



Surface-modified nanoscale carbon black used as sorbents for Cu(II) and Cd(II)

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ABSTRACT

Commercial carbon blacks often have low adsorption capacity for metal ions. Surface modification of them by appropriate physical and chemical treatments could improve their absorption capacities, and hence extend their environmental application. A surface-modified nanoscale carbon black was prepared by oxidizing the carbon black with 65% HNO₃. Batch experiments showed that the adsorption quantities of Cu(II) or Cd(II) on this modified carbon black (MCB) were significantly increased compared with those on the parent one, and the maximum adsorption quantities of Cu(II) and Cd(II) on the MCB were 438 and 282 mmol kg⁻¹, respectively. The desorption percentages of Cu(II) or Cd(II) from the MCB increased with the increasing quantities initially adsorbed. In the binary system of Cu(II) and Cd(II), these two metal ions exhibited competition on the MCB, preferential for Cu(II). It could be concluded that the MCB had very good adsorption properties for the metal ions, and could be applied in the purification of wastewater containing such metal ions.

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1. Introduction

Heavy metals are of great concern because of their extreme toxicity even at low concentration and tendency to be accumulated in food chain. Among the commonly encountered metals of concern, Cu and Cd are hazardous and have been included in the Priority Pollutants List by the United States Environmental Protection Agency (USEPA). Copper is a toxic heavy metal to soil microorganisms, but it is also an essential nutrient at a trace level, while Cd has no known physiological function for plants or humans, and even the smallest quantities can have adverse effects on organisms. Copper sulfate has been used as an algicide since the early 1900s in eutrophic lakes and is still widely used today. In addition to that, large amounts of input of agricultural chemicals and manures from intensive farming easily resulted in soil Cu contamination [1]. Cadmium is a contaminant usually related to mining industry. Once these heavy metals were released into the environment, they can be accumulated in surface soil, and further enriched in plants and animals by food chain, and do harm to people's health [2]. Therefore, removal of heavy metals from wastewater or immobilization of them in soil by an appropriate treatment becomes necessary.

Most of modified carbon adsorbents (MCAs) were prepared by oxidation of activated carbon with NaClO, HNO₃ and KMnO₄, which have shown good adsorption abilities for metal ions, like Cu, Ni, Cd, Pb, Ag, Am and rare earth elements [3–12]. The sorption mecha-

nisms appear mainly attributable to chemical interactions between the metal ions and the surface functional groups of the MCAs. Stafiej and Pyrzynska [13] found that such MCAs can be well employed as adsorbent for divalent metal ions, and the affinity order of the metal ions towards MCAs was Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II).

Carbon black (CB) is an industrial form of soot used as filler in rubber compounds, or in automobile tires. The particle size of CB is partially in the nanometer range with average values between 20 and 300 nm from different sources [14]. However, such carbon blacks often show low adsorption capacity for metal ions. It is interesting to develop CB-based adsorbents for removal of metal ions from water.

Contaminated waters and soils commonly contain many kinds of metals, like Cu, Cd, Pb, Zn, Cr, Ni, and so on. Competition among these metal ions affecting overall removal capacity by carbon black or activated carbon has not been extensively evaluated [15,16]. Mohan and Singh [17] found that the sorption capacities of Cd and Zn on activated carbon in single- and multi-component decreased in the following order for their adsorption in multi-component system: Cd > Cd–Cu > Cd–Zn > Cd–Cu–Zn for Cd; Zn > Zn–Cu > Zn–Cd > Cd–Cu–Zn for Zn. The adsorption capacities of activated carbon for Cd(II) and Zn(II) decreased more in ternary systems as compared to binary systems. Li et al. [18] studied the individual and competitive sorption of Pb(II), Cu(II) and Cd(II) ions on HNO₃ oxidized carbon nanotubes (CNTs). The maximum sorption capacities calculated by applying the Langmuir equation to single ion adsorption isotherms were 97.1 mg g⁻¹ for Pb, 24.5 mg g⁻¹ for Cu, and 10.9 mg g⁻¹ for Cd at an equilibrium concentration of 10 mg l⁻¹. The sorption capacities of CNTs for the

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three metal ions are in the order of $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)}$. The sorption capabilities of CNTs without competition are much higher than those with competition.

The purposes of this study were to evaluate the adsorption of Cu(II) or Cd(II) from single and binary solutions on a modified carbon black (MCB) after strong oxidation with HNO_3 , and examine the effect of their interaction on the sorption of Cu(II) and Cd(II) ions by the MCB. The study aimed at developing a good material for further in situ remediation of a Cu and Cd contaminated soil.

2. Materials and methods

2.1. Modification of nanoscale carbon black

A commercial nanoscale carbon black (CB) with particle size of 20–70 nm was purchased from Jinan Carbon Black factory, Shandong Province, China. This carbon black was further oxidized with 65% HNO_3 for modification by refluxing 10 g of carbon black with 150 ml HNO_3 (65%) in a conical flask at 110 °C for 120 min. The MCB was filtered, washed with deionized water until the pH of the filtrate became stable and finally dried in a vacuum oven at 110 °C for 24 h. The specific surface areas of the CB and MCB determined by the BET method in a Micrometrics Accusorb 2100E were 1259 and 643 $\text{m}^2 \text{g}^{-1}$, respectively. Oxidation increased the functional groups of CB but destroyed its structure.

2.2. Determination of zeta potential of the CB and MCB

The CB and MCB suspensions (0.4g l^{-1}) containing 0.01 M NaNO_3 as background electrolyte were prepared at different pH values. The suspensions were dispersed ultrasonically at a frequency of 40 kHz and a power of 300 W for 1 h, and then shaken for 20 h at 25 °C. After equilibrated for two days, the zeta potential was measured using a JS94C⁺ micro-electrophoresis instrument (Powereach Instruments, Shanghai, China) and the suspension pH was also determined.

2.3. FTIRs of the MCB

Infrared spectra (IR) of the MCB were recorded using a Perkin-Elmer 2000 FTIR spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector covering the frequency range 500–4000 cm^{-1} . The sample cell was purged with nitrogen gas throughout data collection to exclude carbon dioxide and water vapor. Ten milligrams of the dried samples were even dispersed in 200 mg of spectroscopic grade KBr to record the spectra.

2.4. Adsorption isotherms of Cu(II) and Cd(II) on the CB and MCB with different ionic strengths

Adsorption isotherms of Cu(II) and Cd(II) were measured by adding 0.100 g of CB or MCB to 20 ml of 0.001, 0.01, or 0.1 M NaNO_3 solution containing 12.5 mM of 2-(N-morpholino)ethanesulfonic acid (MES, pH 5.5) as buffer in a 50 ml centrifuge tube. Then, 5.0 ml of 0.001, 0.01, or 0.1 M NaNO_3 solution with different concentrations (0–10.0 mM) of $\text{Cu(NO}_3)_2$ or $\text{Cd(NO}_3)_2$ was added. The final volume of 25.0 ml resulted in the suspension Cu(II) or Cd(II) concentrations to be 0, 0.2, 0.4, 1.0, 1.6 and 2.0 mM. Preliminary adsorption kinetics showed that the adsorption of Cu(II) or Cd(II) on the CB and MCB reached equilibrium within 2 h. Therefore, the centrifuge tubes were continuously shaken at 25 °C for 2 h, centrifuged at $9000 \times g$ for 10 min, and then filtered through a 0.45 μm membrane filter. Solution pH was measured by a pH electrode (Leichi Instruments, Shanghai, China). The Cu(II) or Cd(II) concentration in the filtrate was determined by AAS. The amount of Cu(II) or Cd(II) adsorbed was calculated from the difference in concentrations

between the initial and equilibrium solutions. The experiments were performed in duplicate.

For competitive adsorption of Cu(II) and Cd(II) in binary system, the two metal ions were mixed by fixing one while changing the another, with the concentrations the same as in the single system. The procedures for the testing and analysis were also the same as described above.

2.5. Desorption of Cu(II) and Cd(II) from the MCB

Immediately following the adsorption of Cu(II) or Cd(II) from solutions, the centrifuged residues were weighed to determine the amount of occluded solution (to be able to take the metal dissolved in this solution into the account while calculating desorption), and were then re-suspended in 25 ml of 0.1 M NaNO_3 and equilibrated at 25 °C for 2 h before centrifugation of the suspension, and removal and filtration of the supernatant. Copper(II) or Cd(II) concentrations in the pooled supernatant were measured as described above, and desorbed amounts of Cu(II) or Cd(II) were calculated and expressed as a percentage of the previously adsorbed [19].

2.6. Adsorption edges of Cu(II) and Cd(II) on the MCB

The pH-adsorption edges of Cu(II) and Cd(II) on the MCB were performed by adding 0.100 g of MCB to 20 ml of 0.01 M NaNO_3 solution in a 50 ml centrifuge tube. Then, 5.0 ml of 0.01 M NaNO_3 solution with 5.0 mM Cu(II) or Cd(II) as nitrate salts was added. To obtain different pH levels, one or two drops of various concentrations of HNO_3 or NaOH solution were added to the tubes, and the final concentration of Cu(II) or Cd(II) was 1.0 mM. The centrifuge tubes were continuously shaken at 25 °C for 2 h, centrifuged at $9000 \times g$ for 10 min, and then filtered through a 0.45 μm membrane filter. Solution pH was measured by a pH electrode (Leichi Instruments, Shanghai, China). The procedures for testing and analysis were also the same as described above.

3. Results and discussion

3.1. Adsorption isotherms of Cu(II) and Cd(II) on the CB and MCB with different ionic strengths

Fig. 1 illustrated the adsorption isotherms of Cu(II) and Cd(II) on the CB and MCB at pH 5.5 with different ionic strengths. Although the specific surface area of MCB was much lower than that of CB, the adsorption quantities of Cu(II) and Cd(II) on the MCB were much higher than those on the CB. The result indicated that the physical adsorption, which was dependent on specific surface area, is not the main mechanism. Increasing adsorption of Cu(II) and Cd(II) on the MCB might be ascribed to increasing the amount of functional groups after oxidation of the CB surface.

The IR spectra of the CB and MCB were presented in Fig. 2. Compared with the CB, the MCB exhibited some characteristic peaks at wavenumbers of 1580, 1709 and 3424 cm^{-1} , which were associated with hydroxyl groups or carbonyl groups, carboxylic acids and hydroxyl groups [13], respectively. The increased amounts of these functional groups resulted in an increasing surface cation exchange and complexation capacity of the CB [18]. The zeta potentials of both the CB and MCB were shown in Fig. 3. The MCB has a more negative zeta potential than the CB, which is consistent with the conclusion that oxidation increased the functional groups of CB surfaces.

Adsorption isotherms of Cu(II) and Cd(II) on the CB and MCB were fitted by Freundlich and Langmuir models. Freundlich equation was expressed as:

$$q_e = K_f C_e^{1/n}$$

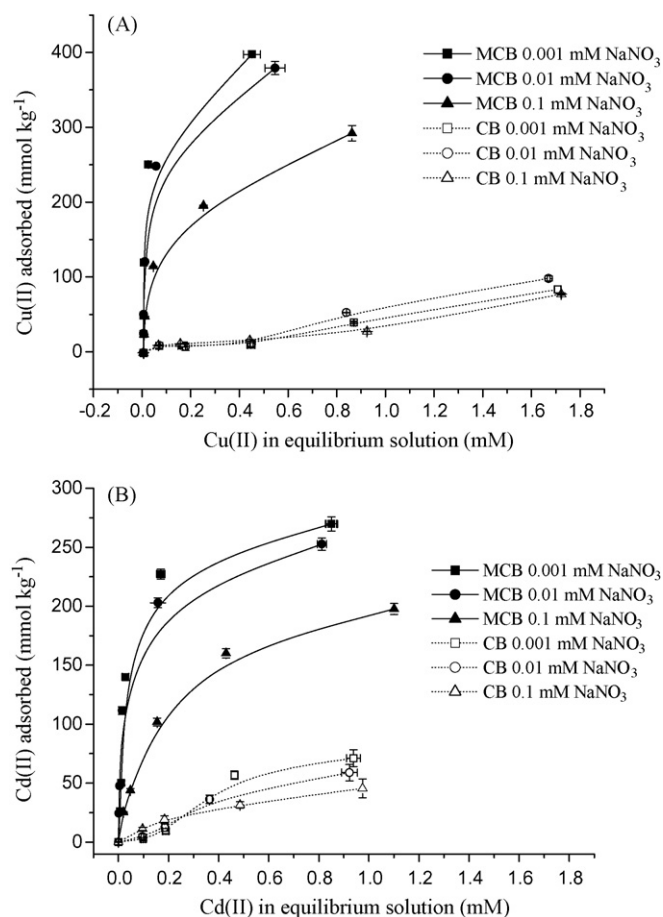


Fig. 1. Adsorption isotherms of Cu(II) (A) and Cd(II) (B) on the CB and MCB in the presence of 0.001, 0.01, and 0.1 M NaNO₃ solution.

where C_e (mg l^{-1}) was the equilibrium concentration of the solute, q_e (mg kg^{-1}) was the adsorbed quantity of Cu(II) or Cd(II). K_F and n were Freundlich constants which gave an estimate of the adsorption capacity and intensity, respectively. The values of the calculated Freundlich constants K_F and $1/n$ were listed in Table 1. The adsorption isotherms of Cu(II) and Cd(II) on the MCB fit the Freundlich isotherm well (R^2 : 0.789–0.971). In each case, the value of n was above 1, indicating that the adsorption was favorable.

The Langmuir isotherm was originally developed to represent chemisorption on a set of distinct adsorption sites. The common form of the Langmuir isotherm was expressed as:

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e}$$

where q_e was the adsorption quantity of metals on adsorbent (mg g^{-1}), C_e was the concentration of metals in equilibrium solution (mg l^{-1}), and K_L was the Langmuir adsorption constant which

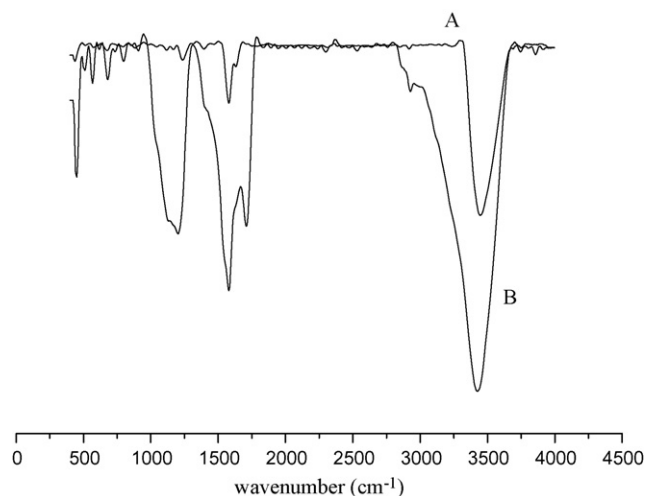


Fig. 2. The Fourier-transformed infrared spectra of the CB (A) and MCB (B).

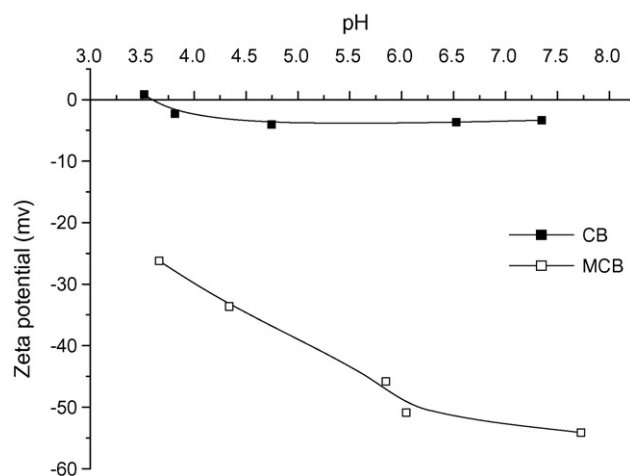


Fig. 3. Zeta potential of the CB and MCB.

related to the adsorption energy. The values of R^2 were 0.887–0.999, suggesting these adsorption events fitted the Langmuir isotherm quite well.

The two models for the adsorption isotherms of Cu(II) and Cd(II) on the MCB were compared in Table 1, where the Langmuir model was more applicable than the Freundlich one, since the correlation coefficients for the former were higher than the latter. Mohan and Chander [15] also found that Freundlich and Langmuir models fit the adsorption isotherms of metal ions on activated carbons well, but Langmuir isotherm fits the data better in single component systems whereas the Freundlich one was better in multi-component systems.

Table 1

Parameters for the adsorption isotherm of Cu(II) and Cd(II) on the MCB in single component system at pH 5.5 with different concentrations of NaNO₃.

	NaNO ₃ (M)	Langmuir isotherm			Freundlich isotherm		
		q_{\max} (mmol kg^{-1})	K_L (l kg^{-1})	R^2	K_F (mmol kg^{-1})	$1/n$	R^2
Cu(II)	0.001	438 ± 70.2	29.9 ± 13.7	0.887	558 ± 139	0.39 ± 0.12	0.789
	0.01	417 ± 43.7	22.1 ± 7.30	0.954	503 ± 95.9	0.39 ± 0.10	0.857
	0.1	311 ± 28.9	9.80 ± 3.20	0.973	322 ± 29.2	0.43 ± 0.07	0.953
Cd(II)	0.001	282 ± 14.2	26.3 ± 5.0	0.986	306 ± 42.1	0.29 ± 0.07	0.895
	0.01	245 ± 9.4	55.0 ± 9.40	0.991	283 ± 26.5	0.26 ± 0.04	0.951
	0.1	234 ± 3.4	5.04 ± 0.22	0.999	201 ± 12.9	0.42 ± 0.06	0.969

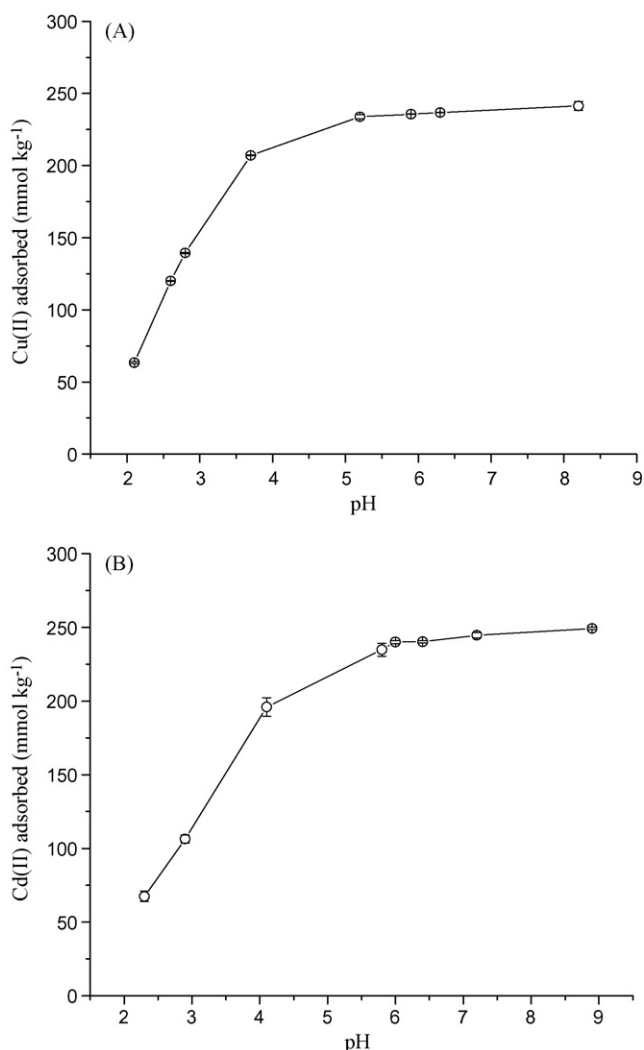


Fig. 4. Effect of pH on the adsorptions of Cu(II) (A) and Cd(II) (B) by the MCB (initial concentrations of both Cu(II) and Cd(II) were 1.0 mM in 0.01 M NaNO₃ solution).

The maximum sorption quantities calculated by applying the Langmuir equation to single ion adsorption isotherms on the MCB were 438 and 282 mmol kg⁻¹ for Cu(II) and Cd(II), respectively. The

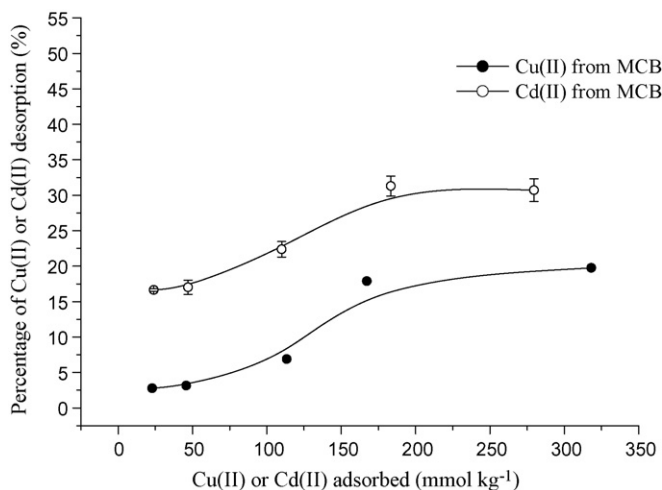


Fig. 5. Desorption of Cu(II) and Cd(II) from the MCB expressed as percent of the initial amount of Cu(II) and Cd(II) adsorbed at pH 5.5 in 0.01 M NaNO₃ solution.

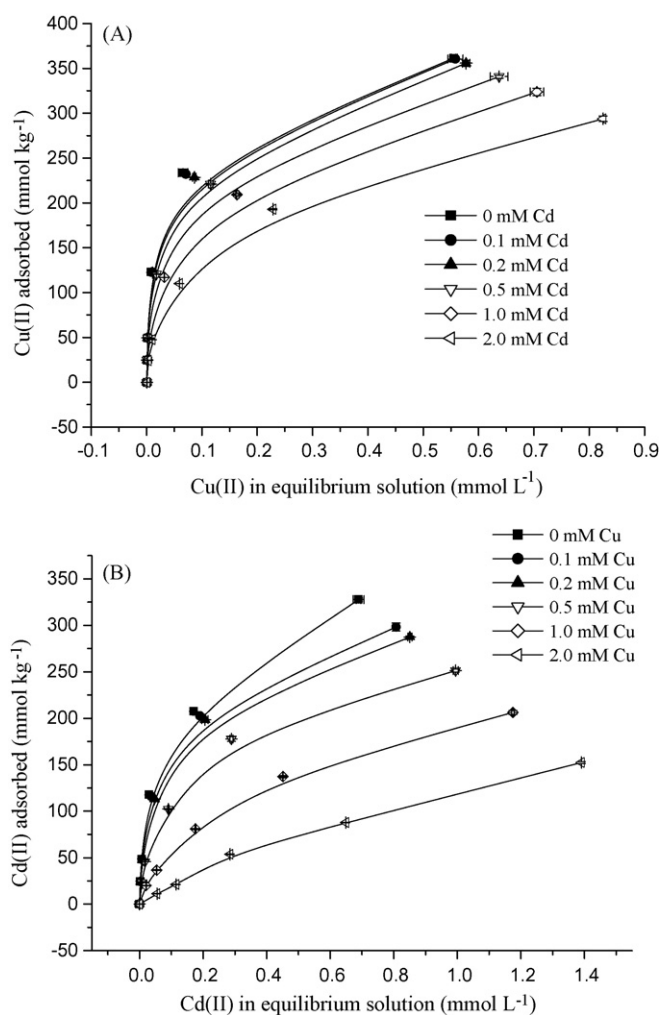


Fig. 6. Adsorption isotherms of Cu(II) and Cd(II) on the MCB in binary component system (initial concentrations of Cu(II) and Cd(II) varied from 0 to 2.0 mM, pH 5.5) in 0.01 M NaNO₃ solution.

sorption capacities of the two metal ions on the MCB were in the order of Cu(II) > Cd(II). This result matched well with their hydrated ionic radii Cu(II) (4.19 Å) < Cd(II) (4.26 Å) and the ionic radii Cu(II) (0.73 Å) < Cd(II) (0.95 Å).

The ionic strengths of 0.001, 0.01 and 0.1 M NaNO₃ were chosen to investigate their effect on the adsorption of Cu(II) or Cd(II) on the MCB (Fig. 1). The adsorption capacities of Cu(II) or Cd(II) on the MCB decreased with increasing ionic strength. This might be attributed to two factors. First, Cu(II) or Cd(II) ions formed electrical double layer complexes with the MCB, and the adsorption sites were occupied when the competing salt was added. The second factor was the influence of ionic strength on the activities of Cu(II) or Cd(II) ions, which limited their transfer to the MCB surfaces. Li et al. [18] also found that the adsorption of Cu(II), Cd(II), and Pb(II) on CNTs decreased with increasing ionic strengths.

3.2. pH-adsorption edges of Cu(II) and Cd(II) on the MCB

Fig. 4 presented the adsorption edges of Cu(II) and Cd(II) on the MCB at different equilibrium solution pH. The solution pH had a significant effect on the adsorption of Cu(II) or Cd(II). In general, heavy metal adsorption was small at low pH. Adsorption then increased at intermediate pH from near zero to near complete adsorption over a relatively small pH range; this pH range was referred as the

Table 2
Parameters for the adsorption isotherm of Cu(II) and Cd(II) on the MCB in binary component system.

		Langmuir isotherm			Freundlich isotherm		
		q_{\max} (mmol kg ⁻¹)	K_L (l kg ⁻¹)	R^2	K_F (l kg ⁻¹)	$1/n$	R^2
Cu(II)	0 mM Cd	353 ± 28.0	49.0 ± 16.9	0.970	456 ± 54.7	0.32 ± 0.06	0.937
	0.1 mM Cd	352 ± 29.4	46.3 ± 17.1	0.967	453 ± 48.1	0.32 ± 0.05	0.950
	0.2 mM Cd	346 ± 31.3	40.2 ± 16.4	0.962	440 ± 38.7	0.32 ± 0.04	0.965
	0.5 mM Cd	342 ± 30.9	25.1 ± 9.50	0.967	409 ± 29.0	0.33 ± 0.04	0.976
	1.0 mM Cd	341 ± 30.7	13.9 ± 4.64	0.973	377 ± 19.3	0.37 ± 0.03	0.987
	2.0 mM Cd	329 ± 27.9	7.81 ± 2.16	0.981	325 ± 13.3	0.40 ± 0.03	0.991
Cd(II)	0 mM Cu	340 ± 33.0	14.5 ± 5.35	0.969	381 ± 17.3	0.36 ± 0.03	0.991
	0.1 mM Cu	308 ± 22.5	14.7 ± 4.14	0.980	330 ± 19.2	0.35 ± 0.04	0.982
	0.2 mM Cu	305 ± 19.3	11.8 ± 2.72	0.986	315 ± 19.1	0.36 ± 0.04	0.980
	0.5 mM Cu	285 ± 17.7	6.48 ± 1.29	0.990	260 ± 14.0	0.40 ± 0.03	0.982
	1.0 mM Cu	278 ± 15.0	2.33 ± 0.30	0.996	194 ± 6.10	0.52 ± 0.04	0.993
	2.0 mM Cu	335 ± 40.0	0.59 ± 0.11	0.997	120 ± 2.40	0.73 ± 0.03	0.997

pH-adsorption edge. At high pH values, solution metal ions were completely removed [20].

Adsorption of Cu(II) or Cd(II) on the MCB increased with the increasing solution pH. Most of the metals were adsorbed on the MCB when pH was above 5.5. This might be attributed to the surface charge development of the MCB and the concentration distribution of Cu(II) or Cd(II) speciation, which both were pH-dependent. At low pH, the adsorption of Cu(II) or Cd(II) on the MCB was low because of the competition of H⁺ with Cu(II) or Cd(II) on the adsorption sites. The surfaces of MCB had negative charges in a wide pH range, and Cu(II) or Cd(II) carried a positive charge either as Cu(OH)⁺ and Cd(OH)⁺. In this case, adsorption occurred by electrostatic attraction. Li et al. [21] found that the removal of Pb(II) from water by oxidized CNTs was highly dependent on the solution pH value, which affected the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbates. And the adsorption capacity of the CNT for Pb(II) increased with the pH value from 3.0 to 7.0. It was well known that metal adsorption occurs via ion-exchange mechanism and pH level of the aqueous solution influenced the adsorption of metal ions due to competition with hydrogen ions. As the pH level increased, the concentration of H⁺ ions as competitor decreased, while Cu(II) or Cd(II) adsorption increased.

3.3. Desorption of Cu(II) and Cd(II) from the MCB

Fig. 5 showed the desorption of Cu(II) and Cd(II) from the MCB expressed as percent of the initial amount of Cu(II) or Cd(II) adsorbed at pH 5.5 in 0.01 M NaNO₃ solution. Clearly, the proportions of Cu(II) or Cd(II) desorbed depended on the quantities initially adsorbed. Desorption of Cu(II) increased from 2.8% to 20% with increase of Cu(II) loadings from 22.8 to 318 mmol kg⁻¹ on the MCB, and Cd(II) desorption increased from 16.6% to 30% with increase of Cd(II) loadings from 23.9 to 280 mmol kg⁻¹. The desorption of Cu(II) and Cd(II) increased with increasing initial solution Cu(II) and Cd(II) concentrations, indicating that they were adsorbed more strongly at the beginning. The MCB was a good material to immobilize Cu(II) and Cd(II) from aqueous solutions.

3.4. Competitive adsorption of Cu(II) and Cd(II) on the MCB

The competitive adsorption isotherms of Cu(II) and Cd(II) on the MCB under different initial concentrations (0–2 mM) were given in Fig. 6. The parameters obtained from Langmuir and Freundlich models were listed in Table 2. Freundlich isotherms described Cu(II) and Cd(II) isotherms in binary systems well. Adsorption quantities of Cu(II) and Cd(II) were inhibited by each other. The decrement in adsorption capacity of Cd(II) was greater than that of Cu(II). Therefore, the adsorption of Cd(II) was impeded more significantly by

Cu(II). Based on the Freundlich isotherm, the adsorption capacities of Cu(II) decreased from 456 to 325 mmol kg⁻¹ in the presence of 2.0 mM Cd(II), and Cd(II) decreased from 381 to 120 mmol kg⁻¹ with 2.0 mM Cu(II). Competitive adsorption induced a decrease in equilibrium adsorption capacity but the percent of decrease depended on coexisting metal ions. Singh and Yenkie [22] had reported similar results using granular activated carbon columns. Carbon black had good adsorption properties and high capacity for Cu(II) and Cd(II), and could be applied for the purification of heavy metals in aqueous solution.

4. Conclusions

Adsorption of Cu(II) and Cd(II) on the MCB was much higher than those on the parent one. In the binary system of Cu(II) and Cd(II), they exhibited competitive adsorption, and the adsorption of Cd(II) was significantly impeded by Cu(II). The modified carbon black had good adsorption properties and high capacity for Cu(II) and Cd(II), and could be expected for application in the purification of heavy metals in aqueous solution.

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