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Simultaneous adsorption of aniline and Cu^{2+} from aqueous solution using activated carbon/chitosan composite

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ABSTRACT

A multifunction adsorbent, activated carbon (AC)/chitosan composite, was synthesized by incorporating AC into chitosan based on the ratio of AC to chitosan being 1/1. The simultaneous adsorption of aniline and Cu^{2+} from aqueous solution onto AC/chitosan composite was investigated by a batch procedure. These results showed that an adsorbent dosage of 0.3 g was appropriate, and a contact time of 210 min was convenient for reaching adsorption equilibriums for aniline and Cu^{2+}. The simultaneous adsorption of aniline and Cu^{2+} was realized in a wide pH range. The adsorption process obeyed the pseudo-second-order kinetic model. The adsorption behaviors of aniline and Cu^{2+} followed Freundlich and Langmuir, respectively. No obvious competitive adsorption existed between Cu^{2+} and aniline.

Keywords: Activated carbon/chitosan composite; Aniline; Cu^{2+}; Simultaneous adsorption

1. Introduction

Inorganic and organic environmental contaminants pose a serious problem, because most of them do not undergo degradation. Aniline is frequently applied as raw material in the manufacture of dyes, rubbers, pharmaceutical preparation, plastic, and paint. It is a toxic pollutant and its presence in wastewater even in very low concentrations has been shown to be harmful to aquatic life [1]. Cu^{2+} is an essential trace nutrient to human where it can be found in tissues, liver, muscle, and bones. However, in excessive amounts, it is toxic, which can lead to liver disease, several neurological defects, and in severe cases, death [2]. Effluents containing Cu^{2+} are widely discharged from industries, such as electroplating and mining, and have to be removed before entering the environment [3].

There are many methods for the removal of organic pollutants or heavy metals from wastewater, such as adsorption, chemical oxidation, membrane process, biological treatment, etc. [4–7]. Among these methods available, adsorption has been considered as an effective method for the removal of toxic pollutants from aqueous environment due to its simplicity of design, ease of operation, and high efficiency [8–11]. Besides, adsorption is an energy-conserving technology in the field of wastewater treatment.

The adsorbent used commonly in wastewater treatment system is activated carbon (AC) because it has a well-developed pore structure and high-internal surface area. Further, AC can remove highly odorous dissolved organic compounds from industrial effluents. Chitosan is a natural product derived by deacetylation

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from chitin. Chitosan has the properties of high hydrophilicity, non-toxicity, and biodegradability. Moreover, it is abundant in nature [12]. Chitosan has been proved to be a particularly interesting adsorbent in the field of industrial wastewater treatment, especially the removal of heavy metals due to its high content of amino (–NH_2) and hydroxy (–OH) functional groups, which have high activity as adsorption sites [13].

Though there has been much interest in the use of AC or chitosan as adsorbents to remove pollutants due to their advantages, almost all of these studies were single systems [14,15]. As we known, both industrial wastewater and domestic sewage are often a mixture of many compounds containing organic and inorganic pollutants, such as aromatic compounds and heavy metals. The interactions of these compounds may mutually enhance or mutually inhibit adsorption capacity. Recently, simultaneous adsorption of various organic and inorganic pollutants has increasingly attracted attention [16,17]. However, there are no reports about using chitosan or AC to remove organic and inorganic pollutants from aqueous solutions simultaneously as far as we know.

In this investigation, an adsorbent, AC/chitosan composite, was synthesized by incorporating AC into chitosan. Aniline and Cu^{2+} were selected as model organic and heavy metal pollutants, respectively. Simultaneous adsorption characteristics of the obtained adsorbent towards aniline and Cu^{2+} were examined in detail with batch experiments.

2. Materials and methods

2.1. Materials

Chitosan [weight–average molecular weight = 100,000 Da, degree of deacetylation = 90%] was purchased from the M/s Sinopharm Group Chemical Reagent Limited Company (China). A commercial AC powder was provided by the M/s Company of Xinhua AC in Taiyuan, Shanxi Province (China). Aniline and copper sulfate were obtained from M/s Aladdin (analytical grade) and used without further purification. Aniline stock solution of 1,000 mg/L was prepared by dissolving 1.00 g of aniline in 1 L of deionized water.

The aniline concentration was determined by a double beam UV–vis spectrophotometer (M/s Unicam UV-2, China) at 545 nm by the naphthyl ethylenediamine azo-photometry. Stock copper solution of 1,000 mg/L was prepared by dissolving 3.9295 g of copper sulfate in 1 L of deionized water. The copper concentration in the solution was determined by flame atomic adsorption spectrometry (M/s TAS 990 F, Persee, China). A pH meter (M/s Leici pHs-3c, Shanghai, China) was used to measure the pH of solutions in experiments and pH adjustments of solutions have been done by diluted HCl and NaOH. Other chemical reagents used in this study were of analytical grade and all experiments were conducted in duplicate and the average values were used for analysis.

2.2. Preparation of AC/chitosan composite

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

2.3. Adsorption of aniline and Cu^{2+}

The adsorption of aniline and Cu^{2+} onto AC/chitosan composite was evaluated by using a batch procedure. The factors affecting the simultaneous adsorption of aniline and Cu^{2+} onto AC/chitosan composite including the ratio of AC to chitosan, adsorbent dosage, initial aniline (or Cu^{2+}) concentration, pH value of initial solutions, and contact time were investigated. Besides, the adsorption isotherms and kinetics of aniline and Cu^{2+} were measured. In all adsorption experiments, a certain amount of adsorbent was placed in a 100 mL erlenmeyer flask, into which 50 mL of solution was added. The experiments were performed in a temperature-controlled water bath shaker at 200 rpm. When the defined time attained, the resultant solution was filtered by filter paper. Aniline or Cu^{2+} concentration was then measured. The adsorption experiments were conducted at 293 K, and a mixed solution of aniline and Cu^{2+} with concentrations of 50 and 100 mg/L, respectively, was tested if no special instructions.

3. Results and discussion

3.1. Effect of the ratio of AC to chitosan on adsorption

A series of AC/chitosan composite was prepared by changing the ratio of AC to chitosan to investigate the effect of such a ratio on adsorption. The results are shown in Fig. 1. Original AC and original chitosan have low removal towards Cu^{2+} and aniline, respectively. However, they show obviously high removal towards aniline and Cu^{2+}, respectively. For aniline, this composite almost remained high removal towards aniline when the ratio of AC to chitosan in this composite material changed from 1/0.5 to 1/1.25. However, the removal towards aniline 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 aniline. For Cu^{2+}, a slight increase in Cu^{2+} removal was observed when the ratio of AC to chitosan changed from 1/0.5 to 1/1.875. This trend can be explained by the fact that when the ratio of AC to chitosan decreases, the content of chitosan in this composite increased, thus promoting the removal towards Cu^{2+}. Considering the removal of aniline and Cu^{2+}, as well as the compatibility between AC and chitosan, the ratio of AC to chitosan was fixed at 1/1 in this composite.

3.2. Effect of adsorbent dosage on adsorption

In this experiment, the adsorbent dosage varied from 0.1 to 0.5 g. As shown in Fig. 2, the removal towards aniline and Cu^{2+} increased from 84.0 to 97.0% and from 61.0 to 98.4%, respectively, when the adsorbent dosage increased from 0.1 to 0.3 g. This increase in removal may be attributed to the increasing sites available for adsorption as increasing adsorbent dosage [18]. However, these removals remained almost constant when the dosage exceeded 0.3 g. The constant removal resulted from the adsorption of aniline and Cu^{2+} saturated. This study utilized 0.3 g of adsorbent dosage for the following experiments.

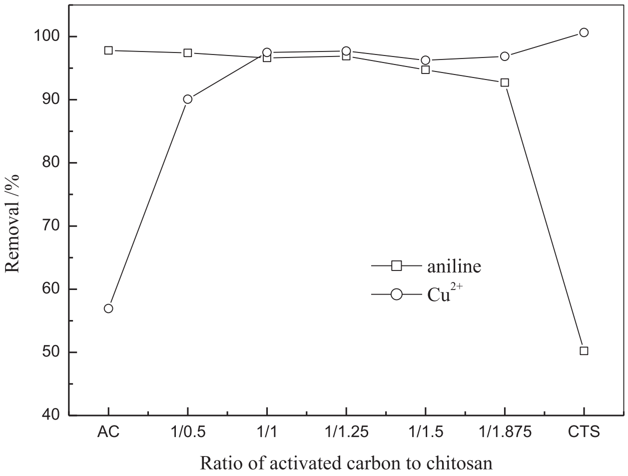

Fig. 1. Effect of the ratio of AC to chitosan on adsorption. Adsorbent dosage: 0.3 g; initial aniline –Cu^{2+} concentration: 50 and 100 mg/L; temperature: 20℃; at natural pH; contact time: 40 min.

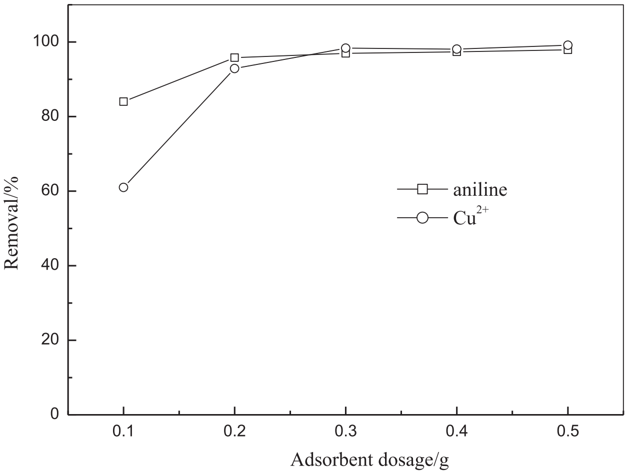

Fig. 2. Effect of adsorbent dosage on adsorption. Initial aniline–Cu^{2+} concentration: 50 and 100 mg/L; temperature: 20℃; at natural pH; contact time: 40 min.

3.3. Effect of initial aniline and Cu^{2+} concentrations on adsorption

Adsorption experiments were performed in single systems to investigate the effect of initial aniline (or Cu^{2+}) concentration on adsorption. The results in Fig. 3 show that the removal toward both aniline and Cu^{2+} decreased when increasing the concentrations of aniline and Cu^{2+}. The removal towards aniline decreased from 97.6 to 78.8% when the initial aniline concentration increased from 20 to 250 mg/L. The removal towards Cu^{2+} decreased from 97.1 to 70.3% when the initial Cu^{2+} concentration increased from 100 to 600 mg/L. This decrease in removal can be explained by the fact that at low concentrations, the ratio of available sites to initial concentration was high, thus increasing the removal. However, at high concentrations, this ratio became low, thus decreasing the removal [19]. When initial aniline and Cu^{2+} concentrations are lower than 150 and 300 mg/L, respectively, these removals of aniline and Cu^{2+} were higher than 85%.

3.4. Effect of pH value of solutions on adsorption

The initial pH of a system is known to be an important parameter for adsorption due to the influence of pH value of solutions on the adsorbent surface

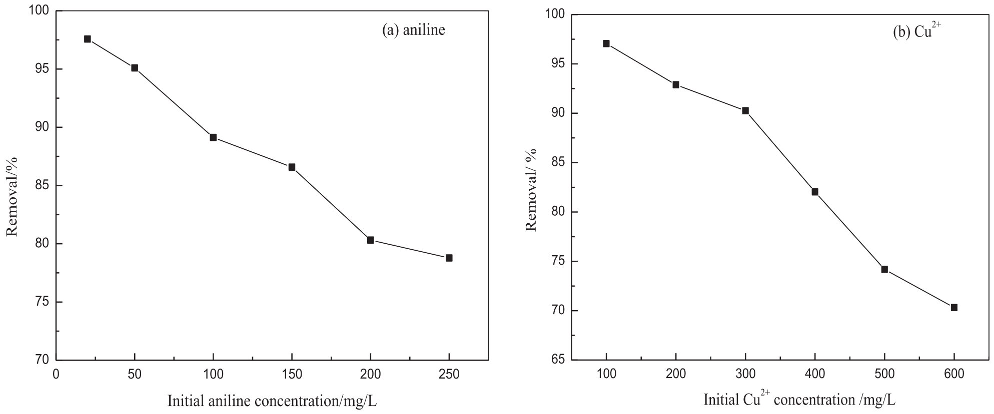

Fig. 3. Effect of initial aniline and Cu^{2+} concentrations on adsorption. Adsorbent dosage: 0.3 g; temperature: 20℃; at natural pH; adsorption time: 40 min.

properties and existing forms of aniline or Cu^{2+}. The pH values of solutions ranging from 4 to 9 were investigated in order to avoid the solubility of chitosan in acid and the precipitation of Cu^{2+} in alkali. A mixed solution of aniline and Cu^{2+} with concentrations of 50 and 20 mg/L, respectively, was tested. The results are shown in Fig. 4. It was found that the adsorption of aniline and Cu^{2+} did not favor at low pH values. For aniline, the pKa value of aniline at 20℃ is approximately 4.6 [20]. When the pH value of the solution exceeds the pK_a of aniline, aniline molecules exist in the solution. When the pH value of the solution is lower than 4.6, aniline molecules are ionized to the positively charged anilinium ions, and a part of $–NH_2$ groups in chitosan was protonated into $–NH_3^+$. At low pH (<5), it was difficult for anilinium ions to approach AC due to the repulsive interaction between $–NH_3^+$ and anilinium ions, thus low removal towards aniline was observed. However, at high pH (>5), high removal towards aniline may be attributed to this fact that aniline molecules were prone to be adsorbed onto AC in this composite by the Van der Waals force. For Cu^{2+}, at low pH (<5), the chelation between Cu^{2+} and chitosan weakened due to the protonation of $–NH_2$ groups in chitosan, resulting in low removal towards Cu^{2+}. However, at high pH, high removal was observed. This high removal may be attributed to the form of hydroxide precipitation ($Cu(OH)_2$). In this study, the removal towards Cu^{2+} was performed by adsorption. Therefore, the pH of the solution should be lower than the critical pH of hydroxide precipitation in order to avoid the form of hydroxide precipitation. In this study, the pH values of solutions were unadjusted because the pH values of mixed solution tested were in the range of 5–6.

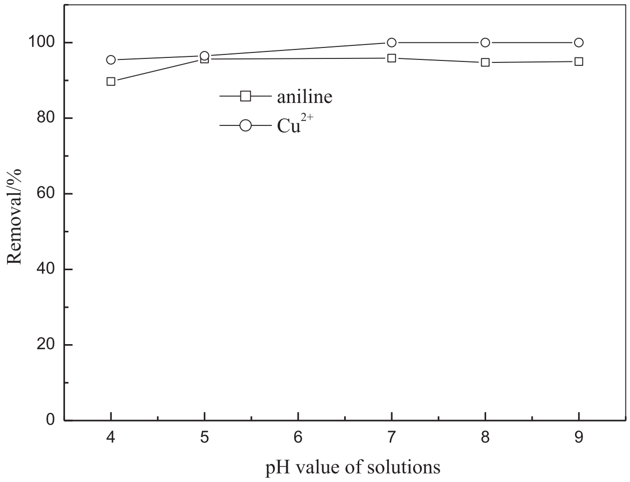

Fig. 4. Effect of pH of solutions on adsorption. Initial aniline–Cu^{2+} concentration: 50 and 20 mg/L; adsorbent dosage: 0.3 g; temperature: 20℃; adsorption time: 40 min.

3.5. Effect of contact time on adsorption

Fig. 5 shows the removal towards aniline and Cu^{2+} at different contact time. With increasing contact time, the removal towards aniline 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 and 210 min are adequate to attain the adsorption equilibrium for aniline and for Cu^{2+}, respectively. The results show that aniline was adsorbed quickly by this composite compared with Cu^{2+} when aniline and Cu^{2+} existed in solutions simultaneously. This is because that the adsorption of aniline onto this composite was mainly realized by the Van der Waals force between aniline and AC, which was attributed to a physical adsorption, the adsorption of aniline was conducted quickly. However, Cu^{2+} was mainly adsorbed by the

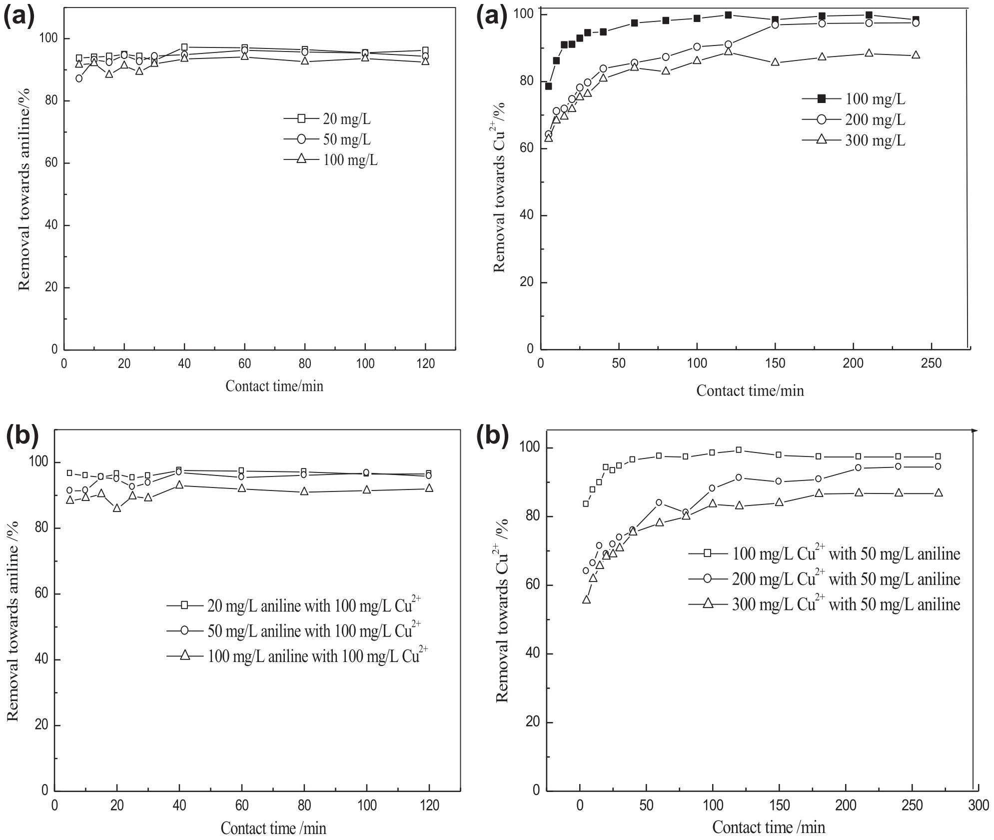

Fig. 5. Effect of contact time on aniline (a) and Cu^{2+} (b) adsorption. Adsorbent dosage: 0.3 g; temperature: 20℃; at natural pH.

chelation between Cu^{2+} and chitosan, which was attributed to a chemical adsorption, thus this adsorption was a slow process relative to the physical adsorption. Also, the results suggest that aniline and Cu^{2+} were adsorbed at different adsorptive sites in this composite. Considering that no significant increase in the removal towards aniline or Cu^{2+} occurred after 210 min, the equilibrium time of 210 min was chosen and used in subsequent experiments.

To examine the controlling mechanism of the adsorption process further, the kinetic models are often used to test the experimental data. In this study, the adsorption kinetics of both aniline and Cu^{2+} were analyzed according to the pseudo-second-order Lagergren equation [21] (Eq. (1)).

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

where q_e (mg/L) and q_t (mg/L) are the amounts of adsorbed aniline (or Cu^{2+}) on this composite at equilibrium and at time t, respectively. k_2 (g/mg/min) is rate constant for pseudo-second-order model and $k_2 q_e^2$ is the initial adsorption rate of aniline (or Cu^{2+}). The slope and intercept of the plot t/q_t vs. t (Fig. 6) 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 pseudo-second-order model was much more closer to the experimental adsorption capacity q_e (exp) for various aniline (or Cu^{2+}) concentrations whether in single systems or in mixed systems confirming the applicability of pseudo-second-order model. These results are also confirmed by high-correlation coefficient values (>0.999) for pseudo- second-order model (Table 1). Hence, the pseudo-second-order model can represent their sorption kinetics well. The pseudo-second-order rate constant (k_2) decreased as the initial aniline (or Cu^{2+}) concentrations increased. Besides, it was observed that the rate constant, k_2 values for aniline and Cu^{2+} were obtained at 0.154 and 0.061 g/mg/min, respectively, when a mixed solution with 50 mg/L aniline and 100 mg/L Cu^{2+} was tested. This result indicated again that aniline was prone to be adsorbed

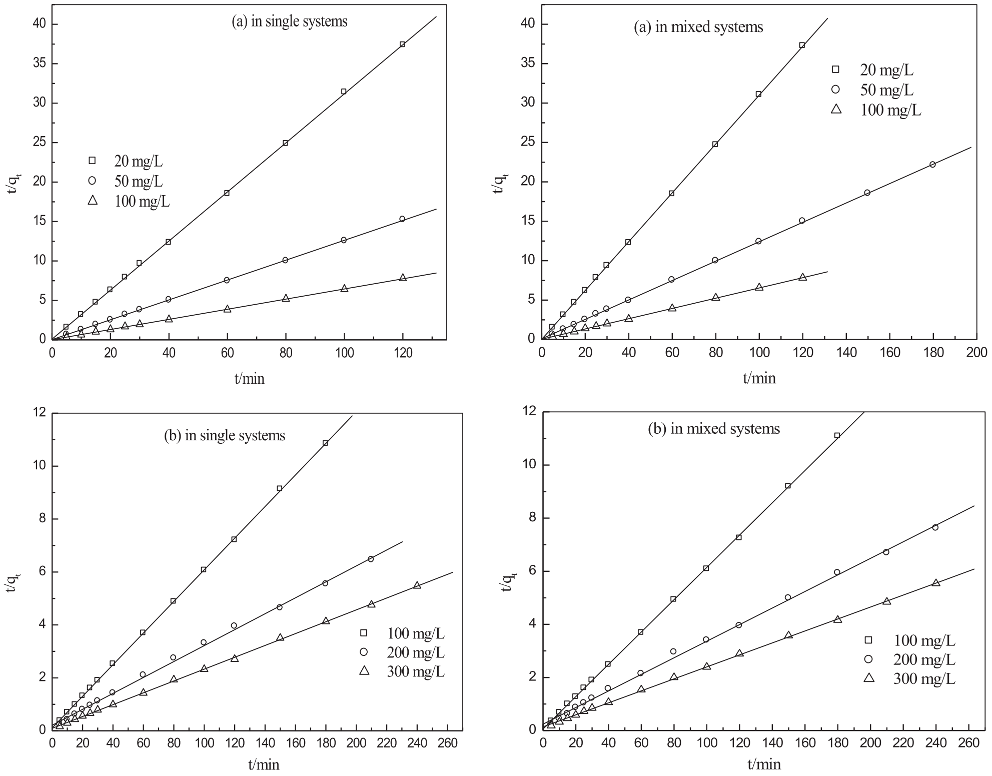

Fig. 6. Pseudo second-order kinetics model for the adsorption of aniline (a) and Cu^{2+} (b) in single and mixed systems. Adsorbent dosage: 0.3 g; temperature: 20℃; at natural pH.

Table 1
Pseudo-second-order parameters for the adsorption of aniline and Cu^{2+}

Parameters Adsorbate	Concentration/mg/L	Single systems k_2	q_e (cal)	q_e (exp)	R^2	Mixed systems k_2	q_e (cal)	q_e (exp)	R^2
Aniline	20	1.107	3.214	3.235	0.9999	5.754	3.226	3.247	1.0000
	50	0.543	7.941	8.023	0.9999	0.154	8.125	7.957	0.9999
	100	0.186	15.547	15.683	0.9999	0.122	15.361	15.320	0.9999
Cu^{2+}	100	0.034	16.734	16.595	1.0000	0.061	16.439	16.227	0.9999
	200	0.006	33.223	32.492	0.9991	0.007	32.051	31.480	0.9992
	300	0.004	44.683	43.867	0.9998	0.004	44.346	43.346	0.9997

quickly as compared with Cu^{2+} when they coexisted in solution, which was consistent with the above phenomenon mentioned.

3.6. Adsorption isotherms

To describe solid–liquid adsorption systems, two isotherms, namely Langmuir and Freundlich have been adopted. Langmuir model assume that there are fixed numbers of active sites on the surface of adsorbent [22]. However, each of this active site is only available for one absorbate molecule to be occupied. Once all the active sites were fully occupied, the surface of the adsorbent will form a homogeneous surface of monolayer adsorption. To explain the behavior of the adsorption on the equilibrium condition, the linearized form of Langmuir equation was applied and can be represented by the following:

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

where C_e (mg/L) is aniline (or Cu^{2+}) 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 homogeneous monolayer at this adsorbent, and b (L/mg) denotes Langmuir constant to give an account on adsorption energy. The intercept and slope of the linear plot between C_e/q_e vs. C_e gives Langmuir constant, b and q_e, respectively.

Freundlich isotherm has been used to characterize the heterogeneous surface of the adsorbent [23]. It is valid for multilayer adsorption on the surface of the adsorbent where there is possibility that the amount of adsorbate being adsorb on the adsorbent surface is not constant. Its linearized form can be expressed as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where K_f (mg/g(L/mg)$^{1/n}$) 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 depict the constant log K_f. In addition, the value of n obtained expressed the favorability of the adsorption process. To exemplify, value of $n > 1$ shows a favorable adsorption.

To compare the results between Langmuir and Freundlich for the adsorption of aniline (or Cu^{2+}) onto this composite, the parameters as obtained from the linearized plots (Figs. 7 and 8) are listed in Table 2. From Table 2, the values of the correlation coefficient for Freundlich isotherms were found to be higher than the ones for Langmuir, thus the adsorption of aniline onto this composite followed Freundlich isotherm whether in single systems or in mixed systems, as shown in Fig. 8. However, 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 aniline onto this composite. Besides, the adsorption of aniline was favorable due to the values of Freundlich constant n (>1). However,

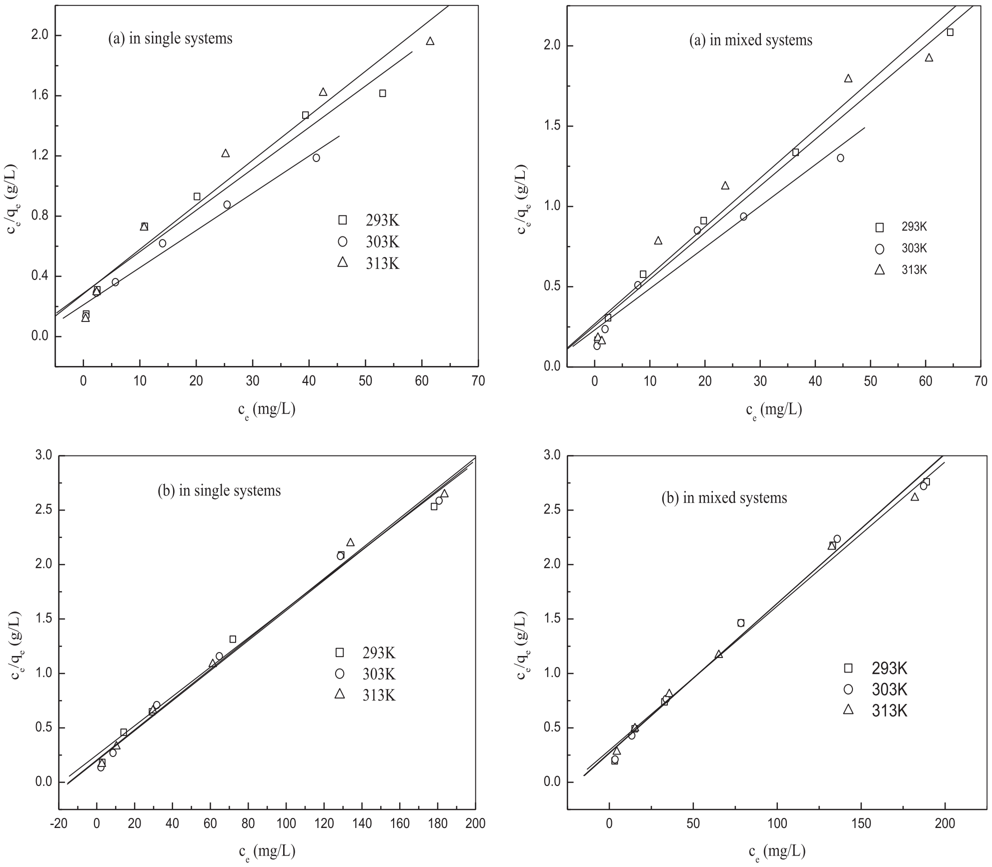

Fig. 7. Langmuir isotherm for the adsorption of aniline (a) and Cu^{2+} (b) in single and mixed systems. Adsorbent dosage: 0.3 g; at natural pH; contact time: 210 min.

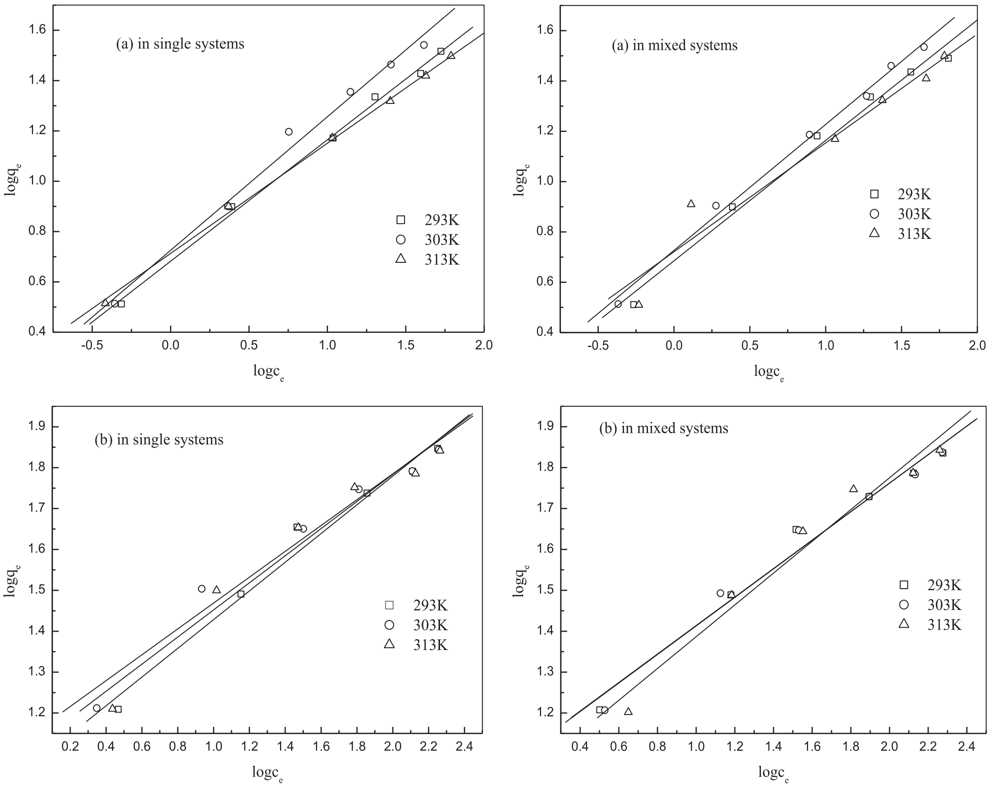

Fig. 8. Freundlich isotherm for the adsorption of aniline (a) and Cu^{2+} (b) in single and mixed systems. Adsorbent dosage: 0.3 g; at natural pH; contact time: 210 min.

the adsorption of Cu^{2+} was described well by Langmuir isotherm due to higher correlation coefficients as compared with Freundlich isotherm. The adsorption capacities both in single systems and in mixed systems were found to closely correspond with each other. This result indicated that the presence of aniline also had no obvious effect on the adsorption of Cu^{2+} onto this composite.

Based on the above analyses, a conclusion can be drawn that there was no competitive adsorption between Cu^{2+} and aniline. In other words, within the concentration ranges used in the present study, the

Table 2
Langmuir and Freundlich isotherm parameters for the adsorption of aniline and Cu^{2+}

Isotherms		Langmuir			Freundlich		
Adsorbate	Temperature (K)	Q (mg/g)	b (L/mg)	R^2	K_f (mg/g(L/mg)$^{1/n}$)	n	R^2
Aniline in single systems	293	36.32	0.096	0.9968	4.809	2.071	0.9983
	303	40.44	0.117	0.9903	5.315	1.884	0.9947
	313	33.80	0.104	0.9952	5.165	2.282	0.9973
Aniline in mixed systems	293	34.41	0.114	0.9930	4.845	2.089	0.9952
	303	38.84	0.112	0.9971	5.327	1.997	0.9976
	313	33.07	0.112	0.9775	5.260	2.311	0.9757
Cu^{2+} in single systems	293	74.35	0.054	0.9950	11.95	2.849	0.9887
	303	72.36	0.070	0.9956	14.21	3.162	0.9855
	313	71.99	0.068	0.9964	13.19	3.014	0.9803
Cu^{2+} in mixed systems	293	72.83	0.051	0.9956	11.59	2.866	0.9907
	303	72.62	0.052	0.9950	11.63	2.871	0.9883
	313	73.47	0.045	0.9967	9.955	2.574	0.9835

adsorption of Cu^{2+} onto this composite was not affected by the presence of aniline, and vice versa. As mentioned in Section 3.5, the adsorption of aniline 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 chitosan in this composite. They were adsorbed at different sites in this composite. No obvious competitive adsorption existed between Cu^{2+} and aniline just because of their different adsorption sites. Similar results have been obtained by Lee et al. [24]. In their investigation of the simultaneous sorption of lead and chlorobenzene by organobentonite no significant competition is found between the sorption chlorobenzene and lead due to their different sorption sites.

4. Conclusions

This work confirmed the potential use of AC/chitosan composite as a good adsorbent for simultaneous removal of aniline and Cu^{2+} from aqueous solution. In this study, these factors affecting the simultaneous adsorption of aniline and Cu^{2+} including the ratio of AC to chitosan, adsorbent dosage, pH value of solutions, contact time, and initial aniline (or Cu^{2+}) concentration were investigated. The result showed that the optimal ratio of AC to chitosan was 1/1, and the adsorbent dosage was 0.3 g. When initial concentrations of aniline and Cu^{2+} were lower than 150 and 300 mg/L, respectively, the removal towards aniline and Cu^{2+} was higher than 85%. A contact time of 210 min was convenient for reaching adsorption equilibriums for aniline and Cu^{2+}. The adsorption kinetics for both aniline and Cu^{2+} followed the pseudo-second-order equation well. Aniline was prone to be adsorbed quickly compared with Cu^{2+} when they coexisted in solution. No obvious competitive adsorption existed between Cu^{2+} and aniline.

Acknowledgments

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References

[1] F. An, X. Feng, B. Gao, Adsorption of aniline from aqueous solution using novel adsorbent PAM/SiO_2, Chem. Eng. J. 151 (2009) 183–187.

[2] J.Y. Uriuadams, C.L. Keen, Copper, oxidative stress, and human health, Mol. Aspects Med. 26 (2005) 268–298.

[3] C.M. Futalan, C.C. Kan, M.L. Dalida, C. Pascua, M.W. Wan, Fixed-bed column studies on the removal of copper using chitosan immobilized on bentonite, Carbohydr. Polym. 83 (2011) 697–704.

[4] L.L. Li, L.L. Fan, M. Sun, H.M. Qiu, X.J. Li, H.M. Duan, C.N. Luo, Adsorbent for chromium removal based on graphene oxide functionalized with magnetic cyclodextrin–chitosan, Colloids Surf., B 107 (2013) 76–83.

[5] S. Chelliapan, P.J. Sallis, Removal of organic compound from pharmaceutical wastewater using advanced oxidation processes, J. Sci. Res. India 72(4) (2013) 248–254.

[6] S.H. Lin, R.S. Juang, Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review, J. Environ. Manage. 90(3) (2009) 1336–1349.

[7] M. Zupanc, T. Kosjek, M. Petkovšek, M. Dular, B. Kompare, B. Širok, Željko Blažeka, E. Heath, Removal of pharmaceuticals from wastewater by biological processes, hydrodynamic cavitation and UV treatment, Ultrason. Sonochem. 20(4) (2013) 1104–1112.

[8] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye Amido Black 10B by hen feather, Environ. Sci. Pollut. Res. 20 (2013) 260–269.

[9] A. Mittal, D. Jhare, J. Mittal, Adsorption of hazardous dye Eosin Yellow from aqueous solution onto waste material De-oiled Soya: Isotherm, kinetics and bulk removal, J. Mol. Liq. 179 (2013) 133–140.

[10] H. Daraei, A. Mittal, M. Noorisepehr, F. Daraei, Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, Environ. Sci. Pollut. Res. 20 (2013) 4603–4611.

[11] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: experimental & theoretical approaches, Desalin. Water Treat. 52 (2014) 1307–1315.

[12] V.M. Boddu, K. Abburi, J.L. Talbott, E.D. Smith, R. Haasch, Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent, Water Res. 42 (2008) 633–642.

[13] Y.H. Zhu, J.J. Hu, J. Wang, Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan, J. Hazard. Mater. 221–222 (2012) 155–161.

[14] Z. Modrzejewska, Sorption mechanism of copper in chitosan hydrogel, React. Funct. Polym. 73(5) (2013) 719–729.

[15] P.C. Mishra, M. Islam, R.K. Patel, Removal of lead(II) by chitosan from aqueous medium, Sep. Sci. Technol. 48(8) (2013) 1234–1242.

[16] G.P. Agnieszka, M. Marek, P. Stanisław, S. Dariusz, Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA, Chem. Eng. J. 179 (2012) 140–150.

[17] W.W. Tang, G.M. Zeng, J.L. Gong, Y.X. Liu, X.-Y. Wang, Y.Y. Liu, Z. Liu, L. Chen, X.R. Zhang, D.Z. Tu, Simultaneous adsorption of atrazine and Cu(II) from wastewater by magnetic multi-walled carbon nanotube, Chem. Eng. J. 211–212 (2012) 470–478.

[18] A. Bhatnagar, E. Kumar, M. Sillanpää, Fluoride removal from water by adsorption—A review, Chem. Eng. J. 171 (2011) 811–840.

[19] N. Viswanathan, C.S. Sundaram, S. Meenakshi, Sorption behaviour of fluoride on carboxylated cross-linked chitosan beads, Colloids Surf., B 68 (2009) 48–54.

[20] Y.P. Chang, C.L. Ren, J.C. Qu, X.G. Chen, Preparation and characterization of Fe_3O_4/graphene nanocomposite and investigation of its adsorption performance for aniline and *p*-chloroaniline, Appl. Surf. Sci. 261 (2012) 504–509.

[21] L.J. Dong, Z.L. Zhu, H.M. Ma, Y.L. Qiu, J.F. Zhao, Simultaneous adsorption of lead and cadmium on MnO_2-loaded resin, J. Environ. Sci. 22(2) (2010) 225–229.

[22] B. Subramanyam, A. Das, Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil, Int. J. Environ. Sci. Technol. 6(4) (2009) 633–640.

[23] N. Barka, A. Assabbane, A. Nounah, L. Laanab, Y. Ichou, Removal of textile dyes from aqueous solutions by natural phosphate as a new adsorbent, Desalination 235 (2009) 264–275.

[24] J.J. Lee, J.J. Choi, J.-W. Park, Simultaneous sorption of lead and chlorobenzene by organobentonite, Chemosphere 49 (2002) 1309–1315.