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Journal of Hazardous Materials B137 (2006) 909–914

Journal of Hazardous Materials

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Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions

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Received 29 November 2005; received in revised form 6 March 2006; accepted 8 March 2006
Available online 18 April 2006

Abstract

In this work, adsorption of Cu(II) ions on sawdust (SD) and activated sawdust (ASD) has been studied by using batch adsorption techniques. The equilibrium adsorption level was determined to be a function of the pH, initial Cu(II) concentration, and adsorbent dosage. The equilibrium nature of Cu(II) adsorption has been described by the Freundlich and Langmuir isotherms. The experimental adsorption data were fitted to the Langmuir adsorption model both sawdust and activated sawdust. The equilibrium capacity of sawdust and activated sawdust were 5.432 and 13.495 mg copper per g adsorbent, respectively at room temperature and natural pH. The maximum adsorption capacity was obtained at the maximum zeta potential value that −74.5 mV (pH 5) for activated sawdust and at −48.4 mV (pH 4) for sawdust. It was observed that activated sawdust was a suitable adsorbent than sawdust for removal of Cu(II) from aqueous solutions.
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Keywords: Copper (II); Activated sawdust; Adsorption isotherm; Zeta potential

1. Introduction

Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. Heavy metal ions such as Cu(II), Cd(II), Hg(II), Zn(II), Pb(II) etc., have long been recognized as ecotoxicological hazardous substances and their chronic toxicities and accumulation abilities in living organism have been of great interest in the last years [1]. Therefore, the removal of heavy metals from waters and wastewaters are important to protect public health and wildlife. Copper and its compounds are ubiquitous in the environment and thus copper is found frequently in surface water [2]. The primary sources of copper in industrial wastewaters are metal-process pickling baths and plating baths. Copper may also be present in wastewater from a variety of chemical manufacturing processes employing copper salts or copper catalyst [3]. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers [4]. Heavy metals can successfully be recovered from solution by precipitation as hydroxides or carbonates, by membrane filtration and by capture on synthetic ion exchangers.

These methods, but, are much less efficient for concentrations lower than about 100 mg/L for which they can be prohibitively expensive and can even fail to achieve legal limits. For these low concentrations it is preferable to use sorption techniques [5]. The adsorption technique, being very effective and economic for removal of metals from wastewater, is one of the preferred methods for removal of toxic contaminants from water. There are many studies for removing Cu(II) ions from aqueous solutions by using adsorption. It has been reported that sago processing waste [6], algae [7], wheat shell [8], seafood processing waste sludge [9] and sawdust [1,22] have been studied to define the adsorption capacity of copper ions. Sawdust is a widely available and abundant natural material. Sawdust has been used as adsorbent for Cr(VI) [10,11], several dyes [12,13] and copper [2,4]. However, without any activation these materials like sawdust have low adsorption capacities. So, many reports have appeared in recent years on the preparation of activated carbon from various cheaper and alternative materials. The use of activated carbon that obtained from alternative materials has been reported in many studies, for example, furfural [14], hazelnut shell [15], agricultural solid waste [16].

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doi:10.1016/j.jhazmat.2006.03.014

The aim of this work was to increase the adsorption capacity of sawdust by activated its surface. Comparison of adsorption capacities of sawdust and activated sawdust were made to measure the effect of several parameters, i.e., initial Cu(II) concentration, initial pH, adsorbent dosage for removal of Cu(II) ions from aqueous solutions.

2. Materials and methods

2.1. Copper

Cu(II) stock solution was prepared from an analytical grade sulfate salt, copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), in a concentration of 10^3 mg/L. In the preparation of the aqueous solution of $CuSO_4{\cdot}5H_2O$, distilled water was used. Test samples of various concentrations (range between 30–150 mg/L) were prepared from this stock solution. Initial pH of the Cu(II) solutions was 5.5 before addition adsorbents.

2.2. Sawdust (SD)

Sawdust of poplar tree (Samsun Clone) was used as an adsorbent for the adsorption of copper ions. Adsorbent was obtained from massive panel factory. Samsun clone poplar trees are solely grown in Samsun (Turkey). Before set up of all experiments, the sawdust was sieved through a 35-mesh sieve then washed with hot distilled water, and finally dried at sunlight.

2.3. Activated sawdust (ASD)

Sawdust was treated with 1N H_2SO_4 in the ratio of 1:2 (sawdust/H_2SO_4; w/v) at 150 °C for 24 h. The heated material was washed distilled water and soaked in 1% sodium bicarbonate solution overnight to remove residual acid. Then the material was dried in an oven at 105 °C for 24 h [17].

The adsorption capacities and the feasible removal rates must be substantially boosted by the modification techniques. In addition, when these chemicals are immobilised at the surface of activated carbon the removal mechanism also changes. The impurities are not only removed by adsorption on the surface of the untreated carbon but it could be removed by a surface attraction chemical bonding phenomenon on the newly added chemicals. The interaction that might occur during metal ions removal with untreated activated carbon, that metal ions are exchanged with the acidic function groups present on the carbon surface.

$$M^{n+} + n(\text{–COOH}) \leftrightarrow (\text{–COO})_n M + nH^+$$

Metal ion removal by activated sawdust might occur due to surface complex formation and exchange between metal ions an acidic functional groups [18].

2.4. Experimental set-up and analysis

Adsorption experiments were carried out using the batch technique at room temperature (20 °C). Initial Cu(II) concentrations were prepared in the range 30, 50, 70, 100 and 150 mg/L. In each adsorption experiments, 250 ml aqueous solution of Cu(II) of desired concentrations and pH was added SD or ASD in a 250 ml erlenmeyer flask. These 250 ml flasks were stirred in a shaker (Rosi 1000) at 200 rpm for 1 h. The analysis of Cu(II) in the final aqueous solutions was carried out complexometrically with EDTA. pH measurements were obtained using pH meter (WTW Multiline P4), while zeta potential measurements were carried out in a Zeta-Meter (Zeta-Meter 3.0 + 542,USA).

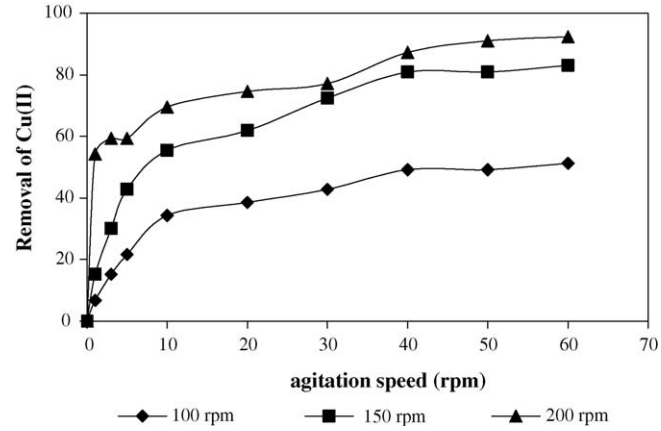

Fig. 1. Effect of agitation speed on removal of Cu(II) ions by 5 g/L of ASD at room temperature (20 °C), initial natural pH, Cu(II) = 50 mg/L.

3. Results and discussion

3.1. Effect of agitation speed and initial Cu(II) concentrations

Effect of agitation speed on Cu(II) removal by ASD is presented in Fig. 1. Agitation speed ranging between 100 and 200 rpm was maintained. The amount of adsorbed Cu(II) ions (mg/g) increased with increase in agitation speed. The removal of Cu(II) was found to be 51.29%, 83.06% and 92.38% for 100, 150 and 200 rpm agitation speed, respectively. So, all subsequent experiments conducted at an agitation speed of 200 rpm.

The experimental results of adsorption of Cu(II) ions on adsorbents (SD and ASD) at various concentrations are shown in Fig. 2a and b. The rate of Cu(II) removal increased considerably as the contact time increased for both adsorbents. The removal of Cu(II) ions is high in the first 10 min. Thereafter, the rate significantly decreases and eventually approaches zero, finally the equilibrium point has been attained. These changes in the rate of removal may be due to the fact that, initially all adsorbents sites are vacant and the solute concentration gradient is high. When the initial concentrations of Cu(II) solution are increased from 30 to 150 mg/L, the percent of adsorption decreases with increasing concentration for both adsorbents. Cu(II) concentration was increased from 30 to 150 mg/L, the removal of Cu(II) decreased from 96.47% to 43.87% for ASD, while it decreased from 68.23% to 17.40% for SD. But, the adsorption density (mg/g) increased with increasing in Cu(II) concentrations. The percent Cu(II) removal at equilibrium increased from 5.79 to 13.16 mg/g as the Cu(II) concentration was increased from 30 to 150 mg/L for ASD while it increased from 4.09 to 5.22 mg/g

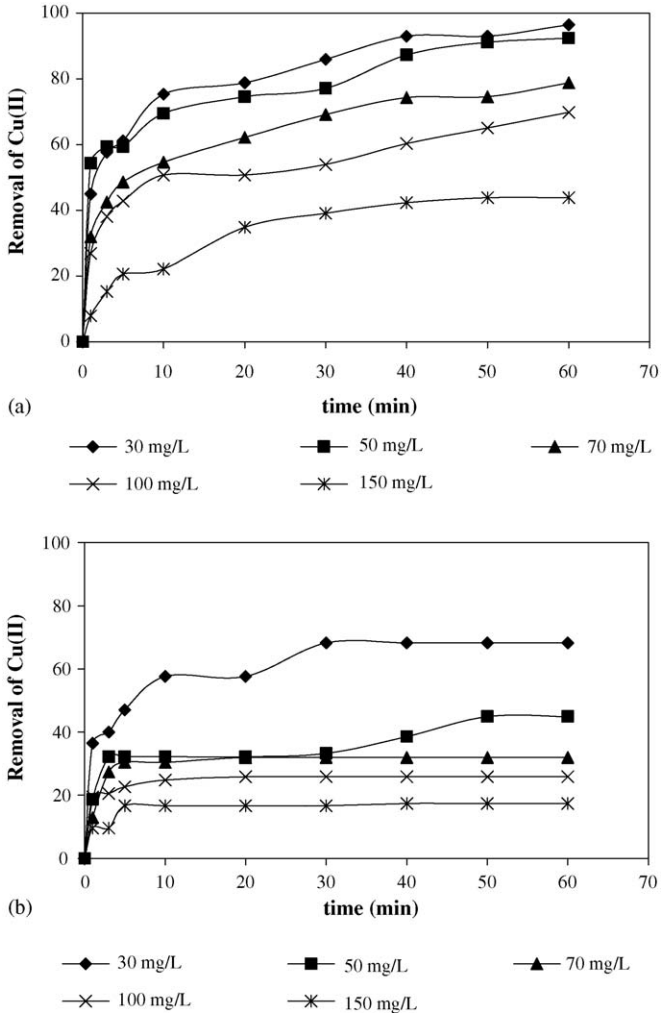

Fig. 2. (a) Effect of initial Cu(II) concentration on removal of Cu(II) ions by 5 g/L of ASD at room temperature (20 °C), initial natural pH, 200 rpm agitation speed. (b) Effect of initial Cu (II) concentration on removal of Cu(II) ions by 5 g/L of SD at room temperature (20 °C), initial natural pH, 200 rpm agitation speed.

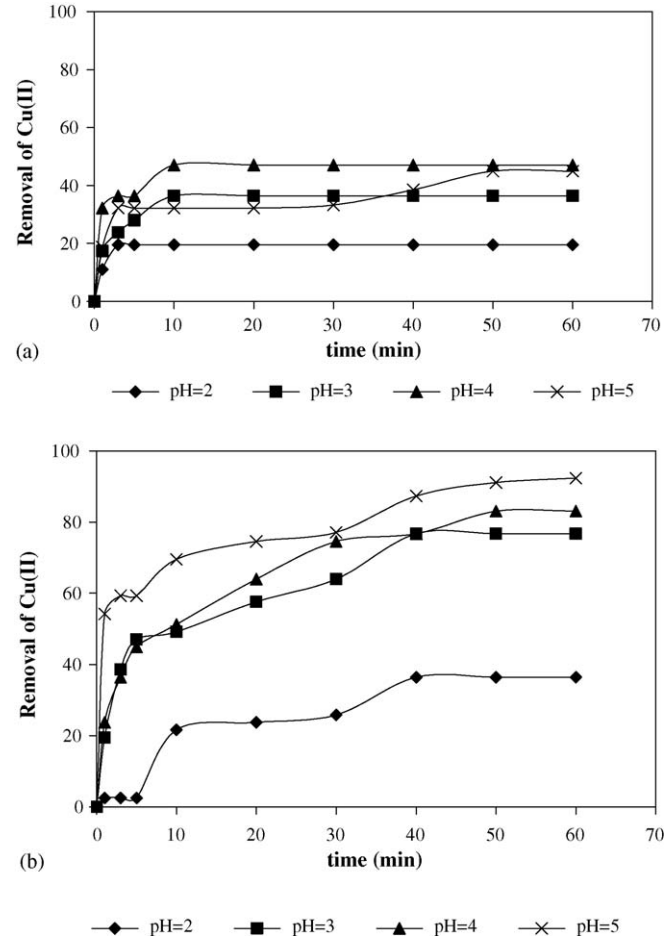

Fig. 3. (a) Effect of initial solution pH on removal of Cu(II) ions by 5 g/L of SD dose at room temperature (20 °C), 200 rpm agitation speed, Cu(II) = 50 mg/L. (b) Effect of initial solution pH on removal of Cu(II) ions by 5 g/L of ASD dose at room temperature (20 °C), 200 rpm agitation speed, Cu(II) = 50 mg/L.

for SD. It is clear that the removal of Cu(II) depends on the concentration of Cu(II). So, the adsorption capacity of ASD was higher than SD for removal of Cu(II) even at high copper concentration. 50 mg/L of Cu(II) concentration was selected for the followed experiments.

3.2. Effect of pH

pH is one of the most important parameters controlling the adsorption process [19]. Hydrogen ions affect metal complexation because they have a great affinity for many complexing and ion-exchange sites [20]. Low pH leads to an increase in H ion concentration in the system and the surface of the ASD acquires positive charge by absorbing H ions. As the carbon surface is positively charged at low pH, the electrostatic attraction between the ASD surface and copper ions leads to decrease. So, it was seen from Fig. 3a and b that the adsorption of Cu(II) ions decreased at low pH (<3). As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decrease. So, the adsorption of copper increased. Negatively charged site on the ASD and SD is favour the adsorption of copper ions due to electrostatic attraction. This is because of the sawdust surface which is negatively charged after activation and is attractive for copper ions. The removal of copper ions decreased with decreasing pH for SD and ASD. The optimum pH that providing maximum removal of copper was 5 for ASD (92.38%), while it was 4 for SD (47.05%) adsorbent. The copper adsorption by SD and ASD was significantly affected over the pH range of 2–5. Similar results were reported using algae at pH 4.5 [7], wheat shell as the adsorbent at pH 5 [8]. At pH values higher than 5.5, natural pH of copper solutions, Cu II ions precipitated and so adsorption studies at these pH values could not be performed.

The effect of pH on the removal of Cu(II) was also checked zeta potential values of adsorbents. The suspensions containing 0.5 g/50 mL solids were prepared. The pH of the suspension was measured prior to zeta potential measurement. The zeta potential was measured for at least three independent suspensions. The average value was reported. Both SD and ASD zeta potential values were negative. However, the degree of zeta potential of SD is lower than that of ASD, resulting in a smaller

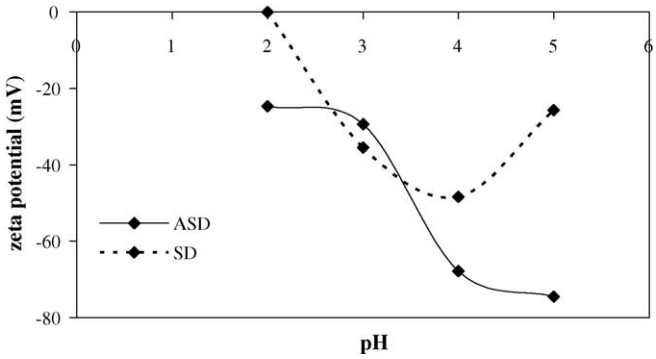

Fig. 4. Effect of pH on zeta potential value (Initial Cu(II) concentrations = 50 mg/L, SD and ASD concentration 5 g/L).

electrostatic attraction zeta potential. Maximum zeta potential value was obtained as −74.5 mV for ASD at pH 5 and it was obtained as −48.4 mV for SD at pH 4.

It can be seen that Figs. 3a, b and Fig. 4, there is a relationship between initial solution pH, zeta potentials and adsorption efficiencies. The percent of maximum adsorption (92.38%) and zeta potential value (−74.5 mV) were obtained at the same pH 5 for ASD. Similar result was determined which maximum adsorption efficiency (47.05%) and zeta potential value (−48.4 mV) at the same pH 4 for SD.

3.3. Effect of adsorbent dose

The percent adsorption increased as the SD and ASD dose were increased (1–10 g/L) at 50 mg/L copper concentration (Fig. 5a and b). Removal of Cu(II) increased from 40.70% to 100%, as the ASD dose was increased from 1 to 10 g/L for ASD adsorption. Similarly, removal of Cu(II) increased 25.87% to 61.88% for SD adsorption. Increase in adsorption with the dose can be attributed to increased surface area and availability of more adsorption sites. But for ASD adsorption, there is no more increase in the percent of adsorption, because it remains constant (100%) after 5 g/L of ASD dose.

3.4. Adsorption isotherms

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies in sorption give the capacity of the sorbent. It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent [21].

In order to investigate the sorption isotherm, two equilibrium models were analysed. These models are Langmuir and Freundlich isotherm.

The well known expression of the Langmuir model is given by Eq. (1):

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

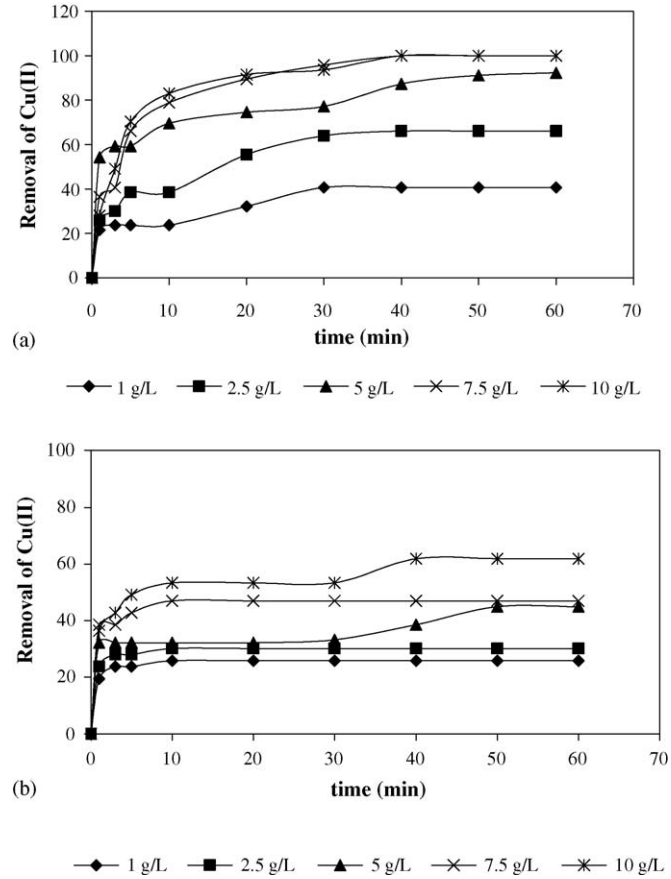

Fig. 5. (a) Effect ASD dose for removal of Cu(II) at room temperature (20 °C), natural initial pH, 200 rpm agitation speed, Cu(II) = 50 mg/L. (b). Effect SD dose for removal of Cu(II) at room temperature (20 °C), natural initial pH, 200 rpm agitation speed, Cu(II) = 50 mg/L.

and the linear form of this equation can be given as

$$\frac{C_e}{(x/m)} = \frac{1}{(b.q_{max})} + \left(\frac{1}{q_{max}}\right) C_e \quad (2)$$

where q_e (mg/g) is the adsorption capacity equilibrium solute concentration, C_e (mg/L) is the unadsorbed copper concentration in solution at equilibrium. q_{max} is the maximum amount of the copper bound per unit weight of adsorbent to form a complete monolayer on the surface (mg/g) and b is a Langmuir constant related to the energy of adsorption (L/mg). Generally, the Langmuir equation applies to the cases of adsorption on completely homogeneous surfaces where interactions between adsorbed molecules are negligible [23].

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The Freundlich equation

Table 1
The comparison of the individual constants obtained from Langmuir and Freundlich adsorption isotherms for both materials

Adsorbate	Langmuir isotherm			Freundlich isotherm		
	q_{max}	b	r^2	K_f	n	r^2
ASD	13.495	0.665	0.998	6.408	5.173	0.884
SD	5.432	0.179	0.996	3.233	10.101	0.873

is commonly presented as:

$$q_e = Kf.C_e^{1/n} \quad (3)$$

In Eq. (4), it has been given the linear form of Eq. (3);

$$\text{Log}\, q_e = \log Kf + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

where K_f and n are the Freundlich constants for the system. K_f and n are indicators of adsorption capacity and adsorption intensity, respectively.

The applicability of Langmuir and Freundlich sorption isotherms are analyzed by plotting C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$, respectively. The values of the Langmuir constants (q_{max} and b) and Freundlich constants (K_f and n) with the correlation coefficients are presented in Table 1 for two adsorbents.

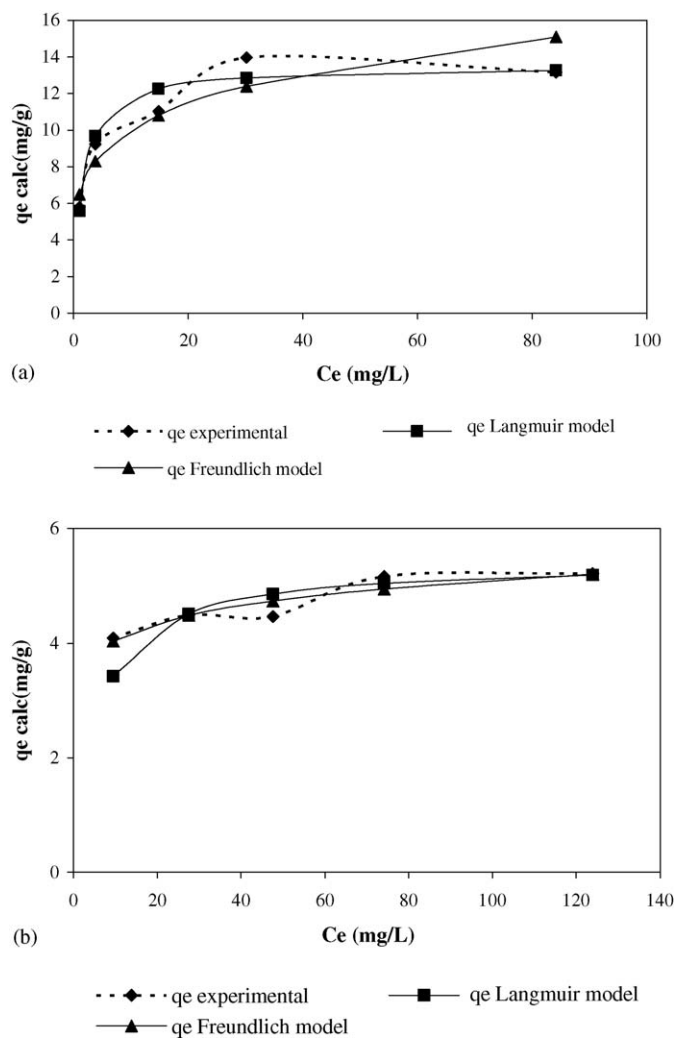

Fig. 6. (a) The comparison of q_e values: experimental, Langmuir and Freundlich adsorption model for Cu(II) adsorption on ASD (5 g/L of ASD dose at room temperature (20 °C), natural initial pH, 200 rpm agitation speed). (b) The comparison of q_e values: experimental, Langmuir and Freundlich adsorption model for Cu(II) adsorption on SD (5 g/L of SD dose at room temperature (20 °C), natural initial pH, 200 rpm agitation speed).

Table 2
Previously reported adsorption capacities of various low-cost adsorbents for Cu(II)

Low-cost adsorbents	Adsorption capacity (mg/g) of Cu(II), q_{max}	Reference
Tea waste	8.64	[1]
Sawdust	1.79	[4]
Wheat shell	8.34	[8]
ASD	13.495	This study
SD	5.432	This study
Peanut hulls	9	[22]
Peanut pellets	12	[22]
Sawdust	8.45	[23]

The values of the correlation coefficient (r^2) (see Table 1) indicate that the Langmuir isotherm has been best fitted for the adsorption of copper on ASD and SD. The monolayer saturation capacities of Cu(II) ions, q_{max} are 13.495 and 5.432 mg/g for ASD and SD, respectively. Using the Langmuir and Freundlich constants and mass balance equation, theoretical amount of copper adsorbed per gram of ASD and SD were determined and compared with experimental data (Fig. 6a and b). It can be seen from these figures, the values of experimental q_e were more close to the values of q_e which calculated by using Langmuir constants than the values of q_e which calculated by using Freundlich constants. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir model hints surface homogeneity of the adsorbent. Because, the experimental results best fit the Langmuir model for ASD ($r^2 = 0.998$), this leads to the conclusion which shows the more homogeneous nature of the ASD.

The adsorption capacities of previously some other materials and ASD and SD reported are given in Table 2.

4. Conclusions

The performances of two adsorbents (ASD and SD) to remove Cu(II) ions from aqueous solution have been investigated. It was found that the adsorption capacity of sawdust increased by the activation of its surface area. Equilibrium isotherms have been measured experimentally and analysed. The Langmuir model was found to best describe the data. This leads to the conclusion which shows the more homogeneous nature of the ASD. According to Langmuir isotherm, the maximum adsorption capacity of sawdust was 5.432 mg/g, at the same experimental conditions, while it was 13.495 mg/g after its surface was activated (ASD) with sulphuric acid. Adsorption of Cu(II) ions is dependent on its initial concentrations, ASD and dosages and pH of the Cu(II) solutions. The most effective pH was 5.0 and 4.0 for ASD and SD, respectively. The maximum removal efficiency was 47.05% at pH 4.0 for SD while removal efficiency for ASD raised to a maximum of 92.38% at pH 5.0.

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