsorption is almost constant. Therefore, an adsorbent weight of 70 g L^{-1} was considered to be sufficient for the removal of copper and was selected for all further experiments.

3.5. Effect of contact time

The effect of contact time on adsorption of Cu(II) was investigated by varying the time from 5 to 100 min using 70 g L^{-1} adsorbent weight as shown in Fig. 5. Increase in percentage adsorption with increase in contact time is due to more time required for Cu(II) ions to make complex with low-rank Pakistani coal up to 70 min; after this, no increment is observed because of unavailability of active sites. Finally, 70-min contact time was selected for further experiments.

3.6. Kinetic explanation

The adsorption data was applied to the Morris–Weber [30] equation:

$$q_t = K_p t^{0.5} \tag{3}$$

where q_t (mg g^{-1}) is the adsorbed concentration at time (t). K_p is the intraparticle diffusion rate constant of the Morris–Webber equation. The value of K_p was calculated from the slope by plotting q_t against $t^{0.5}$ (Fig. 6) and was found to be 3×10^{-3} mg (g $min^{-0.5}$).

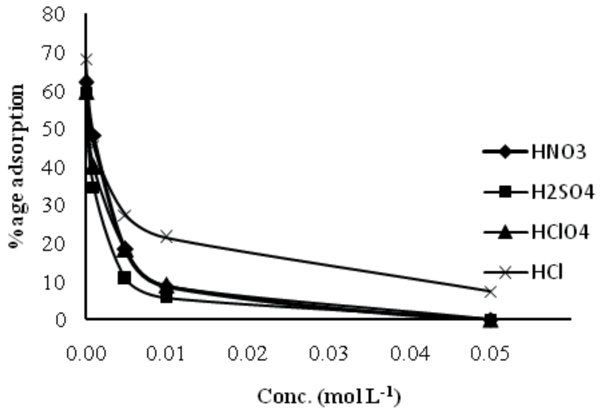

Fig. 3. Effect of percentage adsorption of copper ions on low-rank Pakistani coal as a function of acid concentration (C_i = 10 mg L^{-1}, coal dosage = 50 g L^{-1}, t = 50 min, T = 297 K).

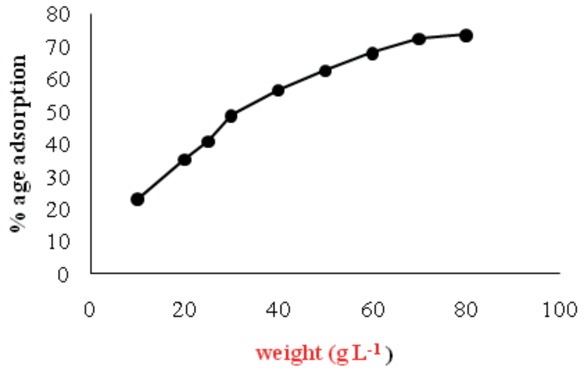

Fig. 4. Effect of adsorbent weight on the adsorption of copper ions (C_i = 5 mg L^{-1}, pH = 5, t = 30 min, T = 297 K).

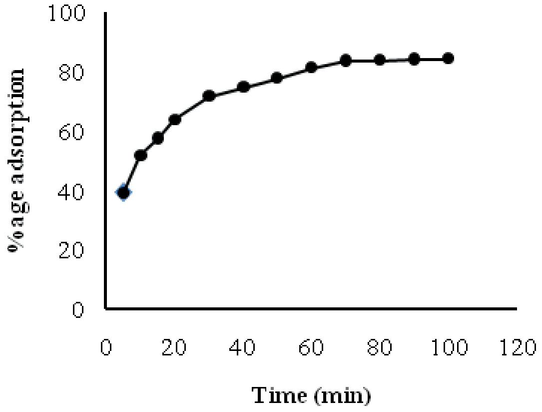

Fig. 5. Influence of equilibration time on the adsorption of copper ions on low-rank Pakistani coal (C_i = 5 mg L^{-1}, pH = 5, coal dosage = 70 g L^{-1}, T = 297 K).

In order to verify the rate-controlling step, the adsorption kinetic data of Fig. 5 was subjected to the equations of film and particle diffusion.

When film diffusion is the rate-controlling process, the equation [31] is:

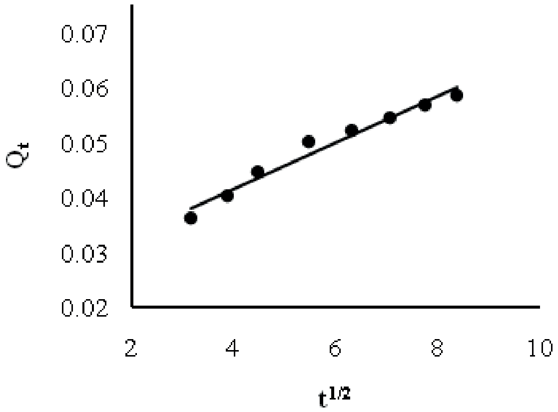

Fig. 6. Morris–Weber plot of copper ions adsorption on low-rank Pakistani coal.

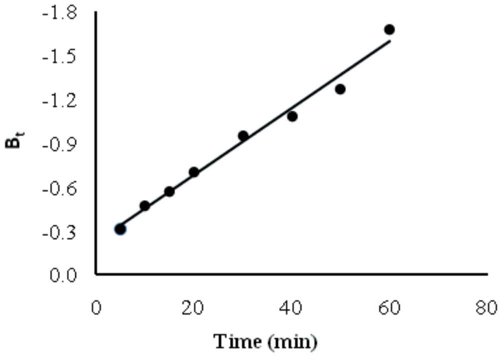

Fig. 7. Reichenberg plot of copper ions adsorption on low-rank Pakistani coal.

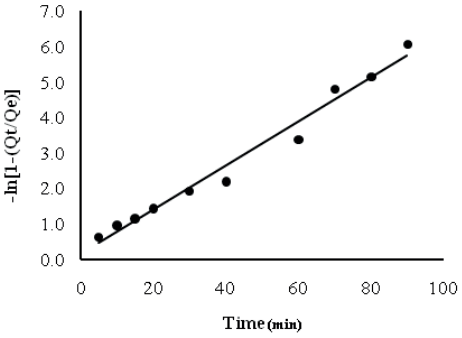

Fig. 8. Plot of $-\ln(1 - Q_t/Q_e)$ vs. t for adsorption of copper ions.

$$-In(1-F) = Rt \tag{4}$$

where

$$F = \frac{q_t}{q_e} \tag{5}$$

where q_t and q_e are the amount of copper ions adsorbed on low-rank Pakistani coal at time t (min.), and at equilibrium time (min), R is the film diffusion rate constant when $-\ln(1–F)$ was plotted vs. time (t); a straight line was obtained (Fig. 7), which did not pass through the origin. This shows that film diffusion is not only involved in the kinetics of copper ion adsorption on low-rank Pakistani coal.

On the other hand, for the particle diffusion to be the rate-controlling process, the following relationship [32] was subjected to the kinetic data of Fig. 5:

$$B_t = -In(1-F) - 0.4977 \tag{6}$$

By plotting B_t against t (Fig. 8), a straight line was obtained with a small intercept. This represents that intraparticle diffusion is the rate-controlling step.

In order to evaluate kinetic adsorption parameters, the obtained kinetic adsorption data of copper ions on coal was fitted to the first-order Lagergren (Eq. 7) and pseudo-second-order (Eq. 8) rate equations using the linearized form as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

where q_e (mg g^{-1}) is the amount of copper adsorbed at equilibrium; q_t (mg g^{-1}) is the amount of copper adsorbed at any time t (min), and K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the rate constants of the first-order and pseudo-second-order models, respectively. 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 0.987 and 0.999, respectively. The determined kinetic parameters for the first-order and pseudo-second-order models are shown in Table 3.

The higher R^2 value and good correspondence between the determined (0.064 mg Cu g^{-1}) and the experimental (0.059 mg Cu g^{-1}) values of adsorption capacity confirm that the experimental kinetic data are in agreement with the pseudo-second-order model as shown in Fig. 9.

3.7. *Effect of initial metal concentration*

The influence of copper concentration on the efficiency of adsorption was investigated under the optimized conditions of contact time 70 min., adsorbent dose 70 g L^{-1} and the pH 5.0. The initial concentration of copper was varied

Table 3
Kinetic parameters for the adsorption of copper 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
0.0509	0.062	0.987	0.064	15.625	0.9999

Note: Experimentally measured q_e = 0.059 mg g^{-1}.

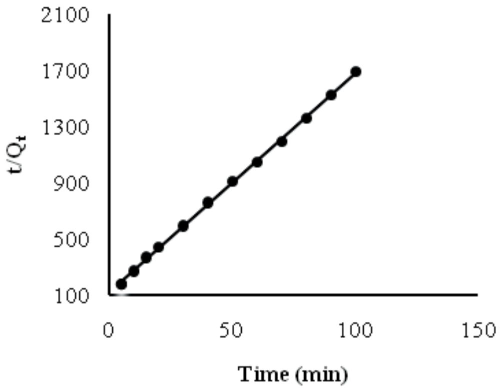

Fig. 9. Pseudo-second-order plot of copper ions adsorption on low-rank Pakistani coal.

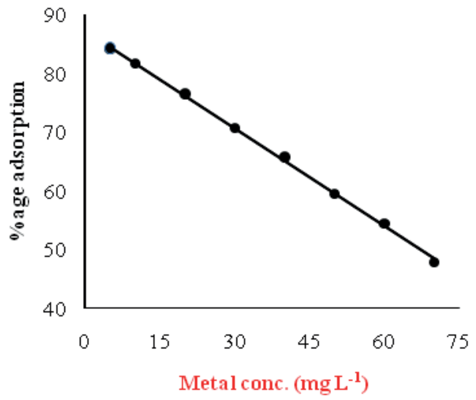

Fig. 10. Adsorption effect of copper ions as a function of its own concentration on low-rank Pakistani coal (coal dosage = 70 g L^{-1}, pH = 5, t = 70 min, T = 297 K).

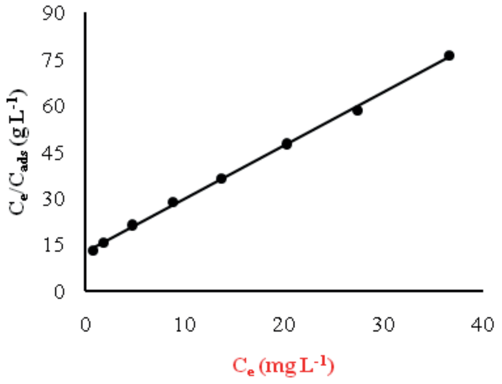

Fig. 11. Langmuir plot for the adsorption of copper ions on low-rank Pakistani coal.

from 5 to 70 mg L^{-1}, and the results are shown in Fig. 10. The adsorption efficiency decreased with an increase in the concentration of copper. This is explicable on the bases of the relatively smaller number of active sites in a fixed amount of adsorbent at a higher concentration of copper.

3.8. Adsorption isotherms

To explain experimental data, adsorption isotherm equations are used. Adsorption equilibrium calculations are used to determine the maximum adsorption capacity. Parameters and assumptions of these equilibrium isotherms provide information about adsorption mechanism and the nature of surface and affinity of the adsorbent. Analysis of the relationship between the adsorption capacity of low-rank Pakistani coal and copper ion concentration at equilibrium was performed using the equations of Langmuir, Freundlich and Dubinin–Radushkevich (D–R).

The Langmuir model represents adsorption on completely homogenous surfaces with no lateral interaction between adsorbed ions. The experimental data for the adsorption of copper on low-rank Pakistani coal have been tested in the light of Langmuir mode of adsorption. It was found that the data obeyed Langmuir adsorption isotherm over the entire concentration range studied.

The Langmuir isotherm was analyzed in the following linear form:

$$\frac{C_e}{C_{ad}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{9}$$

where C_{ad} is the concentration of copper adsorbed at equilibrium (mg g^{-1}); C_e is the equilibrium concentration of copper in solution (mg L^{-1}). Q and b are Langmuir constants. A plot of C_e/C_{ad} vs. C_e yields a straight line (Fig. 11). This linear plot supports the applicability of the Langmuir isotherm model in the present work. The values of Langmuir constants Q and b determined from the slope and intercept of the plot in Fig. 11 and were found to be 4.242 and 0.014 L mg^{-1}, respectively.

Table 4 summarizes the comparison of copper ions adsorption capacities by various adsorbents. Coal has higher adsorption capacity than different adsorbents

Table 4
Comparison of adsorption capacity of different adsorbents for the removal of copper ions from aqueous solution

SI. No.	Adsorbent	Capacity (mg g^{-1})	Reference
1	Nigerian brown coal	0.066	[4]
2	Kolubara lignite	4.045	[16]
3	Granular active carbon	3.60	[17]
4	Coconut husk	3.07	[18]
5	Palm fiber	2.0	[19]
6	Saw dust	1.74	[20]
7	Fly ash	1.38	[21]
8	Aspergillus oryzae	0.79	[22]
9	Low-rank Turkish coals	1.62	[23]
10	Saw dust (oak tree)	3.60	[24]
11	Jute fibers	4.23	[25]
12	Sugar beet pulp	0.15	[26]
13	Lignite and humic substances	1.486	[27]
14	Pomegranate peel	1.32	[28]
15	Pakistani coal	4.242	Present study

presented in Table 4, indicating a promising future of low-rank Pakistani coal for removal of copper ion from aqueous solutions.

Freundlich adsorption isotherm is the relationship between the concentration of metal uptake per unit mass of the adsorbent (C_{ad}) and the concentration of copper at equilibrium (C_e).

Freundlich equation is as follows:

$$C_{ad} = KC_e^{\frac{1}{n}} \tag{10}$$

The Logarithmic form of the equation can be written as

$$\log C_{ad} = \log K + \frac{1}{n}\log C_e \tag{11}$$

where $1/n$ and K are Freundlich constants representing the intensity of adsorption and adsorbent capacity, respectively. These constants were calculated from the slope and the intercept of the Freundlich plot (Fig. 12) and were found to be 0.447 and 10.422 mg g^{-1}, respectively.

The D–R isotherm was also applied in its linearized form to classify the physical or chemical adsorption.

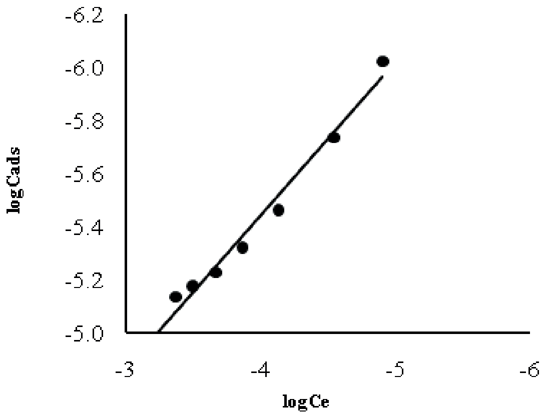

Fig. 12. Freundlich plot for the adsorption of copper ions on low-rank Pakistani coal.

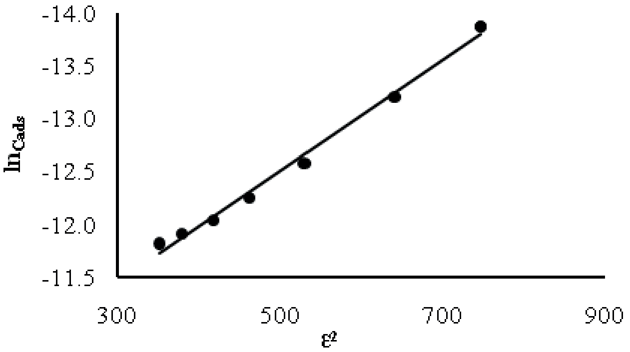

Fig. 13. D–R plot for the adsorption of copper ions on low-rank Pakistani coal.

The D–R equation is as follows:

$$C_{ad} = C_m \exp(-\beta \in^2) \tag{12}$$

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

$$\in = RT\text{In}\left(1 + \frac{1}{C_e}\right) \tag{13}$$

where R is the ideal gas constant; T is the temperature in K; C_e is the equilibrium concentration of copper in solution.

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

$$\text{In}C_{ad} = \text{In}C_m - \beta \in^2 \tag{14}$$

A straight line was obtained when lnC_{ad} is plotted against $\in^2$ (Fig. 13) indicating that copper ions adsorption also obeys the D–R equation. From the linear plot, value of β determined was 4×10^{-3} K J^2 mol^{-2}. By substituting the value of β, the mean adsorption energy (E_s) was determined as follows:

$$E_s = \frac{1}{(-2\beta)^{1/2}} \tag{15}$$

The numerical values of adsorption energy in the range of 1–8 KJ mol^{-1} indicate the physical sorption, and more than 8 KJ mol^{-1} predicts chemical sorption [33,34]. The calculated value of E_s from Eq. (15) was 11.236 KJ mol^{-1}, predicted chemical sorption or ion exchange process.

3.9. Effect of temperature

The adsorption of 10 mg L^{-1} of copper ions on low-rank Pakistani coal was carried out using optimized conditions at different temperatures varying from 283 to 333 K, and the results are shown in Table 5. It was found that the copper ions adsorption increases with the rise in temperature.

Van't Hoff plot was used to determine $\Delta H°$ and $\Delta S°$ from the slope and intercept, respectively, by using the relation [29,35,36]:

$$\text{I}\,n K_c = \frac{\Delta S^o}{\Delta R} - \frac{\Delta H^o}{RT} \tag{16}$$

where K_c is equilibrium constant; $\Delta S°$ is the change in entropy; $\Delta H°$ is the enthalpy change for the process; R is gas constant and T is absolute temperature.

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

$$K_c = \frac{C_{eq\cdot S}}{C_{eq\cdot L}} \tag{17}$$

Table 5
Adsorption studies of copper ions on low-rank Pakistani coal as a function of temperature

Low-rank Pakistani coal	70 g L^{-1}
Contact time	70 min
Volume equilibrated	10 mL
pH	5
Copper ion concentration	10 mg L^{-1}

Temp. (K)	1/T (K^{-1})	Concentration adsorbed (mg L^{-1})	Concentration in bulk (mg L^{-1})	K_c	lnK_c
283	3.534×10^{-3}	7.850	2.150	3.640	1.292
288	3.472×10^{-3}	8.400	1.600	5.235	1.655
293	3.413×10^{-3}	8.850	1.150	7.675	2.038
303	3.300×10^{-3}	9.385	0.615	15.222	2.723
313	3.195×10^{-3}	9.705	0.295	32.819	3.491
323	3.096×10^{-3}	9.825	0.175	56.010	4.026
333	3.003×10^{-3}	9.915	0.085	116.373	4.757

where $C_{eq.S}$ is equilibrium concentration of copper adsorbed on the adsorbent (mg L^{-1}), and $C_{eq.L}$ is equilibrium concentration of copper in solution (mg L^{-1}).

ΔG° and ΔS° for the specific adsorption process have also been calculated using the following relations:

$$\Delta G^o = -RT\text{In}K_c \tag{18}$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \tag{19}$$

ΔH° and ΔS° were calculated by plotting lnK_c vs. 1/T as shown in Fig. 14. The calculated values of ΔG°, ΔH° and ΔS° have been presented in Table 6. The negative values of ΔG° represent that the adsorption of copper on low-rank Pakistani coal is a spontaneous process. The increase in the numerical value of –ΔG° with the increase in temperature represents that the adsorption process of copper ions on coal is more favorable at higher temperatures. The positive values of enthalpy change (ΔH°) indicate the endothermicity of the adsorption process. Since diffusion is an endothermic process, it was observed that increased solution temperature resulted in increased adsorption of copper ions [35]. The positive value of ΔS° represents increase in the degree of freedom of the adsorbed species.

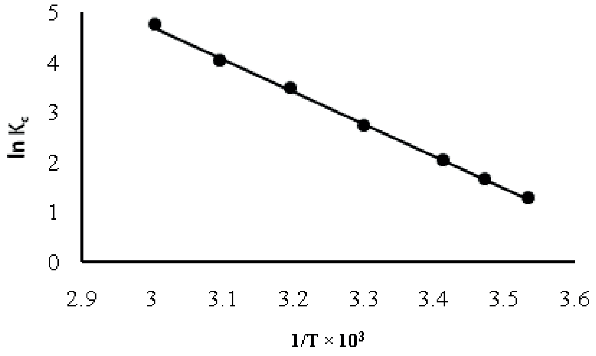

Fig. 14. Van't Hoff plot for the adsorption of copper ions on low-rank Pakistani coal (C_i = 10 mg L^{-1}, coal dosage = 70 g L^{-1}, pH = 5, t = 70 min).

3.10. Effect of cations and anions

The presence of other cations and anions in the adsorptive medium may interfere the environment and solution chemistry of the concern metal, which influence the adsorption efficiency of an adsorbent. Therefore, using the optimized conditions, the adsorption of 10 mg L^{-1} of copper ions on low-rank Pakistani coal was also examined in the presence of 50 mg L^{-1} concentrations of various cations and anions. All the anions were used as their sodium salts, while for cations the nitrate salts were used. The results are

Table 6
Calculated thermodynamic parameters for adsorption of copper ions on low-rank Pakistani coal

Temperature (K)	ΔG° (KJ mol^{-1})	ΔH° (KJ mol^{-1})	ΔS° (JK^{-1} mol^{-1})
283	–3.040	53.877	0.201
288	–3.964		0.201
293	–4.965		0.201
303	–6.859		0.200
313	–9.085		0.201
323	–10.811		0.200
333	–13.170		0.201

summarized in Table 7. The results show that adsorption of copper on coal was decreased in the presence of Al^{3+}, Se^{2+}, B^{3+}, Pb^{2+}, Zn^{2+} and Fe^{3+} up to 21.9%. While the adsorption of copper on low-rank Pakistani coal was not decreased significantly in the presence of anions except $C_2O_4^{2-}$ This decrease in the adsorption of copper may be due to the competitor action of cations or the formation of stable compounds/complexes with anions for the active sites on the surface of low-rank Pakistani coal.

Table 7
Influence of cations and anions on the adsorption of 10 mg L^{-1} of copper ions on coal

Cations		Anions	
Ions	% adsorption	Ions	% adsorption
None	82.20	None	82.20
Na^{+}	82.70	NO_3^{-}	82.30
K^{+}	81.10	$C1O^{-}_{4}$	79.10
Mg^{2+}	79.30	PO^{3-}_{4}	88.70
Sr^{2+}	80.70	$C1^{-}$	79.80
Co^{2+}	78.70	Br^{-}	82.20
Mn^{2+}	79.70	I^{-}	83.65
Ni^{2+}	77.40	F^{-}	85.90
Zn^{2+}	41.30	CN^{-}	83.50
Fe^{3+}	70.60	CO_3^{2-}	82.85
Pb^{2+}	72.70	NO^{-}_{2}	78.40
Cr^{3+}	64.50	S^{2-}	80.80
B^{3+}	35.66	$C_2O_4^{2-}$	57.50
$A1^{3+}$	60.30	HCO_3^{-}	83.50
Ge^{2+}	77.35	BO_3^{-}	80.20
Sb^{3+}	83.40	Citrate	85.00

3.11. Scanning electron microscope studies

The scanning electron microscope (SEM) images of low-rank Pakistani coal and loaded copper were recorded and are shown in Fig. 15. In the SEM micrograph the bright spots indicate the rough and porous surface of the adsorbent before adsorption, which is one of the causes increasing adsorption capacity. The loaded SEM images indicate the adsorption of copper on the coal. It is clearly seen that the caves, pores and surfaces of adsorbent were covered by copper, and therefore, the surface has become smooth. It is evident that after adsorption of copper the adsorbent structure has changed.

4. Conclusion

Low-rank Pakistani coal has good adsorption characteristics for the removal of copper ions from aqueous solutions. The adsorption of copper on coal follows the pseudo-second-order rate equation. The adsorption data obeyed the Langmuir, Freundlich and D–R isotherms. The uptake of copper was increased with the rise in temperature. The thermodynamic quantities, that is, $\Delta G°$ and $\Delta H°$, represent spontaneity and endothermicity of copper ion adsorption on low-rank Pakistani coal. On the basis of this study, it is concluded that the abundantly available, efficient, inexpensive and eco-friendly coal has great potential for the removal of copper ions from polluted environmental aqueous systems.

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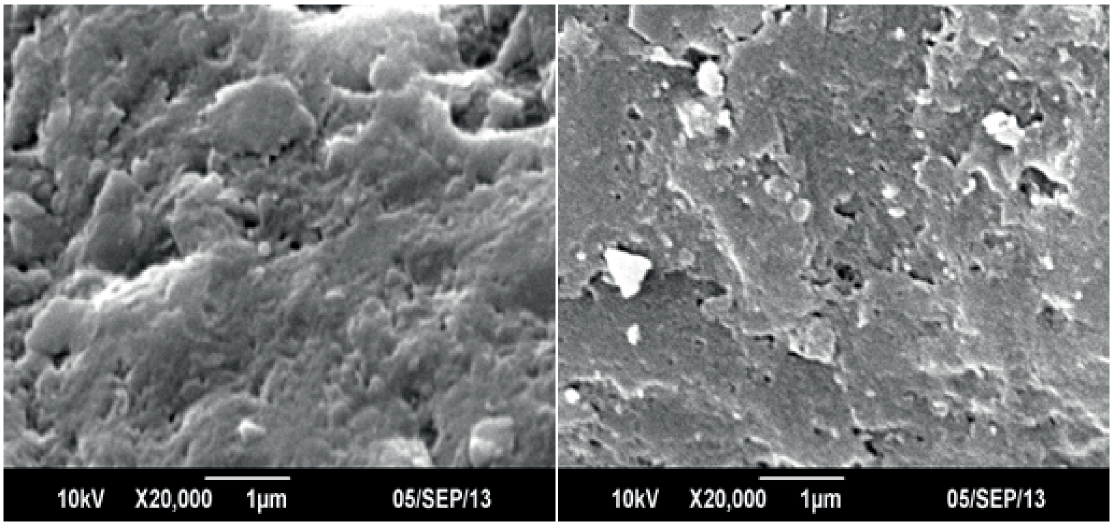

Fig. 15. SEM image of the low-rank Pakistani coal before and after copper ions adsorption.

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