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Adsorption of copper ions onto activated carbon from capsicum straw

Jianxin Shou[a], Muqing Qiu[b,*]

[a]*Department of Life Science, Shaoxing University Yuanpei College, Shaoxing 312000, P.R. China, Tel. +86 575 88345098; email: shoujx@126.com (J. Shou)*
[b]*College of Life Science, Shaoxing University, Shaoxing 312000, P.R. China, Tel./Fax: +86 575 88345007; email: qiumuqing@126.com (M. Qiu)*

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ABSTRACT

Activated carbon was obtained from capsicum straw by chemical activation using KOH as an activator. Then, it was used as an adsorbent for the removal of copper ions from aqueous solution. The effects of various parameters such as contact time, initial copper ion concentration, and temperature on copper ions adsorption by activated carbon were investigated. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption. Kinetic adsorption data were analyzed by the pseudo-first-order kinetic model, the pseudo-second-order model, and the intraparticle diffusion model, respectively. The thermodynamics parameters were also calculated. The activated carbon was found to be both effective and economical.

Keywords: Adsorption; Copper; Activated carbon; Capsicum straw

1. Introduction

The presence of metal ions in municipal or industrial wastewater and their potential impact have been a subject of scientific environmental studies for a long time because of their extreme toxicity even at low concentrations, and their tendency to accumulate in the food chain [1–3]. In particular, copper pollution is arising from copper mining and smelting, brass manufactural, and electroplating industries. Excessive uptake of copper in human body can cause capillary damage, hepatic toxicity, and renal damage [4]. Copper, as well as arsenic and mercury, is recognized as one of the most toxic heavy metal ions to mammalians. Long-term inhalation of copper-containing sprays is linked with an increase rate of lung cancer in exposed workers. Hence, it is necessary to remove copper ions from wastewater in order to protect human health and the environment [5].

The common methods for removing metal ions from wastewater include adsorption, bio-sorption, complexation, chemical precipitation, solvent extraction, reverse osmosis, ion exchange, filtration, and membrane processes. Among them, adsorption is a highly effective and economical method to remove metal ions from the aqueous solution. The process is governed by a number of parameters that determine the efficiency level of an adsorbent [6–8].

Activated carbons are materials owning complex porous structures with associated energetic as well as chemical inhomogeneities. Their structural heterogeneity is a result of the existence of micropores, mesopores, and macropores of different sizes and shapes. Activated carbon is one of the most important

*Corresponding author.

adsorbents. The main application of this adsorbent is for separation and purification of gaseous- and liquid-phase mixtures [9–12]. However, appropriate properties and cost of adsorbent materials are the key aspects for practical applications when dealing with metal ion wastewater. One way to reduce the cost of adsorbent production is using inexpensive precursors such as agricultural by-products and wastes. In recent years, fruit stones and agricultural by-products like almond shell, peanut shells, coir pith, chestnut, pistachio-nut shells, corn, and palm stones are of particular interest because they are generated as by-products from food processing and agricultural industries in amounts sufficient for large-scale production of activated carbon [13–15]. It was demonstrated that agricultural by-products and various bio-sorbent materials have promising capacities to remove a variety of pollutants. More importantly, some researchers observed that these materials exhibited higher affinity in bonding heavy metal ions [16–18]. Capsicum straw is one of the most widely planted crops in China. Abundance in production and relatively low price make capsicum straw attractive precursor for the activated carbon production. However, it received little attention in investigating capsicum straw-derived carbons and its efficiency on adsorption of heavy metal ions.

In this study, activated carbon was obtained from capsicum straw by chemical activation using KOH as an activator. Then, it was used for removal of copper ions from the aqueous solution. The effects of temperature, contact time, and initial copper ion concentration on copper ion adsorption by activated carbon were investigated. The adsorption isotherms, kinetics, and thermodynamics of the model compound over the activated carbon were also determined and discussed in detail.

2. Materials and methods

2.1. Preparation of the adsorbents

The capsicum straw was obtained from Shaoxing City in Zhejiang Province of P.R. China. The capsicum straw was dried at 378 K for 12 h, to achieve constant weight, then comminuted and sieved into a uniform size of 120 mesh. The 50 g of the capsicum straw was soaked stilly with 100 mL 10% KOH solution in 250 mL Erlenmeyer flasks for 24 h at room temperature. Then, it was dried again at 378 K for 12 h to constant weight and was carbonized at 973 K in a muffle furnace for 60 min. The product of 120-mesh activated carbon was thus obtained and then stored for later adsorption experiments.

2.2. Adsorption experiments

Adsorption experiments were conducted in a set of 250-mL Erlenmeyer flasks containing 0.10 g of activated carbon and 100 mL of copper ion solutions with various initial concentrations (20, 30, 40, and 50 mg/L). The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature (293, 303, and 313 K) and 200 rpm. The samples were filtered, and the residual concentration of copper ion was analyzed by atomic absorption spectrophotometry.

2.3. Analytical methods

The textural characteristics of activated carbon including surface area, pore volume, and pore size distribution were determined using standard N_2-adsorption techniques. The surface physical morphology of activated carbon was observed by a scanning electron microscope.

The amount of adsorbed copper ion q_t (mg/g) at different time was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of copper ion, respectively. V (L) is the solution volume, and m (g) is the mass of adsorbent used.

2.4. Statistical analyses of data

All experiments were repeated in duplicate, and the data of results were expressed as the mean and the standard deviation (SD). The value of the SD was calculated by Excel software. All data were analyzed by the Langmuir and Freundlich adsorption models to test for the effects of temperature and initial copper ion concentration. The kinetic adsorption data were discussed using the pseudo-first-order model and pseudo-second-order model. All error estimates given in the text and error bars in figures were SD of means (mean ± SD). All statistical significance was noted at $\alpha = 0.05$ unless otherwise noted.

3. Results and discussion

3.1. Characterization of activated carbon

The surface of activated carbon was observed using scanning electron microscopy as shown in

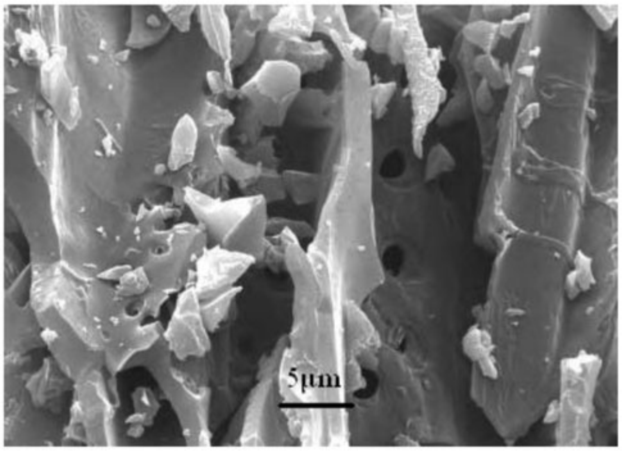

Fig. 1. SEM image of activated carbon.

Fig. 1. It can be seen from the micrograph that the activated carbon contains porous structures and presents an adequate morphology for copper ions adsorption.

The characteristics of activated carbon are obtained from the standard N_2-adsorption techniques. The BET surface area is 676 m^2/g, the total pore volume is 0.72 cm^3/g and the nominal pore size is 1.21 nm. In addition, the content of C, N, and H in activated carbon is 86.24, 1.13, and 0.25%, respectively. It shows that activated carbon has a large specific surface area.

3.2. Adsorption kinetics

The influence of contact time on the removal of copper in solution by activated carbon is shown in Fig. 2.

It can be concluded that adsorption rate of copper ion increases sharply at short contact time and slowed gradually as equilibrium was approached. It may be due to the availability of initial large number of vacant surface active sites for adsorption, the adsorption rate is very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to the repulsive forces between copper ion adsorbed on solid surface and copper ion from solution.

In order to investigate the mechanism of copper ions sorption, three models were used in this study.

The linear pseudo-first-order model of Lagergren is given as follows [19]:

$$\ln (q_e - q_t) = \ln q_e - k_1 \times t \tag{2}$$

where $q_e$and q_t are the amounts of copper ions absorbed onto the adsorbent (mg/g) at equilibrium and at t, respectively. k_1 is the rate constant of first-order adsorption (min^{-1}).

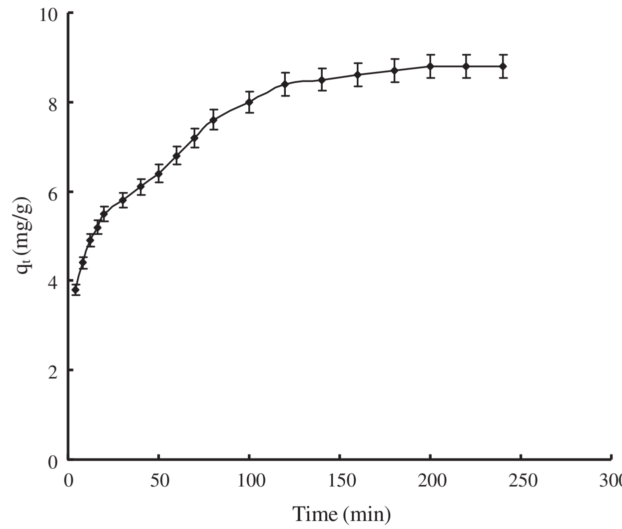

Fig. 2. Effect of contact time on adsorption of copper ion in solution onto activated carbon.
Notes: Experimental conditions: 0.10 g of activated carbon, 20 mg/L of initial copper ion concentration, 120 meshes of particle size, 293 K, 200 rpm and pH 5.0.

The pseudo-second-order kinetic model developed by Ho and Mckay [20] is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 is the rate constant of second-order adsorption (g/mg min^{-1}).

The intraparticle diffusion model can be expressed as follows:

$$q_t = k_i t^{\frac{1}{2}} \tag{4}$$

where k_i is the constant of intraparticle diffusion rate. It is obtained from the slope of the straight line of q_t vs. $t^{\frac{1}{2}}$.

The adsorption kinetic models were shown in Fig. 3. The rate constant (k_1, k_2, and k_i), correlation coefficient R^2, and equilibrium adsorption density of q_e could be derived from this line.

The validity of the exploited models is verified by the correlation coefficient (R^2). R^2 values of the pseudo-first-order model, the pseudo-second-order model, and the intraparticle diffusion model for

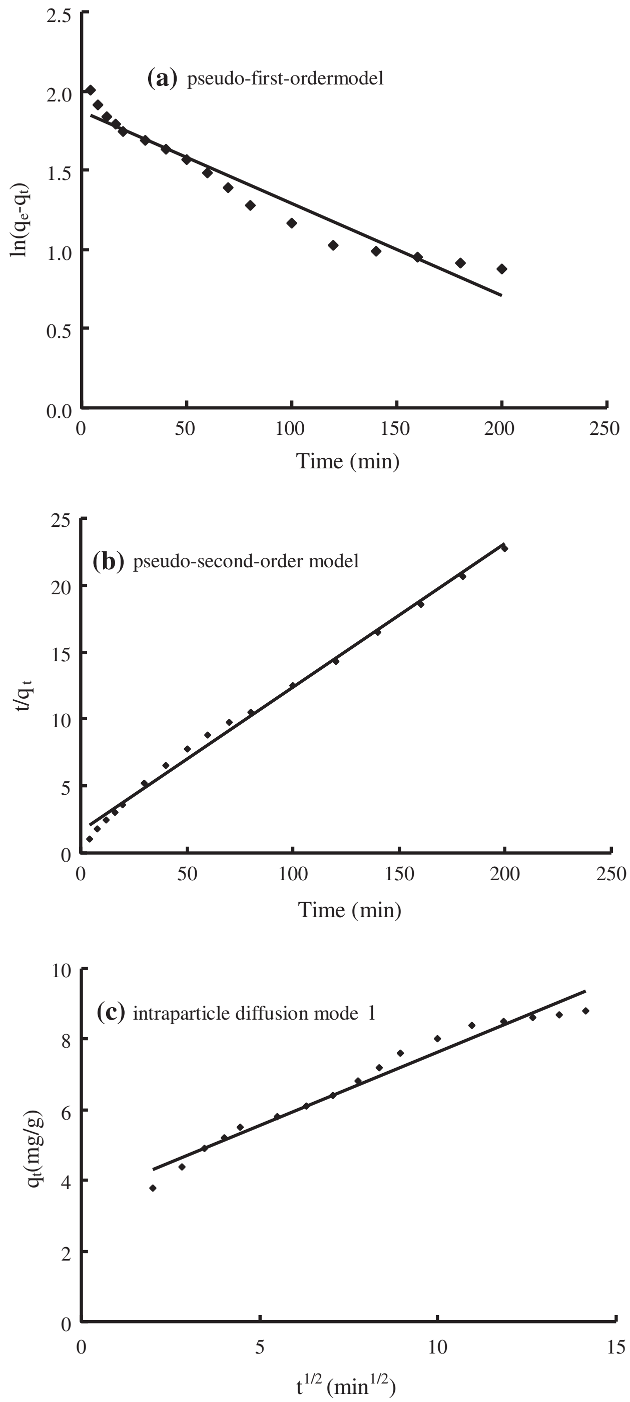

Fig. 3. (a) Pseudo-first-order model for adsorption of copper ion onto activated carbon at 293 K. (b) Pseudo-second-order model for adsorption of copper ion onto activated carbon at 293 K. (c) Intraparticle diffusion model for adsorption of copper ion onto activated carbon at 293 K. Notes: Experimental conditions: 0.10 g of activated carbon, 20 mg/L of initial copper ion concentration, 120 meshes of particle size, 293 K, 200 rpm and pH 5.0.

adsorption of copper ion onto activated carbon were 0.9421, 0.9943, and 0.969, respectively. This result confirmed that the adsorption of copper ion onto activated carbon better fits to pseudo-second-order kinetic model. It implies that the predominant process is chemisorption, which involves in a sharing of electrons between the adsorbate and the surface of the adsorbent [21]. The results obtained from this experiment agreed with those found by Nadeem et al. [22] for the adsorption of lead onto chemically modified activated carbon.

3.3. Adsorption isotherms

The capacity of an adsorbent can be described by its equilibrium sorption isotherm. The Langmuir and Freundlich adsorption models are commonly adopted to investigate the adsorption behavior of materials and the correlation among adsorption parameters. Accordingly, equilibrium data were simulated by the Langmuir [23] and Freundlich models [24].

The Langmuir isotherm equation is represented by the following Eq. (5):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where C_e is the equilibrium concentration of copper ions (mg/L), q_e is the amount of copper ions adsorbed (mg/g), q_m is the maximum adsorption capacity of copper ions (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

The Freundlich isotherm equation is described by the following Eq. (6):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

where K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity, respectively.

The corresponding values of Langmuir and Freundlich isotherms for copper ions adsorption on activated carbon were listed in Table 1. The results indicate that the Langmuir isotherm fits better than the Freundlich isotherm, which may be due to the homogeneous distribution of active sites onto activated carbon. The value of R_L is between 0 and 1, which indicates the heterogeneity of the adsorbents and favorable adsorption [25]. The maximum adsorption capacity obtained from the Langmuir isotherm is 21.93 mg/g. This result is a higher adsorption capacity

Table 1
Equilibrium model parameters for the adsorption of copper ion onto activated carbon

Langmuir model			Freundlich model		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
21.93	0.065	0.9841	0.131	0.4958	0.9384

Notes: Experimental conditions: 0.10 g of activated carbon, 120 meshes of particle size, contact time of 200 min, 293 K, 200 rpm and pH 5.0.

compared with other adsorbents reported in the previous studies, such as 12.42 mg/g by sago waste, 17.15 mg/g by prawn shell, 10.34 mg/g by wheat shell, and 6.74 mg/g by walnut shell [14]. The results show that activated carbon from capsicum straw should be a promising sorbent for copper ion in aqueous solution.

3.4. Effect of temperature and thermodynamics parameters

The effect of temperature was shown in Fig. 4. It was found that the adsorption rate of copper ion increased with increasing solution temperature from 293 to 313 K. It also indicated that the adsorption is an endothermic process. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites, or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of the activated carbons at higher temperatures. Similar findings have been reported by other researchers working on the removal of heavy metal ions from the aqueous solution by activated carbon [26,27].

The thermodynamic parameters of free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were used to describe thermodynamic behavior of the adsorption of copper ions onto the activated carbon. These parameters were calculated from the following equations [28].

$$\Delta G^0 = -RT \ln K_a \tag{7}$$

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

$$K_a = \frac{q_e}{C_e} \tag{9}$$

where T is the solution temperature (K), K_a is the adsorption equilibrium constant, R is the gas constant

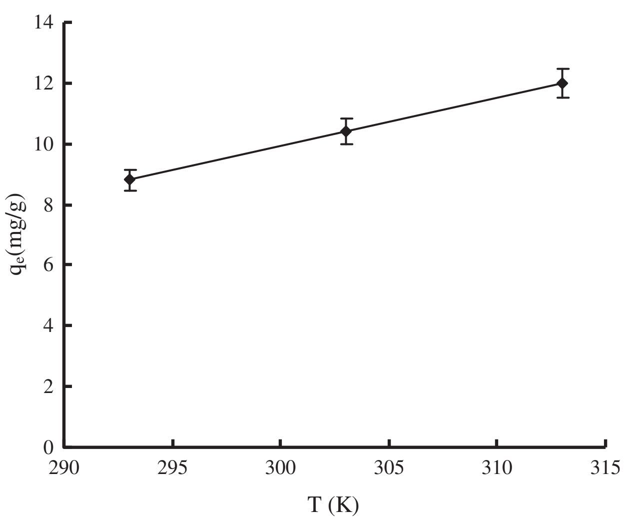

Fig. 4. Effect of temperature on adsorption of copper ion onto activated carbon.
Notes: Experimental conditions: 0.10 g of activated carbon, 20 mg/L of initial copper ion concentration, 120 meshes of particle size, contact time of 200 min, 200 rpm and pH 5.0.

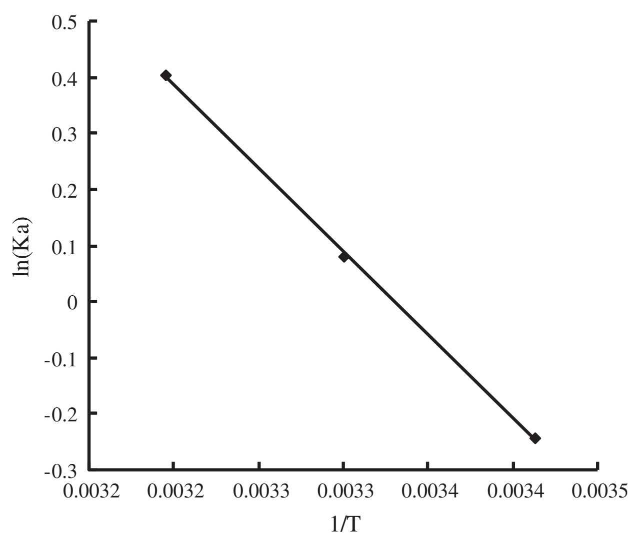

Fig. 5. Determination thermodynamic parameters for adsorption of copper ion onto activated carbon.
Notes: Experimental conditions: 0.10 g of activated carbon, 20 mg/L of initial copper ion concentration, 120 meshes of particle size, contact time of 200 min, 200 rpm and pH 5.0.

Table 2
Thermodynamic parameters for the adsorption of copper ion onto activated carbon

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
293	0.588	24.641	0.082
303	−0.201	24.641	0.082
313	−1.055	24.641	0.082

Notes: Experimental conditions: 0.10 g of activated carbon, 120 meshes of particle size, contact time of 200 min, 200 rpm and pH 5.0.

(8.314 J/mol K^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g), and C_e is the equilibrium concentration of the adsorbate (mg/L).

Thermodynamic parameters (ΔH^0,ΔS^0, and ΔG^0) for copper ions adsorption were evaluated using Eqs. (7)–(9). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of ln K_a vs. $1/T$ (Fig. 5).

The values of ΔH^0,ΔS^0, and $\Delta G^0$are listed in Table 2. The positive value of ΔG^0 indicated a chemical adsorption process at 293 K. As the temperature increases, the value of ΔG^0 decreases. It indicated that higher temperatures resulted in less driving force and less adsorption capacity. Above 303 K, the negative values of ΔG^0 indicates that the adsorption of copper ion onto activated carbon is spontaneous and thermodynamically favorable. The positive value of ΔH^0 indicated that the sorption process was endothermic in nature. The positive value of ΔS^0 showed the increasing randomness at solid/solution interfaced with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

4. Conclusions

Activated carbon was obtained from capsicum straw by chemical activation process. The adsorption studies for the removal of copper ion from aqueous solutions were carried out. The activated carbon contains porous structures and presents an adequate morphology for copper ions adsorption. It was shown that the pseudo-second-order kinetic model better described the sorption data. The adsorption isotherm studies showed that Langmuir isotherm fits better than the Freundlich isotherm. The maximum adsorption capacity obtained from the Langmuir isotherm is 21.93 mg/g. The positive value of ΔG^0 indicated a chemical adsorption process at 293 K. As the temperature increases, the value of ΔG^0 decreases. Above 303 K, the thermodynamic parameters showed a spontaneous, thermodynamically favorable, and endothermic adsorption.

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