

Simultaneous adsorption of phenol and Cu²⁺ from aqueous solution by activated carbon/chitosan composite

Qian Liu*, Bingchao Yang**, Lujie Zhang*, and Ruihua Huang*[†]

*College of Science, Northwest A&F University, Yangling, Shaanxi 712100, China

**Xi'an Institute of Geology and Mineral Resource, Xi'an, Shaanxi 710054, China

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Abstract—A multifunction adsorbent was synthesized by incorporating AC into CTS, and the ratio of AC to CTS was 1/1. The resultant was called activated carbon (AC)/chitosan (CTS) composite. The simultaneous adsorption of phenol and Cu²⁺ from aqueous solution onto AC/CTS composite was investigated by a batch procedure. The adsorption processes for both Cu²⁺ and phenol obeyed the pseudo second-order kinetic model. Phenol was prone to be adsorbed more quickly as compared with Cu²⁺ when they coexisted in solution. The adsorption behavior of both phenol and Cu²⁺ followed the Langmuir isotherm. The maximum adsorption capacities of phenol and Cu²⁺ were 34.19 mg/g and 74.35 mg/g at 293 K, respectively. No obvious competitive adsorption existed between phenol and Cu²⁺.

Keywords: AC/CTS Composite, Phenol, Cu²⁺, Simultaneous Adsorption

INTRODUCTION

Inorganic and organic environmental contaminants pose a serious problem, because most of them do not undergo degradation. Inorganic elements occurring in various oxidation states are specific types of impurities, as they often have different degrees of toxicity depending on the particular oxidation state [1]. The study of simultaneous removal of phenol and Cu²⁺ from aqueous solution is important since Cu²⁺ ions and organic co-pollutants, including phenol and naphthalene, often originate from industrial sources of wastewater, such as leather tanning, photographic-filmmaking, wood preservation, petroleum refining and agricultural activity [2]. A wide range of organic pollutants including phenol, naphthalene and trichloroethylene (TCE) have been found at high concentrations in water containing heavy metals; co-pollutants of heavy metals often reach anoxic aquatic environments including groundwater aquifers, lake and river sediments and anaerobic sludge digesters.

The adsorption process is one of the most efficient methods for removing pollutants from wastewater. The advantages of adsorption process include its simplicity in operation, low cost (compared to other separation processes) and no sludge formation [3]. The adsorbent used commonly in wastewater treatment systems is AC (AC) because it has a well-developed pore structure and high internal surface area. AC can also remove highly odorous dissolved organic compounds from industrial effluents, but it is not widely applied for disposing practical wastewater because of its high cost. The coating of AC with biomaterial is a new method for the modification of AC properties. By this modification, much lower quantities of AC are needed in the adsorption process and removal process is changed to a cost-effective and environmentally benign process. CTS is a biomaterial derived by deacetylation from the polysaccharide chitin.

CTS, which is abundant in nature, has high hydrophilicity, non-toxicity, and biodegradability [4]. It has proven to be a particularly interesting adsorbent in the treatment of wastewater, especially the removal of heavy metals due to its high content of amino (-NH₂) and hydroxy (-OH) functional groups, which have high activity as adsorption sites [5].

Though there has been much interest in the use of AC or CTS as adsorbents to remove pollutants due to their advantages, almost all of these studies were single systems [6,7]. However, there are no reports about using CTS or AC to remove organic and inorganic pollutants from aqueous solutions simultaneously as far as we know.

We synthesized an adsorbent, AC/CTS composite, by incorporating AC into CTS. Phenol and Cu²⁺ were selected as model organic and heavy metal pollutants, respectively. Simultaneous adsorption of phenol and Cu²⁺ by AC/CTS composite was examined in detail with batch experiments.

MATERIALS AND METHODS

1. Materials

CTS [weight-average molecular weight (MW)=100,000 Da, degree of deacetylation (dd)=90%] was purchased from the Sinopharm Group Chemical Reagent Limited Company (China). AC powder was used without further purification. Phenol and copper sulfate with five water molecules were obtained from Aladdin (analytical grade) and used without further purification. A stock phenol solution of 1,000 mg/L was prepared by dissolving 1.00 g of phenol in 1 L of deionized water.

The phenol concentration was determined by a double beam UV-Vis spectrophotometer (Unicam UV-2, China) at 510 nm by the 4-amino-antipyrine photometry. Stock copper solution of 1,000 mg/L was prepared by dissolving 3.9295 g of copper sulfate with five water molecules in 1 L of deionized water. The copper concentration in the solution was determined by flame atomic adsorption spec-

[†]To whom correspondence should be addressed.

E-mail: huangrh20022002@aliyun.com

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trometry (TAS 990 F, PERSEE, China). Surface morphology of samples was determined by field emission scanning electronic microscope (FE-SEM) (Hitachi S4800). All other chemical reagents used in this work were of analytical grade. The pH of the solution tested was adjusted by adding 0.1 mol/L HCl or NaOH solutions.

2. Preparation of AC/CTS Composite

CTS powder was dissolved into 2% (v/v) acetic acid, thereby obtaining a 2 wt% solution. AC power was then added in this solution to a certain proportion. The mixture was coated in culture vessels and then dried at 60 °C to form membranes. Subsequently, these membranes were soaked in 0.1 mol/L NaOH solution to separate from the culture vessels. The membranes were washed with deionized water to neutral pH and were then dried at 60 °C. The dry membranes were ground to obtain 200-mesh size particles that were then used for adsorption studies.

3. Adsorption of Phenol and Cu^{2+}

Batch experiments were conducted in the adsorption of phenol and Cu^{2+} onto AC/CTS composite. The factors affecting the simultaneous adsorption of phenol and Cu^{2+} onto AC/CTS composite including the ratio of AC to CTS, adsorbent dosage, initial phenol (or Cu^{2+}) concentration, pH value of initial solution, and contact time were investigated.

Adsorption isotherm studies were conducted by mixing 0.3 g adsorbent with 50 mL solutions of various phenol and Cu^{2+} concentrations in 100 mL Erlenmeyer flasks. 0.1 mol/L HCl or NaOH solution was used for pH adjustment. After shaking at 200 rpm for a fixed time and temperature, a solution sample was taken out from

the adsorption system and analyzed for the concentration of the adsorbate.

Adsorption kinetic experiments were carried out by batch adsorption method at 293 K on a shaker at 200 rpm, using 100 mL conical flasks with 50 mL solutions and 0.3 g adsorbent. Contact time was from 5 to 240 min. Separate flasks were prepared for each time interval and only one flask was taken for the desired time.

RESULTS AND DISCUSSION

1. SEM Analysis

Fig. 1 shows the SEM micrographs of AC and AC/CTS composite under the different magnifications (1000 and 3000). From Fig. 1, AC/CTS composite had a more developed honeycomb structure compared with raw AC. Besides, this composite became rigid relative to raw CTS. The rigidity would endow this composite with good settlement. During the adsorption experiments, we truly observed that this composite could subside rapidly.

2. Effect of the Ratio of AC to CTS on Adsorption

A series of AC/CTS composite was prepared by changing the ratio of AC to CTS to investigate the effect of such a ratio on adsorption. As shown in Fig. 2, single AC and single CTS have low removal towards Cu^{2+} and phenol, respectively. However, CTS/AC composite shows relatively high removal towards both phenol and Cu^{2+} . For phenol, this composite almost remained high removal towards phenol when the ratio of AC to CTS in this composite material changed from 1/0.5 to 1/1.5. However, the removal towards phenol

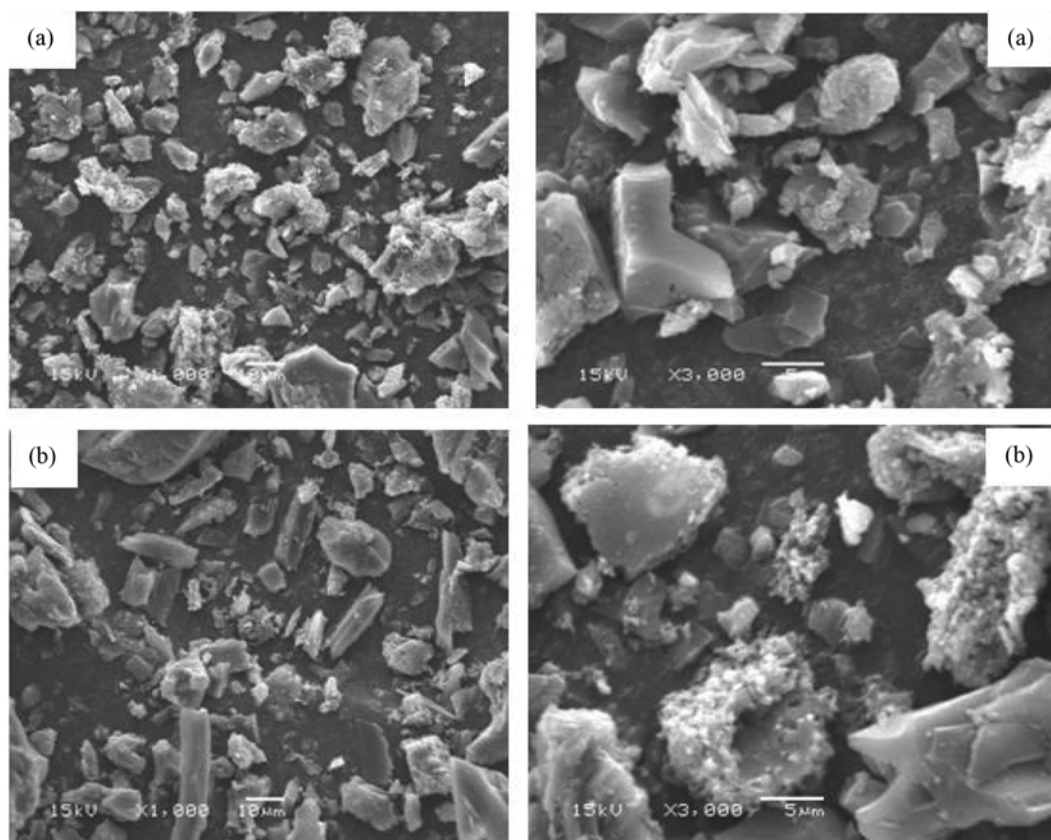


Fig. 1. SEM images of activated carbon (a) and activated carbon/chitosan composite (b).

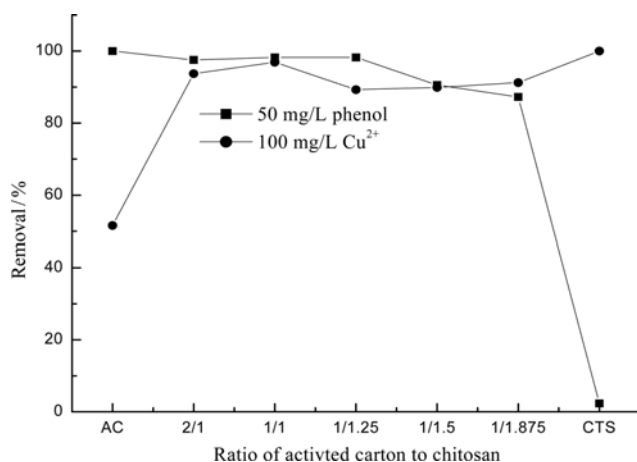


Fig. 2. Effect of the ratio of activated carbon to chitosan on adsorption. Adsorbent dosage: 0.3 g; initial phenol-Cu²⁺ concentration: 50 and 100 mg/L; temperature: 20 °C; natural pH; contact time: 40 min.

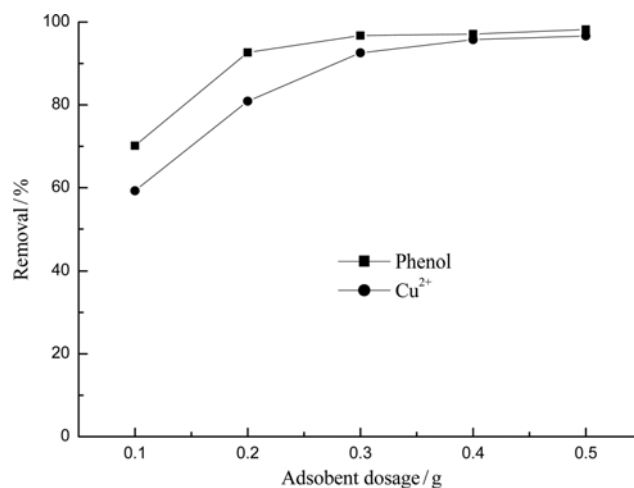


Fig. 3. Effect of adsorbent dosage on adsorption. Initial phenol-Cu²⁺ concentration: 50 and 100 mg/L; temperature: 20 °C; natural pH; contact time: 40 min.

decreased slowly with a further decrease in this ratio. A decrease in this ratio indicates a decrease in AC content in this composite. Decreasing content of AC resulted in a reasonable decrease in the removal towards phenol. For Cu²⁺, a slight increase in Cu²⁺ removal was observed when the ratio of AC to CTS changed from 1/0.5 to 1/1.875. This trend can be explained by the fact that when the ratio of AC to CTS decreases, the content of CTS in this composite increases, thus promoting the removal towards Cu²⁺. Considering the removal of phenol and Cu²⁺ as well as the compatibility between AC and CTS, the ratio of AC to CTS was fixed at 1/1 in this study.

Based on the above investigation, the preparation of AC/CTS composite is listed as follows: the ratio of AC to CTS was fixed at 1/1 in the film-forming solution. Other processes are presented in Section 2.2. AC/CTS composite obtained under these conditions was used for the subsequent experiments.

3. Effect of Adsorbent Dosage on Adsorption

As shown in Fig. 3, the removal towards phenol and Cu²⁺ increased from 70.1% to 98.2% and from 59.2% to 96.7%, respectively, when the adsorbent dosage increased from 0.1 g to 0.3 g. This increase

in removal may be attributed to the increasing sites available for adsorption as increasing adsorbent dosage [8]. However, a further increase in adsorbent dosage beyond 0.3 g exhibited no extra improvement in removal. Considering this removal and relatively less adsorbent dosage, 0.3 g of adsorbent dosage was selected for following studies.

4. Effect of Initial Phenol and Cu²⁺ Concentration on Adsorption

Adsorption experiments were performed in single systems to investigate the effect of initial concentration on adsorption. Fig. 4 shows that the removal towards both phenol and Cu²⁺ decreased with increasing phenol and Cu²⁺ concentration in single systems. The removal towards phenol decreased from 98.2% to 75.6% when the initial phenol concentration increased from 20 mg/L to 250 mg/L. The removal towards Cu²⁺ decreased from 97.1% to 70.3% when the initial Cu²⁺ concentration increased from 100 mg/L to 600 mg/L. This decrease can be explained by the fact that at low concentrations, the ratio of available sites to initial concentration is high, thus increasing the removal. However, at high concentrations, this

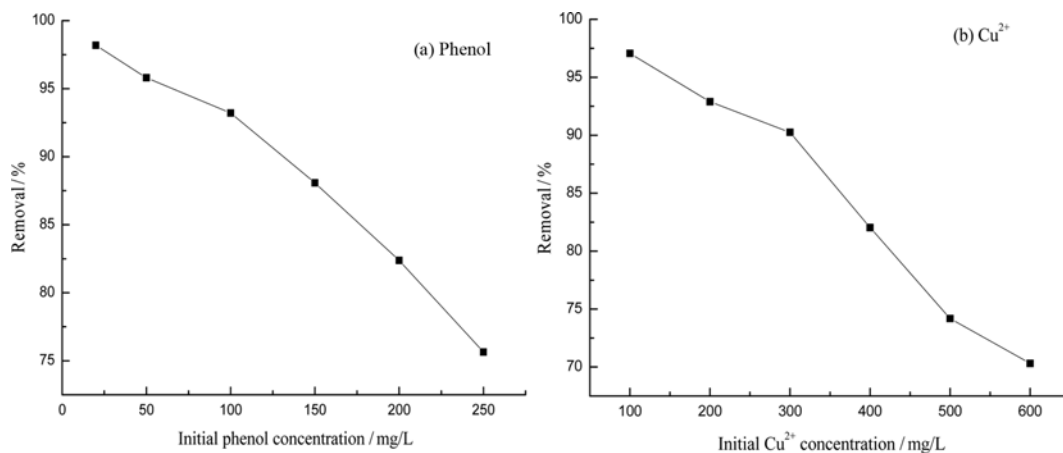


Fig. 4. Effect of initial phenol and Cu²⁺ concentrations on adsorption. Adsorbent dosage: 0.3 g; temperature: 20 °C; natural pH; contact time: 40 min.

ratio becomes low, thus decreasing the removal [9]. When phenol and Cu^{2+} concentrations were lower than 200 mg/L and 400 mg/L, respectively, the removal towards phenol and Cu^{2+} was higher than 80%.

5. Effect of pH Value of Solutions on Adsorption

The pH value of solution from which adsorption occurs may influence the extent of adsorption. In general, initial pH value may enhance or depress the uptake. The pH values of solutions ranging from 4 to 10 were investigated in order to avoid the solubility of CTS in acid and the precipitation of Cu^{2+} in alkali. The results are shown in Fig. 5. The pH of the solutions affects the existing form of phenol. The pK_a value of phenol at 20 °C is approximately 10 [10]. When the pH of the solution is lower than the pK_a of phenol, phenol molecules exist in the solution. Consequently, when the pH of the solution exceeds 10, phenol molecules are ionized to the negatively charged phenolate ions. Although the existing form of phenol varies with the pH of solutions, such pH has a minimal influence on phenol removal (Fig. 5). This condition may be attributed to the adsorption of phenol onto AC, the surface properties of which are unaffected by pH due to AC coated by CTS film. For Cu^{2+} , at low pH (<5), the chelation between Cu^{2+} and CTS weakened due to the protonation of $-\text{NH}_2$ groups in CTS, resulting in low removal towards Cu^{2+} . However, at high pH, high removal was observed, which may be attributed to the form of hydroxide precipitation ($\text{Cu}(\text{OH})_2$). In this study, the removal towards Cu^{2+} was performed by adsorption. Therefore, the pH of the solution should be lower than the critical

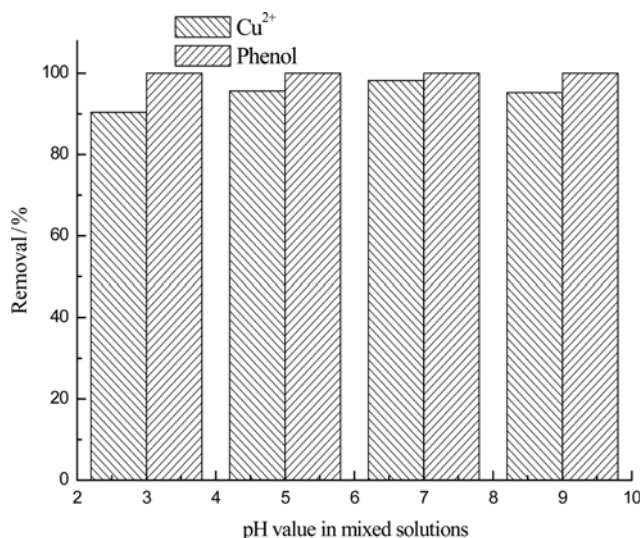


Fig. 5. Effect of pH of solutions on adsorption. Initial phenol- Cu^{2+} concentration: 50 and 20 mg/L; adsorbent dosage: 0.3 g; temperature: 20 °C; contact time: 40 min.

pH of hydroxide precipitation in order to avoid the form of hydroxide precipitation. Considering the removal towards phenol and Cu^{2+} , the pH value of mixed solution tested was in the range of 5-6 in subsequent adsorption experiments.

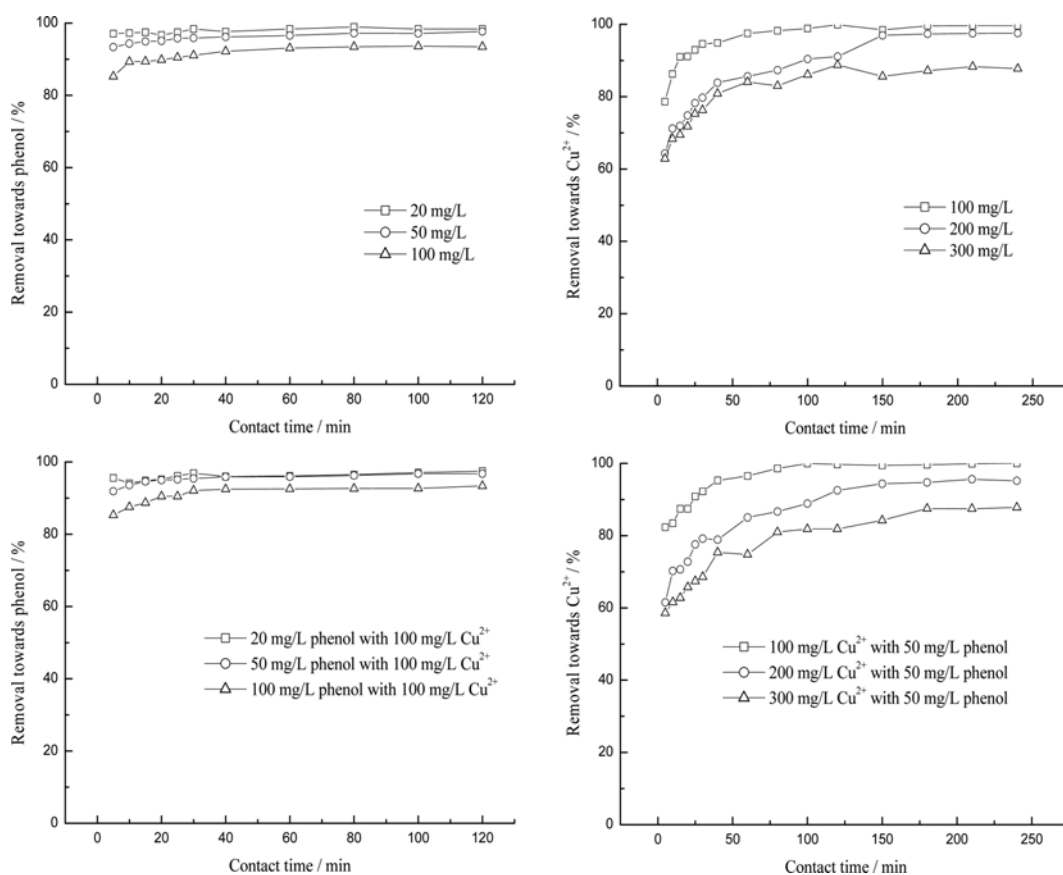


Fig. 6. Effect of contact time on adsorption. Adsorbent dosage: 0.3 g; temperature: 20 °C; the single and mixed phenol and Cu^{2+} solutions with different concentrations were tested.

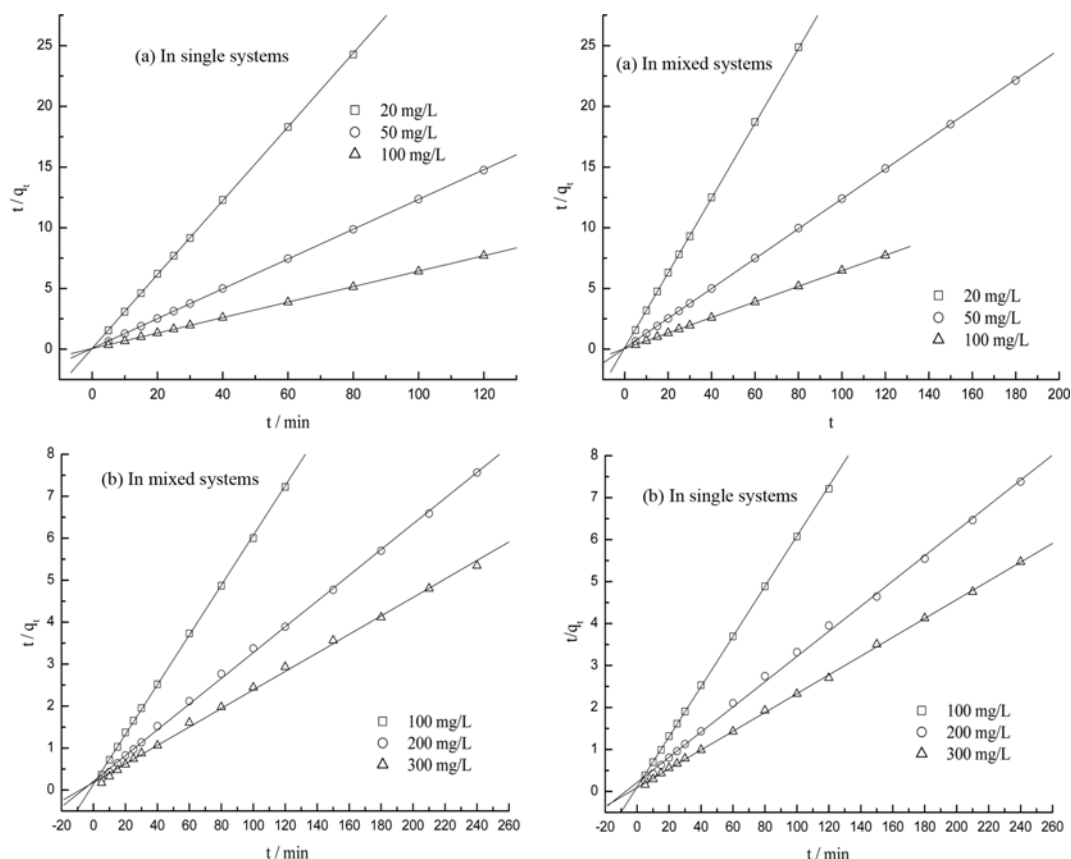


Fig. 7. Pseudo second-order kinetic model for phenol (a) and Cu^{2+} (b) adsorptions in single and mixed systems. Adsorbent dosage: 0.3 g; temperature: 20 °C; at natural pH.

6. Effect of Contact Time on Adsorption

The removal towards phenol and Cu^{2+} at different contact time is shown in Fig. 6. With increasing contact time, the removal towards phenol reaches a platform in a short time, while the removal towards Cu^{2+} increases slightly and then gradually approaches a constant value denoting equilibrium. Approximately 40 min and 180 min are adequate to attain the adsorption equilibrium for phenol and for Cu^{2+} , respectively. The results show that phenol was adsorbed more quickly compared with Cu^{2+} when phenol and Cu^{2+} existed in solutions simultaneously by this composite. This is because the adsorption of phenol onto this composite was mainly realized by the van der Waals force between phenol and AC, the adsorption of phenol onto AC/CTS composite was attributed to a physical adsorption; thus it was conducted quickly. However, Cu^{2+} was mainly adsorbed by the chelation between Cu^{2+} and CTS; thus the adsorption of Cu^{2+} onto AC/CTS composite was attributed to a chemical adsorption. The chemical adsorption was often a slow process relative to the physical one. Also, these results suggest that phenol and Cu^{2+} were adsorbed at different adsorptive sites in AC/CTS composite. Considering that no significant increase in the removal towards aniline or Cu^{2+} occurred after 180 min, the equilibrium time of 180 min was chosen and used in subsequent experiments.

To illustrate the adsorption process and provide insights into possible reaction mechanisms, a pseudo-second-order kinetic model [11] (Eq. (1)) was used to fit the experimental data, which can be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1)$$

where q_t (mg/L) and q_e (mg/L) are the amounts of adsorbed phenol (or Cu^{2+}) on this composite at equilibrium and at time t , respectively; k_2 (g/mg/min) is the rate constant for pseudo-second-order model, and $k_2 q_e^2$ is the initial adsorption rate of phenol (or Cu^{2+}). The slope and intercept of the plot t/q_t versus t (Fig. 7) denotes the rate constant and adsorption capacity, respectively. The parameters as obtained from the linearized plots are given in Table 1. As observed, the calculated adsorption capacity q_e (cal) for the pseudo-second-order model was much more closer to the experimental adsorption capacity q_e (exp) for various phenol (or Cu^{2+}) concentrations whether in single systems or in mixed systems, confirming the applicability of the pseudo-second-order model. Table 1 shows a linear relationship with very high correlation coefficients ($R^2 > 0.999$) between t/q_t and t for both phenol and Cu^{2+} , indicating that the adsorption processes of phenol and Cu^{2+} by the adsorbent followed the pseudo-second-order kinetic model quite well. The pseudo-second-order rate constant (k_2) decreased as the initial phenol (or Cu^{2+}) concentrations increased. We also observed that the rate constant, k_2 values for phenol and Cu^{2+} were obtained at 0.128 and 0.017 g/mg/min, respectively, when a mixed solution with 50 mg/L phenol and 100 mg/L Cu^{2+} was tested. This result indicated again that phenol was prone to be adsorbed more quickly compared with Cu^{2+} when they coexisted in solution, which was consistent with the above phe-

Table 1. Pseudo-second-order parameters of phenol and Cu²⁺

Parameters		Single systems				Mixed systems			
Adsorbate	Concentration/mg/L	k ₂	q _e (cal)	q _e (exp)	R ²	k ₂	q _e (cal)	q _e (exp)	R ²
Phenol	20	1.026	3.288	3.279	1.0000	0.527	3.247	3.248	1.0000
	50	0.163	8.149	8.137	1.0000	0.128	8.130	8.131	1.0000
	100	0.054	15.694	15.573	1.0000	0.063	15.603	15.560	1.0000
Cu ²⁺	100	0.023	16.734	16.595	1.0000	0.017	16.863	16.605	0.9999
	200	0.003	33.322	32.513	0.9994	0.003	32.605	31.725	0.9996
	300	0.002	44.683	43.867	0.9998	0.002	45.393	44.904	0.9991

nomena mentioned.

7. Adsorption Isotherms

To optimize the design of an adsorption system to remove phenol and Cu²⁺ from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. Several models have been used in the literature to describe the experimental data of adsorption isotherms. The Langmuir model is the most frequently employed model and given by Subramanyam and Das [12]:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

where C_e (mg/L) is phenol (or Cu²⁺) equilibrium concentration in the solution; q_e (mg/g) is the adsorption capacity, q_e (mg/g) represents maximum amount of adsorption required to form a homoge-

neous monolayer at this adsorbent, and b (L/mg) denotes Langmuir constant to give an account of adsorption energy. The intercept and slope of the linear plot between C_e/q_e versus C_e gives Langmuir constant, b and q_e , respectively.

The Freundlich isotherm is another frequently employed model that has been used to characterize the heterogeneous surface of the adsorbent [13]. Its linearized form can be expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where K_f (mg/g) and n are Freundlich constants for the adsorption capacity of the adsorbent and the intensity of adsorption, respectively. From the linearized equation of Freundlich, the slope of the graph represents the constant $1/n$, while the intercept depicts the

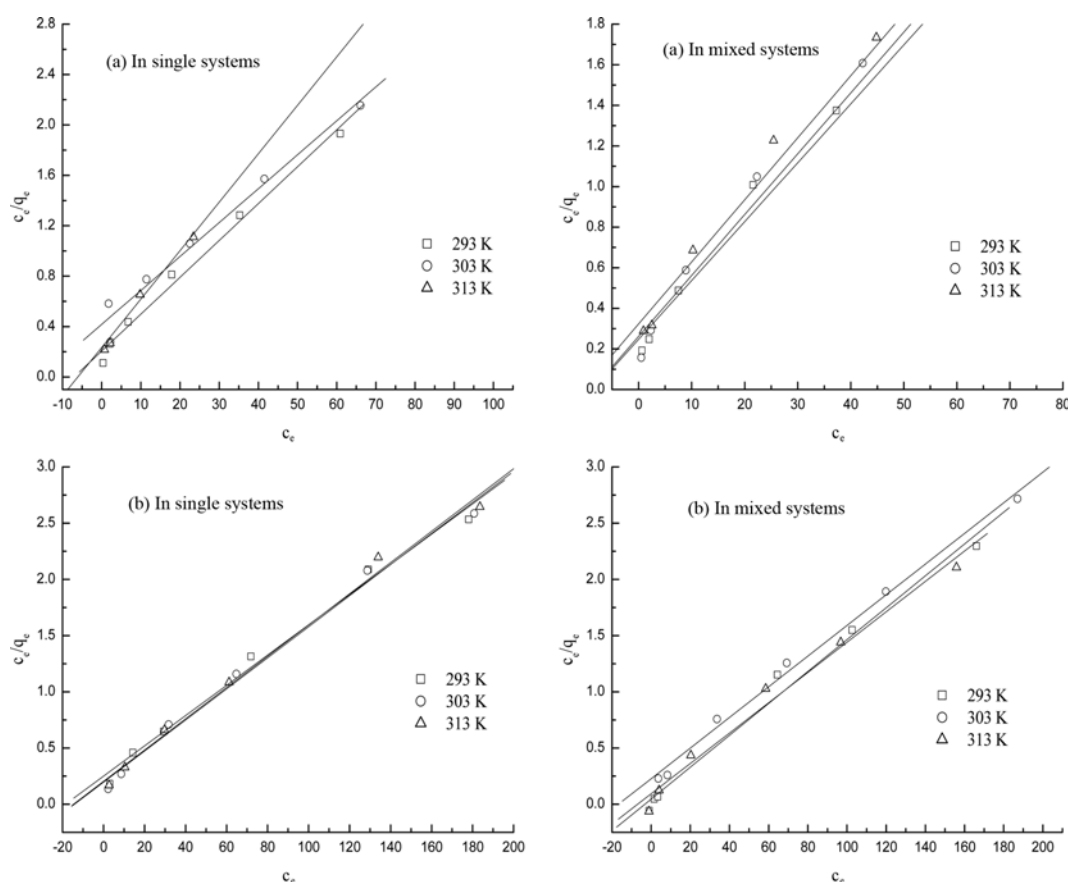


Fig. 8. Langmuir isotherm for phenol (a) and Cu²⁺ (b) adsorption in single and mixed systems. Adsorbent dosage: 0.3 g; natural pH; contact time: 180 min.

constant $\log K_f$. In addition, the value of n obtained expresses the favorability of the adsorption process. To exemplify, a value of $n > 1$ shows favorable adsorption.

The linear plots about Langmuir and Freundlich models are shown in Fig. 8 and Fig. 9, respectively. Comparisons of the experimental data and model fits of the two isotherms for phenol and Cu^{2+} are presented in Table 2. The Langmuir isotherm better described the adsorption of phenol and Cu^{2+} with the higher correlation coefficient, R^2 , and the correlation coefficients were higher than 0.98; thus the adsorption of phenol and Cu^{2+} onto this composite both followed Langmuir isotherms whether in single systems or in mixed systems. The adsorption capacities obtained in single systems were similar to the ones in mixed systems under the same adsorption temperature, suggesting the presence of Cu^{2+} had no obvious effect on the adsorption of phenol onto this composite, and vice versa. Besides, the adsorption of phenol and Cu^{2+} was favorable due to the values

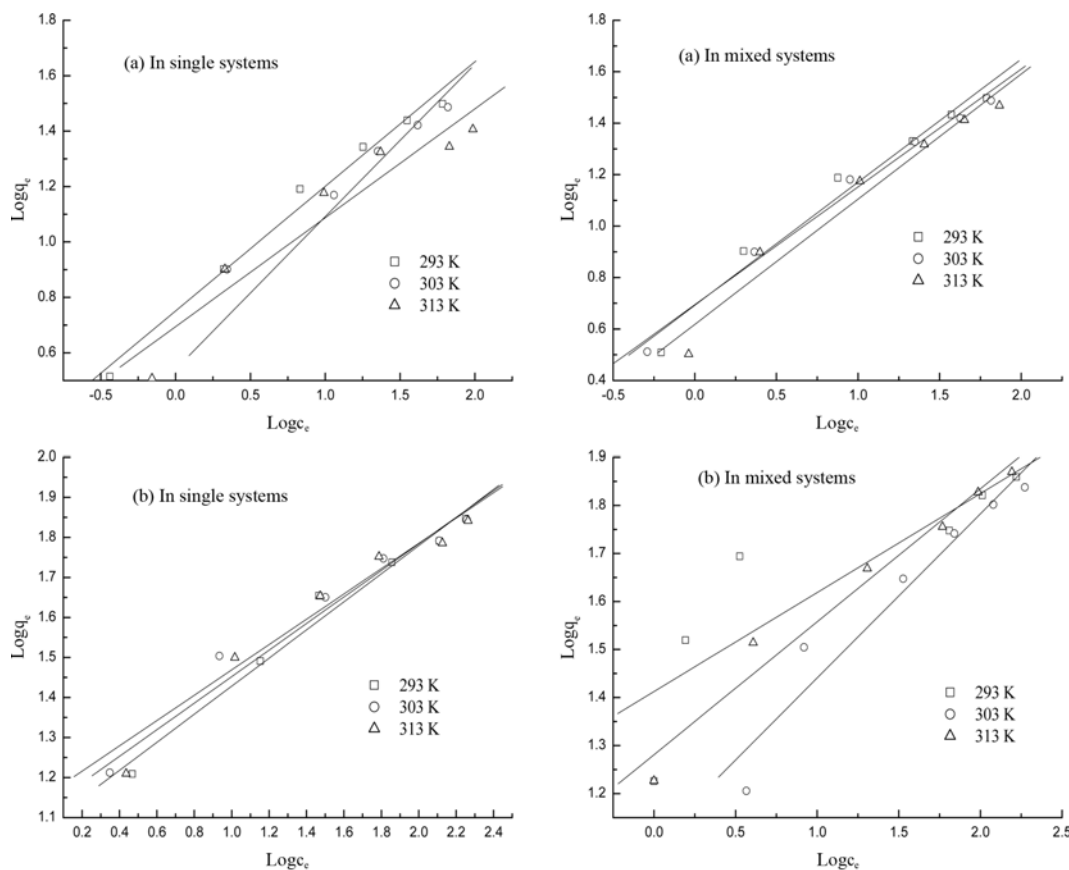


Fig. 9. Freundlich isotherm for phenol (a) and Cu^{2+} (b) adsorption in single and mixed systems. Adsorbent dosage: 0.3 g; natural pH; contact time: 180 min.

Table 2. Langmuir and Freundlich isotherm parameters of phenol and Cu^{2+} onto the adsorbents

Isotherms		Langmuir			Freundlich		
Adsorbate	Temperature/K	Q (mg/g)	b (L/mg)	R^2	$K_f (\text{mg/g}(\text{L/mg})^{1/n})$	n	R^2
Phenol in single systems	293	34.188	0.062	0.9949	0.057	2.224	0.9930
	303	37.147	0.065	0.9873	0.002	1.817	0.9475
	313	26.008	0.165	0.9964	0.026	2.545	0.9588
Phenol in mixed systems	293	34.483	0.117	0.9927	0.025	2.091	0.9856
	303	33.367	0.114	0.9918	0.026	2.183	0.9938
	313	32.712	0.095	0.9953	0.008	2.055	0.9816
Cu^{2+} in single systems	293	74.349	0.054	0.9950	2.105	2.849	0.9887
	303	72.359	0.070	0.9956	4.139	3.162	0.9855
	313	71.994	0.068	0.9964	3.113	3.014	0.9803
Cu^{2+} in mixed systems	293	70.522	0.307	0.9937	31.585	4.851	0.8647
	303	73.368	0.060	0.9973	2.570	2.927	0.9670
	313	74.129	0.145	0.9919	11.881	2.612	0.9853

of the Freundlich constant n (>1), which represents an advantageous adsorption condition. Therefore, the Freundlich exponent $1/n$ gave an indication of the favorability of phenol and Cu^{2+} adsorption by the adsorbent.

Based on the above analyses, a conclusion can be drawn that there was no competitive adsorption between phenol and Cu^{2+} . Within the concentration ranges used in the present study, the adsorption of phenol onto this composite was not affected by the presence of Cu^{2+} , and vice versa. As mentioned in section 3.6, phenol was mainly adsorbed onto AC in this composite by the van der Waals force, while Cu^{2+} was mainly adsorbed by the chelation between Cu^{2+} and CTS in this composite. No obvious competitive adsorption existed between Cu^{2+} and phenol just because of their different adsorption sites in this composite. Similar results have been obtained by Lee et al. [14]. In their investigation of the simultaneous sorption of lead and chlorobenzene by organobentonite, no significant competition was found between the sorption chlorobenzene and lead due to their different sorption sites.

CONCLUSIONS

AC/CTS composite was an effective adsorbent for the removal towards phenol and Cu^{2+} from aqueous solution. The removal towards phenol and Cu^{2+} was considerably affected by the ratio of AC to CTS, initial pH value, adsorbent dosage, initial phenol (or Cu^{2+}) concentrations and contact time. These results show that the optimal ratio of AC to CTS is 1/1, and the adsorbent dosage is 0.3 g. When the pH value of mixed solution tested was in the range of 5–6, AC/CTS composite had high removal towards phenol and Cu^{2+} . A contact time of 180 min was convenient for reaching adsorption equilibrium for both phenol and Cu^{2+} . When phenol and Cu^{2+} concentrations were lower than 200 mg/L and 400 mg/L, respectively, the removal towards phenol and Cu^{2+} was higher than 80%. The adsorption process obeyed the pseudo second-order kinetics model well. Phenol was prone to be adsorbed quickly compared with Cu^{2+} when they coexisted in solution. Langmuir isotherm model described the experimental equilibrium data for phenol and Cu^{2+} both in single

and mixed systems. No obvious competitive adsorption existed between phenol and Cu^{2+} .

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