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Competitive Adsorption of Pb(II), Cu(II), and Cd(II) Ions on Wheat-Residue Derived Black Carbon

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ABSTRACT: The competitive adsorption properties of the heavy metal ions Pb(II), Cu(II), and Cd(II) ions in binary and ternary systems on black carbon (BC) isolated from the burning residue of wheat straw were studied in batch systems. The BC samples were characterized by Fourier transform infrared spectroscopy (FTIR). Equilibrium and kinetic adsorption data showed that the selectivity of metal ions on BC followed the order of Pb(II) > Cu(II) > Cd(II). Kinetic studies were performed, and the rate kinetics was fitted well with the pseudosecond-order model. The Freundlich adsorption isotherm was applicable to the adsorption process, and its constants were evaluated.

1. INTRODUCTION

Heavy metals are discharged from various industries such as electroplating, metal finishing, textile, storage batteries, mining, ceramic, and glass. Heavy metals removal from industrial wastewater has become an important issue because of environmental concerns. Among the heavy metals of public concern, lead and cadmium have received much attention, probably because of their toxicity. The adverse effects of lead, cadmium, and copper have been reported.[1] Presently, numerous processes have been used to remove heavy metals from wastewaters which principally include chemical precipitation, ion-exchange, reverse osmosis, coagulation and flocculation, membrane separation, biosorption, and adsorption.

Among these methods, the adsorption process is highly effective and economical due to its low initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances.[2] Activated carbon is the most widely used adsorbent due to its large specific surface area, microporous structure, active functional groups, and so forth.[3] However, its use is likely limited due to its high cost and low selectivity, which have led many workers to search for more economic substitutes.[4−10] Black carbon (BC), a significant extrinsic carbonaceous component arising from the incomplete combustion of fossil fuels and biomass, is regarded as a potential contaminant adsorbent in soils and sediments.[11,12] Numerous studies have demonstrated that BC in soils is a highly effective adsorbent for organic contaminants (including pesticides).[13−15] Recently, some researchers have applied BC as an adsorbent to remove heavy metal ions from aqueous solutions. Qiu et al.[16] evaluated the adsorptive ability of BC isolated from the burning residue of rice straw and wheat straw for lead ions and suggested the electrostatic interaction between positively Pb(II) and negatively charged functional groups as the primary adsorptive forces. In our previous study, the Cr(VI) reaction mechanism and adsorption performance with wheat-residue derived BC were elucidated, and some physicochemical properties such as surface morphology, specific surface area, zero point of charge (pH_{ZPC}), and surface acidity/basicity, and so forth, have been reported.[17]

In general, contaminated water contains more than one heavy metal. It is thus of more interest to investigate the adsorption equilibrium and kinetics of multiple heavy metal ions in wastewater. As a continuation of our effort in developing BC for heavy metal removal from wastewater, we attempted to examine the competitive adsorption properties of heavy metals Pb(II), Cu(II), and Cd(II) on BC in binary and ternary systems in this work.

2. MATERIALS AND METHODS

2.1. Materials and Sample Preparation. Lead nitrate, copper nitrate, cadmium nitrate, hydrochloric acid, hydrofluoric acid, nitric acid, and sodium hydroxide were purchased from the Shanghai Chemical Reagent Company (Shanghai, China) and were of analytical reagent (A.R.) grade. The wheat straw (*Triticum aestivum L.*) was collected from the croplands of Yuntai District (Lianyungang, China). The BC samples were prepared according to Wang et al.[17]

2.2. Infrared Spectroscopy. The Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Fourier transform infrared spectrometer (FT/IR-5300). The powders were blended with IR-grade KBr in an agate mortar and pressed into tablets.

2.3. Adsorption of Heavy Metal Ions. Pb(II), Cu(II), and Cd(II) solutions were prepared from $Pb(NO_3)_2$, $Cu(NO_3)_2\cdot 3H_2O$, and $Cd(NO_3)_2\cdot 4H_2O$. The speciation distribution of the heavy metal ions studied was calculated using the Medusa computer program developed by the Royal Institute of Technology (KTH), Sweden.

The adsorption equilibrium measurements of the binary and ternary metal ion systems were carried out at 25 °C. About 0.5 g of a BC sample was placed in a 100 mL conical flask containing 50 mL of heavy metal solution with initial concentration ranges from (2 to 20) $mmol\cdot L^{-1}$. The pH of the solution was maintained at 5.0 by using nitric acid to avoid metal precipitation at a high pH.

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Table 1. Metal Solutions Used to Study Competitive Kinetics (25 °C and pH 5)

system	solution mixture
binary	20 $\text{mmol}\cdot\text{L}^{-1}$ Pb^{2+} + 20 $\text{mmol}\cdot\text{L}^{-1}$ Cu^{2+}
	20 $\text{mmol}\cdot\text{L}^{-1}$ Pb^{2+} + 14 $\text{mmol}\cdot\text{L}^{-1}$ Cu^{2+}
	20 $\text{mmol}\cdot\text{L}^{-1}$ Pb^{2+} + 20 $\text{mmol}\cdot\text{L}^{-1}$ Cd^{2+}
	20 $\text{mmol}\cdot\text{L}^{-1}$ Pb^{2+} + 14 $\text{mmol}\cdot\text{L}^{-1}$ Cd^{2+}
	20 $\text{mmol}\cdot\text{L}^{-1}$ Cu^{2+} + 20 $\text{mmol}\cdot\text{L}^{-1}$ Cd^{2+}
ternary	20 $\text{mmol}\cdot\text{L}^{-1}$ Pb^{2+} + 20 $\text{mmol}\cdot\text{L}^{-1}$ Cu^{2+} + 20 $\text{mmol}\cdot\text{L}^{-1}$ Cd^{2+}

For the kinetic experiments, 1.5 g of a dried BC sample was added into 250 mL of a solution containing multiple heavy metal ions with the initial concentrations shown in Table 1. The suspension was withdrawn at a given time interval and rapidly filtered through a 0.45 μm nylon membrane filter. The filtrate was collected for subsequent measurements of the concentrations of the heavy metal ions by using an inductive-coupled plasma-atomic emission spectrometer (ICP-AES, CAP6300, Thermo Scientific).

The amounts of metals adsorbed by the adsorbent (q) in the sorption system was calculated using the mass balance equation:

$$q = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where V is the solution volume (L), m is the amount of adsorbent (g), and C_0 and C_e ($\text{mmol}\cdot\text{L}^{-1}$) are the initial and equilibrium metal concentrations, respectively.

3. RESULTS AND DISCUSSION

3.1. Speciation of Aqueous Metal Ions. The speciation of metal ions in an aqueous solution significantly influences their interaction with a solid adsorbent.[18] In this study, the metal solutions applied were prepared from nitrate compounds. The speciation distribution of the three metals versus pH at the metal ionic concentration of 10 $\text{mmol}\cdot\text{L}^{-1}$ are presented in Figure 1. It is found that at pH < 5.0, Pb(II), Cu(II), and Cd(II) species are present totally in ionic states, namely, Me^{2+} and $MeNO_3^{+}$, where Me represents Pb, Cu, and Cd. With increasing pH, Pb^{2+}, Cu^{2+}, and Cd^{2+} species starts to hydrolyze and entirely precipitate into $Pb(OH)_2$ and CuO at pH > 6.0, whereas formation of $Cd(OH)_2$ starts at a higher pH value. Accordingly, divalent metal ions (Pb^{2+}, Cu^{2+}, and Cd^{2+}) are believed to be the major species with a small amount of $PbNO_3^{+}$, $CuNO_3^{+}$, and $CdNO_3^{+}$ under the experimental conditions applied in this study (pH 5.0).

3.2. Competitive Adsorption Isotherms of Binary or Ternary Metal Ions. The competitive adsorption isotherms of the metal ions in binary systems Pb(II)/Cu(II), Pb(II)/Cd(II), and Cu(II)/Cd(II) on BC are presented in Figure 2. As can be seen from Figure 2, in Pb(II)/Cu(II) and Pb(II)/Cd(II) binary mixture systems, Pb(II) ions are always favorably adsorbed on BC over Cu(II) and Cd(II) ions. In Cu(II)/Cd(II) binary system, Cu(II) ions are favorably adsorbed on BC over Cd(II) ions. The possible reason may be due to the selectivity of ion exchange in multicomponent systems, and the selectivity of metal ions on BC follows the order Pb(II) > Cu(II) > Cd(II). This trend is matched with the reverse order of hydrated ionic radii but does not coincide with the values of other parameters listed in Table 2. Choy and McKay[23] studied the sorption of metal ions onto bone char. As bone char removes the metal ions from solution by both ion adsorption and ion exchange effects, the selectivity properties should be similar to BC. The selectivity of bone char followed Cu(II) > Cd(II) > Zn(II). Lee and Moon[24] studied the sorption of metal ions onto natural zeolites, and the resultant trend is also matched with the reverse order of the hydrated ionic radii Pb(II) > Cu(II) > Cd(II). However, Lv et al.[18] investigated the competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on the microporous titanosilicate ETS-10 and found the affinity order of $Pb^{2+} > Cd^{2+} > Cu^{2+}$. The results mentioned demonstrate that the competitive adsorption of heavy metal ions from aqueous solution seems to be affected by a combination of factors corresponding to the physicochemical characteristics of both the solution and the solid adsorbent itself.

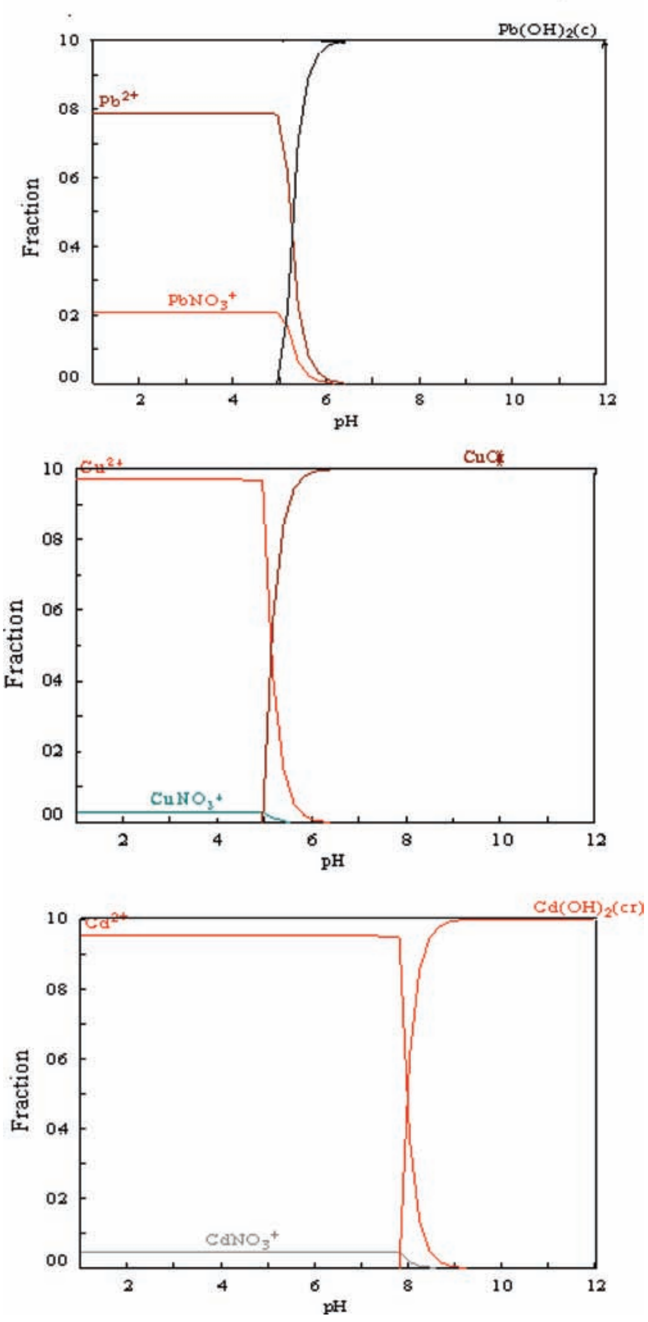

Figure 1. Species fraction diagrams versus pH (10 $\text{mmol}\cdot\text{L}^{-1}$ lead nitrate, copper nitrate, and cadmium nitrate).

Relationship with the Hard Soft Acids and Bases (HSAB) Principle. Essentially, the HSAB theory on hard or soft acids and bases establishes that hard acids prefer to coordinate to hard bases and soft acids to soft bases.[25] The cations Pb^{2+} (absolute hardness, η, 8.5) and Cu^{2+} (absolute hardness, η, 8.3) are considered to be Pearson's borderline Lewis acids, while Cd^{2+} belongs to Pearson's soft Lewis acid according to the Pearson's classification.[25,26] It should be stressed that, although Cd^{2+} has been termed a soft metal in accordance with the classification of Pearson, in fact, Cd^{2+} is regarded as a borderline ion of slightly less class B (soft) character than Cu^{2+} as a result of the lower product of its electronegativity and ionic radius.[27,28] These classifications also correlate well with the present results (Pb(II) > Cu(II) > Cd(II)).

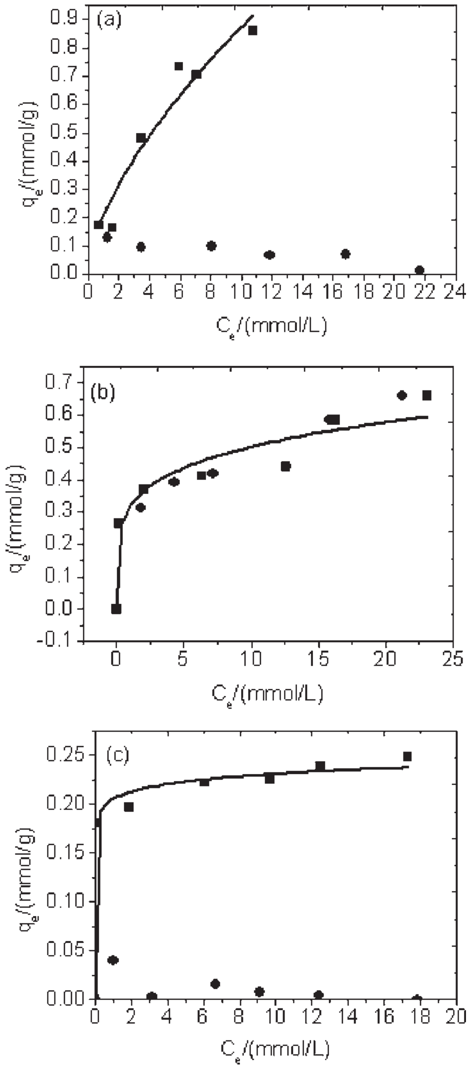

Figure 2. Competitive adsorption isotherms of binary metal ions on BC [a: Pb(II) (■)/Cu(II) (●); b: Pb(II) (■)/Cd(II) (●); c: Cu(II) (■)/Cd (II) (●)] (reaction temperature: 25 °C, pH 5, adsorbent concentration: 10 g·L^{-1}; reaction time: 5 h).

The Freundlich isotherm equation was applied to the single metal isothermal data and is written as

$$q_{e,i} = k_{f,i} C_{e,i}^{\ 1/n_i} \qquad (2)$$

where $k_{f,i}$ $((\text{mg}\cdot\text{g}^{-1})/(\text{mg}\cdot\text{L}^{-1})^{1/n})$ and n_i are the constants of Freundlich equation, respectively.

The experimental data were successfully fitted to the Freundlich model (Table 3 and Figure 2). Compared to the fitting result by the Freundlich equation, the experimental data did not conform to the Langmuir model (data not shown). The empirical form of Freundlich isotherm is applicable to monolayer adsorption (chemisorption) and multilayer adsorption (van der Waals adsorption).[29] Some authors explain that the Langmuir equation corresponds to a dominant ion-exchange mechanism, while the Freundlich isotherm shows adsorption-complexation reactions take place in the adsorption process.[30] It is pointed out that it is worthy of being further investigated to identify the interaction mechanism only from the point of view of correlation to the isotherms.

3.3. Competitive Adsorption Kinetics of Binary or Ternary Metal Ions. The competitive adsorption kinetics of binary systems Pb(II)/Cu(II) and Pb(II)/Cd(II) with different ratios of initial concentrations and the binary system Cu(II)/Cd(II) and ternary system Pb(II)/Cu(II)/Cd(II) with an equal ratio are shown in Figures 3 to 5. In the Pb(II)/Cu(II) system, it can be seen that the uptake of Pb(II) ions was rapid at the beginning and was followed by the subsequent slower removal of Pb(II) which continued for a relatively long period of time until the adsorption equilibrium was attained. The uptake kinetics of Cu(II) exhibited a different trend: in the early stage a maximum was reached and then decreased progressively as the contact time was prolonged. This phenomenon has been attributed to the competition between Pb(II) and Cu(II) for the active sites on the BC surface.[18] Although an increase in the initial concentration of Cu(II) ions gave rise to a decline in the adsorption amounts of Pb(II), there was no evident difference in the competitive adsorption behavior of both metal species.

Similar adsorption kinetics were observed in the other binary and the ternary systems (Figures 4 and 5). If metals are competing for the same active sites on an adsorbent, those metals with a

Table 3. Freundlich Parameters for Heavy Metal Ions Pb(II), Cu(II), and Cd(II) in a Binary System

metal species	k_f	$1/n$	r
Pb(II) in Pb(II)/Cu(II) system	0.204	0.631	0.970
Pb(II) in Pb(II)/Cd(II) system	0.316	0.201	0.970
Cu(II) in Cu(II)/Cd(II) system	0.206	0.051	0.995

Table 2. Some Physicochemical Parameters of Selected Heavy Metal Ions in Solutions

	effective ionic radius[19]	ionic potential[20]	enthalpy of hydration[21]	hydrolysis constants[22]	hydrated radius[20]
	(r_{eff})/nm	Z^2/r_{eff}	kJ·mol^{-1}	pK_h	nm
Pb^{2+}	0.143	2	−1556	7.8	0.401
Cu^{2+}	0.087	2.6	−2174	7.5	0.419
Cd^{2+}	0.124	2.3	−1882	11.7	0.426

stronger affinity can replace others with a weaker affinity. Therefore, the results show that the Pb(II) affinity to BC is the highest among the three metals studied, followed by that of Cu(II), and then Cd(II), which is in accordance with the order observed in the equilibrium experiments.

The kinetic data were fitted to the pseudosecond-order kinetic model suggested by Ho and McKay.[31] The kinetic rate equation can be written as follows

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (3)$$

where q_t is the amount adsorbed at time t (mmol·g^{-1}) and k is the equilibrium rate constant of the second-order sorption (g·mmol^{-1}·min^{-1}). Nonlinear regressions using a least-squares fitting program (Origin 7.0, OriginLab Corp., Northampton, MA) were conducted to acquire the best estimate of all constants.

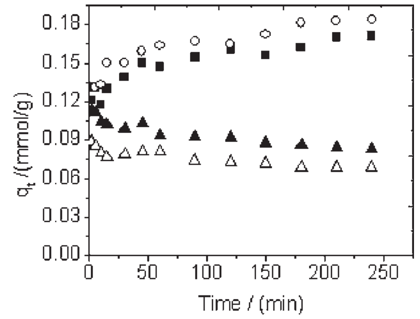

Figure 3. Competitive adsorption kinetics in Pb(II)/Cu(II) system [20 mmol·L^{-1} Pb^{2+} (■) + 20 mmol·L^{-1} Cu^{2+} (▲), 20 mmol·L^{-1} Pb^{2+} (○) + 14 mmol·L^{-1} Cu^{2+} (△)] (reaction temperature: 25 °C, pH 5, adsorbent concentration: 15 g·L^{-1})).

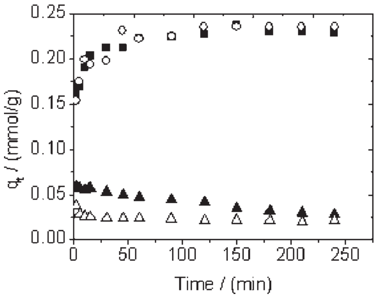

Figure 4. Competitive adsorption kinetics in Pb(II)/Cd(II) system [20 mmol·L^{-1} Pb^{2+} (■) + 20 mmol·L^{-1} Cd^{2+} (▲), 20 mmol·L^{-1} Pb^{2+} (○) + 14 mmol·L^{-1} Cd^{2+} (△)] (reaction temperature: 25 °C, pH 5, adsorbent concentration: 15 g·L^{-1}).

The kinetic parameters acquired from fitting results are summarized in Table 4. The high correlation coefficients (r) implied that the kinetic data fitted the pseudosecond-order equation well and also adsorption of metal ions on those samples was closer to chemisorption.[31]

3.4. FTIR Analyses. Figure 6 shows the infrared spectra of the virgin BC and the BC contacted with the acidic Cu(II) solution. The infrared spectra of the Pb(II)−BC and Cd(II)−BC were similar to those of Cu(II), and thus these data are not shown. The most prominent peak at around 3446 cm^{-1} was attributed to

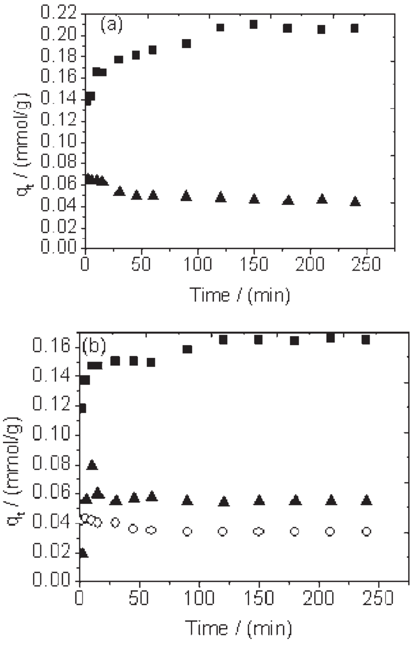

Figure 5. Competitive adsorption kinetics of (a) 20 mmol·L^{-1} Cu^{2+} (■) + 20 mmol·L^{-1} Cd^{2+} (▲), and (b) 20 mmol·L^{-1} Pb^{2+} (■) + 20 mmol·L^{-1} Cu^{2+} (▲) + 20 mmol·L^{-1} Cd^{2+} (○) (reaction temperature: 25 °C, pH 5, adsorbent concentration: 15 g·L^{-1}).

Table 4. Pseudosecond-Order Kinetics Parameters for Heavy Metal Ions Pb(II), Cu(II), and Cd(II) in a Binary System

	q_e	k	
metal species	mmol·g^{-1}	g·mmol^{-1}·min^{-1}	r
Pb(II) in Pb(II)/Cu(II) System			
20 mmol·L^{-1} Pb^{2+} + 20 mmol·L^{-1} Cu^{2+}	0.1529	8.0151	0.9653
20 mmol·L^{-1} Pb^{2+} + 14 mmol·L^{-1} Cu^{2+}	0.1721	2.8391	0.9891
Pb(II) in Pb(II)/Cd(II) System			
20 mmol·L^{-1} Pb^{2+} + 20 mmol·L^{-1} Cd^{2+}	0.2256	3.9027	0.9884
20 mmol·L^{-1} Pb^{2+} + 14 mmol·L^{-1} Cd^{2+}	0.2289	3.4527	0.9861
Cu(II) in Cu(II)/Cd(II) System			
20 mmol·L^{-1} Cu^{2+} + 20 mmol·L^{-1} Cd^{2+}	0.1963	3.9303	0.9771
Pb(II) in Pb(II)/Cu(II)/Cd(II)			
20 mmol·L^{-1} Pb^{2+} + 20 mmol·L^{-1} Cu^{2+} + 20 mmol·L^{-1} Cd^{2+}	0.1596	8.0305	0.9926

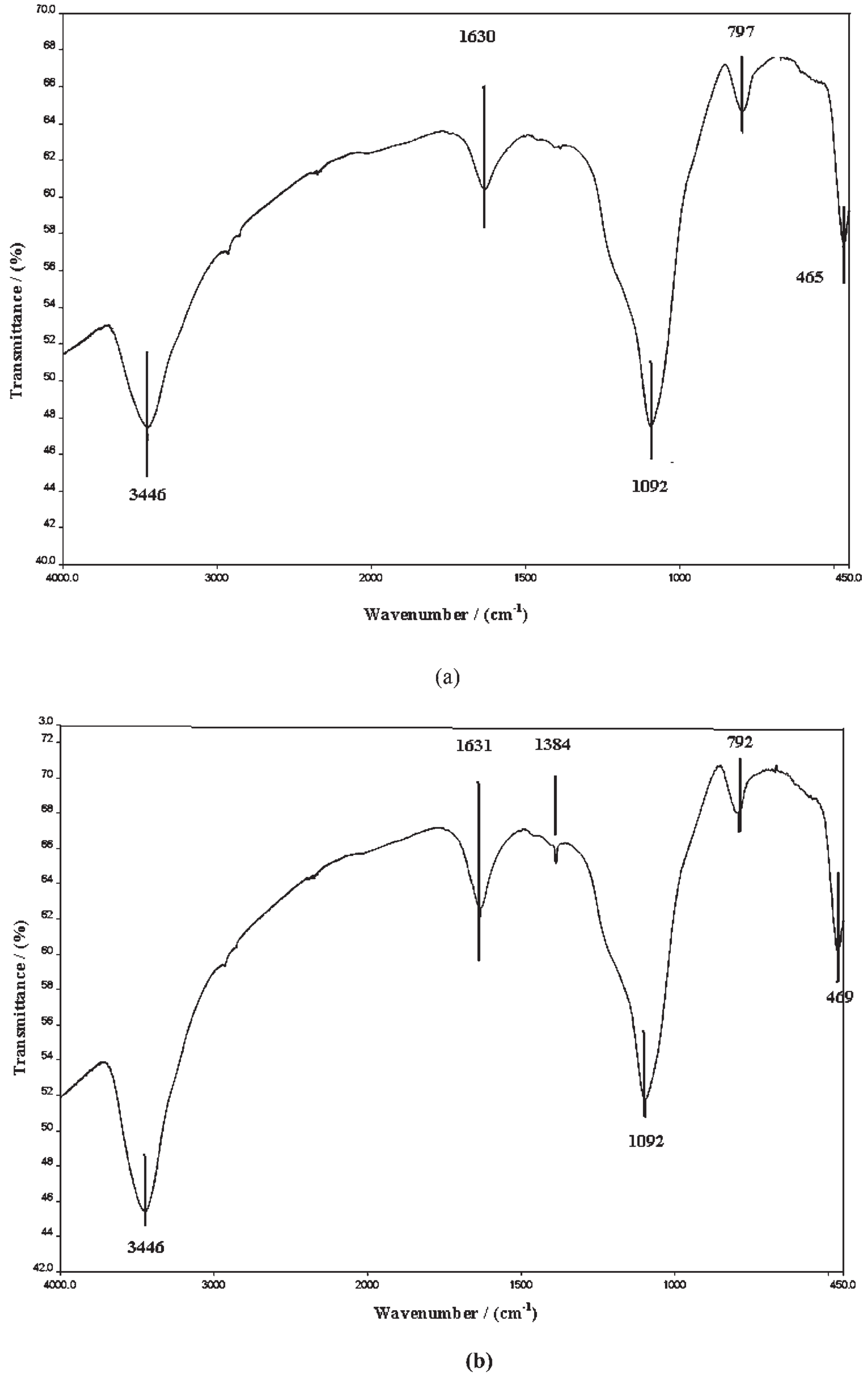

Figure 6. FTIR spectra of (a) untreated BC and (b) Cu(II)-loaded BC.

phenolic hydroxyl stretching vibration, and the band at 1630 cm^{-1} represented contribution from aromatic C=O stretching (quinines or conjugated ketone).[32] The bands at (1092 and 797) cm^{-1} were assigned to aliphatic ether (C—O) stretching and aliphatic CH_2 deformation, respectively.[16] The Cu(II) adsorption induced some small modifications of the IR spectrum (Figure 6b). The neo-formed sharp absorption peak at 1384 cm^{-1} was confidently assigned to the C—O^{-} stretching of carboxylate anion,[33] indicating likely interactions between the carboxylate anion (—COO^{-}) and Cu(II). Similarly, Cu(II) binding with carboxylate groups on humic and fulvic acids have been demonstrated by NMR and FTIR analysis.[34]

4. CONCLUSIONS

A BC sample isolated from the burning residue of wheat straw was applied to investigate the competitive adsorption characteristics of binary and ternary systems of the heavy metals Pb(II), Cu(II), and Cd(II) ions. In batch systems, the competitive adsorption ability of heavy metal ions in a binary or a ternary system toward BC followed Pb(II) > Cu(II) > Cd(II). Such a trend is matched with the reverse order of the hydrated ionic radii of the heavy metal species. The equilibrium behavior of heavy metals with a stronger affinity toward BC could be fitted by the Freundlich isotherm very well while the adsorption kinetics of the metal ions could be well-fitted to the pseudosecond-order equation.

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■ REFERENCES

(1) Meng, Z. Q. *Environmental Toxicology*; China Environmental Science Press: Beijing, P. R. China (in Chinese).

(2) Dupont, L.; Guillon, E. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. *Environ. Sci. Technol.* **2003**, *37*, 4235–4241.

(3) Chen, J. P.; Lin, M. Equilibrium and kinetics of metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modeling studies. *Water Res.* **2001**, *35*, 2385–2394.

(4) Dönmez, G.; Aksu, Z. Removal of chromium (VI) from saline wastewaters by *Dunaliella* species. *Proc. Biochem.* **2002**, *38*, 751–762.

(5) Loukidou, M. X.; Zouboulis, A. I.; Karapantsios, T. D.; Matis, K. A. Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*. *Colloids Surf., A* **2004**, *242*, 93–104.

(6) Park, D.; Yun, Y.; Park, J. M. Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia sp*. *Chemosphere* **2005**, *60*, 1356–1364.

(7) Amir, H. M.; Dariush, N.; Forugh, V.; Shahrokh, N. Tea waste as an adsorbent for heavy metal removal from industrial wastewaters. *Am. J. Appl. Sci.* **2005**, *1*, 372–375.

(8) Wang, X. S.; Li, Z. Z.; Sun, C. Removal of Cr(VI) from aqueous solutions by low-cost biosorbents: marine macroalgae and agricultural by-products. *J. Hazard. Mater.* **2008**, *153*, 1176–1184.

(9) Wang, X. S.; Li, Z. Z.; Tao, S. R. Removal of chromium (VI) from aqueous solution using walnut hull. *J. Environ. Manag.* **2009**, *90*, 721–729.

(10) Wang, X. S.; Tang, Y. P.; Tao, S. R. Kinetics, equilibrium and thermodynamic study on removal of Cr(VI) from aqueous solutions using low-cost adsorbent alligator weed. *Chem. Eng. J.* **2009**, *148*, 217–225.

(11) Pignatello, J. J.; Kwon, S.; Lu, Y. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. *Environ. Sci. Technol.* **2006**, *40*, 7757–7763.

(12) Zhu, D. Q.; Pignatello, J. J. Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. *Environ. Sci. Technol.* **2005**, *39*, 2033–2041.

(13) Yang, Y.; Sheng, G. Enhanced pesticide sorption by soils containing particulate matter from crop burns. *Environ. Sci. Technol.* **2003**, *37*, 3635–3639.

(14) Cornelissen, G.; Gustafsson, Ö. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. *Environ. Sci. Technol.* **2004**, *38*, 148–155.

(15) Chen, J.; Zhu, D.; Sun, C. Effect of heavy metals on the sorption of hydrophobic organic compounds to wood charcoal. *Environ. Sci. Technol.* **2007**, *41*, 2536–2541.

(16) Qiu, Y.; Cheng, H.; Xu, C.; Sheng, G. D. Surface characteristics of crop-residue-derived black carbon and lead (II) adsorption. *Water Res.* **2008**, *42*, 567–574.

(17) Wang, X. S.; Chen, L. F.; Li, F. Y.; Chen, K. L.; Wan, W. Y.; Tang, Y. J. Removal of Cr(VI) with wheat-residue derived black carbon: reaction mechanism and adsorption performance. *J. Hazard. Mater.* **2010**, *175*, 816–822.

(18) Lv, L.; Hor, M. P.; Su, F.; Zhao, X. S. Competitive adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on microporous titanosilicate ETS-10. *J. Colloid Interface Sci.* **2005**, *287*, 178–184.

(19) Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **1976**, *A32*, 751–767.

(20) Huheey, J. E. Inorganic Chemistry. *Principles of Structure and Reactivity*; Harper and Row: New York, 1978.

(21) Friedman, H. J.; Krishnan, C. V. Water: A Comprehensive Treatise. *Aqueous Solutions of Simple Electrolytes*, Vol. 3; Franks, F., Ed.; Plenum Press: New York, 1973.

(22) Yatsimirksii, K. B.; Vasil'ev, V. P. *Instability Constants of Complex Compounds*; Pergamon Press: Elmsford, NY, 1960.

(23) Choy, K. K. H.; McKay, G. Sorption of metal ions from aqueous solution using bone char. *Environ. Int.* **2005**, *31*, 845–854.

(24) Lee, D. H.; Moon, H. Adsorption equilibrium of heavy metals on natural zeolites. *Korean J. Chem. Eng.* **2001**, *18*, 247–256.

(25) Pearson, R. G. Hard and soft acids and bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(26) Pearson, R. G. Chemical hardness and bond dissociation energies. *J. Am. Chem. Soc.* **1988**, *110*, 7648–7690.

(27) Nieboer, E.; Richardson, D. H. S. The replacement of the nondescript term "heavy metals" by a biologically and chemically significant classification of metal ions. *Environ. Pollut. Ser. B* **1980**, *1*, 3–6.

(28) Alfarra, A.; Frackowiak, E.; Beguin, F. The HSAB concept as a mans to interpret the adsorption of metal ions onto activated carbons. *Appl. Surf. Sci.* **2004**, *228*, 84–92.

(29) Yang, C. Statistical mechanical study on the Freundlich isotherm equation. *J. Colloid Interface Sci.* **1998**, *208*, 379–387.

(30) Pangday, K. K.; Prasad, G.; Singh, V. N. Copper (II) removal from aqueous solutions by fly ash. *Water Res.* **1985**, *19*, 869–873.

(31) Ho, Y. S.; McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* **2000**, *34*, 735–742.

(32) Muñoz-González, Y.; Arriagada-Acuña, R.; Sota-Garrido, G.; García-Lovera, R. Activated carbons from peach stones and pine swadust by phosphoric acid activation used in clarification and decolorization processes. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 39–47.

(33) Xu, S. C. *Organic Chemistry*; Higher Education Press: Beijing, China, 1983.

(34) Leenheer, J. A.; Brown, G. K.; McCarthy, P.; Cabaniss, S. E. Models of metal binding structures in fulvic acid from the Suwanner river, Georgia. *Environ. Sci. Technol.* **1998**, *32*, 2410–2416.