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A B S T R A C T

Sorption of copper (Cu^{2+}) by untreated and treated (bleaching and hydrolysis) aspen wood fibers, cellulose and lignin was examined to understand the Cu^{2+} sorption behavior by these natural sorbents. All sorbents were characterized by solid-state ^{13}C NMR and FTIR. Bleaching broke up aromatic structures and increased hydrophilicity of the fibers, whereas hydrolysis decreased carbohydrate content, producing a more hydrophobic structure. Copper sorption was a function of pH; the percentage of Cu^{2+} sorption steadily increased from pH 1.5 to 4.5 with a maximum sorption amount at around pH 5.5 for all the materials. All isotherms fitted well to the Langmuir equation. Bleached sample (BL) had a highest sorption capacity, followed by untreated (UTR), cellulose (CEL), and hydrolyzed (HHY), while lignin (LIG) had little Cu^{2+} sorption under the studied conditions. The results suggested that carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{CHOH}$) in carbohydrates are mainly responsible for Cu^{2+} sorption, and that ion exchange may be a main sorption mechanism for the studied sorbents. Additionally, the sorption capacity for Cu^{2+} on all sorbents decreased with the increase of the initial concentrations of Ca^{2+} , Na^+ or Al^{3+} . Copper sorption decreased rapidly at low initial concentrations of Ca^{2+} , Na^+ or Al^{3+} . However, the decline of Cu^{2+} sorption slowed down when initial Na^+ and Ca^{2+} concentration was higher than 0.05 M or initial Al^{3+} concentration was greater than 0.005 M, indicating that specific adsorption may be taking place. Therefore, the majority of sorbed Cu^{2+} to aspen wood fibers could be through ion exchange (especially, for UTR, BL and CEL), while a fraction of sorbed Cu^{2+} via inner-sphere complex (or specific adsorption).

Keywords:

Heavy metal
Water treatment
Ion exchange
Ionic strength
Modified wood fibers
Specific sorption

1. Introduction

Copper (Cu^{2+}) is one of the most widespread heavy metal contaminants in the environment (O'Connell et al., 2006) and one of the most toxic heavy metals to living organisms. High Cu^{2+} levels in drinking water can cause vomiting, abdominal pain, nausea and diarrhea. Elevated Cu^{2+} concentrations have been detected in urban stormwater runoff (Hares and Ward, 1999). Major sources of Cu^{2+} in non-industrial areas include runoff from road surfaces and parking lots, automobile corrosion, building materials, and lawn fertilizers. Industrial sources of Cu^{2+} pollution include manufacturing processes, smelting and refining, electricity generation, refuse and waste-water treatment.

Copper removal from wastewater and urban stormwater runoff has received great attention, and a number of physical and chemical methods are now used to remove Cu^{2+} from water, including ion exchange, reverse osmosis, chemical precipitation, membrane technologies, and electrochemical treatment. Of these methods, precipitation by chemical and electrochemical methods are the most widely used treatments to remove Cu^{2+} from wastewater

(Wang and Chen, 2006). However, the disposal of the precipitates and the ineffectiveness of precipitation at low Cu^{2+} concentration are problematic (Wang and Chen, 2006). Additionally, precipitation can only reduce the dissolved metal concentration to the solubility product level, which is often much higher than the discharge permit standards (Brown et al., 2000). Ion exchange treatment is the second most widely used method for Cu^{2+} removal (Wang and Chen, 2006). However, this method is rarely economical, although it can reduce Cu^{2+} to a very low level (Tiravanti et al., 1997). Similarly, activated carbon can efficiently remove heavy metals from drinking water, but it is too costly to treat wastewater (Sun and Shi, 1998) or to clean runoff/stormwater. Overall, most Cu^{2+} treatment methods fail to meet the pollution control limits and/or the adsorbents/chemical agents are too expensive (Saha et al., 2003). This is especially the case when treating urban runoff water, because (1) the Cu^{2+} concentrations in runoff are usually not as high as those in wastewater from industrial plants, and (2) the runoff volume is large. For these reasons, interest in innovative methods to clean up contaminated water has been increasing. Many natural materials such as peat, sawdust, peanut and hazelnut shells have been studied for treating metal-contaminated wastewater (Brown et al., 2000). The results of these studies showed that Cu^{2+} sorption using natural materials is effective, efficient, and

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economical in comparison to traditional methods for water decontamination (O'Connell et al., 2006) because biomass materials are abundant and readily available at a very low cost.

Cadmium (Cd^{2+}) sorption to biomass depends on the initial pH of the reaction mixture because pH dramatically influences surface activities of sorbents (Horsfall and Spiff, 2004). According to Pagnanelli et al. (2000) cell walls of *Arthrobacter* sp. have many functional groups, such as carboxylate, hydroxyl, amide, and amino groups that are attractive binding sites for Cu^{2+} . Wang and Chen (2006) showed that both ion exchange and complexation are processes facilitating Cu^{2+} sorption on biosorbents. Surface complexation in particular is a predominant mechanism in metal binding especially because of the complexing ability of carboxylic moieties. Merdy et al. (2002) reported that carboxylic and alcoholic coordination sites, in addition to phenolic groups, could be involved in the complexation with metal cations as shown by X-ray photoelectron spectroscopy (XPS) measurements. Cabral (1992) reported that complexation was the only mechanism responsible for Cu^{2+} and other heavy metals removal from aqueous solution when they studied the accumulation of metal cations by *Pseudomonas syringae*. Relative to surface complexation, ion exchange becomes important when cell walls of natural biomass contain a high percentage of polysaccharides as basic building blocks. Under these circumstances, ion exchange between divalent metal ions and counter ions of the polysaccharides is considered a main mechanism (Venkobachar, 1990). Ion exchange was also found to be responsible for Cu^{2+} biosorption by the fungi *Lucidum* and *Aspergillus niger* (Muraleedharan and Venkobachar, 1990).

Ion exchange, however, can be hindered by the presence of other ions. For instance, Wolf et al. (1977) observed that increasing aqueous Ca^{2+} concentration resulted in decreasing sorption on humic substances of heavy metals, including Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} . However, Cu^{2+} sorption on suspended particulate matter was not significantly affected by Ca^{2+} concentration ranging from 2.5×10^{-4} to 0.1 M over a pH range from 3 to 9 (Lu and Allen, 2001). They also found that ionic strength (I) did not have any noticeable influence on Cu^{2+} sorption if $I > 0.01$ M when NaNO_3 was used instead of $\text{Ca}(\text{NO}_3)_2$. However, a small but noticeable decrease in Cu^{2+} sorption with increasing I at low ionic strength ($I < 0.01$ M) was detected. Dissanayake and Weerasooriya (1981) observed that the presence of Na^+ (as 0.01 M Na_2SO_4) reduced the Cu^{2+} sorption to peat and attributed this to the presence of mono-valent ions which buffered the sorption sites. In another study, Merdy et al. (2002) observed that Ca^{2+} did not compete with Cu^{2+} for adsorption sites on lignin straw, indicating that Ca^{2+} occupies nonspecific sites whereas Cu^{2+} ions are specifically adsorbed on lignin straw. Therefore, as one may see from the above brief review, opposing views exist on the influence of ionic strength and the presence of competing cations on Cu^{2+} sorption.

In addition to ion exchange effects, pH is a main factor determining Cu^{2+} removal efficiency by natural sorbents. For instance, Lu and Allen (2001) reported that Cu^{2+} starts to precipitate as Cu^{2+} hydroxide when the pH is greater than 6. Also, the Cu^{2+} sorption distribution coefficient (K_D) to suspended particulate matter increased in the pH range from 6 to 7, and the maximum K_D value was found for pH 7–8. At higher pH values the K_D value decreased and Cu^{2+} precipitated.

In this study, we examined the influence of pH and ionic strength on Cu^{2+} sorption to aspen wood fibers. The hypothesis was that Cu^{2+} sorption onto aspen wood is facilitated by ion exchange and the presence of Ca^{2+} , Na^+ and Al^{3+} would decrease Cu^{2+} sorption. The particular objectives of this study were 1) to examine the sorption behaviors of Cu^{2+} on treated and untreated aspen wood fibers, and 2) to examine the effect of pH and ionic strength on Cu^{2+} sorption. The following summarizes the methods used to test the hypothesis and examines the result from the Cu^{2+}

sorption experiments performed with treated and untreated aspen wood.

2. Materials and methods

2.1. Sorbent

Untreated aspen wood (UTR) dry fibers were obtained from the American Excelsior Company, Arlington, TX. Bleaching (BL) and hydrolysis (HHY) were used to remove specific chemo-structural components from aspen wood fibers. Details of these two treatment methods can be found in Huang et al. (2006) and are summarized in Table S1. In addition to UTR, BL, HHY samples, cellulose (CEL) and lignin (LIG) were used as sorbents. The latter two were purchased from Sigma–Aldrich Chemical Co.

2.2. Sorbate

Cu nitrate [$\text{Cu}(\text{NO}_3)_2 \times 5\text{H}_2\text{O}$, >99% purity], sodium nitrate [NaNO_3], calcium nitrate [$\text{Ca}(\text{NO}_3)_2$], and aluminum nitrate [$\text{Al}(\text{NO}_3)_3 \times 9\text{H}_2\text{O}$] were purchased from Sigma–Aldrich Chemical Co. and used as received. A certified standard solution of $1000 \mu\text{g mL}^{-1}$ of Cu^{2+} was purchased from the Fisher Company and used for preparation of standard curves.

2.3. Characterization of sorbents

Dry weight-based C, H, and N contents of all samples were determined using a Vario ELIII elemental analyzer (Elementar, Germany) with the oxygen concentration calculated by mass difference. Solid-state ^{13}C NMR spectra were obtained with a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at the ^{13}C frequency of 75 MHz. Except for the number of scans (3000–6000), the instrument was run under the same conditions as the one used by Wang and Xing (2007). Within the 0–220 ppm chemical shift range, the structural carbon assignments were: aliphatic carbons (0–50 ppm), methoxyl carbons (50–61 ppm), carbohydrate carbons (61–96 ppm), anomeric carbons (96–109 ppm), aromatic carbons (109–165 ppm), carboxyl and carbonyl carbons (163–190 ppm), and ketone carbons (190–220 ppm). All samples were analyzed by a diffuse reflectance infrared Fourier transform (DRIFT) spectrophotometer (Perkin–Elmer, MA), following the procedure of Chen et al. (2005).

2.4. pH effect on sorption

The pH experiments were conducted using 8 mL-vials for UTR, BL, HHY, CEL and LIG at an initial concentration of $\sim 3.5 \mu\text{g mL}^{-1}$ Cu^{2+} . The pH values of the solutions ranged from 1.50 to ~ 6.00 and were adjusted with 0.01–1 M HNO_3 or 0.01–1 M NaOH . The vials were sealed with Teflon screw caps and kept shaking for three days at $23 \pm 1^\circ\text{C}$.

2.5. Sorption experiments

Cu^{2+} sorption was investigated by batch experiments in 8 mL-vial with ~ 8.4 mL of solution. A pH value of 5.5 was used for sorption isotherms to avoid formation of $\text{Cu}_2(\text{OH})_2^{2+}$, $\text{Cu}(\text{OH})_2^0$ and $\text{Cu}(\text{OH})^+$. The pH values of the solution were adjusted with 0.01–1 M HNO_3 or 0.01–1 M NaOH . Each isotherm had 9–10 concentration points; each point, including blanks (i.e., solution without wood fibers) was run in duplicate. The initial Cu^{2+} concentrations ranged from 0.01 to $8 \mu\text{g mL}^{-1}$ in deionized water. The vials were sealed with Teflon screw caps and kept shaking for three days at $23 \pm 1^\circ\text{C}$. After equilibration, the solutions were filtered

with glass filters (0.45 μm) and approximately 3 mL of the filtered solution was taken for analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Optima 3400 DV, Perkin-Elmer, CT). Sorbed Cu^{2+} concentrations were determined by mass balance calculations. The sorption data were fitted by the Langmuir equation,

$$q = q_{\max} b C_e / (1 + b C_e)$$

where q is the amount of solute adsorbed per unit weight of sorbent $\mu\text{g g}^{-1}$, C_e is solute equilibrium concentration, $\mu\text{g mL}^{-1}$, $q_{\max}$ is the maximum adsorption capacity of the sorbent, $\mu\text{g g}^{-1}$, and b is the adsorption affinity constant, $\text{mL } \mu\text{g}^{-1}$.

2.6. Effect of ionic strength and cations (Na^+ , Ca^{2+} and Al^{3+}) on Cu^{2+} sorption

Experiments were conducted with five samples (UTR, BL, HHY, CEL and LIG) at an initial concentration of $\sim 3.5 \mu\text{g mL}^{-1}$ Cu^{2+} (as background solution). From stock solutions of NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$, test solutions at the concentrations (0.0001 M, 0.005 M, 0.025 M, 0.05 M, 0.1 M and 0.2 M) were prepared in background solution (i.e., $3.5 \mu\text{g mL}^{-1}$ Cu^{2+}). The vials containing the various wood samples submerged in the test solutions were shaken for three days at $23 \pm 1^\circ\text{C}$ at $\sim\text{pH}$ 5.5 for Ca^{2+} and Na^+ with Cu^{2+} and pH 3.75 for Al^{3+} with Cu^{2+} .

3. Results and discussion

3.1. Solid-state ^{13}C NMR

^{13}C NMR results of the five wood samples are presented in Fig. 1 and Table 1. The ^{13}C NMR spectra illustrate that bleaching and hydrolysis caused structural modifications of aspen wood matrix. In particular, the peaks around 21 ppm and 172 ppm were attributed to methyl C and carbonyl C in acetyl groups of hemicelluloses, respectively (Martinez et al., 1991). The 56 ppm peak was from the lignin's methoxy groups (OCH_3) (Huang et al., 2006). The signals located at 83 ppm and 88 ppm were from C-4 in amorphous and crystalline celluloses, respectively. The peaks between 71 ppm and 74 ppm were assigned to C-2, C-3, and C-5 in cellulose, whereas the strong peak at 104 ppm was associated with anomeric

Fig. 1. Solid-state ^{13}C NMR spectra of UTR (untreated), BL (bleached), HHY (high temperature hydrolyzed) wood fibers, CEL (cellulose) and LIG (lignin). Aliphatic C (0–109 ppm), aromatic C (109–163 ppm) and COOH/C=O (163–220 ppm).

carbon (C-1). The peaks in the region of 131–137 ppm were assigned to the ring carbons in which the ring was not substituted by strong electron donors such as oxygen and nitrogen (Schnitzer and Preston, 1983). The multiple peaks in the range from 145–163 ppm were from the carbons of phenolic components, mainly the syringyl and guaiacyl units in lignin (Hawkes et al., 1993). The peak at 146 ppm was from C-4 in guaiacyl unit with free phenolic OH at C-4 (Hawkes et al., 1993) whose signal is strong in both HHY and LIG. There is almost no signal of $-\text{COOH}$, $-\text{COO}-$ and aromatic carbons for CEL or of carbohydrate carbons for LIG, which is consistent with their structures. Overall, the NMR results demonstrate that bleaching and hydrolysis of the wood effectively increased its hydrophilic and hydrophobic properties, respectively.

3.2. DRIFT

The DRIFT spectra between 4000 cm^{-1} and 450 cm^{-1} for the five samples are shown in Fig. 2. A broad and strong band in the region from 3324 cm^{-1} to 3346 cm^{-1} was assigned to the stretching vibration of hydroxyl group, indicative of hydrogen bonding (Chen et al., 2005). A strong methylene/methyl vibration was observed at 2895 cm^{-1} in UTR, BL and CEL, and 2939 cm^{-1} for HHY and LIG.

The absorption bands at 1740 cm^{-1} mainly arose from the carbonyl (C=O) linkage in acetyl ester groups from hemicelluloses (Ajuong and Redington, 2004). Because carbonyl groups occur abundantly within the polymer components of wood, they tend to dominate in the branched-chain hemicellulose polymer (Kimura et al., 1992). It is evident that ester carbonyl groups of hemicelluloses dominated in both UTR and BL. However, this DRIFT band became obscure in HHY because hemicellulose was readily decomposed under acidic conditions (Yang et al., 2004). Conversely, the absorption bands around 1704 cm^{-1} in HHY and LIG were attributed to carbonyl stretching of unconjugated ketone and conjugated carboxylic groups in lignin (Matuana et al., 2001).

The absorption bands at 1595 cm^{-1} and 1505 cm^{-1} were assigned to aromatic ring carbon skeletal stretching (Ajuong and Redington, 2004; Yang et al., 2004). The 1595 cm^{-1} band was also attributive to the stretching of conjugated C=O group (Pandey, 1999). These two bands were similar in UTR and HHY, but almost completely disappeared in BL. In contrast, these bands became very strong in the HHY, indicating that bleaching caused the cleavage of aromatic ring.

Absorption bands around 1462 cm^{-1} and 897 cm^{-1} were ascribed to CH and CH_2 units. The band at 1462 cm^{-1} was assigned to CH deformation in methyl and methylene in syringyl unit from lignin (Herring et al., 2004). It became sharper and stronger after hydrolysis, but weaker after bleaching. The band at 897 cm^{-1} was assigned to CH_2 wagging from carbohydrates (Pandey, 1999; Herring et al., 2004). Its relative intensity was strong in UTR and BL, but almost disappeared in HHY and no signal in LIG.

Absorption bands at 1273 cm^{-1} , 990 cm^{-1} and 617 cm^{-1} were from C–O single bond in carbohydrates (Kimura et al., 1992). Generally, the intensities of these bands were decreasing in the following order: BL, UTR, CEL, HHY and LIG. This underlined that hemicelluloses and parts of cellulose were easy to hydrolyze in an acidic environment. However, the absorption band at 1250 cm^{-1} was attributable to C–O single bonds in lignin (Pandey, 1999). High intensity of this peak was observed in the spectra of HHY and LIG. These data again suggest that the relative lignin content was higher after hydrolysis, but lower after bleaching. This finding is in good agreement with the NMR results.

3.3. Effect of pH on Cu^{2+} sorption

Our results showed (Fig. 3) that pH greatly affected Cu^{2+} sorption onto UTR, BL, CEL and HHY. The amount of Cu^{2+} sorption stea-

Table 1
Structural carbon distributions (%) as obtained from ^{13}C NMR integration.

Sample	Distribution of C (%) chemical shift, ppm ^a								Aliphatic ^b C (%)	Aromatic ^c C (%)
	0–50	50–61	61–96	96–109	109–145	145–163	163–190	190–220		
UTR	9.20	8.00	50.6	12.4	8.30	5.90	4.20	1.40	80.2	14.2
BL	5.30	2.60	61.7	15.0	5.00	2.60	5.90	2.10	84.5	7.5
HHY	15.9	10.9	25.1	10.0	25.0	7.70	2.60	2.80	62.0	32.7
CEL	0	1.6	75.3	17.6	0	0	2.8	2.7	94.5	0
LIG	13.5	14.0	9.1	6.6	34.0	15.3	3.3	4.3	43.2	34.0

^a Within the 0–220 ppm chemical shift range, structural carbon assignments were: aliphatic carbons (0–50 ppm), methoxyl carbons (50–61 ppm), carbohydrate carbons (61–96 ppm), anomeric carbons (96–109 ppm), aromatic carbons (109–165 ppm), carboxyl and carbonyl carbons (163–190 ppm), and ketone carbons (190–220 ppm).

^b Total aliphatic carbon region (0–109 ppm).

^c Total aromatic carbon region (109–163 ppm).

Fig. 2. DRIFT spectra of UTR (untreated), BL (bleached), HHY (high temperature hydrolyzed) wood fibers, CEL (cellulose) and LIG (lignin).

Fig. 3. Effect of pH on Cu^{2+} sorption on UTR (untreated, ▲), BL (bleached, ◆), HHY (high temperature hydrolyzed, ◇) wood fibers and CEL (cellulose, △).

dily increased from an initial pH value of 1.5–4.5, and a maximum sorption amount was observed at around pH 5.5 for all the samples. This result is consistent with the results reported by Caliman and Gavrilescu (2008) according to whom Cu^{2+} displayed a maximal or near maximal sequestration at a pH value near to the dissociation constant of carboxylic acids ($\text{pK}_a \approx 5$) in brown algal biomass. This may be explained by competition of excess hydrogen

ions with Cu^{2+} for sorption sites at low pH value, whereas at higher pH fewer H^+ ions compete with Cu^{2+} . This argument is similar to the study of Kalavathy et al. (2005), which suggested that heavy metal cations displace H^+ from free hydroxyl groups of cellulose, hemicelluloses and lignin.

Compared to other samples, BL exhibits a sharp increase in Cu^{2+} sorption from pH 2 to pH 4. A possible reason is that BL has more –COOH groups as demonstrated by the results from the DRIFT and NMR spectra. As shown by Pagnanelli et al. (2005), metal ions mainly exchanged with –COOH groups of natural biomass between pH 1.5 and 5, while at higher pH, phenol groups become more active Cu^{2+} sorption sites. Similar results were observed by Plette et al. (1996). Contrary to these studies, the increase of Cu^{2+} sorption at higher pH in our experiment was not significant, indicating phenol groups in the wood matrix contributed little Cu^{2+} sorption capacity. This is consistent with the sorption results determined for samples HHY and LIG (not shown), which had low COOH group densities, but comparably many phenol groups.

For CEL, Cu^{2+} may be sorbed onto the outer surface of the microfibrils by complex formation with hydroxyl groups (Michie, 1961) and ion exchange with H^+ . Also, ion exchange may play the main role in Cu^{2+} sorption according to the decreased Cu^{2+} sorption with the increase of Na^+ concentrations (Fig. S1).

3.4. Sorption isotherms

The results of the Cu^{2+} sorption experiments are shown in (Fig. 4 and Table S2). All data were fitted with the Langmuir equation and it was found that except for sample LIG, the fit with the Langmuir equation was quite good.

Sample BL had the highest sorption and sorption did not reach maximum capacity within our experimental concentration range. The possible reason is that bleaching introduces oxygen-containing

Fig. 4. Cu^{2+} sorption isotherms by UTR (untreated, ▲), BL (bleached, ◆), HHY (high temperature hydrolyzed, ◇) wood fibers and CEL (cellulose, △).

groups (Table S3), this may be due to formation of –COOH groups by oxidation of benzene rings, making the surface of the wood more hydrophilic and amenable to enhanced Cu²⁺ sorption (Saha et al., 2003). Conversely, hydrolysis removed carbohydrate moieties from the wood, which led to the increase of hydrophobic structure and reduced Cu²⁺ sorption. With regard to sample CEL, Cu²⁺ may exchange with H⁺ in hydroxyl groups, or Cu²⁺ may be adsorbed as a monolayer on the outer surface of the microfibrils by complex formation with hydroxyl groups of the cellulose molecules (Michie, 1961). Lignin data fitted a linear isotherm and its Cu²⁺ sorption was negligible as compared to BL and UTR. This result differs from those of previous studies (Lebow and Morrell, 1995). For instance, Lebow and Morrell (1995) reported Cu²⁺ uptake by lignin and concluded that phenolic hydroxyl groups were the primary reaction sites.

3.5. Effect of ionic strength

The sorption capacity of Cu²⁺ on all sorbents decreased markedly with the increasing Ca²⁺, Na⁺ or Al³⁺ concentrations when the initial concentration of Ca²⁺ or Na⁺ was less than 0.05 M or of Al³⁺ was less than 0.0005 M (Figs. S1 and S2). The dramatic decrease of Cu²⁺ sorption at low Ca²⁺, Na⁺ or Al³⁺ concentrations in contrast to at their high concentrations indicates that competitive sorption between Ca²⁺, Na⁺ or Al³⁺ and Cu²⁺ was occurring. That is, at low co-sorbate concentrations, more sorption sites were occupied by Cu²⁺ ions, while at high ion concentrations Cu²⁺ was losing the competition for sorption sites. This trend in decreasing Cu²⁺ sorption at low co-sorbent concentration is indicative of ion exchange. Also, comparing the effects of co-sorbate at a same ionic strength, the presence of Ca²⁺ decreased Cu²⁺ sorption more extensively than Na⁺ did. This is because Ca²⁺ has stronger exchange ability with Cu²⁺ than with Na⁺, which further confirms that ion exchange is a main sorption mechanism. This is consistent with the results reported by Wolf et al. (1977), but different from the results observed by Lu and Allen (2001). In the case of Lu and Allen (2001), it was found that ionic strength (2.2 × 10^{−3}–0.1 M NaNO₃) did not significantly influence Cu²⁺ sorption to suspended particulate matter. However, at initial Na⁺ and Ca²⁺ concentration greater than 0.05 M or Al³⁺ concentration higher than 0.005 M, specific adsorption (i.e., formation of inner-sphere complexes) might be taking place because the sorbed Cu²⁺ did not substantially decrease with further ionic strength increase, probably due to the strong irreversible bonding between Cu²⁺ and functional surface groups (Stumm and Morgan, 1996).

In conclusion, our results demonstrate that solution pH greatly affected Cu²⁺ sorption onto aspen wood fibers and that maximum sorption occurred at around pH 5.5 independent of which kind of treatment the wood samples had undergone. The results also suggested that carboxyl (–COOH) and hydroxyl (–CHOH) in carbohydrates are the main contributors to Cu²⁺ sorption to aspen wood fibers and CEL. Additionally, the Cu²⁺ sorption capacity of all sorbents was influenced by the presence of Ca²⁺, Na⁺ or Al³⁺. Except HHY, ion exchange was identified as a main sorption mechanism in this study, while specific adsorption may also take place for a fraction of sorbed Cu²⁺. Taking all together, the results described herein could be critical for developing novel and low-cost wood-based treatment technologies for polluted runoff and wastewater.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.04.030.

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