

## Research Article

# Effects of Cu(II) on the Adsorption Behaviors of Cr(III) and Cr(VI) onto Kaolin

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The adsorption of Cr(III) or Cr(VI) in the absence and presence of Cu(II) onto kaolin was investigated under pH 2.0–7.0. Results indicated that the adsorption rate was not necessarily proportional to the adsorption capacity. The solutions' pH values played a key role in kaolin zeta potential ( $\zeta$ ), especially the hydrolysis behavior and saturation index of heavy metal ions. In the presence of Cu(II),  $q^{\text{mix}}_{\text{Cr(III)}}$  reached the maximum adsorption capacity of  $0.73 \text{ mg}\cdot\text{g}^{-1}$  at pH 6.0, while the maximum adsorption capacity for the mixed Cr(VI) and Cu(II) system ( $q^{\text{mix}}_{\text{Cr(VI)}}$ ) was observed at pH 2.0 ( $0.38 \text{ mg}\cdot\text{g}^{-1}$ ). Comparing the adsorption behaviors and mechanisms, we found that kaolin prefers to adsorb hydrolyzed products of Cr(III) instead of  $\text{Cr}^{3+}$  ion, while adsorption sites of kaolin surface were occupied primarily by Cu(II) through surface complexation, leading to Cu(II) inhibited Cr(VI) adsorption. Moreover, Cr(III) and Cr(VI) removal efficiency had a positive correlation with distribution coefficient  $K_d$ . Cr(III) and Cr(VI) removal efficiency had a positive correlation with distribution coefficient  $K_d$  and that of adsorption affinities of Cr(III) or Cr(VI) on kaolin was found to be  $K_d \text{ Cr(III)} < K_d \text{ Cr(III)-Cu(II)}$  and  $K_d \text{ Cr(VI)} > K_d \text{ Cr(VI)-Cu(II)}$ .

## 1. Introduction

Heavy metal pollution, as a potential threat to human beings due to toxicity and carcinogenicity, can cause serious environmental problems [1, 2]. Chromium, including Cr(III) and Cr(VI), is one of most toxic metals from the hazardous heavy metal list. Chromium is widely used in mining, electroplating, fossil fuel combustion, wood preservatives, textiles, and so forth [3, 4]. It has also been noted that weathering of chrome ore and chromium containing wastewater irrigation usually cause severe pollution to soil and water [5, 6]. Compared with Cr(III), Cr(VI) has greater toxicity, mobility, and potential carcinogenic properties [7, 8]; thus their environmental behaviors might be different.

Kaolin is one of the most well-known natural clays, available worldwide in rocks and soils. As crystalline aluminosilicate, kaolin possesses permanent negative surface charge, making it a good adsorbent for heavy metals [8, 9]. Therefore,

kaolin controls the distribution and transport of heavy metals in the aqueous and soil environments [10]. Previous studies have reported that Cr(III) and Cr(VI) adsorption onto kaolin can be affected by solution pH, metal concentrations, contact time, and the presence of other metal ions. In addition, pH is an important aqueous chemistry variable that affects both the surface charge of adsorbent and the speciation of heavy metal, resulting in the different adsorption behavior of metals on adsorbent surfaces and intraparticle processes [11, 12]. For example, the removal efficiency of both Cr(III) and Cr(VI) by kaolin increased with increasing pH up to 5.0 [13, 14], yet when using synthesized kaolin, the adsorption capacity of Cr(VI) decreased as pH increased [15]. A lot of work has been done on the use of low-cost adsorbents for removal of Cr(III) or Cr(VI) in a single system, while the adsorption behaviors of Cr(III) or Cr(VI) on soils and clay minerals in the presence of other heavy metals have increasingly gained attention.

Cu(II) is an essential element for plant growth and has been widely used in antiseptics, feed additives, and organic fertilizers [16]. The adsorption of multiple metal ions onto kaolin has been investigated, and  $\text{Cu}^{2+}$  was reported to inhibit  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  adsorption [17, 18], while it promoted the Cr(III) adsorption on kaolin at pH 2.0–6.0 [14]. As for the Cr(VI) adsorption behaviors, phosphate-P inhibited the adsorption of Cr(VI) on modified kaolin because of competitive adsorption [19]. Cu(II) also gradually decreased the removal efficiency of  $\text{Cr}_2\text{O}_7^{2-}$  on mesoporous silica as the pH increased due to protonation [20]. However, Xu et al. found that the adsorption of  $\text{CrO}_4^{2-}$  on red soil was remarkably enhanced by an increase in both  $\text{Cu}^{2+}$  dose and pH [21]. To the best of our knowledge, only a few studies reported the combined effects between adsorption of Cu(II) and Cr(VI) by modified minerals and various soils [22–24], and those studies mainly focus on the removal efficiency. Nevertheless, limited work has been reported on the effects of  $\text{Cu}^{2+}$  on aqueous Cr adsorption behaviors and the controlling mechanisms on kaolin.

To fill this information gap, the main objectives of this study were (1) to study the competitive adsorption characteristics of two different valence states of Cr(III, VI) with or without Cu(II) on kaolin; (2) to evaluate the effect of pH on adsorption of Cr(III) or Cr(VI) by kaolin; and (3) to explore the competitive adsorption mechanisms of Cr(III) or Cr(VI) on kaolin in the absence and presence of Cu(II).

## 2. Materials and Methods

**2.1. Materials and Chemicals.** Kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , MW = 258 g·mol<sup>-1</sup>), containing 89% of kaolinite, 5% of quartz and 6% of alunite [25], was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd., China. Stock solutions containing 300 mg·L<sup>-1</sup> Cr(III), 200 mg·L<sup>-1</sup> Cr(VI), and 200 mg·L<sup>-1</sup> Cu(II) were prepared by dissolving  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in that order, in deionized water (DW), respectively. The concentration of Cr(III) is higher than Cr(VI), because Cr(III) hydrolysis very fast in aqueous solution and the soil maximum contaminate level for Cr(III) in China is 300 mg·L<sup>-1</sup>. All reagents used in this study were of analytical grade (AG) and obtained from Xilong Chemical Reagent Co. (Beijing, China).

**2.2. Kaolin Characterization.** For understanding the adsorption mechanisms, the physiochemical properties of kaolin were characterized using multiple techniques. The cation exchange capacity (CEC) of kaolin was determined using the ammonium acetate (pH = 7.0) method and flame photometric detection [26]. The specific surface area (SSA) and pore size distribution of kaolin were determined by the  $\text{N}_2$  gas adsorption-desorption isotherm via the Brunauer-Emmett-Teller (BET) method (V-Sorb 2800P; Beijing Gold Spectrum Technology Co. Ltd., China). The zeta potential ( $\zeta$ ) was determined by dynamic light scattering (DLS, Zetasizer Nano ZSP, Malvern, UK) to study the surface charges of kaolin. All the zeta potential measurements were carried every 2 min for 15 min at 25°C.

**2.3. Batch Adsorption Experiments.** The first experiment was performed to evaluate the effect of contact time. These adsorption experiments of Cr(III) and Cr(VI) were conducted in the absence and presence of Cu(II) at room temperature ( $25 \pm 1^\circ\text{C}$ ). First, 10.0 g kaolin was placed into a 500 mL polyethylene bottle, containing 400 mL of Cr(III), Cr(VI), Cr(III)-Cu(II), or Cr(VI)-Cu(II) solutions (pH =  $4.5 \pm 0.1$ ). The concentrations of Cr(III), Cr(VI), and Cu(II) were 300 mg·L<sup>-1</sup>, 200 mg·L<sup>-1</sup>, and 200 mg·L<sup>-1</sup>, respectively. Then, samples were completely mixed using a magnetic stirrer at a speed of 200 rpm and collected at different time intervals (i.e., 5, 10, 15, 20, 30, 40, 60, 80, 100, and 120 min). Finally, samples were immediately filtered with 0.45  $\mu\text{m}$  polycarbonate filters for further analysis.

The second experiment was done to determine the effect of initial concentration. At first, 0.5 g of kaolin was added into 20.0 mL single solutions of Cr(III) or Cr(VI) and the binary solutions of Cr(III)-Cu(II) or Cr(VI)-Cu(II) ( $25 \pm 1^\circ\text{C}$ , pH =  $4.5 \pm 0.1$ ). These solutions were completely mixed on a reciprocal shaker at 200 rpm for 120 min. The concentrations of Cr(III) in the single solutions were 20, 40, 60, 80, 100, 150, 200, 250, and 300 mg·L<sup>-1</sup>, whereas Cr(VI) concentrations in single solutions ranged from 20 to 200 mg·L<sup>-1</sup>. For the Cr-Cu binary solutions, Cu(II) was added in equal concentrations as Cr(III) or Cr(VI). After the adsorption of Cr on kaolin reached equilibrium, the supernatants of samples were collected via centrifugation at 4000 rpm for 15 min. The concentrations of chromium in supernatants were measured by atomic absorption spectrometry (AAS, Z-2000, Hitachi, Japan).

The third experiment investigated the effect of solution pH on adsorption. Effects of solution pH on Cr adsorption were conducted following the same procedures as described in the second experiment under variable pH conditions (i.e., pH = 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0). The concentrations of Cr(III), Cr(VI), and Cu(II) were 300 mg·L<sup>-1</sup>, 200 mg·L<sup>-1</sup>, and 200 mg·L<sup>-1</sup>, respectively.

**2.4. Data Analysis.** The amounts of adsorbed chromium at a given time  $t$  ( $q_t$ , mg·g<sup>-1</sup>) and at equilibrium ( $q_e$ , mg·g<sup>-1</sup>) were calculated using

$$q_t = \frac{(c_0 - c_t) \times V}{m},$$

$$q_e = \frac{(c_0 - c_e) \times V}{m},$$
(1)

where  $c_0$  (mg·L<sup>-1</sup>) is the initial Cr(III) or Cr(VI) concentration,  $c_t$  and  $c_e$  (mg·L<sup>-1</sup>) are the Cr(III) or Cr(VI) concentrations at any time  $t$  and at equilibrium  $e$ ,  $m$  is the mass of kaolin added (g), and  $V$  is the solution volume (L).

The adsorption capacity of Cr(III) or Cr(VI) in single and binary solutions was referred to  $q^0$  and  $q^{\text{mix}}$ , respectively. Accordingly, the promoting efficiency (PE) and inhibitory

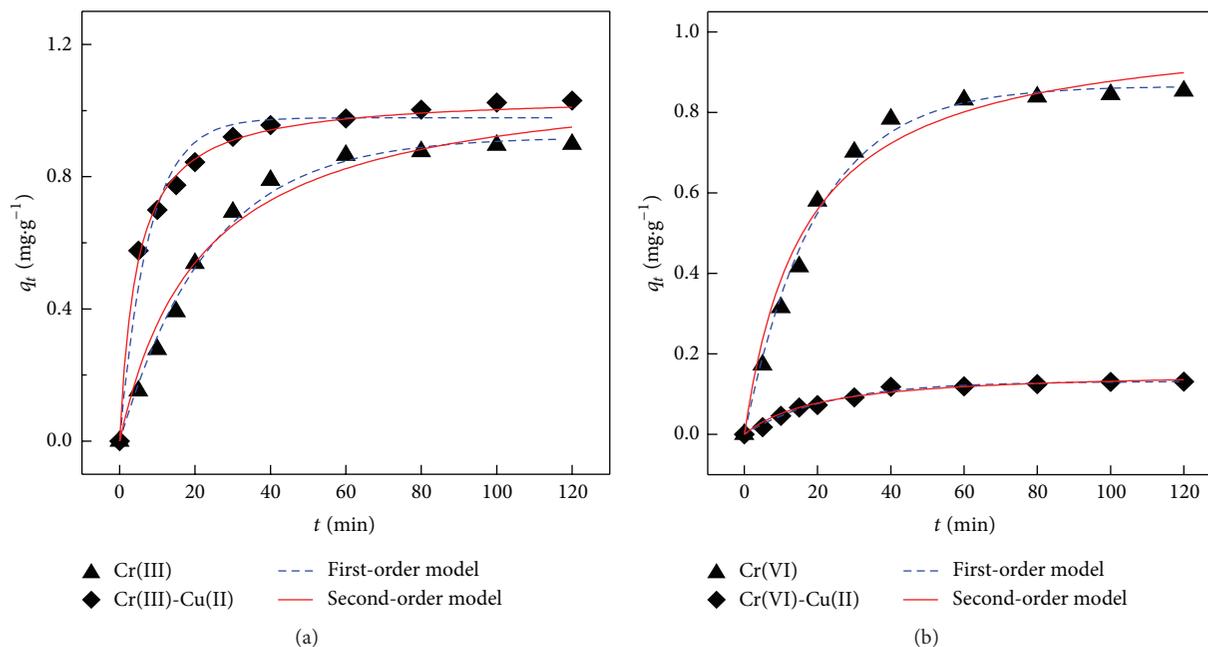


FIGURE 1: The Cr(III) (a) or Cr(VI) (b) adsorption kinetics onto kaolin in the absence and presence of Cu(II). The ▲ and ◆ are the measured data. The dashed and solid curves are fittings using pseudofirst-order and second-order models, respectively (adsorption conditions:  $c_0$  for Cr(III) = 300 mg·L<sup>-1</sup>, for Cr(VI) and Cu(II) = 200 mg·L<sup>-1</sup>, pH = 4.5, and temperature = 25°C).

efficiency (IE) of Cu(II) for Cr(III) or Cr(VI) adsorption were calculated as follows [17]:

$$\begin{aligned} \text{PE} (\%) &= \frac{q^{\text{mix}} - q^0}{q^0} \times 100\%, \\ \text{IE} (\%) &= \frac{q^0 - q^{\text{mix}}}{q^0} \times 100\%. \end{aligned} \quad (2)$$

### 3. Results and Discussion

**3.1. The Physicochemical Characterization of Kaolin.** The physicochemical properties, such as the cation exchange capacity (CEC), specific surface area (SSA), and micropore volume and pore size, are highly relevant to the adsorption capacity of kaolin and, thus, were measured. The CEC and SSA of kaolin were  $9.1 \pm 0.36$  meq·100 g<sup>-1</sup> and  $14.93 \pm 0.32$  m<sup>2</sup>·g<sup>-1</sup>, respectively. In general, the CEC of kaolin should be within 3~15 meq·100 g<sup>-1</sup> [19], and our CEC value fell within this range. The pore volume of kaolin was  $0.167 \pm 0.27$  cm<sup>3</sup>·g<sup>-1</sup>, which was almost the same value reported by Rida et al. ( $0.118$  cm<sup>3</sup>·g<sup>-1</sup>) [9]. The pore diameter of kaolin was  $12.59 \pm 0.49$  nm, and similar values were reported by Wu et al. [25]. The zeta potential values of kaolin surfaces were similar ( $-41.5 \pm 5.0$  mV) over our experimental pH range (pH 2.0–7.0).

**3.2. Effect of Contact Time on Cr(III) and Cr(VI) Adsorption.** The effects of contact time on the adsorption of Cr(III) and Cr(VI) in the absence and presence of Cu(II) onto kaolin were shown in Figure 1. For all scenarios, the adsorption capacity

( $q_t$ ) increased with increasing contact time. It was found that all the adsorption process could be divided into two distinctive phases ( $t < 40$  min and  $t > 40$  min). Moreover, adsorption rate of Cr(III) and Cr(VI) was relatively fast for the first 40 min; then the amount of adsorbed Cr(III) and Cr(VI) ions onto kaolin continued to increase slightly and reached their maximum values and adsorption equilibrium onto kaolin at 120 min [27]. The long time required to establish equilibrium may indicate that the adsorption process is diffusion controlled physical adsorption [28]. Therefore, the contact time of 120 min was chosen in all adsorption experiments of this study.

Interestingly, the presence of Cu(II) showed opposite effects on the adsorption of Cr(III) and Cr(VI) on kaolin. At equilibrium, the adsorption capacity of Cr(III) onto kaolin in binary solution ( $q^{\text{mix}} = 1.030$  mg·g<sup>-1</sup>) was slightly higher than that in single solution ( $q^0 = 0.898$  mg·g<sup>-1</sup>), indicating increased Cr(III) adsorption on kaolin in the presence of Cu(II). Adversely, at equilibrium, the adsorption capacity of Cr(VI) in binary solution ( $q^{\text{mix}} = 0.131$  mg·g<sup>-1</sup>) was much lower than that in the single solution ( $q^0 = 0.853$  mg·g<sup>-1</sup>), indicating an inhibitory effect of Cu(II) on Cr(VI) adsorption. Therefore, Cr(VI) was removed faster than Cr(III) in single solutions, while Cr(III) was more easily adsorbed by kaolin than Cr(VI) in the presence of Cu(II).

**3.3. Adsorption Kinetics Models.** Besides adsorption capacity at equilibrium, the adsorption kinetic studies can also provide information on adsorption rate, rate-controlling steps, and mechanism of the adsorption process. In this study, to gather this information, our experimental data were fitted

TABLE 1: Comparison of rate constants calculated based on pseudofirst-order and pseudosecond-order models.

Adsorbed solution	$q_{e,exp}$ (mg·g <sup>-1</sup> )	Pseudofirst-order kinetic model			Pseudosecond-order kinetic model		
		$q_{e,cal}$ (mg·g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{e,cal}$ (mg·g <sup>-1</sup> )	$k_2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$R^2$
Cr(III)	0.898	0.920	0.042	0.993	1.120	0.042	1.000
Cr(III)-Cu	1.030	0.978	0.130	0.967	1.049	0.209	0.963
Cr(VI)	0.853	0.865	0.051	0.993	1.040	0.052	0.976
Cr(VI)-Cu	0.131	0.132	0.043	0.990	0.162	0.270	0.981

TABLE 2: Intraparticle diffusion model for Cr(III) and Cr(VI) adsorption in single and binary solution.

Adsorbed solution	Film diffusion			Pore diffusion			Intraparticle diffusion		
	$C^a$	$k_{p1}^b$	$R^2$	$C^a$	$k_{p2}^b$	$R^2$	$C^a$	$k_{p3}^b$	$R^2$
Cr(III)	0.176	0.146	0.997	0.065	0.136	0.993	0.778	0.011	0.952
Cr(III)-Cu	0.307	0.122	0.996	0.577	0.061	0.974	0.844	0.017	0.958
Cr(VI)	0.210	0.168	0.988	0.315	0.004	0.966	—	—	—
Cr(VI)-Cu	0.027	0.023	0.971	0.315	0.004	0.966	—	—	—

<sup>a</sup>The unite of  $C$  is mg·g<sup>-1</sup>; <sup>b</sup>the unite of  $k_{pi}$  is mg·g<sup>-1</sup>·min<sup>-0.5</sup>.

to three different adsorption kinetic models, including the pseudofirst-order kinetic model (see (3)), the pseudosecond-order model (see (4)), and the intraparticle diffusion model (see (5)) [1, 22]. One has

$$q_t = q_e (1 - e^{-k_1 t}), \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}, \quad (4)$$

$$q_t = k_{pi} t^{0.5} + C, \quad (5)$$

where  $t$  is the contact time of adsorption experiment (min);  $q_e$  (mg·g<sup>-1</sup>) and  $q_t$  (mg·g<sup>-1</sup>) are, respectively, the adsorption capacity at equilibrium and at any time  $t$ ;  $k_1$  (min<sup>-1</sup>) is the first-order rate constant;  $k_2$  (g·mg<sup>-1</sup>·min<sup>-1</sup>) is the rate constant of pseudosecond-order model; and  $k_{pi}$  (mg·g<sup>-1</sup>·min<sup>-0.5</sup>) is the intraparticle diffusion rate constant, which can be calculated from the slope of the linear plots of  $q_t$  versus  $t^{0.5}$ .

The corresponding parameters of the pseudofirst-order and pseudosecond-order models were summarized in Table 1. It is clear that both models were successful in describing the adsorption process of Cr(III, VI) onto kaolin to a better extent than the intraparticle diffusion model (Table 2). The values of coefficient of determination  $R^2$  (>0.960) were relatively high. This suggested that the rate of the adsorption process was preferably controlled by physical adsorption on surface and chemisorption [22, 29]. As a comparison of the adsorption rate constants  $k_1$  and  $k_2$ , Table 1 shows that adsorption rate of both Cr(III) and Cr(VI) onto kaolin in binary solutions was greater than in single solutions. Meanwhile,  $k_2$  values were higher for Cr(VI) in both single and binary solutions than for Cr(III). Although Cr(VI) has a higher valence state and a larger adsorption rate than Cr(III), Cr(VI) existed mainly in the form of  $Cr_2O_7^{2-}$  and  $HCrO_4^-$  at pH = 4.5 [1]. Thus Cu(II) could have been easily adsorbed by negatively charged kaolin, thus inhibiting the adsorption of Cr(VI) (Figure 1(b)), while  $k_2$  was larger in the Cr(III)-Cu binary solution. Moreover,

specific adsorption properties of Cr(III) may concerned due to the atomic weight, electronegativity, ionic potential, and hydrolysis. The adsorption capacity of kaolin was so small that the adsorption saturation was achieved quickly. Hence, kaolin could have been easily adsorbed Cr(III) and reached the adsorption equilibrium, causing Cu(II) to enhance the adsorption of Cr(III) onto kaolin (Figure 1(a)). Thus, we conclude that the adsorption rate was not necessarily proportional to the adsorption capacity.

The intraparticle diffusion model has been widely used to explain the diffusion mechanisms and sites of heavy metals in adsorbent, and the rate-controlling steps affecting the adsorption kinetics typically involved film diffusion, pore diffusion, and intraparticle diffusion [22, 30]. The details of the three types of mechanisms are in Supporting Information (see S1 Mechanisms of intra-particle diffusion model in Supplementary Material available online at <http://dx.doi.org/10.1155/2016/3069754>). Figure 2(a) shows that the adsorption of Cr(III) onto kaolin in both single and binary solutions involved all three diffusion steps, which is consistent with the result of Saleh et al. [31]. However, in both single and binary solutions, kaolin adsorption of Cr(VI) involved only film diffusion and pore diffusion mechanisms (Figure 2(b)), which agrees with the results of Gan et al. [22]. It illustrated that Cr(III) was adsorbed on the interior sites of kaolin followed by intraparticle diffusion.

Table 2 shows the intraparticle diffusion model constant values. The intraparticle diffusion rate constant in the first stage was higher than in the last two stages ( $k_{p1} > k_{p2} > k_{p3}$ ) in both Cr(III) and Cr(VI) adsorption. It illustrated that the first step adsorption was an instantaneous diffusion process on the exterior surface of kaolin. When the exterior surface reached saturation, Cr(III) or Cr(VI) ions entered the interior channels of kaolin on the second stage with increased diffusion resistance and occupied the exchangeable positions of interior kaolin within the crystalline structure [22, 32], resulting in decreased diffusion rates ( $k_{p2}$ ). Therefore, the film diffusion was considered as the rate-limiting step and

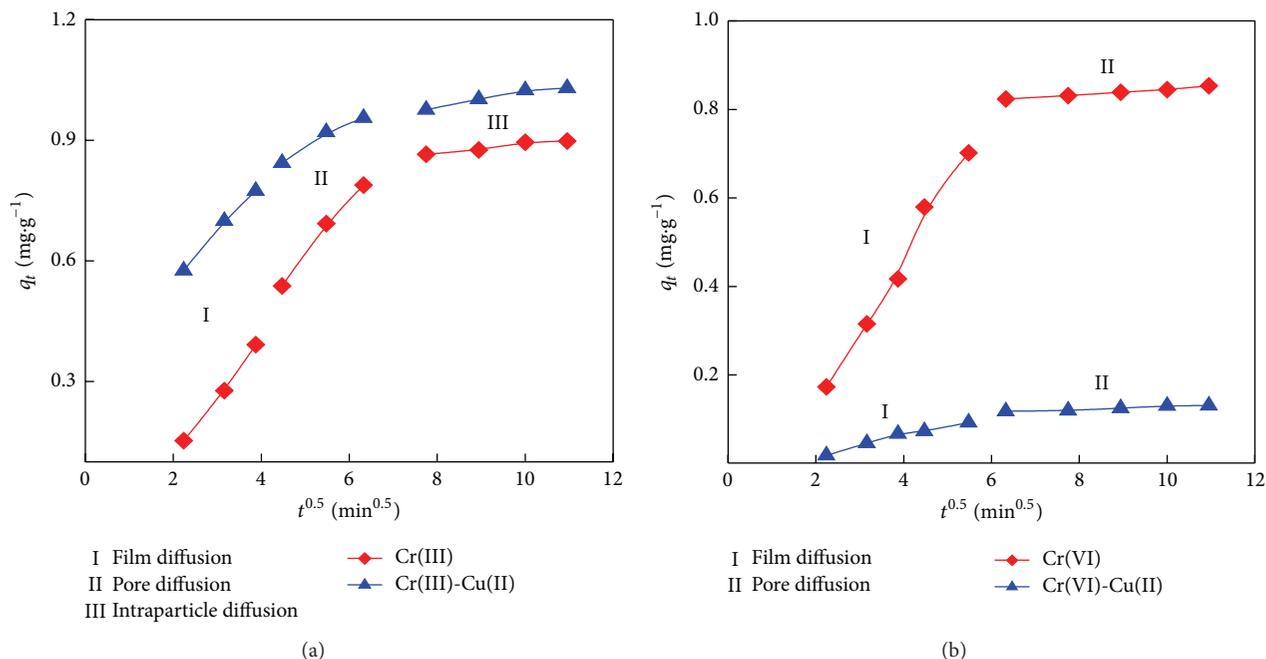


FIGURE 2: Intraparticle diffusion plots for Cr(III) (a) or Cr(VI) (b) adsorption onto kaolin in the absence and presence of Cu(II) (adsorption conditions: initial concentration for Cr(III) = 300 mg·L<sup>-1</sup>, for Cr(VI) and Cu(II) = 200 mg·L<sup>-1</sup>, temperature = 25°C, pH = 4.5, and equilibrium time = 120 min).

both Cr(III) and Cr(VI) were adsorbed on the boundary-layer and surface adsorption sites of kaolin. This agrees with the research of Debnath and Ghosh [33].

**3.4. Adsorption Isotherms.** Adsorption isotherms provided fundamental physicochemical data to assess the adsorption capacity of adsorbent and evaluate their interactions with adsorbate. Two typical isotherm models, the Langmuir isotherm model (see (6)) and the Freundlich isotherm model (see (7)) were employed to fit our experimental data, and their nonlinear forms are shown as follows [34, 35]:

$$q_e = \frac{q_m K_l c_e}{1 + c_e}, \quad (6)$$

$$q_e = K_f c_e^{1/n}, \quad (7)$$

where  $c_e$  is Cr concentration in the solution (mg·L<sup>-1</sup>);  $q_e$  is Cr concentrations in the solid adsorbent (mg·g<sup>-1</sup>);  $q_m$  is the saturated adsorption capacity (mg·g<sup>-1</sup>);  $K_f$  is a constant related to the adsorption capacity (mg<sup>1-1/n</sup>·L<sup>1/n</sup>·g<sup>-1</sup>);  $K_l$  is a constant related to the energy of adsorption (L·g<sup>-1</sup>); and  $n$  is the adsorption intensity, while  $1/n$  is a function of the strength of the adsorption [1].

The fitting of adsorption isotherms was achieved using Origin 8.5 software, and the fitted curves are shown along adsorption isotherms in Figure 3. Adsorption isotherm parameters ( $K_l$ ,  $q_m$ ,  $K_f$ , and  $1/n$ ) and correlation coefficients ( $R^2$ ) of Cr(III) and Cr(VI) adsorption in single and binary solutions onto kaolin are summarized in Table 3. The values of  $R^2$  from the Langmuir model were higher than from the

Freundlich model for all scenarios. Therefore, the Langmuir model was more suitable for describing Cr(III) and Cr(VI) adsorption in both single and binary solutions. This indicated that both Cr(III) and Cr(VI) were adsorbed on kaolin surface by physical or chemical adsorption, which occurred on the monolayer molecular layer. The conclusions were in accordance with the kinetic results of adsorption. The adsorption of Cr(III) and Cr(VI) has been well described by the Langmuir model ( $R^2 > 0.978$ ), which were in agreement with the adsorption of Cr(III) or Cr(VI) onto kaolin in single solution [36]. A positive correlation between the coefficient  $K_l$  in the Langmuir model and saturation adsorption  $q_m$  was observed, which could explain the different adsorption behaviors of Cr(III, VI) in single and binary solution (Figure 3). However, the favorable adsorption process can be described by the heterogeneity factor  $1/n$  [37]. Table 3 showed that all the values of  $1/n$  in the Freundlich model are less than 1 (0.293–0.764), implying heterogeneous energy site for both Cr(III) and Cr(VI) adsorption on kaolin.

**3.5. Effects of pH on Cr(III) Removal.** The solution's pH is considered to be an important parameter in heavy metal adsorption, as the pH values can affect the speciation of metal ions and the surface properties of adsorbents [12, 31]. The adsorption capacities ( $q_e$ ) of Cr(III) in the absence and presence of Cu(II) increased with pH (pH 2.0–7.0), as shown in Figure 4(a). Over the pH range, enhanced Cr(III) adsorption was observed in the presence of Cu(II), which was consistent with Cr(III) adsorption on bentonite in Cu(II)-Cr(III) solution [38]. Chantawong et al. also found that kaolin exhibited a significant affinity to Cr<sup>3+</sup>, followed by Zn<sup>2+</sup>,

TABLE 3: Parameters of isotherms for the removal of Cr(III) or Cr(VI) by kaolin in single and binary solutions.

Adsorbed solution	Langmuir model			Freundlich model		
	$K_l$ (L·g <sup>-1</sup> )	$q_m$ (mg·g <sup>-1</sup> )	$R^2$	$K_f$ (mg <sup>1-1/n</sup> ·L <sup>1/n</sup> ·g <sup>-1</sup> )	$1/n$	$R^2$
Cr(III)	0.083	1.018	0.991	0.308	0.764	0.958
Cr(III)-Cu	0.595	1.441	0.997	0.493	0.554	0.959
Cr(VI)	3.367	0.878	0.985	0.628	0.293	0.956
Cr(VI)-Cu	0.134	0.595	0.978	0.070	0.710	0.912

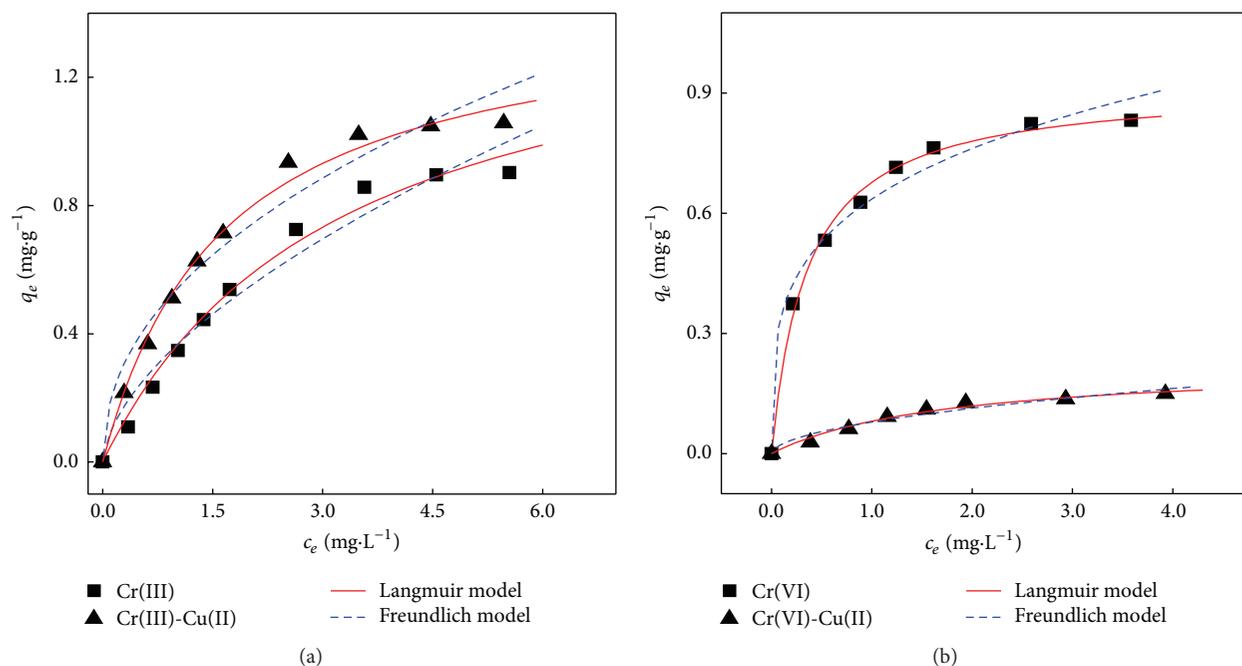


FIGURE 3: Isotherm plots for Cr(III) (a) or Cr(VI) (b) adsorption by kaolin in single and binary solutions at the fitting of Langmuir and Freundlich isotherm models (adsorption conditions: temperature = 25°C, pH = 4.5, and equilibrium time = 120 min).

TABLE 4: Effects of Cu(II) on Cr(III) and Cr(VI) adsorption onto kaolin under different pH values.

	pH					
	2.0	3.0	4.0	5.0	6.0	7.0
Cr(III)						
$q^{\text{mix}}/q^0$	1.59	2.06	1.80	1.74	1.53	1.31
PE (%)	58.7	106	80.0	73.5	52.9	30.6
Cr(VI)						
$q^{\text{mix}}/q^0$	0.91	0.35	0.07	0.15	0.18	0.51
IE (%)	9.14	64.8	93.0	84.7	82.4	49.5

$\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$  in mixture solution, indicating that  $\text{Cr}^{3+}$  was adsorbed preferentially on kaolin surface compared to  $\text{Cu}^{2+}$  [39]. Moreover,  $\text{Cr}^{3+}$  has higher valence and smaller ionic radius (0.061 nm) compared with  $\text{Cu}^{2+}$  (0.070 nm) [38], which can also explain the preferential adsorption of Cr(III) on kaolin. The PE values were calculated (Table 4); the strongest promoting effect (i.e., highest PE value) of Cu(II) for Cr(III) adsorption was observed at pH = 3.0 (PE = 106%). In addition, the initial solution pH 6.0–7.0 had significant effects

( $P > 0.05$ ) on Cr(III) which was adsorbed by kaolin in both the absence and presence of Cu(II).

To understand the effects of pH on Cr(III) adsorption, the speciation of Cr(III) and saturation index (SI) with respect to  $\text{Cr}(\text{OH})_3$  were calculated in the absence of Cu(II) by Visual MINTEQ as shown in Figures 4(a) and 4(b). It was reported that, for minerals with low dielectric constants, such as quartz and kaolin, the mineral surfaces preferred to adsorb the hydrolyzed products of metal ions (e.g.,  $\text{Cr}(\text{OH})^{2+}$ ,  $\text{Cr}_2(\text{OH})_2^{4+}$ , and  $\text{Cr}(\text{OH})_2^+$ ) instead of the unhydrolyzed metal ions (e.g.,  $\text{Cr}^{3+}$ ) [40]. According to the Cr(III) speciation diagram (Figure 5(a)), over the pH range of 2.0–5.0 and with increasing pH, more  $\text{Cr}^{3+}$  ions were hydrolyzed, resulting in promoted Cr(III) adsorption onto kaolin. With further increases of pH over the range of 5.0–7.0 in Figure 5(b), the solution became supersaturated with respect to  $\text{Cr}(\text{OH})_3$ . The precipitation of  $\text{Cr}(\text{OH})_3$  at the higher pH range can promote the removal of Cr(III) from solution (Supporting Information 2).

In addition, the kaolin surface exhibited a positive charge from pH 4.8 to 6.5 in Figure 6(a), indicating that a large amount of Cr(III) was adsorbed onto the kaolin surface by

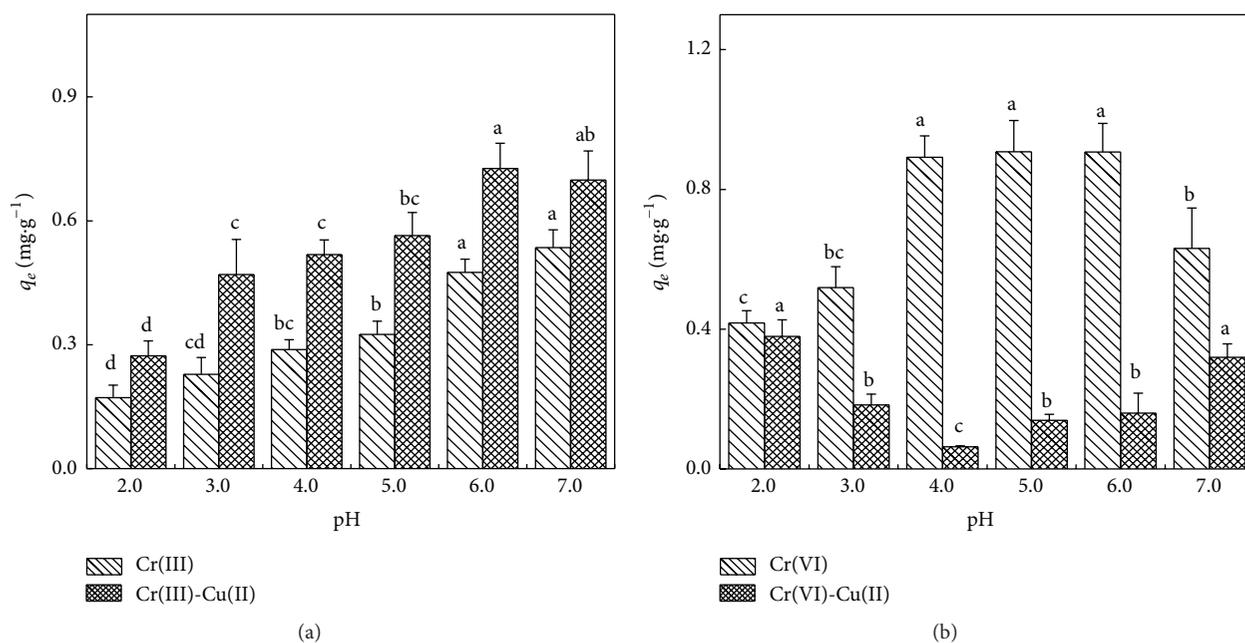


FIGURE 4: Influence of pH on the adsorption capacities of Cr(III) (a) or Cr(VI) (b) onto kaolin. Note: the lowercase letters in figure above are the 5% significant level by using LSD method under the same Cr treatment, but under different pH (adsorption conditions:  $c_0 = 300 \text{ mg}\cdot\text{L}^{-1}$  for Cr(III),  $c_0 = 200 \text{ mg}\cdot\text{L}^{-1}$  for Cr(VI),  $V = 20 \text{ mL}$ ,  $m = 0.50 \text{ g}$ , temperature =  $25^\circ\text{C}$ , and equilibrium time = 120 min).

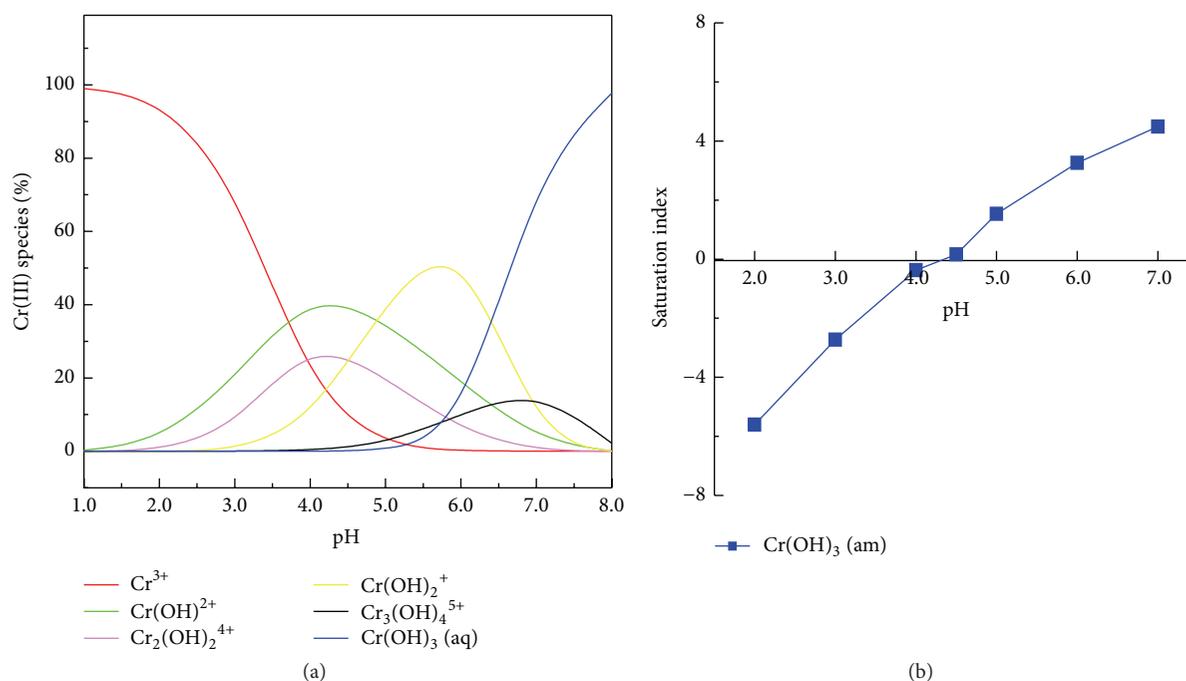


FIGURE 5: The speciation pH plot of Cr(III) (a) in absence of Cu(II) and the saturation index with respect to  $\text{Cr}(\text{OH})_3$  in solution with  $300 \text{ mg}\cdot\text{L}^{-1}$  Cr(III) at  $25^\circ\text{C}$ .

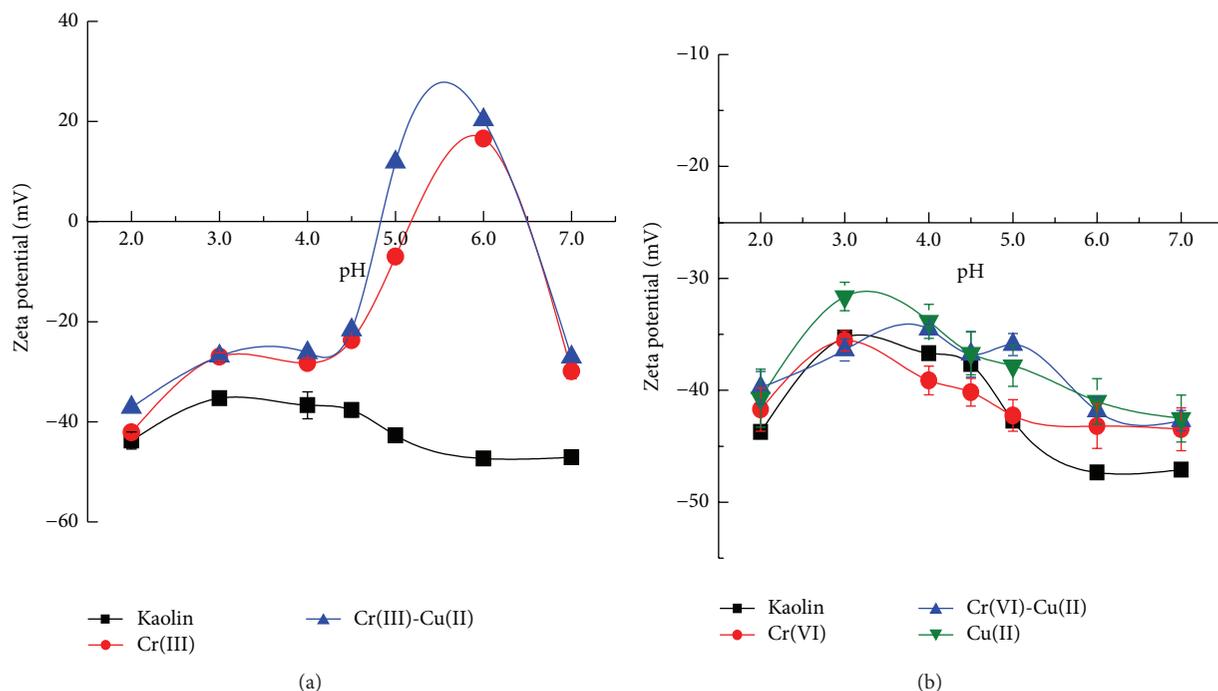


FIGURE 6: The zeta potential curve for original kaolin and kaolin after adsorbed Cr(III) (a) or Cr(VI) (b) in absence and presence of Cu(II).

specific adsorption. The similar changes were reported for the adsorption of Cr(III) onto iron hydroxide particles sorbents [40] and two Tunisian mineral clays [41]. When zeta potential changed into positive charge, the dominant adsorption mechanism of Cr(III) onto kaolin was precipitation in both single and binary solutions in Figure 5(b).

**3.6. Effects of pH on Cr(VI) Removal.** As shown in Figure 4(b), in the absence of Cu(II), the values of  $q_{\text{Cr(VI)}}^0$  increased with rising pH up to 5.0. Similar trend has been reported by Li et al. [36], where  $q_{\text{Cr(VI)}}^0$  on kaolin reached the maximum at pH 4.0–6.0. On the contrary, in the presence of Cu(II), the values of  $q_{\text{Cr(VI)}}^{\text{mix}}$  decreased with increasing pH and reached the minimum value at pH = 4.0. The values of  $q_{\text{Cr(VI)}}^{\text{mix}}$  increased thereafter at pH > 4.0. Over the whole pH range (2.0 to 7.0),  $q^{\text{mix}}/q^0$  were less than 1 for Cr(VI), indicating that the presence of Cu(II) inhibited Cr(VI) adsorption onto kaolin. Shen et al. [24] also found that Cu(II) and Cr(VI) exhibited the competition onto the nano- $\text{Fe}_3\text{O}_4$  magnetic polymers surface. The calculated IE values show that the strongest inhibitory effect (the lowest IE) of Cu(II) for Cr(VI) adsorption occurred at pH = 2.0 (IE = 9.14%). In addition, in the absence of Cu(II), the initial solution on pH 4.0–6.0 showed statistically higher ( $P > 0.05$ ) adsorption capacity of kaolin for Cr(VI) in Figure 4(b), while in the presence of Cu(II) the adsorption capacity of kaolin for Cr(VI) is statistically ( $P > 0.05$ ) at initial pH = 2.0 and pH = 7.0 compared to other pH.

Though there exist different types of Cr(VI) species, the total concentration of soluble Cr(VI) modeled by Visual MINTEQ remains stable without reduction at different pH (Figure 7(a)), which were consistent with the finding of

Chen et al. [7]. In Cr(VI)-Cu(II) solution, the zeta potential of kaolin was still negatively charged after adsorbing ions (Figure 6(b)). Therefore, the negatively charged adsorption sites of the kaolin surfaces were occupied by  $\text{Cu}^{2+}$  through electrostatic attraction [42], decreasing the adsorption site on kaolin surface, thus reducing the adsorption of Cr(VI). However, Xu et al. reported that Cu(II) could promote the adsorption of Cr(VI) on red soils [21], which was contrary to our result. Moreover, with continually increasing pH, some mineral precipitations (e.g., antlerite and brochantite) of Cu(II) formed at pH = 5.0 (Figure 7(b)), reducing the concentration of Cu(II) and releasing some adsorption sites on kaolin surface.

**3.7. Comparing Cr(III) and Cr(VI) Removal.** Effects of pH on the adsorption capacity of Cr(III) and Cr(VI) in the absence and presence of Cu(II) were different. The adsorption capacity for Cr(III) was smaller than for Cr(VI) ( $q_{\text{Cr(III)}}^0 < q_{\text{Cr(VI)}}^0$ ) under all pH values in the absence of Cu(II). As mentioned, both the surface charge and framework of kaolin were negative, indicating Cr(VI) removal not through electrostatic adsorption instead of specific adsorption. Meanwhile, Chen et al. found that some active sites of kaolin, such as Al-OH- and Si-OH- groups, can be occupied by Cu(II) through surface complexation [38]. Therefore, Cu(II) could inhibit the adsorption of Cr(VI) on kaolin.

Some researchers found that the distribution coefficient ( $K_d$ ) is a useful parameter for comparing the adsorptive capacity for any particular ion, and a high  $K_d$  value indicates a high metal retention by the solid phase through adsorption and chemical reactions [38, 43]. The effect of Cu(II) on Cr(III,VI) adsorption could also be explained by the distribution

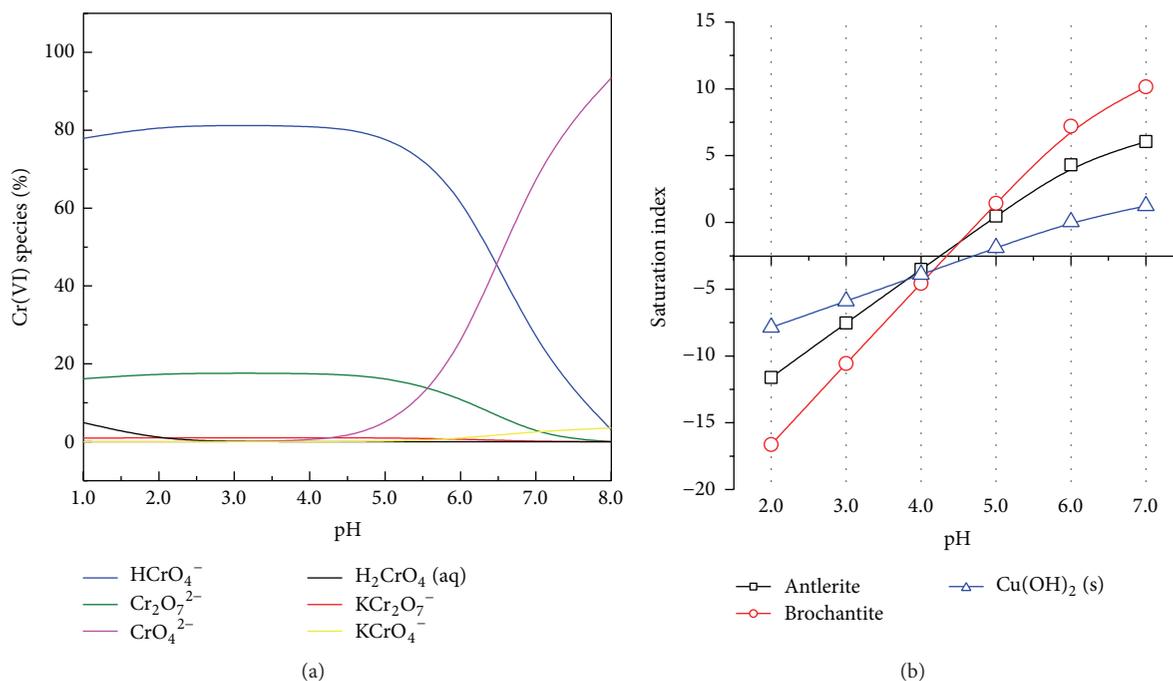


FIGURE 7: The speciation pH plot of Cr(VI) (a) in absence of Cu(II) and the saturation index with mineral precipitations in solution with  $200 \text{ mg}\cdot\text{L}^{-1}$  Cr(VI) and  $200 \text{ mg}\cdot\text{L}^{-1}$  Cu(II) at  $25^\circ\text{C}$ .

TABLE 5:  $K_d$  value of Cu(II) on Cr(III) and Cr(VI) adsorption onto kaolin under different pH values.

$K_d$ ( $\text{L}\cdot\text{mg}^{-1}$ )	pH					
	2.0	3.0	4.0	5.0	6.0	7.0
Cr(III)	14.56	19.41	24.55	27.87	41.26	46.68
Cr(III)-Cu(II)	23.30	40.84	45.08	49.37	64.50	61.84
Cr(VI)	110.19	138.92	250.97	256.28	255.83	171.43
Cr(VI)-Cu(II)	99.65	46.78	15.79	35.42	40.81	82.98

coefficient ( $K_d = q_e/c_e$ ). Table 5 shows that all  $K_d$  values of Cr(III) under pH 2.0–7.0 in the presence of Cu(II) were higher in the presence than in the absence of Cu(II); namely,  $K_d \text{ Cr(III)-Cu(II)} > K_d \text{ Cr(III)}$ , indicating that Cu(II) promoted the adsorption of Cr(III). Similar results showing Cr(III) higher affinity to kaolinite [44], bentonite [38], and subsoil [45] than Cu(II) have been reported. In contrast,  $K_d \text{ Cr(VI)-Cu(II)} < K_d \text{ Cr(VI)}$  indicating that Cu(II) inhibited the adsorption capacity of kaolin for Cr(VI). Therefore, the adsorption capacity had a positive correlation with distribution coefficient  $K_d$  in Table 5. Moreover,  $K_d$  was an effective evaluation index for adsorption behaviors of both Cr(III) and Cr(VI) in the absence and presence of Cu(II). In addition, the comparison of other low-cost adsorbents for Cr(III) and Cr(VI) removal in the absence and presence of other heavy metals, values of the adsorption capacity, and optimum pH of other adsorbents from the literature are given in Supporting Information (Table S1 and Table S2). It is clear from Table 5 that the adsorption capacities of kaolin for Cr(III) and Cr(VI) are comparable with the other adsorbents shown in Tables S1 and S2.

## 4. Conclusion

This study demonstrated that the adsorption behaviors and mechanisms of Cr(III) and Cr(VI) onto kaolin under pH 2.0–7.0, in the absence or presence of Cu(II), were remarkably different. The zeta potential results showed that only adsorbed Cr(III) changed the zeta potential of kaolin from negative to positive. Therefore, Cr(III) was adsorbed onto kaolin through electrostatic attraction at pH below 4.0. The main adsorption mechanisms were physic-chemical adsorption and mineral precipitation with pH > 4.0. The specific adsorption occurred at pH 4.8–6.5, indicating that Cr(III) was adsorbed in the interior of kaolin. Electrostatic adsorption and protonation were the dominant adsorption mechanisms of Cr(VI).

Further studies need to focus on the influence of different coexisting anions on kaolin adsorption behaviors of these heavy metals. Also, these heavy metal adsorption behaviors or mechanisms should be verified through quartz crystal microbalance dissipation (QCM-D) measurements.

## Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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