Selective Removal of Copper(II) from Aqueous Solutions Using Fine-Grained Activated Carbon Functionalized with Amine

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To develop an effective transition-metal-ion adsorbent material, functionalization of amine ($-NH_2$) onto fine-grained activated carbon (AC) was performed via the electrophilic aromatic substitution of nitro ($-NO_2$) groups onto the aromatic backbone of the AC, followed by reduction of $-NO_2$ to $-NH_2$. Fourier transform infrared, Brunauer−Emmett−Teller surface area analysis, gravimetric method, and batch metal ion adsorption experiments were performed in parallel on unmodified AC and amine-functionalized AC (NH_2-AC). The competitive adsorption of transition-metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}) was measured in batch experiments at pH 2.0−5.8. Metal ions favored the NH_2-AC over the unmodified AC. Based on the distribution coefficients (K_d), the NH_2-AC had an affinity for metal ions in decreasing order of $Cu^{2+} \gg Pb^{2+} > Ni^{2+} > Cd^{2+}$. On the NH_2-AC, the copper adsorption equilibrium was reached within 1 min with a saturation loading capacity of 0.86 mmol of Cu/g, 2.5 times greater than that on the unmodified AC. The Langmuir and Redlich−Peterson isotherm models were used successfully to characterize the Cu^{2+} adsorption isotherms. Having K_d values up to 100 000, the NH_2-AC is a useful adsorbent material for removing Cu^{2+} from aqueous wastes.

Introduction

Copper is commonly used in the electrical industry, the electroplating industry, and agricultural poisoning and as an algicide in water purification. Copper can cause liver and kidney damage when present at high concentrations in the human body. Like many other transition-metal ions, copper is very mobile in the environment and can accumulate in the food chain. Copper metal readily corrodes in water to yield copper ions (Cu^{2+}), which are of more concern to the Environmental Protection Agency (EPA) than copper metal because they exhibit high acute and chronic toxicity to aquatic organisms that results in their death.[1] The EPA has issued water quality criteria for copper ions, identifying the level of copper ions that water can contain without causing harm to aquatic species (i.e., 9.2 ppb for acute criterion and 6.5 ppb for chronic criterion in freshwater).[1] Copper is also regulated under the Safe Drinking Water Act (SDWA), the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), and the Superfund Amendment and Reauthorization Act (SARA).[1] Given these regulatory limits and the fact that the total release of copper in the United States, according to the 2000 Toxic Release Inventory (TRI), was approximately 630 000 tons/year, there is a need to find a cost-effective way to remove copper ions from aqueous environments.

A number of studies have been performed on the removal of copper ion from aqueous solutions by modified and unmodified natural adsorbents such as pine barks,[2] scrap and ground rubbers,[2] softwood sawdust,[3] peat,[4] peanut hulls,[2,5] lignite,[6] chitosan in prawn shells,[7] corncobs,[8] and kudzu.[9] Although these materials are considered inexpensive, the saturation uptakes of copper

ion on these materials are low, which makes these materials become less cost-effective and more cumbersome when used in large-scale water treatment applications. For example, the saturation uptakes of copper ions on pine barks, softwood sawdust, rubbers, and peanut hulls are below 15 mg of Cu^{2+}/g, those on peat and lignite are between 15 and 30 mg of Cu^{2+}/g, and that on kudzu is a little over 30 mg of Cu^{2+}/g. The pH range where these materials work is also limited to around neutral pH. In addition, the adsorption kinetics on most natural materials is slow. For instance, at experimental conditions of a 5 g/L solids-to-solution ratio and an initial Cu^{2+} concentration of 10 mg/L, it takes about 20 min to reach copper adsorption equilibrium using peanut pellets and peanut hulls[5] or about 50 min using chitosan in prawn shells.[7]

For large-scale water treatment applications, researchers have focused on immobilizing organic functional groups on silica and polymers to selectively remove transition-metal ions from aqueous wastes for many years. However, attaching functional groups to activated carbons (ACs) is still relatively new. Unmodified ACs have been used to sequester metal ions from aqueous wastes[10−16] because they offer high surface area, fast adsorption kinetics, and mesoporous structure. Also, they often contain some functional groups, such as carboxyls, phenols, esters, and ketones, as a result of the oxidation of AC precursors (e.g., coal, almond shells, peat, and wood) under air or steam at high temperature. However, these inherent functional groups are present at low concentrations, which results in a low metal ion adsorption capacity, and are also not engineered to specific needs for metal removal. Functionalized AC has potential advantages as an adsorbent: ACs can be engineered to have higher surface areas than silica materials of a similar mass, ACs do not break down or dissolve in basic solutions (pH >9) as do silica materials, ACs do not shrink or swell with changes in the solution

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pH as do polymers, and, most importantly, AC is cheaper than most silica and polymers.

At the Pacific Northwest National Laboratory, we have successfully immobilized different organic functional groups (i.e., amine, sulfonate, amide, chloromethyl, phosphoryl, and sulfenyl groups) on fine-grained AC via electrophilic substitutions of the benzene rings of the ACs. This synthetic methodology is straightforward. The amounts of the functional groups that can be obtained on the ACs are not limited by adsorption equilibrium as in the adsorption methodology used in some studies[17,18] to immobilize commercial ligands onto ACs. Also electrophilic substitutions of the benzene rings do not require significant pretreatment of ACs to increase the amounts of the specific surface carbon groups (i.e., hydroxyl carbon groups and acid chlorides) in order for the anchoring of organic molecules to succeed.[19] One successful electrophilic aromatic substitution of AC is the synthesis of amine-functionalized AC (NH_2-AC), in which nitro ($-NO_2$) groups are installed on the aromatic backbone of AC and then subsequently reduced to $-NH_2$ groups.

The objective of this study is to propose NH_2-AC as a new adsorbent material for better and faster removal of copper ion (Cu^{2+}) from aqueous solutions. The particular Darco KB-B AC (Aldrich Co.) was chosen as the starting material because of its extremely high surface area (1600 m^2/g), low Fe content, and mesoporosity (primary pore diameter of 40 Å). A competitive adsorption study was performed to determine the selectivity of NH_2-AC for common divalent transition-metal ions. Equilibrium and kinetics studies were performed to assess the saturation adsorption capacities and the adsorption rate of this material for copper ion.

Experimental Section

Preparation and Characterization of Functional AC. The AC used in this study was Darco KB-B (Aldrich Co.) in a wet powder form. This AC was manufactured by phosphoric activation, followed by steam oxidation of wood chips. A polydisperse pore structure is normally obtained, in which a small amount of microporous pores (<20 Å) are found together with a large amount of mesoporous pores (~40 Å), and all pores are virtually smaller than 200 Å. The Fourier transform infrared (FTIR) spectra of the material were obtained by collecting 200 scans for a wavenumber range of 4000−400 cm^{-1} on a Nicolet Magna-IR 860 spectrometer. The KBr-to-sample weight ratio was 1250:1. The FTIR results show that the Darco KB-B AC clearly contains both hydroxyls (3428 cm^{-1})[20] and carboxylic acids (1700 cm^{-1}).[20]

The AC was functionalized with amine groups in a two-step process as follows:
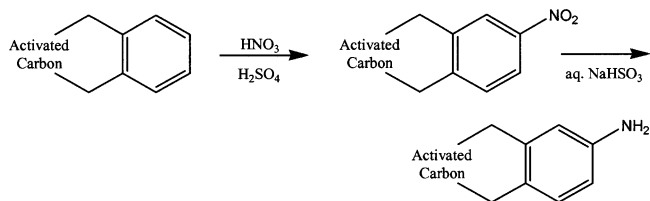
The first step involved an electrophilic substitution for the nitration of AC. At 0 °C (an ice bath), 50 mL of concentrated (18 M) sulfuric acid (H_2SO_4) was added slowly to 50 mL of concentrated (15.7 M) nitric acid

Table 1. Typical Experimental Conditions for Batch Competitive Adsorption Isotherms

condition	value
mass of AC or NH_2-AC (m_s, g)	0.05
volume of metal ion solution (V, mL)	10.0
initial concentration of each metal ion ($C_{i,0}$, mmol/L)	0.5
solvent solution (pH = 2)	0.05 M $NaNO_3$
solvent solution (pH > 2)	0.05 M CH_3CO_2Na
pH (held constant in each batch)	2.0−5.8
contact time (h)	2
mixing speed (rpm)	200
temperature (°C)	25

(HNO_3). Then, a 8.97 g quantity of as-received AC was slowly added to the acid mixture and stirred for 50 min. The mixture was filtered and washed with deionized (DI) water and subsequently 2-propanol. The filtrate was then air-dried at ambient temperature. The resulting product from the first step was nitrobenzene. A 14% weight gain was found to correlate to 3.0 mmol of $-NO_2$/g or 3.7 mmol of $-NH_2$/g (dry weight). THe FTIR spectrum (not shown) of the NO_2-AC contains N−O stretches[20] at 1340 and 1534 cm^{-1}.

The second step is the conversion of nitroarene to aniline in a procedure adapted from Redemann and Redemann.[21] A 5.05 g quantity of treated AC (equivalent to 47.6 mmol of NO_2^-), 50 mL of water (2.78 mol), 20 mL of 15 N ammonium hydroxide (0.30 mol), and a stir bar were placed in a 250 mL round-bottom flask and stirred for 10 min. A 28 g (160 mmol) quantity of sodium hydrosulfite ($Na_2S_2O_4$) was added to this solution slowly and allowed to stir overnight at room temperature. An exothermic reaction was observed during the addition of $Na_2S_2O_4$. A reflux condenser was fitted on the flask and water-cooled to avoid solvent evaporation due to the increase in the solution temperature. A 20 mL volume of 17.5 M glacial acetic acid (0.35 mol) was diluted in 100 mL of water and was then added to the solution and stirred for 5 h at reflux (100 °C). The solution was then cooled to room temperature, filtered, washed with a copious amount of water, followed by 2-propanol, and finally air-dried. The final product is NH_2-AC. A 7.9% weight lost was correlated to 3.0 mmol of $-NO_2$/g or 3.7 mmol of $-NH_2$/g (dry weight). The elemental analyses of NO_2-AC and NH_2-AC for H and O by an independent company (Galbraith Laboratories, Inc., Knoxville, TN) showed the approximate decrease of O and increase of H by 3.8 mmol/g (dry weight) as NO_2-AC was reduced to NH_2-AC. This demonstrates a complete reduction of $-NO_2$ to $-NH_2$. The Brunauer−Emmett−Teller analysis using a Quantachrome Autosorb 6B showed a decrease in the surface area density from 1587 to 820 m^2/g after the functionalizations with $-NH_2$, while the primary pore size remained constant at 3.8 nm. The decrease in the surface area density was due to the weight gain of the functionalized materials, not a reduction of the surface area.

Competitive Adsorption. The pH-dependent adsorption isotherms of metal ions on as-received AC and NH_2-AC were measured in batch experiments. The experimental conditions are summarized in Table 1. A 0.05 g quantity of AC and a 10 mL volume (solution-to-solids ratio = 200) of a diluted multicomponent metal ion solution were shaken in a polyethylene bottle at a speed of 200 rpm and room temperature for a total contact time of 2 h. Each metal ion, including four transition-metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+}), had an equimolar (0.5 mmol/L) initial concentration. To

maintain essentially constant ionic strength and pH, the multicomponent metal ion solution was prepared by diluting the stock solutions (comprised of 10 000 mg/L of each metal ion in a 1−4% HNO_3 solution) with a diluent containing 0.05 M $NaNO_3$ (for pH 2) or 0.05 M sodium acetate (CH_3CO_2Na) solutions (for pH 3−6). The solution pH was then adjusted to a nominal pH of 2, 3, 4, or 6 by adding a 0.1 M HNO_3 solution and/or a 0.1 M NaOH solution. The pH was controlled to less than 6 to prevent hydroxide precipitation of metal ions. The pH values of the solution before and after each batch experiment were measured. After the batch experiments, the metal-loaded AC material was filtered through a 0.2 μm Nylon filter in a polypropylene housing. Both initial and final solutions (before and after the batch experiment) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin-Elmer, Optima 3000 DV). The percent removal is given by the percent change of the metal ion concentration in the solution before and after addition of the adsorbent. The adsorption capacity, Q or q, is given in milligrams or millimoles of metal ion loaded per gram (dry weight) of adsorbent as follows:

$$Q = \frac{(C_0 - C_f)V}{m_s} \tag{1}$$

where C_0 and C_f are the initial and final metal ion concentrations in solution (mg/L), V is the solution volume (L), and m_s is the mass of AC or NH_2-AC (g).

Sorption Isotherm Experiments. To determine the metal ion adsorption capacity of the ACs, a 0.05 g quantity of AC or NH_2-AC and a 10.0 mL volume of a copper ion solution were shaken in a polyethylene bottle in the same fashion as that described for the competitive adsorption experiments. Copper ion solutions were obtained by diluting the stock solution (comprised of 10 000 mg/L of Cu^{2+} in a 2% HNO_3 solution) with a 0.05 M CH_3CO_2Na diluent solution. The initial copper concentrations ranged from 10 to 1000 mg/L.

Metal Ion Adsorption Kinetics Experiment. The copper adsorption kinetics experiment was performed in a fashion similar to that of the competitive adsorption batch experiments. A 0.5 g quantity of NH_2-AC was dispersed in a 100 mL volume of solution containing 10 mg/L of Cu^{2+}. Sample aliquots were removed for ICP-OES analysis at 0, 0.5, 1, 2, 3, 4, 5, 10, 15, 30, 60, and 120 min.

Results and Discussion

pH Dependency of Adsorption. The functional groups on NH_2-AC bind with metal ions via a coordination process rather than an ion-exchange process. The pH of a solution is an important factor to be considered when using NH_2-AC as a sorbent material. The efficiency of metal ion removal by a sorbent material is dependent not only on the pK_a of the ligand and the stability constant of the metal−ligand complex but also on the pH of the solution.[22] Parts a and b of Figure 1 show the metal ion adsorption capacities as a function of the final pH in solution on the as-received AC and NH_2-AC, respectively. The adsorption of metal ions on these materials behaved in the same fashion: adsorption increased as the pH increased from 2 to 5.8. Each metal ion showed a different sensitivity to pH conditions. The Cd ion behaved in parallel with the Ni ion,
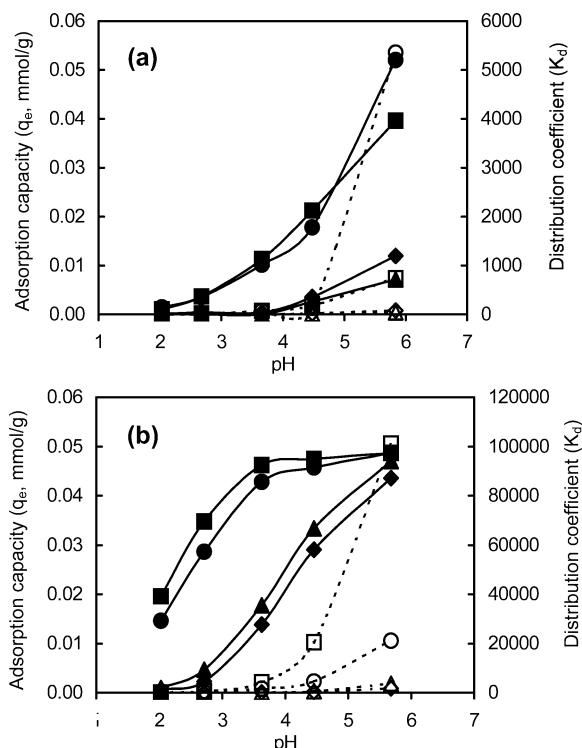

Figure 1. Adsorption capacity and distribution coefficient (K_d) of metal ions as a function of the solution pH on (a) unmodified AC and (b) NH_2-AC. Q: (■) Cu; (●) Pb; (▲) Ni; (◆) Cd. K_d: (□) Cu; (○) Pb; (△) Ni; (◇) Cd. $C_{i,0} = 0.5$ mmol/L; $V/m_s = 200$.

whereas the Cu ion behaved in parallel with the Pb ion. On AC (Figure 1a), the adsorption capacities of Ni and Cd ions were negligible from pH 2 to 4 and increased slightly to 0.007 and 0.012 mmol/g, respectively, as the pH was increased to 5.8. The adsorption capacities for Cu and Pb ions increased significantly from 0 to 0.04 mmol/g (80% removal) and 0.05 mmol/g (100% removal), respectively, as the pH was increased from 2 to 5.8. On NH_2-AC (Figure 1b), the adsorption capacities of Ni and Cd ions were negligible from pH 2 to 3 and increased significantly to 0.045 mmol/g (90% removal) as the pH was increased to 5.7. The adsorption capacities of Cu and Pb ions increased significantly from 0.018 to 0.045 mmol/g as the pH was increased from pH 2 to 4 and remained at approximately 0.05 mmol/g as the pH was increased to 5.7.

NH_2-AC was able to remove between 40% and 90% of Cu^{2+} at between pH 2 and 4, whereas the unmodified AC was able to remove only a negligible amount of Cu^{2+} in the same pH range. The ability to adsorb copper ion at low pH range is important for an adsorbent to be useful for Cu^{2+} removal from concentrated copper-bearing wastes because highly concentrated copper solutions tend to precipitate copper complexes at pH values of less than neutral. For instance, based on the $Cu(OH)_2$ solubility product constant (K_{sp}) of 2×10^{-19} at 25 °C,[23] a 0.5 M Cu^{2+} solution (i.e., normally found in mining industry solutions) starts to precipitate at pH 4.8. On the basis of the pH isotherms in Figure 1b, the K_d values (reflecting the binding affinity) of all metal ions, including Cu^{2+} at pH 2 and below, are negligible, suggesting that the regeneration of NH_2-AC can be easily performed by subjecting the metal-laden NH_2-AC to an acidic solution, and the material is ready for reuse.

Performance Comparison of NH_2-AC versus Unmodified AC. Parts a and b of Figure 1 also show the

distribution coefficients (K_d) of metal ions as a function of the solution pH on the unmodified AC and NH$_2$-AC, respectively. The distribution coefficients are mass-weighted partition coefficients of metal ions between the solid and solution phases and are calculated by

$$K_d = \frac{C_0 - C_f}{C_f} \frac{V}{m_s} \qquad (2)$$

In the experiment, each metal ion was added in solution to have an equimolar concentration. Also, the solution-to-solids ratio, ionic strength, and solution pH were kept constant. Therefore, the distribution coefficients (K_d) can be used to reflect the stability of a metal–ligand complex at a particular pH. The higher its K_d value, the more stable the metal–ligand complex is. The high K_d value of a metal ion is favorable also because it indicates the high affinity of the adsorbent to that metal ion under dilute conditions. To compare the effect of different donor atoms on metal–ligand complex stability, the same metal ion that formed the complexes with those different ligands was considered. On the basis of the K_d values at pH values ranging from 2 to 5.8, each metal ion favored NH$_2$-AC over the unmodified AC. For example, at pH 5.8, the K_d value of Cu^{2+} measured on NH$_2$-AC was approximately 101 000, 140 times higher than that measured on the unmodified AC. Similarly, the K_d value of Pb^{2+} measured on NH$_2$-AC was approximately 21 000, 4 times higher than that measured on the unmodified AC. Amines are known to be versatile ligands, and metal–amine complexes have been known for well over 100 years. The inherent functional groups of an AC prepared by H$_3$PO$_4$ activation of wood are likely to be carboxylic acids, phenolic acids, and phosphonic acids.[24] Amine (–NH$_2$) groups attached to the AC increased the ligand strength of the surface, thereby increasing the affinity of the sorbent material for transition-metal ions.

Selectivity of Metal Ion Adsorption. To determine the affinity of the metal ions toward a given ligand, the stabilities of the complexes (represented by their K_d values) formed by a particular ligand with a series of metal ions in a given oxidation state were compared.[22] On the basis of the K_d values, the Darco KB-B AC is most selective for Pb^{2+}, whereas NH$_2$-AC was most selective for Cu^{2+}. On NH$_2$-AC, at pH 5.7 with a solution-to-solids ratio of 200 and an initial concentration of each metal ion of 0.5 mmol/L, the copper K_d value was 101 000, approximately 5-fold of Pb^{2+}, 30-fold of Ni^{2+}, and 60-fold of Cd^{2+}. The high K_d values also show that NH$_2$-AC was more selective to these transition-metal ions than sodium ions, which were present in the solutions at 100 times higher concentration than the transition-metal ions. The series of the affinity of ligands toward metal ions studied were as follows:

$$\text{Pb} \gg \text{Cu} > \text{Cd} > \text{Ni} \qquad \text{on AC}$$

$$\text{Cu} \gg \text{Pb} > \text{Ni} > \text{Cd} \qquad \text{on NH}_2\text{-AC}$$
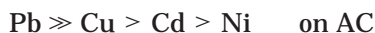
According to Pearson's hard–soft acid–base theory,[25] aniline nitrogen atom is somewhat soft, preferring to undergo reaction with borderline cations such as Cu. The significant difference in selectivity among metal ions with equal charges confirms that the binding between metal ions and NH$_2$ groups is through coordination and not through an ion-exchange process, which normally has poorer selectivity among metal ions with
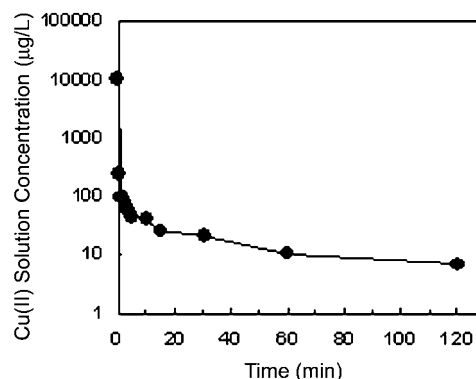

Figure 2. Adsorption kinetics of Cu^{2+} on NH$_2$-AC. $C_0 = 10$ mg/L; $V/m_s = 200$.
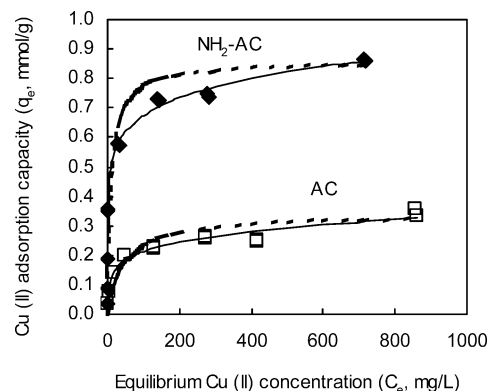

Figure 3. Adsorption isotherms of Cu^{2+} on AC and NH$_2$-AC: (- - -) Langmuir model; (—) Redlich–Peterson model. $V/m_s = 200$.

equal charges. In addition to the hardness–softness of the metal ion and ligand field, the selectivity of a sorbent material toward different metal ions of the same oxidation state is also dependent upon the geometry of the adsorption surface, the stereochemistry, the synergism of the ligands, etc.[26]

Kinetics of Adsorption. Figure 2 shows the temporal profile of Cu^{2+} concentrations in solution contacting NH$_2$-AC. At a solution-to-solids ratio of 200, NH$_2$-AC reduced the Cu^{2+} concentration in solution from 10 mg/L to about 0.1 mg/L (99% removal) within 1 min and to about 0.01 mg/L (99.9% removal) within 60 min. This evidence suggests that copper ions first fill up macropores, then mesopores, and finally micropores of the AC. The removal of more than 99% of Cu^{2+} within the first minute indicates that there was little resistance to both external mass-transfer and intraparticle diffusion. There was little external mass-transfer and chemical resistance because of the hydrophilic properties of the amine groups on the surface, and there was very little intraparticle diffusion resistance because of the rigid pore structures of the AC. As a result, the coordination occurred at a rate as rapid as that of a typical ion-exchange process in which the rate-determining step is the diffusion of counterions rather than the actual chemical exchange reactions at the functional groups.[27]

Sorption Isotherm. The loading capacities of copper ions were measured on the as-received AC and NH$_2$-AC. Figure 3 compares the isotherm curves on both materials. The isotherm curve is the plot of the Cu^{2+} adsorption capacities (mmol/g, dryweight) versus the equilibrium concentrations of Cu^{2+} in solution (mg/L) at room temperature. The average final solution pH was 5.7. On the as-received AC, initially the Cu^{2+} adsorption capacity increased rapidly with increasing Cu^{2+} con-

Table 2. Adsorption Isotherm Constants for Cu(II) on AC and NH$_2$-AC

parameter	AC	NH$_2$-AC
Langmuir Model		
Q_{max} (mg/g)	21.41	54.35
K_L (L/mg)	0.0229	0.0962
r^2	0.963	0.974
Redlich–Peterson Model		
P	0.818	0.880
A (L/g)	3.819	83.739
B (L/mg)^p	0.630	3.379
r^2	0.983	0.998

centration in the solution. Above 100 mg/L of Cu^{2+} in solution, the adsorption capacity increased more slowly and then remained almost constant at 0.35 mmol/g (22 mg/g). On NH$_2$-AC, initially the Cu^{2+} adsorption capacity increased rapidly with increasing Cu^{2+} concentration in the solution. Above 200 mg/L of Cu^{2+} in solution, the adsorption capacity increased more slowly and then remained almost constant at 0.86 mmol/g (55 mg/g). The saturation adsorption capacity of Cu^{2+} on NH$_2$-AC was 2.5 times higher than that on the unmodified AC.

Adsorption isotherm data are often fitted into three empirical models: the Langmuir isotherm model, the Redlich–Peterson isotherm model, and the Freundlich isotherm model. The linearized Langmuir equation[27] is given by

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{1}{Q_{max}} C_e \tag{3}$$

where Q_{max} is the adsorption capacity (mg/g) when all adsorption sites are occupied, C_e is the equilibrium concentration of Cu^{2+}, and the Langmuir constant K_L (L/mg) is derived from the ratio of the adsorption rate constant to the desorption rate constant. The Freundlich equation[29] is given by

$$Q_e = K_F C_e^{1/n} \tag{4}$$

where n and K_F [(mg/g)(L/mg)$^{1/n}$] are the Freundlich constants. The Redlich–Peterson equation[30] is given by

$$Q_e = \frac{A C_e}{1 + B C_e^p} \tag{5}$$

where A, B, and p are the model constants. The exponent p has a value between 0 and 1. If p is 1, the Redlich–Peterson model reduces to the Langmuir model.

Table 2 summarizes the isotherm constants for the Cu^{2+} adsorption on both the as-received AC and NH$_2$-AC. The Langmuir constants were obtained by a linear regression of C_e/Q_e versus C_e (eq 3). The total number of samples (N) was 16. The Fruendlich model was not considered because of its inability to predict the saturation adsorption capacities found in the experimental data. The Redlich–Peterson model constants were obtained by fitting the data directly to eq 5 using a multidimensional unconstrained nonlinear minimization (Nelder–Mead) function called FMINSEARCH of MATLAB, version 6.1. The minimization function (F_{obj}) is defined as

$$F_{obj} = \sqrt{\sum_N (Q_{e,i}^{cal} - Q_{e,i}^{exp})^2}$$

where $Q_{e,i}^{cal}$ and $Q_{e,i}^{exp}$ are the predicted and measured adsorption capacities at each data point, respectively. Figure 3 also shows the predicted Cu^{2+} adsorption isotherms using the Langmuir and Redlich–Peterson isotherm models. On the basis of the correlation coefficients (r^2), the Redlich–Peterson isotherm model, which incorporated the features of both Langmuir and Freundlich isotherm models, represented the data best. The Langmuir isotherm model also satisfactorily described the copper adsorption data. The facts that the Redlich–Peterson exponent p is close to unity and there is reasonable agreement between the data and the Langmuir isotherm model suggest that Cu^{2+} binding occurs via uniform adsorption of submonolayer coverages onto the interfaces throughout these two ACs and not in multilayered clusters, as would be predicted by a nucleation or precipitation mechanism.

Conclusions

The synthesis of amine-functionalized AC was successfully performed via electrophilic aromatic substitution of a fine-grained AC (Darco KB-B) to introduce nitro ($-NO_2$) groups, which were subsequently reduced to amine ($-NH_2$) groups. The amine functional group density was 3.7 mmol/g. On the basis of the distribution coefficients (K_d), the amine-functionalized AC was much more effective than the unmodified AC in sequestering Cu, Pb, Ni, and Cd ions over the pH range of 2.0 to 5.8. The adsorption isotherm and kinetics studies demonstrate that the amine-functionalized AC has a potential use as an adsorbent for the removal of transition-metal ions, especially Cu^{2+}, from aqueous solutions. NH$_2$-AC has many advantages over the solvent extraction and ion-exchange resins. Unlike solvent (liquid–liquid) extraction processes that have a drawback of not being favorable economically for the treatment of dilute solutions,[31] the K_d values of up to 100 000 measured on NH$_2$-AC indicate the high affinity of the adsorbent to the metal ion under dilute conditions. For selective separations, the coordinating adsorbents such as NH$_2$-AC are more favorable than ion-exchange resins[26] because they normally have better selectivity among transition- and heavy-metal ions with equal charges. Conventional ion-exchange resins (e.g., sulfonated resins) also have a high affinity for alkaline and alkaline-earth metal ions (e.g., Ca^{2+}), which are normally present at higher concentrations than the target metal ions (i.e., Cu^{2+}) in most wastewaters; thus, they often lose binding sites to these alkaline and alkaline-earth metals. On the contrary, NH$_2$-AC is highly selective for copper ions even in the presence of excess sodium ions, while it still offers a rapid binding rate, as do most ion-exchange resins, owing to the hydrophilic properties of the amine groups as well as the rigid pore structures of the AC. Functionalized ACs are also cheaper than most silica- and polymer-based adsorbents.

Acknowledgment

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