

## Simultaneous Adsorption of Aniline and Cr(VI) Ion by Activated Carbon/Chitosan Composite

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**ABSTRACT:** Activated carbon/chitosan composite has been used as an adsorbent to remove aniline and Cr(VI) ions from aqueous solutions simultaneously. The effects of preparation conditions such as the ratio of activated carbon to chitosan, crosslinking reagents, crosslinking time, and adsorption conditions including adsorbent dosage, pH value of solution, and contact time on simultaneous adsorption of aniline and Cr(VI) ion were investigated. Experimental results showed that epichlorohydrin was the proper crosslinking reagent, and the ratio of activated carbon to chitosan was kept at 1. When the adsorbent dosage was 4.0 g/L, and the concentrations of aniline and Cr(VI) were lower than 50 and 100 mg/L, respectively, both aniline and Cr(VI) were simultaneously removed at natural pH with high removals (>95%). The presence of Cr(VI) enhanced the adsorption of aniline, while the presence of aniline almost had no influence on the adsorption of Cr(VI). The adsorption processes of both aniline and Cr(VI) followed the pseudo-second-order kinetics model, but the sorption of Cr(VI) was preferential to that of aniline by this composite. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39903.

**KEYWORDS:** adsorption; composites; applications; membranes

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### INTRODUCTION

Inorganic and organic environmental contaminants often exist simultaneously in wastewater, especially in industrial wastewater. 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.<sup>1–3</sup>

Chromium exists in the environment in the trivalent state, that is, in the cationic form as Cr(III), or in the hexavalent state as the Cr(VI) anions:  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{Cr}_2\text{O}_7^{2-}$ . Cr(VI) is toxic to both plants and animals. Cr(VI) is approximately 100 times more toxic than Cr(III). Aniline is an oily and colorless liquid. Chemically, it is a highly acrid poison, which is dangerous for health. It causes an unpleasant taste and odor even at low concentrations in water. During water treatment, a great variety of processes have been developed, such as coagulation/flocculation, membrane separation, advanced oxidation, ion-exchange, and adsorption.<sup>4–7</sup> Of them, adsorption has been considered as an effective process due to its simplicity of design, ease of operation, and high efficiency.

Activated carbon (AC) with large surface area has been attracted for a long time as an efficient adsorbent to adsorb various pol-

lutants. Although AC is favorable to remove natural organic matter such as aniline and phenol, the lack of dispersion of AC powder brings a pity to its further application. Chitosan (CS) is a cationic biopolymer obtained from the deacetylation of chitin which is the second most abundant biopolymer in nature. CS has received considerable attention as an excellent natural adsorbent to remove many heavy metal ions due to the presence of amine groups and hydroxyl groups on the main chain which act as chelation sites for metal ions. However, raw CS is soft and has a tendency to agglomerate or form a gel in aqueous media, rendering most of the amino and hydroxyl groups inaccessible for pollutant binding.<sup>8,9</sup> In addition, raw CS is very sensitive to pH as it can dissolve in acidic medium.<sup>10</sup> CS composites have been proven to have better adsorption capacity and resistance to acidic environment.<sup>11</sup> Different kinds of substances have been used to form composite with CS such as sand,<sup>12</sup> bentonite,<sup>13</sup> fly ash,<sup>14</sup> montmorillonite,<sup>15</sup> and granular AC.<sup>16</sup> However, most adsorption systems focus on single metal ions or organic pollutants, when these composites were used as adsorbents. There are few reports about the simultaneous adsorption of metal-organic pollutants. As we know, 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.<sup>17,18</sup>

In this study, a kind of AC and CS composite was prepared. Cr(VI) and aniline was selected as a model metal and organic pollutant, respectively. Simultaneous adsorption of aniline and Cr(VI) on this composite was investigated. The important factors affecting the adsorption, such as the preparation conditions of this composite and adsorption conditions were studied. Besides, the adsorption isotherms and kinetics were also discussed.

## MATERIALS AND METHODS

### Materials

CS (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 provided by the company of Xinhua AC in Taiyuan, Shanxi Province (China). Aniline was obtained from Aladdin (analytical grade) and used without further purification. Potassium dichromate, acetic acid, and other chemical reagents used in this work were of analytical grade. A stock aniline solution of 1000 mg/L was prepared by dissolving 1.00 g of aniline in 1 L of deionized water. Also, a stock chromium solution of 1000 mg/L was prepared by dissolving 2.828 g of potassium dichromate in 1 L of deionized water.

The concentration of aniline was determined with spectrophotometer (Unicam UV-2) at 545 nm by the *N*-(1-naphthyl)ethylenediamine method. The concentration of total chromium was determined by flame atomic adsorption spectrometry (HITACHI Z-2000). The surface morphology of the adsorbent was visualized by field emission scanning electron microscope (SEM) (S-8400, Japan). Fourier-transform infrared spectroscopy (FTIR) of the samples was taken by using an Avatar-360 IR spectrometer from Nicolet in the wave number range of 400–4000 cm<sup>-1</sup>. The pH value of solution tested was adjusted by adding 0.1M HCl or NaOH solutions.

### Preparation of AC/CS Composite

CS powder was dissolved into 2% (v/v) acetic acid solution, thereby obtaining a 2 wt % solution. AC was then added in CS solution based on the ratio of AC to CS being 1. The mixture was coated in culture vessels and dried at 60°C to form membranes. After these membranes were soaked in 0.1M NaOH solution to separate from the culture vessels, they were washed with deionized water to neutral pH and dried at 60°C in oven. According to the previous study,<sup>19</sup> the dry membranes were crosslinked with epichlorohydrin (ECH) at 60°C. Crosslinked membranes were washed with deionized water to remove any free crosslinking reagents and then treated for 90 min using concentrated HCl at 20°C. The composite obtained was washed with deionized water to neutral pH, and dried at 60°C in oven, which were used for adsorption studies.

### Effect of Adsorption Parameters

Batch adsorption experiments were conducted in 150 mL Erlenmeyer flask, into which 50 mL of solution was added in a

shaker at 200 rpm at 20°C. Subsequently, the adsorbents were separated followed by the analysis of residual aniline (or Cr(VI)) concentrations in supernatant.

In the first set of experiments, the aniline–Cr(VI) mixed solution was tested. The initial concentrations of aniline and Cr(VI) were fixed at 50 and 100 mg/L, respectively. The effect of the preparation conditions of AC/CS composite, which included the ratio of AC to CS, crosslinking reagents, and crosslinking time on the adsorption of aniline and Cr(VI) was investigated. In the second set of experiments, the aniline–Cr(VI) mixed solution was still tested. The initial concentrations of aniline and Cr(VI) were fixed at 50 and 100 mg/L, respectively. The effect of adsorption conditions, which included adsorbent dosage, contact time, and pH of solutions on the adsorption of aniline and Cr(VI) was studied. In the third set of experiments, competitive adsorption studies were conducted when both aniline and Cr(VI) were adsorbed onto AC/CS composite simultaneously. The concentration of Cr(VI) was fixed at 100 mg/L (or aniline 50 mg/L) while the concentration of aniline (or Cr(VI)) varied.

### Adsorption Isotherms

The sorption isotherm experiments were performed in flasks containing 50 mL of 4 g/L AC/CS composite and initial concentrations of aniline varying from 20 to 250 mg/L or Cr(VI) varying from 100 to 500 mg/L at natural pH for 80 min at 273 K. Langmuir, Freundlich, and Redlich-Peterson sorption isotherm models were used to determine the proper isotherm for aniline and Cr(VI) adsorption by this composite. The Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. Langmuir's equation involves two parameters, was expressed as follows:

$$q_e = \frac{q_m b c_e}{1 + b c_e} \quad (1)$$

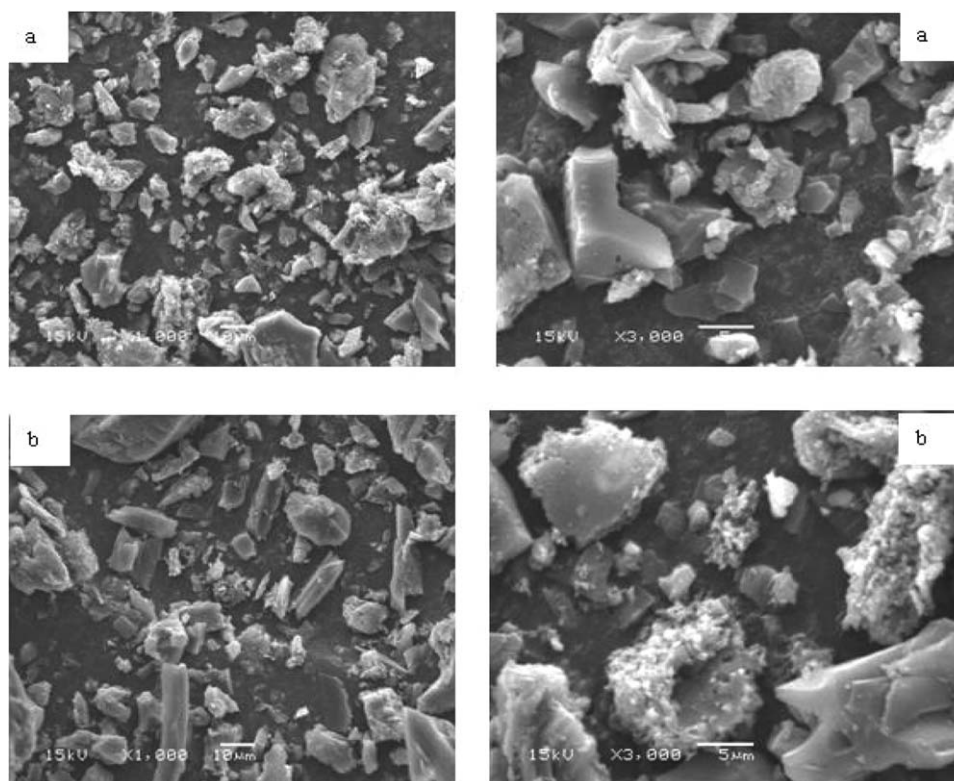
where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g),  $c_e$  is the equilibrium concentration of the solute in the bulk solution (mg/L),  $q_m$  is the maximum adsorption capacity (mg/g), and  $b$  is the constant related to the free energy of adsorption (L/mg).

The Freundlich isotherm describes a heterogeneous system and reversible adsorption and is not restricted to monolayer formation, and is expressed as follows:

$$q_e = K_F c_e^{1/n} \quad (2)$$

where  $K_F$  is a constant, it indicates the relative adsorption capacity of the adsorbent (mg<sup>1-(1/n)</sup> L<sup>1/n</sup>/g) and  $1/n$  is the adsorption intensity.

The Redlich-Peterson isotherm combines elements from both the Langmuir and Freundlich equations, where the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. It is widely used as a compromise between Langmuir and Freundlich systems. Redlich-Peterson isotherm incorporates three parameters and can be applied either in homogenous or heterogeneous systems. It was expressed as follows:



**Figure 1.** SEM images of AC (a) and AC/CS composite (b).

$$q_e = \frac{K_{RP} c_e}{1 + a_{RP} c_e^\beta} \quad (3)$$

where  $K_{RP}$  (L/mg) and  $a_{RP}$  (mg/L) $^\beta$  are Redlich-Peterson isotherm constants and  $\beta$  is the exponent which lies between 1 and 0.

#### Adsorption Kinetics

The effect of contact time on the adsorption of aniline (or Cr(VI)) by AC/CS composite was studied in flasks containing 50 mL of 50 mg/L aniline (or 100 mg/L Cr(VI)) and 4 g/L AC/CS composite at natural pH. The samples were taken from different flasks at predetermined time intervals (from 0 to 120 min), and the remaining aniline (or Cr(VI)) concentrations in supernatant were determined.

To illustrate the adsorption process and provide insights into possible reaction mechanisms, a pseudo-second-order kinetic model was used to fit the experimental data, which can be expressed as:

$$\frac{1}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} \quad (4)$$

where  $k$  (g/mg min $^{-1}$ ) is the pseudo-second-order rate constant,  $q_t$  (mg/g) and  $q_e$  (mg/g) are the adsorbed amount of adsorbate at any time and at equilibrium, respectively.

## RESULTS AND DISCUSSION

### Characterization of AC/CS Composite

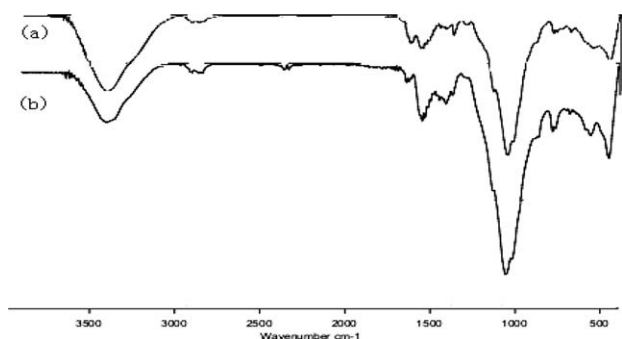
**SEM Analysis.** Figure 1 shows the SEM micrographs of AC and AC/CS composite under the different magnifications (1000 and 3000). From Figure 1, it was found that AC/CS composite had a more developed honeycomb structure compared with raw AC. Besides, this composite became rigid relative to raw CS. The

rigidness would endow this composite with good settlement. During the adsorption experiments, we truly observe that this composite can subside rapidly.

**FTIR Spectra Analysis.** The FTIR spectra of simple AC/CS composite (without crosslinking and treatment of concentrated HCl) and AC/CS composite were measured by an FTIR spectrometer within the range of 400–4000 cm $^{-1}$  wave number and are shown in Figure 2. In FTIR spectra for simple AC/CS composite, the adsorption band around 3420 cm $^{-1}$  can be attributed to the stretching vibration of —OH, extension vibration of N—H bonds<sup>20,21</sup> and adsorption band at 1637 cm $^{-1}$  can be attributed to N—H bending vibrations of NH $_2$  group of CS,<sup>20</sup> and 1384 cm $^{-1}$  confirms —NH deformation vibration in —NH $_2$ .<sup>22</sup> The peaks at 2917, 2870, and 1422 cm $^{-1}$  present C—H aliphatic stretching, —O—CH $_3$  of aldehyde group, stretching vibrations of C=O in carbonyl, and stretching of C—O or O—H deformation in carboxylic acids, respectively.<sup>23</sup> In FTIR spectra for AC/CS composite, an obvious decrease in the peak at 1637 cm $^{-1}$  was observed. This decrease may be attributed to the fact that a part of —NH $_2$  groups in CS was protonated. Besides, it was found that the peaks at 1422 cm $^{-1}$  almost appeared. However, the peak around 3420 cm $^{-1}$  enhanced obviously, which was due to the introduction of —OH groups from the crosslinking reaction between ECH and CS.

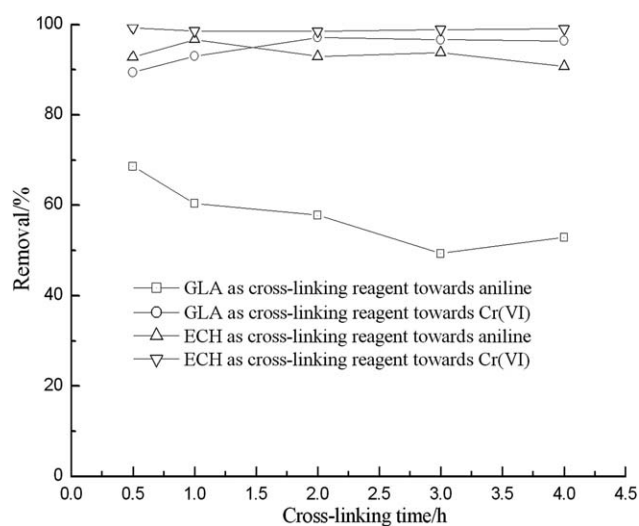
### Effect of the Preparation Conditions of AC/CS Composite on Adsorption

**Effect of Crosslinking Reagents and Crosslinking Time.** The application of CS is limited due to its solubility in acidic conditions and unsatisfied mechanical properties. CS is often crosslinked to overcome these disadvantages. ECH and



**Figure 2.** FTIR spectra of simple AC/CS composite (a) and AC/CS composite (b).

gluteraldehyde (GLA) often act as the crosslinking reagents of CS. Two different types of AC/CS composite were synthesized by using ECH and GLA as crosslinking reagents. Figure 3 shows that the composite obtained by using ECH shows higher removal toward aniline than those obtained by using GLA. This trend can be explained like this. During the preparation process of this adsorbent, AC was dispersed in the membrane-forming solution of CS. The membrane was covered on the surface of AC. After these membranes were crosslinked, the network structure was formed. When GLA acted as crosslinking reagent, the network structure formed may be compact relative to ECH, and aniline was not liable to approach the adsorption sites onto AC, leading to a low removal toward aniline. However, the crosslinking reagents have no influence on the adsorption of Cr(VI) and high removals was observed, which may be attributed to the adsorption of Cr(VI) mainly occurring onto CS. After the composite was treated further by concentrated HCl, a part of  $-\text{NH}_2$  groups were protonated into  $-\text{NH}_3^+$ , and the positive charge of AC/CS composite enhanced, thus facilitating Cr(VI) removal because of the strong electrostatic interaction between

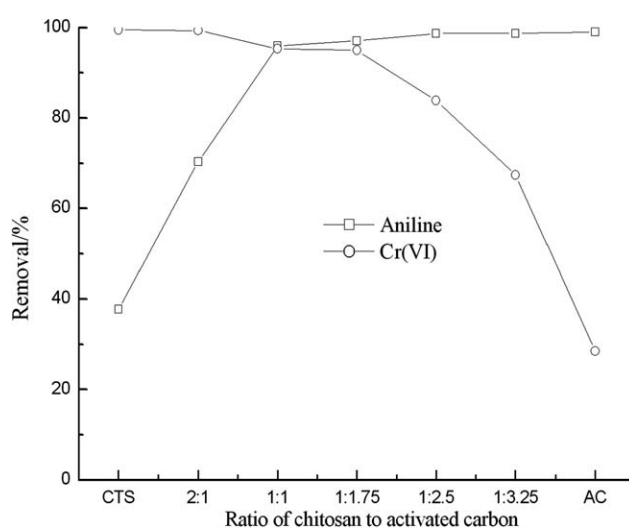


**Figure 3.** Effect of crosslinking reagents and crosslinking time on simultaneous adsorption of aniline and Cr(VI). Adsorption conditions: adsorbent dosage: 4 g/L; initial aniline-Cr(VI) concentration: 50 and 100 mg/L; temperature: 20°C; at natural pH; contact time: 40 min.

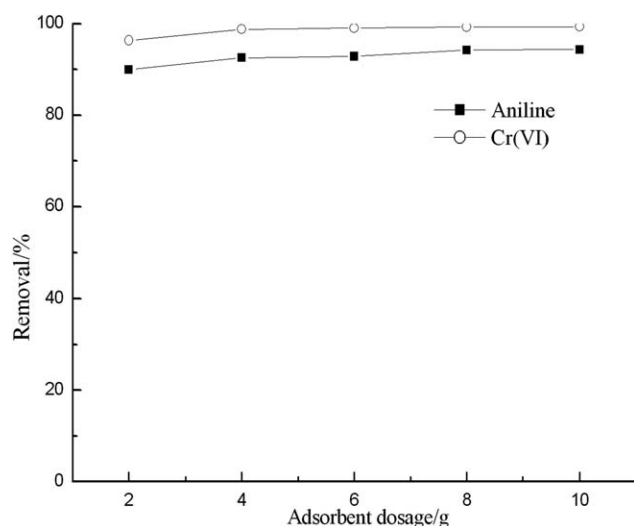
Cr(VI) and  $\text{NH}_3^+$ . Besides, the removal toward aniline decreased due to compact network structure with increasing crosslinking time. Considering the removal of aniline and Cr(VI) together, ECH was selected as the crosslinking reagent and 1 h of crosslinking time was adopted.

**Effect of the Ratio of CS to AC.** A series of AC/CS composite was prepared by changing the ratio of CS to AC to investigate the effect of such ratio on adsorption. The results are shown in Figure 4. Single AC and single protonated crosslinked CS have high removals toward aniline and Cr(VI), respectively. The removal toward aniline increases when decreasing the ratio of CS to AC. A decrease in this ratio indicates an increase in the content of AC or a decrease in the content of CS. As we know, AC often allows high removals toward organic pollutants including aniline.<sup>24</sup> An increase in the content of AC resulted in a reasonable increase in the removal of aniline, afterward a constant removal toward aniline (98.7%) was observed with a further increase in AC. This constant removal may be attributed to the adsorption sites saturated under low aniline concentration tested. However, the removal toward Cr(VI) decreased slightly when the ratio of CS to AC decreased. This trend can be explained like this. When the ratio of CS to AC decreased, that is, the content of CS reduced, the  $-\text{NH}_2$  protonated reduced accordingly, resulting in the decreasing removal of Cr(VI). Considering the removal of aniline and Cr(VI) together, the ratio of CS to AC was fixed at 1.

Based on the above investigation, the preparation of AC/CS composite is listed as follows: the ratio of CS to AC was fixed at 1 in the membrane-forming solution. The membranes were crosslinked with ECH solution for 1 h before being protonated. Other processes were presented in Effect of Ration of Chitosan to AC section. The AC/CS composite obtained under these conditions was used for the subsequent experiments.



**Figure 4.** Effect of the ratio of CS to AC on simultaneous adsorption of aniline and Cr(VI). Adsorption conditions: adsorbent dosage: 4 g/L; initial aniline-Cr(VI) concentration: 50 and 100 mg/L; temperature: 20°C; at natural pH; contact time: 40 min.

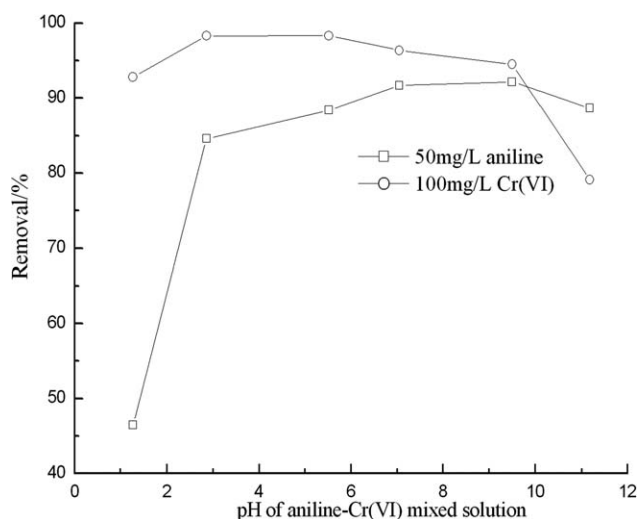


**Figure 5.** Effect of adsorbent dosage on adsorption on simultaneous adsorption of aniline and Cr(VI). Adsorption conditions: adsorbent dosage: 2–10 g/L; initial aniline–Cr(VI) concentration: 50 and 100 mg/L; temperature: 20°C; at natural pH; contact time: 40 min.

### Effect of the Adsorption Conditions on Adsorption

**Effect of Adsorbent Dosage on Adsorption.** The effect of adsorbent dosage on the adsorption process was studied with the constant Cr(VI) and aniline concentrations of 100 and 50 mg/L, respectively, in a mixed solution, and the results are illustrated in Figure 5. It is clear from the figure that the removals of Cr(VI) and aniline increased from 96.3% to 98.7% and from 90.0% to 92.6%, respectively, when the adsorbent dosage increased from 2 to 4 g/L. The increase in removal toward aniline and Cr(VI) from aqueous solution was primarily due to the greater number of active sites available for adsorption as a result of the increased amount of adsorbent. The removal toward Cr(VI) remained almost constant when the dosage exceeded 4 g/L. This trend resulted from the sites that remained saturated during adsorption. However, the removals toward aniline increased with an increase in adsorbent dosage until it was 8 g/L. In this study, 4 g/L of adsorbent dosage was fixed as the optimum dosage which had given relatively high removals toward both aniline and Cr(VI).

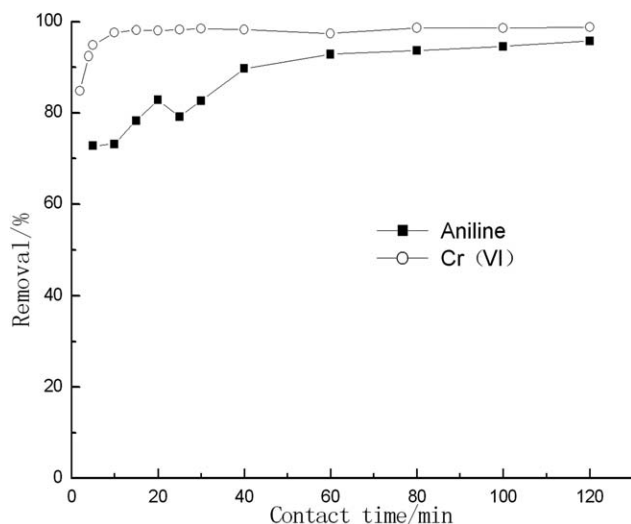
**Effect of the pH Value of the Solutions on Adsorption.** The initial pH of a system is known to be an important parameter for adsorption due to the influence of pH on the surface properties of this adsorbent and ionic forms of Cr(VI) ions or aniline in mixed solution. The effect of the solution pH on the removal of aniline and Cr(VI) by this composite was studied, and the results are presented in Figure 6. The Cr(VI) species may generally be represented in various forms, such as  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{H}_2\text{CrO}_4$ , in the solution as a function of pH. At lower pH values (<2), the Cr(VI) species exist in the form of  $\text{H}_2\text{CrO}_4$ , the electrostatic force between the positively charged surface and Cr(VI) weakened. Thus, less Cr(VI) ions were adsorbed onto this composite within a lower pH. At higher pH value (>10), the Cr(VI) species exist in the form of  $\text{CrO}_4^{2-}$ , a decrease in the adsorption of Cr(VI) may be attributed to the competition between  $\text{CrO}_4^{2-}$  and  $\text{OH}^-$  for adsorption sites on



**Figure 6.** Effect of pH of aniline–Cr(VI) mixed solution on simultaneous adsorption of aniline and Cr(VI). Adsorption conditions: adsorbent dosage: 4 g/L; initial aniline–Cr(VI) concentration: 50 and 100 mg/L; temperature: 20°C; pH: 1–11; contact time: 40 min.

the surface of adsorbent. The high removal toward Cr(VI) can be achieved among a broad solution pH range. For aniline, aniline has a  $\text{pK}_a$  value of 4.63.<sup>25</sup> At an acidic pH of 3.0, aniline will be in the form of anilinium cation. The removal toward aniline from aqueous solution was very low at this pH. This low removal was primarily due to the electrostatic repulsion between the positively charged protonated CS and the positively charged, anilinium cation. The electrostatic repulsion did not facilitate the adsorption of aniline onto AC. Increasing the pH from 3.0 to 8.0, which was higher than the  $\text{pK}_a$  of aniline, aniline was mainly in the molecular form, enhanced the removal toward aniline due to dispersive interactions between aniline and AC. Over a pH of 8.0, the removal toward aniline decreased slightly. Considering the removal of aniline and Cr(VI) together, the adsorption experiments were conducted at natural pH.

**Effect of Contact Time on Adsorption.** The effect of the contact time on the removal of aniline and Cr(VI) by this composite was studied, and the results are shown in Figure 7. For aniline, it is obvious from the figure that the adsorption rate increased dramatically within 40 min as the removal reached 89.8%. Subsequently, a slight increase occurred during the next several minutes and apparent equilibrium was achieved at 100 min. During the initial stage of sorption, a large number of vacant surface sites were available for adsorption. After a lapse of some time, the remaining vacant surface sites were difficult to be occupied due to steric effect, resulting in a relatively long time to reach the equilibrium. For Cr(VI), the removal rate was found to be very rapid during the initial 10 min, and no significant change in Cr(VI) removal was observed after about 10 min. The rapid adsorption during the initial stage of sorption was attributed to the strong electrostatic interaction between Cr(VI) ions and protonated CS in this composite as well as the fast diffusion of Cr(VI) ions. Their adsorption trends as a



**Figure 7.** Effect of contact time on simultaneous adsorption of aniline and Cr(VI). Adsorption conditions: adsorbent dosage: 4 g/L; initial aniline-Cr(VI) concentration: 50 and 100 mg/L; temperature: 20°C; at natural pH; contact time: 5–120 min.

function of contact time indicate that Cr(VI) ions had a faster adsorption rate than aniline.

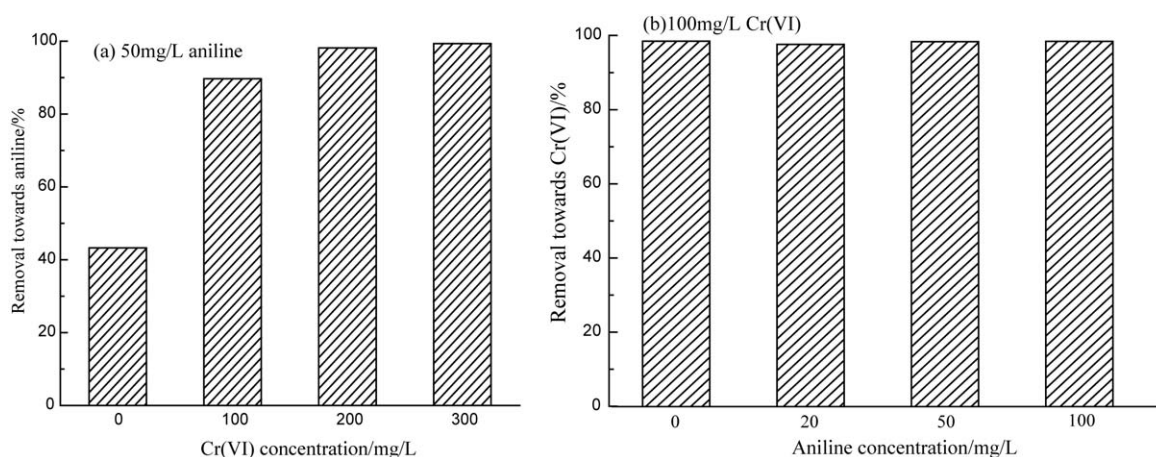
**Adsorption of Aniline in the Presence of Cr(VI).** The removals of aniline by AC/CS composite in the presence and absence of Cr(VI) are shown in Figure 8(a). The presence of Cr(VI) obviously enhanced the adsorption of aniline onto this composite when Cr(VI) concentration was kept at 100 mg/L in Cr(VI)-aniline mixed solution. This increase may be explained like this. As mentioned in Effect of Contact Time on Adsorption section, Cr(VI) ions were adsorbed by this adsorbent faster than aniline. Cr(VI) adsorbed by this composite promoted the adsorption of part aniline due to the formation of Cr(VI)-aniline complex. As Cr(VI) ions' concentrations increased, more Cr(VI) ions were adsorbed on the surfaces of this adsorbent, which facilitated the adsorption of aniline, leading to an increase in the removal toward aniline. When Cr(VI) concentration was 300

mg/L in Cr(VI)-aniline mixed solution, the removal toward aniline reached up to 99.3%.

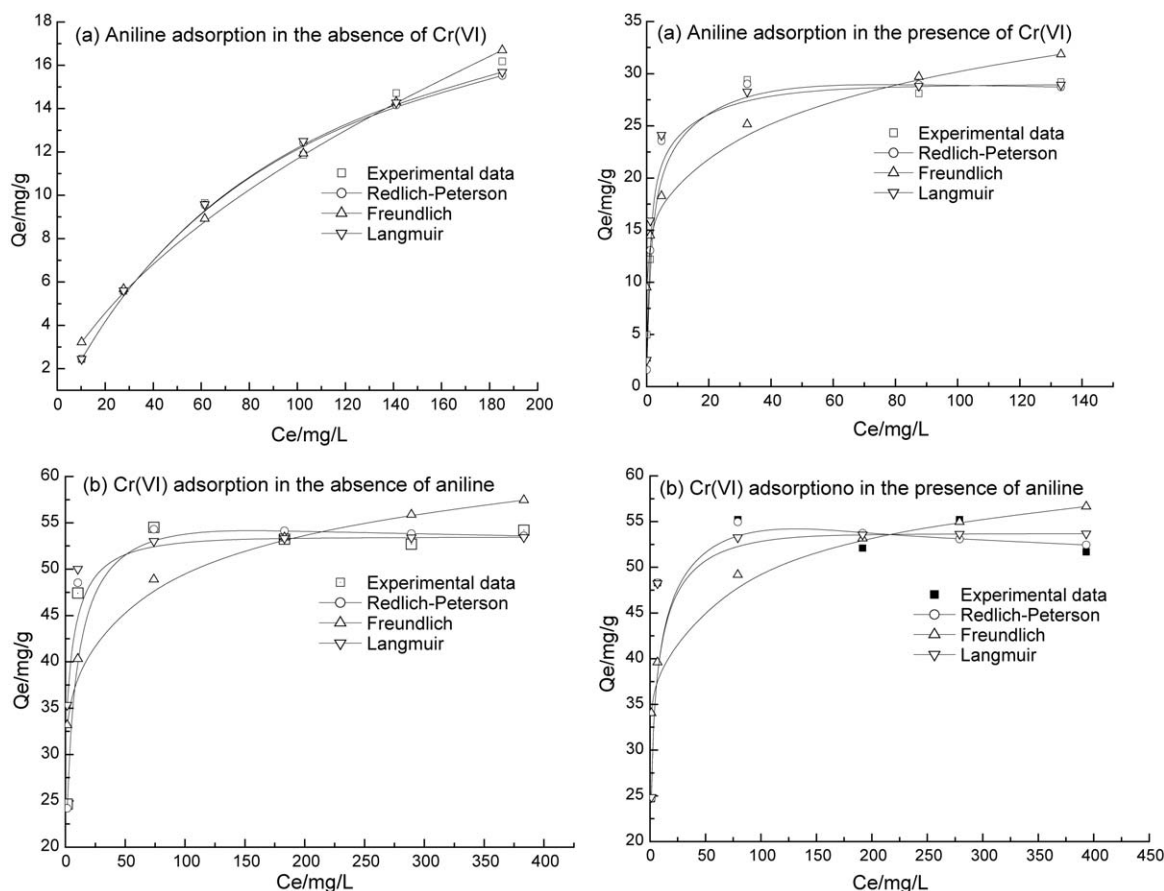
**Adsorption of Cr(VI) in the Presence of Aniline.** The removal of Cr(VI) by this composite in the presence and absence of aniline is shown in Figure 8(b). Results indicate that the presence of aniline almost has no influence on the adsorption of Cr(VI) when aniline concentration varied at 20, 50, and 100 mg/L. The results suggest that no competitive effect was observed for Cr(VI) ions adsorption onto this composite in the presence of aniline. Cr(VI) ions were mainly adsorbed onto this composite by the electrostatic interactions between protonated CS and Cr(VI) ions. Also, the results in Effect of Contact Time on Adsorption section showed that the Cr(VI) ions were adsorbed by this adsorbent faster than aniline. Hence, aniline cannot bring about the steric effect on the adsorption of Cr(VI) in a short adsorption time. Therefore, the adsorption of Cr(VI) ions was not affected by the presence of aniline due to the strong electrostatic interactions between protonated CS and Cr(VI) ions as well as the fast adsorption rate of Cr(VI) by this composite.

#### Adsorption Isotherm

The experimental data fitted to Langmuir, Freundlich, and Redlich-Peterson isotherm equations are shown in Figure 9. These parameters ( $q_m$ ,  $b$ ,  $k_F$ ,  $n$ ,  $k_{RP}$ ,  $a_{RP}$ , and  $\beta$ ) obtained from these isotherms together with correlation coefficient,  $r^2$ , were shown in Table I. From Table I, these three isotherms described the adsorption of aniline well in the absence of Cr(VI). However, when compared with Freundlich isotherm, both Langmuir and Redlich-Peterson isotherms seem to describe the adsorption of aniline in the presence of Cr(VI) due to higher correlation coefficient  $r^2$ , as shown the results in Figure 9(a). Also, it was observed that the two isotherms (namely Langmuir and Redlich-Peterson isotherm) were found to closely correspond with each other, as per expectation (because the Langmuir isotherm is a special case of Redlich-Peterson isotherm, when value of  $\beta$  is unity or so). Therefore, it indicated that the presence of Cr(VI) changed the adsorption characteristic of aniline onto this composite. Besides, Table I shows that the maximum



**Figure 8.** Interactive influence between aniline and Cr(VI) adsorption. Adsorption conditions: adsorbent dosage: 4 g/L; initial 50 mg/L aniline or 100 mg/L Cr(VI); temperature: 20°C; at natural pH; contact time: 40 min.



**Figure 9.** Isotherm models for aniline (a) and Cr(VI) (b) adsorption. Adsorption conditions: adsorbent dosage: 4 g/L; initial aniline concentration: 20–250 mg/L or Cr(VI) concentration: 100–500 mg/L; temperature: 20°C; contact time: 80 min.

adsorption capacity of aniline in the presence of Cr(VI) are 29.15 mg/g at 293 K, which increased by 6.20 mg/g as compared with the one in the absence of Cr(VI). However, the adsorption data for Cr(VI) were better fitted by the Langmuir and Redlich–Peterson isotherms [seen in Figure 9(b)] whether in the presence of aniline or in the absence of aniline, suggesting that the presence of aniline had no influence on the adsorption characteristic of Cr(VI). Also, it was found that the adsorption capacity of Cr(VI) was not affected by aniline.

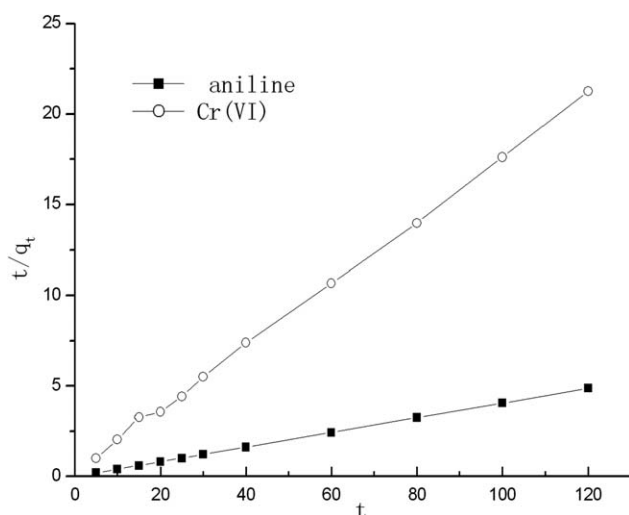
#### Adsorption Kinetics

To examine the controlling mechanism of the adsorption process, kinetic models are often used to test the experimental

data. In this study, the adsorption kinetics of Cr(VI) and aniline were investigated. The linear plots of  $t/q_t$  versus  $t$  for the pseudo-second-order model for the adsorption of aniline and Cr(VI) onto AC/CS composite are shown in Figure 10. The constants and correlation coefficient ( $r^2$ ) for pseudo-second-order kinetic model are presented in Table II. From Table II, the pseudo-second order model had high correlation coefficient ( $r^2 > 0.99$ ). In addition, the calculated  $q_e$  from pseudo-second-order model is very closely similar to experimental  $q_e$  whether for aniline or for Cr(VI) adsorption by this composite. Therefore, the pseudo-second-order model was the best model to predict kinetic behavior of aniline and Cr(VI) adsorption. Besides, it was found that the  $k$  values calculated from the slopes were

**Table I.** Isotherm Parameters for Aniline and Cr(VI) Adsorption by AC/CS Composite

Adsorbate	Langmuir			Freundlich			Redlich-Peterson			
	$q_m$	$b$	$r^2$	$k_F$	$n$	$r^2$	$k_{RP}$	$a_{RP}$	$\beta$	$r^2$
Aniline	22.95	0.0117	0.9963	0.8616	1.761	0.9937	0.2677	0.0113	1.009	0.9987
Aniline/aniline + Cr(VI)	29.15	0.9997	0.9957	14.06	5.979	0.9848	17.56	0.5077	1.035	0.9973
Cr(VI)	53.54	1.371	0.9945	32.07	10.20	0.9847	28.47	0.4668	1.021	0.9963
Cr(VI)/aniline + Cr(VI)	53.79	1.282	0.9937	33.45	11.34	0.9854	32.14	0.4799	1.040	0.9960



**Figure 10.** Adsorption kinetics of aniline and Cr(VI) by pseudo-second-order kinetic model. Adsorption conditions: adsorbent dosage: 4 g/L; initial aniline-Cr(VI) concentration: 50 and 100 mg/L; temperature: 20°C; at natural pH; contact time: 5–120 min.

0.1122 g/mg min<sup>-1</sup> for aniline and 0.3537 g/mg min<sup>-1</sup> for Cr(VI). The result suggested that the sorption of Cr(VI) was preferential to that of aniline by this composite, when Cr(VI) and aniline existed simultaneously in aqueous solution. This phenomenon may be related to the differences in the adsorptive sites. Cr(VI) was adsorbed fast on the surface of this composite by the electrostatic interactions between protonated CS and Cr(VI) ions. However, for aniline, a part of aniline molecules were adsorbed by dispersion interaction of AC, other aniline molecules were adsorbed by the formation of Cr(VI)–aniline complex. When aniline molecules approached AC, these molecules must travel within the pore of CS membrane coated on the surface of AC, thus resulting in a relatively slow adsorptive rate.

## CONCLUSIONS

AC/CS composite combining properties of AC and CS were synthesized for the simultaneous adsorption of aniline and Cr(VI) from aqueous solutions. The results showed ECH was the proper crosslinking reagent, and the ratio of AC to CS was kept at 1. Aniline sorption isotherm data were described by Langmuir, Freundlich, and Redlich-Peterson isotherms, while Cr(VI) sorption isotherm data were fitted well by Langmuir and Redlich-Peterson isotherm. The presence of Cr(VI) enhanced

the adsorption of aniline, and changed the adsorption isotherms of aniline, while the presence of aniline almost had no influence on the adsorption of Cr(VI). Dynamic data for both aniline and Cr(VI) sorption on this composite followed the pseudo-second-order kinetic model.

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**Table II.** Kinetic Parameters for Aniline and Cr(VI) Adsorption by Pseudo-Second-Order Model

Adsorbate	K	q <sub>e,measured</sub>	q <sub>e,calculated</sub>	r <sup>2</sup>
Aniline	0.1122	5.688	5.751	0.9996
Cr(VI)	0.3537	24.62	24.63	1.0000



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