

Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls

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Abstract

Activated carbon prepared from *Ceiba pentandra* hulls, an agricultural solid waste by-product, for the removal of copper and cadmium from aqueous solutions has been studied. Parameters such as equilibrium time, effect of pH and adsorbent dose on removal were studied. The adsorbent exhibited good sorption potential for copper and cadmium at pH 6.0. C=O and S=O functional groups present on the carbon surface were the adsorption sites to remove metal ions from solution. The experimental data was analysed by both Freundlich and Langmuir isotherm models. The maximum adsorption capacity of copper and cadmium was calculated from Langmuir isotherm and found to be 20.8 and 19.5 mg/g, respectively. The sorption kinetics of the copper and cadmium have been analysed by Lagergren pseudo-first-order and pseudo-second-order kinetic models. The desorption studies were carried out using dilute hydrochloric acid solution and the effect of HCl concentration on desorption was also studied. Maximum desorption of 90% for copper and 88% for cadmium occurred with 0.2 M HCl.

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1. Introduction

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms [1]. Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agri-chemicals. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic [2] and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [3]. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs, which are affected by blooms of blue-green alga [4]. Maximum acceptable copper concentration in drinking water is less than 3000 $\mu\text{g}/\text{dm}^3$ [5,6]. Cadmium is introduced into water bodies from smelting, metal plating,

cadmium–nickel batteries, phosphate fertilisers, mining, pigments, stabilizers, alloy industries and sewage sludge. The harmful effects of cadmium include number of acute and chronic disorders such as “itai–itai” disease, renal damage, emphysema, hypertension and testicular atrophy [7]. Hence, removal of copper and cadmium from water and wastewater assumes importance.

The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among all the methods adsorption is highly effective and economical.

Though the use of commercial activated carbon is a well-known adsorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low-cost adsorbents from agriculture wastes such as coconut coirpith [8], sawdust [3], rice husk [9], banana pith [10], cottonseed hulls [11], apple wastes [12], sugarcane bagasse pith [13], peanut hull carbon [14], activated carbons obtained from

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agricultural by-products [15] and Mn-oxide coated granular activated carbon [16] for the removal of copper and cadmium from water and wastewater. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of copper and cadmium from aqueous solutions.

Studies were carried out in the removal of copper and cadmium from aqueous solutions using activated carbon derived from hulls of *Ceiba pentandra*. This tree is widely distributed in the deciduous forests of western and eastern India especially in hotter areas. The plant parts (root, bark, gum and leaf) have high medicinal applications except hulls. Cotton obtained from the fruits is used in stuffing pillows and mattresses. But hulls obtained from the fruits are of no economic importance and are considered as an agricultural waste.

The goal of this research was to demonstrate the efficacy of using carbonised *C. pentandra* hulls for removal of copper and cadmium from aqueous solutions.

2. Experimental

2.1. Instrumentation

A Varian spectra, atomic absorption spectrometer (AAS) with copper/cadmium hollow cathode lamp and air acetylene flame was used for determining copper and cadmium concentrations. An Elico (LI-129) pH meter was used for pH measurements. A mechanical shaker (Macro Scientific Works, Delhi, India) was used for agitating the samples. X-ray diffractometer (X'Pert, Phillips) with Cu $K\alpha_1$ radiation source was used to record the X-ray measurements of the adsorbent. Fourier transform infrared spectrometry (Perkin-Elmer) was used to analyze the organic functional groups in the adsorbent. The transmission spectrum was acquired at a 64 scans with 4 cm^{-1} resolution and the spectrum was corrected for a KBr background.

2.2. Chemicals

All the chemicals used were of analytical reagent grade. Deionised doubly distilled (DDD) water was used throughout the experimental studies. Stock copper and cadmium solutions (1 mg/ml) were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, in 1000 ml of DDD water. Working standards were prepared by progressive dilution of stock copper and cadmium solutions using DDD water. ACS reagent grade HCl, NaOH and buffer solutions (E. Merk) were used to adjust the solution pH.

2.3. Procedure of adsorbent preparation and activation

Waste *Cieba pentandra* hulls were collected from local fields and cut to a small pieces, washed several times with DDD water and left to dry. The carbonisation of hulls was performed in muffle furnace at 200°C for 2 h. Steam activation (SA) of the carbon was carried out using the method described by Warhurst et al. [17]. Finally, the material was sieved to 100-mesh size and stored in desiccator for further use.

2.4. Adsorption studies

Batch adsorption experiments were carried out in a series of stoppered reagent bottles. A weighed amount (0.5 g) of adsorbent was introduced into reagent bottles (100 ml) containing various concentrations with 50 ml aqueous solutions of copper or cadmium. The solution pH was adjusted to the desired value by adding HCl or NaOH. Then, the bottles were shaken at room temperature ($30 \pm 1^\circ\text{C}$) using a mechanical shaker for a prescribed time to attain the equilibrium. The solutions were filtered and the concentrations of metal ions were determined by AAS method. The effects of concentration (40–240 mg/l), contact time (5–80 min), solution pH (3–9) and adsorption dose (0.1–0.9 g) were studied. Blank solutions were treated similarly (without adsorbent) and the recorded concentration by the end of each operation was taken as the initial one.

2.5. Desorption studies

The desorption studies were carried out with varying concentrations of HCl solution. The sorbent, which was removed from filtration, was transferred into stoppered reagent bottles. To this 100 ml of HCl solution was added. The bottles were shaken at room temperature ($30 \pm 1^\circ\text{C}$) using a mechanical shaker. The sorbent was then removed by filtration. The concentrations of copper and cadmium in the aqueous solutions were determined by AAS method.

2.6. Sorption isotherm models

The sorption equilibrium data of copper and cadmium on activated carbon were analysed in terms of Freundlich and Langmuir isotherm model [18]. Freundlich isotherm equation $X/m = k_F C_e^{1/n}$ can be written in the linear form as given below.

$$\log \frac{X}{m} = \log k_F + \frac{1}{n} \log C_e \quad (1)$$

where X/m and C_e are the equilibrium concentrations of copper/cadmium in the adsorbed and liquid phases in mg/g and mg/l, respectively. k_F and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively. Freundlich constants k_F and n can be calculated from the slope and intercept of the linear plot, with $\log(X/m)$ versus $\log C_e$.

The Langmuir sorption isotherm equation $X/m = Q_m k_L C_e / (1 + k_L C_e)$ on linearization becomes

$$\frac{C_e}{(X/m)} = \frac{C_e}{Q_m} + \frac{1}{Q_m k_L} \quad (2)$$

where Q_m and k_L are Langmuir constants which are related to sorption capacity and energy of sorption, respectively and can be calculated from the intercept and slope of the linear plot, with $C_e/(X/m)$ versus C_e .

2.7. Kinetic models

The sorption kinetic data of copper and cadmium on the adsorbent studied was analysed in terms of pseudo-first-order

and pseudo-second-order sorption equations Wu et al. [19]. The pseudo-first-order equation is shown below:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_t (mg/g) denotes the amount of sorption at time t (min) and q_e (mg/g) is the amount of sorption at equilibrium. After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (3) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

The sorption rate constant, k_1 , can be calculated by plotting $\log(q_e - q_t)$ versus t .

The pseudo-second-order equation can be written as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

where k_2 ($\text{g}/(\text{mg min})$) is the rate constant. Integration of Eq. (5) and application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, give

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t \quad (6)$$

The following equation can be obtained on rearranging Eq. (6) into a linear form

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \quad (7)$$

k_2 and q_e can be obtained from the intercept and slope

Table 1

Characteristics of the activated carbon derived from *Ceiba pentandra* hulls

Parameter	Value
Specific surface area (m^2/g)	521.0
pH_{PZC}	5.7
Conductivity ($\mu\text{S}/\text{cm}$)	52
Ash (%)	6.7
Moisture (%)	10.0
Volatile matter (%)	47.0
Matter soluble in water (%)	1.0
Carbon (%)	56.25
Hydrogen (%)	2.60
Nitrogen (%)	0.44
Sulphur (%)	1.49

3. Results and discussion

3.1. Characteristics of the adsorbent

The physical characteristics along with the percentage of carbon, hydrogen, nitrogen and sulphur in the activated carbon made from *C. pentandra* hulls are presented in Table 1. The FT-IR spectrum and X-ray diffraction pattern of the activated carbon are shown in Figs. 1 and 2. The absorption at 3431 cm^{-1} indicates the presence of OH group, which was probably attributed to adsorbed water on the carbon [20,21]. The bands appearing at 1384 and 1595 cm^{-1} are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties, respectively [22]. The additional peaks at 1457 and 1118 cm^{-1} indicate the presence of C–H and S=O groups, respectively [13]. The C=O and S=O

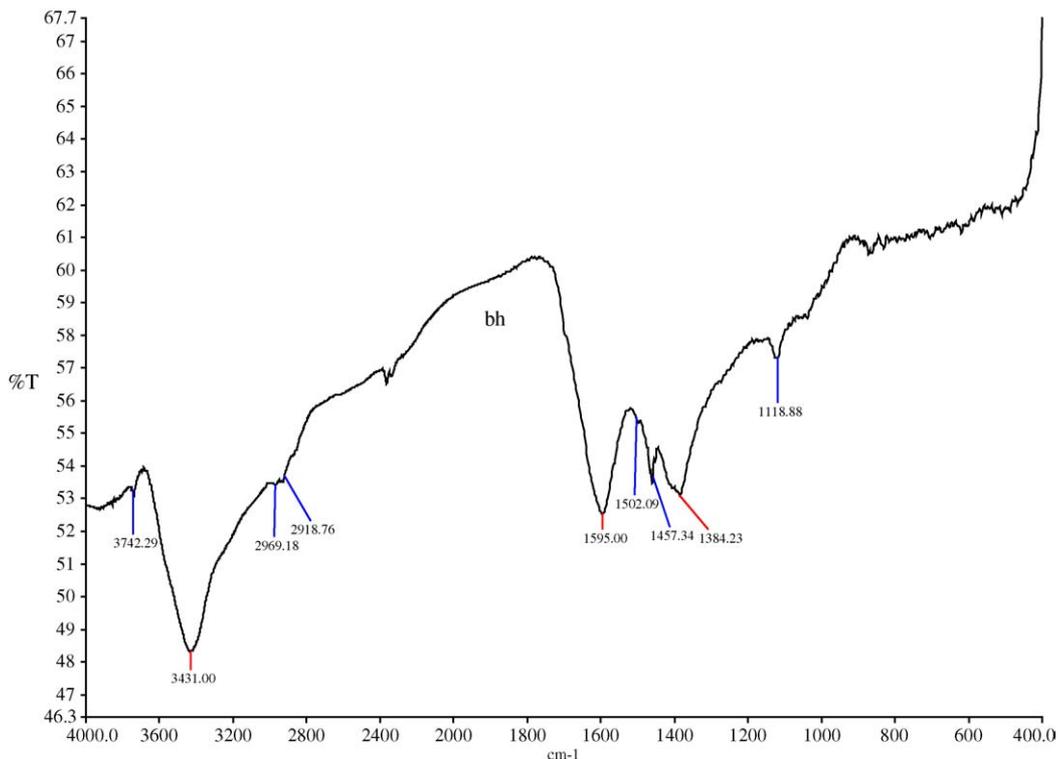


Fig. 1. FT-IR Spectrum of activated carbon derived from *Ceiba pentandra* hulls.

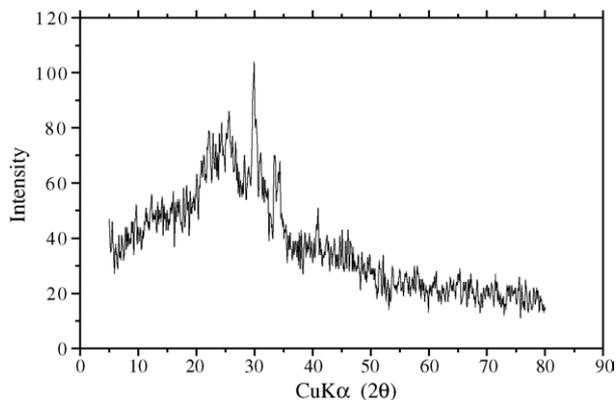
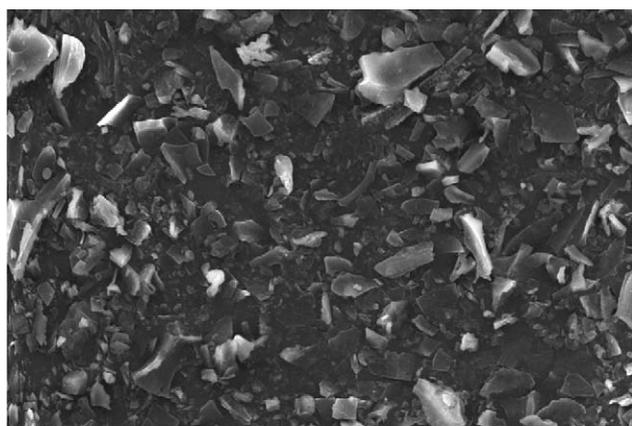
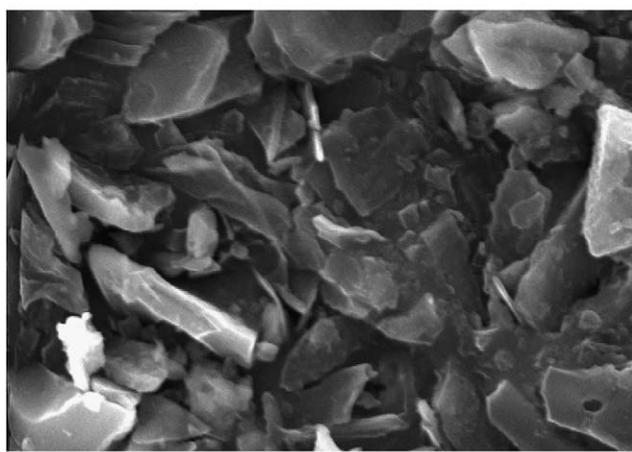


Fig. 2. X-ray diffraction of activated carbon derived from *Ceiba pentandra* hulls.

functional groups show very high coordination with heavy metals. Hence, the good sorption properties of the adsorbent towards copper and cadmium can be attributed to the presence of these functional groups on the adsorbent. Scanning electron microscopic photographs of activated carbon shown in Fig. 3 reveal the surface texture and porosity of the sample. The availability of pores and internal surface is requisite for an effective adsorbent.



(A)



(B)

Fig. 3. SEM photographs of the activated carbon (a) 20 kV, $\times 1000$; (b) 20 kV, $\times 5000$.

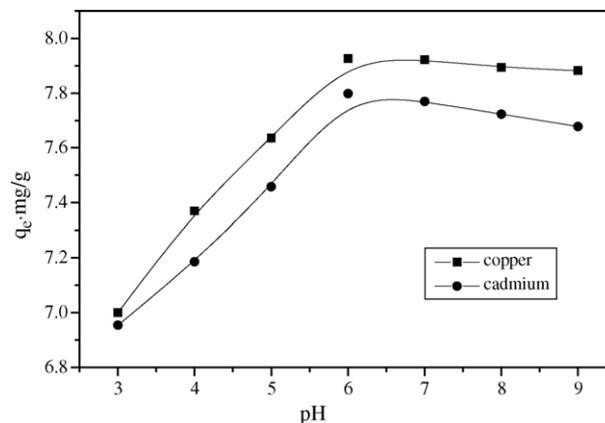


Fig. 4. Effect of pH on removal of copper and cadmium (initial concentration 80 mg/l; contact time 60 min).

3.2. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The binding of metal ions by surface functional groups was strongly pH dependent [23]. The effect of pH on adsorption of copper and cadmium shown in Fig. 4 indicates that copper has greater removal than cadmium at the same pH and initial concentration. The effect of pH can be explained by considering the surface charge on the adsorbent material [13,24]. The point of zero charge (PZC) of the adsorbent (pH_{PZC}) was 5.7, which was determined by the method described by Kinniburgh et al. [25]. Below pH 5.7, the surface is positively charged under these conditions the uptake of metal ions would be quite low due to electrostatic repulsion. With increasing pH (beyond PZC) the negative charge on the surface of adsorbent increases there by enhancing the metal adsorption.

3.3. Effect of carbon dosage

The effect of adsorbent dosage on removal of copper and cadmium has been presented in Fig. 5. The amount of carbon required for quantitative removal of copper and cadmium from 50 ml (80 mg/l) of solution was 0.5 g. The adsorption increased

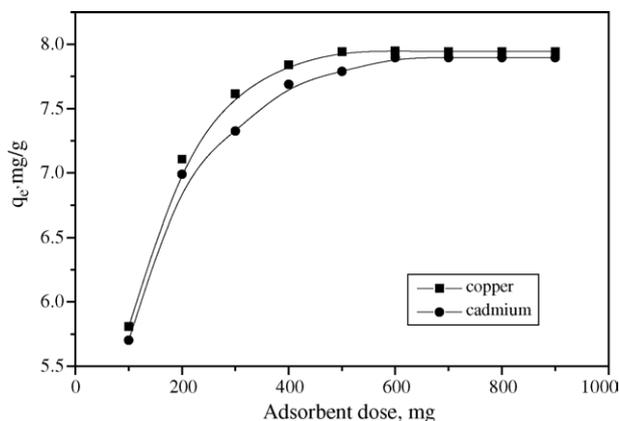


Fig. 5. Effect of adsorbent dose on removal of copper and cadmium (initial concentration 80 mg/l; contact time 60 min; pH 6.0).

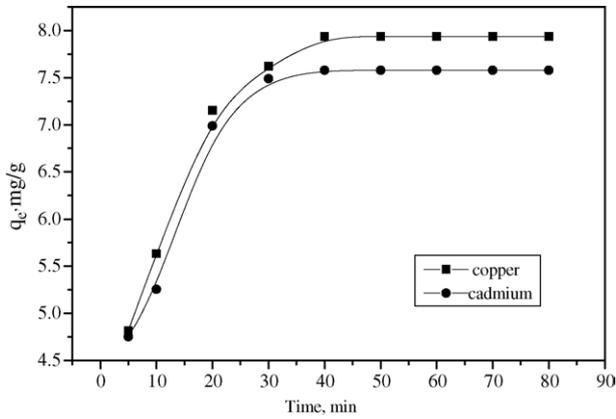


Fig. 6. Effect of contact time on removal of copper and cadmium (initial concentration 80 mg/l; pH 6.0).

up to 20.8 mg/g with adsorbent dose of 0.5 g/50 ml (10 g/l) in the case of copper and then became almost constant. The adsorption was found to be 19.5 mg/g in the case of cadmium for a similar adsorbent dose. It is apparent that the percent removal of copper and cadmium increases in the concentration of the activated carbon due to the greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent.

3.4. Effect of contact time and initial concentration

Fig. 6 shows the effect of contact time on removal of copper and cadmium. Experimental studies were carried out with varying initial metal ion concentrations of copper and cadmium ranging from 40–100 mg/l using 10 g/l of adsorbent dose at pH 6.0 (the results are not shown in Fig. 6). Equilibrium adsorption was established within 40 min for both metal ions at initial concentrations of 80 and 100 mg/l. It is very clear from the results that the agitation time required for maximum uptake of metal ions by activated carbon was dependent on the initial metal ion concentration. This data is important because equilibrium time is one of the parameters for economical wastewater treatment plant application [8]. According to these results, the agitation time was fixed at 1 h for the rest of the batch experiments to make sure that equilibrium was attained.

3.5. Adsorption isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for designing purposes. The sorption data was analysed in terms of Freundlich and Langmuir isotherm models. The fitted constants for Freundlich and Langmuir models along with regression coefficients are summarised in Table 2. The Freundlich and Langmuir isotherms are shown graphically in Figs. 7 and 8. As can be seen from isotherms and regression coefficients, the fit is better with Freundlich model than with Langmuir model. The Langmuir constants Q_m and k_L were 20.8 mg/g and 0.68 for copper and 19.5 mg/g and 0.48 for cadmium, respectively. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless

Table 2
Freundlich and Langmuir constants

	Copper	Cadmium
Freundlich		
k_F	9.06	8.32
n	3.89	4.28
R^2	0.9903	0.9905
Langmuir		
Q_m	20.78	19.59
k_L	0.68	0.48
R^2	0.9624	0.9576

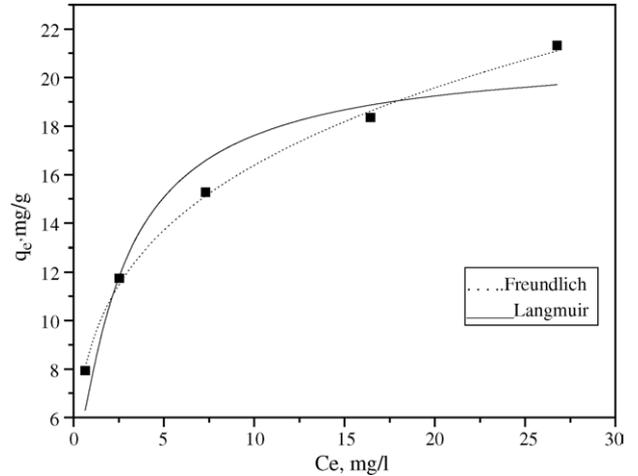


Fig. 7. Adsorption isotherms of copper at pH 6.0.

constant separation factor or equilibrium parameter, R_L , which is defined as

$$R_L = \frac{1}{(1 + k_L C_0)}$$

where k_L is the Langmuir constant and C_0 is the initial concentration of Cu or Cd. The R_L value indicates the shape of the isotherm as follows.

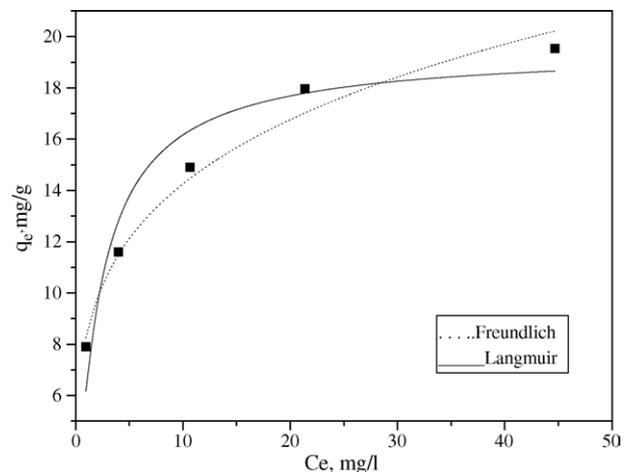


Fig. 8. Adsorption isotherms of cadmium at pH 6.0.

R_L value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

According to McKay et al. [26], R_L values between 0 and 1 indicate favourable adsorption. The R_L values for copper and cadmium were 0.018, 0.014 and 0.025, 0.020, respectively, for concentrations of 80, 100 mg/l. Hence, the adsorption of both metal ions on *C. pentandra* hulls seems to be favourable. The Freundlich constants k_F and n were 9.06, 3.89 for copper and 8.32, 4.28 for cadmium, respectively. It has been shown that 'n' values between 1 and 10 represent beneficial adsorption.

3.6. Sorption kinetics

The kinetics of sorption describing the contact time in the removal of copper/cadmium is one of the characteristics defining efficiency of sorption. The time profile and the order of kinetic models for copper and cadmium are presented in Fig. 9. The rates of sorption of copper and cadmium are rapid on activated carbon, for example, over 70% of copper and cadmium uptake is completed with in 10 min and equilibrium is attained at 40 min. The pseudo-second-order equation shows a good correlation of the experimental results with linearized form. The results indicate that the kinetic behaviour of copper and cadmium on activated carbon can be satisfactorily explained with the pseudo-second-order sorption equation. Compared to the former, the pseudo-first-order equation shows a poor correlation with the experimental data. Hence, the pseudo-second-order equation is useful for the kinetic studies in the present investigation.

3.7. Desorption studies

To achieve practical adsorption, the adsorbate has to be desorbed and spent adsorbent reused. The use of thermal activation

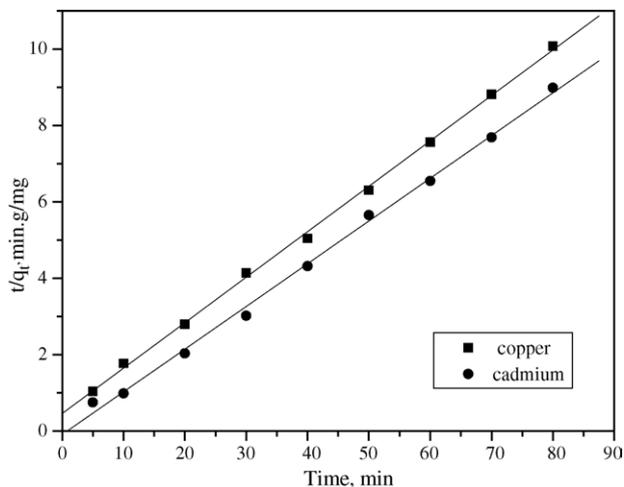


Fig. 9. Time profiles and pseudo-second-order kinetic model for copper and cadmium.

Table 3
Desorption data corresponding to copper

Initial concentration Cu(II) (mg/l)	Removal efficiency	Desorption ^a with HCl			
		0.05 M ^b	0.1 M ^b	0.2 M ^b	0.3 M ^b
40.0	100.0	68.2	80.0	90.0	88.5
60.0	100.0	60.0	73.5	82.3	81.2
80.0	99.2	57.4	70.1	78.4	78.0

^a All values are percent recovery of copper.

^b Concentration of HCl.

Table 4
Desorption data corresponding to cadmium

Initial concentration Cd(II) (mg/l)	Removal efficiency	Desorption ^a with HCl			
		0.05 M ^b	0.1 M ^b	0.2 M ^b	0.3 M ^b
40.0	100.0	78.3	83.4	88.0	86.5
60.0	100.0	67.8	71.2	80.5	78.8
80.0	98.8	56.5	60.5	70.0	67.6

^a All values are percent recovery of cadmium.

^b Concentration of HCl.

to regenerate the adsorbent could require high energy and 5–10% adsorbent loss in each cycle. Hence, studies were attempted to use chemical regeneration for adsorbate desorption. Results relating to desorption of copper and cadmium by HCl are given in Tables 3 and 4. The results showed that with increase in concentration of HCl the desorption also increased but attained a constant with 0.2 M HCl. The data also shows that desorption of copper is more when compared to cadmium.

4. Conclusions

The study indicated that activated carbon prepared from *C. pentandra* hulls could be used as an effective adsorbent material for the treatment of copper and cadmium-bearing aqueous wastewater. The adsorption of copper and cadmium on activated carbon is found to be time, concentration, pH and dose dependent. In the study kinetics of sorption, the pseudo-second-order model provides better correlation of the sorption data than the pseudo-first-order model, this suggests that the rate-limiting step may be chemical sorption rather than diffusion. The material (*C. pentandra* hulls) under consideration is not only economical, but also an agricultural waste product. Hence activated carbon derived from *C. pentandra* hulls would be useful for the economic treatment of wastewater containing copper and cadmium metals.

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