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REMOVAL OF HEAVY METALS FROM WATER WITH FOREST BASED MATERIALS

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Introduction

For 1.5 to 2.5 billion people in the world, clean water is a critical issue (Lepkowski 1999). In the U.S., it is estimated that 90% of all Americans live within 10 miles of a body of contaminated water (Hogue, 2000). The development of filters to clean our water supply is big business. It is estimated that global spending on filtration (including dust collectors, air filtration, liquid cartridges, membranes and liquid macro-filtration) will increase from \$17 billion in 1998 to \$75 billion by 2020 (Noble, 2000). The fastest-growing non-industrial application area for filter media is for the generation of clean water.

One of the prevalent contaminants in our water is metal ions that come from a wide variety of sources including abandoned hard rock and coal mines, highways and large parking lot runoff and natural erosion of minerals. Most methods to remove metal ions from solution are expensive. However, it has been shown that wood and bark are effective in removing metal ions from water (Bryant *et al.*, 1992; Kumar and Dara, 1980; Laszlo and Dintzis, 1994; Randall, 1977).

Materials and Methods

Two methods are presented here that modify wood to increase the sorption of metal ions from contaminated water by increasing the carboxyl content of the cell wall polymers, thus increasing the negatively charged sites that participate in ion exchange with cations. One technique involves grafting citric acid to wood by esterification of a wood hydroxyl group with one of two adjacent carboxylic acid groups of a citric acid

molecule. The other technique involves a two-step oxidation process: First using sodium periodate to selectively cleave adjacent polysaccharide hydroxyl groups, resulting in the formation of a dialdehyde. A second oxidation step with sodium hypobromite converts aldehydes to carboxylates. All treatments were conducted at room temperature.

Citric Acid

Ten ml of 200 g/l ACS Reagent citric acid (anhydrous) was added to 2 g of milled aspen wood and allowed to soak for ½ h. The excess water was removed by oven drying 4 h at 60°C. The dry sample was thermochemically reacted by elevating oven temperature. Separate samples were reacted for 2, 4 and 6 h at 110, 120 and 130°C. Reacted samples were water-rinsed to remove unreacted citric acid and then vacuum oven dried for 16 h at 45°C.

Sodium Periodate

Twenty-five g of milled southern pine wood was mixed in 500 ml solutions containing ACS Reagent sodium periodate (99%). Three concentrations of periodate were used, with separate wood samples, consisting of 1, 2 and 3 % (w/v). Samples were reacted for 24 h, water-rinsed and vacuum oven dried for 16 h at 45°C.

Sodium Hypobromite

ACS Reagent bromine (99.5%) was used to prepare the sodium hypobromite solution immediately before each use. Bromine and sufficient NaOH to yield pH 11 were combined in a 300 ml aqueous solution. Ten g of periodate treated wood was added to three separate concentration levels of the hypobromite. The 1, 2, and 3% (w/v) sodium periodate treated samples were added to 0.3, 0.6 and 0.8% (w/v) solutions of bromine as sodium hypobromite, respectively. Samples were reacted for 24 h, water-rinsed and vacuum oven dried for 16 h at 45°C.

Copper ion Sorption Testing

Cu²⁺ ion was used as standard to determine the efficiency of each modification in removing metal ions from aqueous solutions. The test method involved a 0.1g test sample in 50ml of 50 ppm and a 24 hour equilibrium batch test protocol (pH range 4.6 to 5.2). The wood sorbent was filtered from each standard solution and was analyzed for remaining Cu²⁺ ion with a Jobin Yvon, Ultima, inductively coupled plasma-atomic emission spectrometer instrument.

FTIR Spectroscopy

A Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII Single Reflection ATR accessory was used to monitor changes to carboxylate and ester carbonyl regions of the modified wood, compared with the unmodified wood.

Results and Discussion

Both modification methods resulted in substantial increases to sorption capacity of the wood calculated as Cu²⁺ ion/wood (mg/g). In addition, changes in the FTIR/ATR spectra reflected increases to carboxyl and with citric acid treated, ester carbonyl regions of the modified wood, from that of the unmodified wood.

The greatest increase in sorption capacity with the citric acid method was a 2 h reaction at 130°C, 20% (w/v) citric acid reaction with aspen wood. Weight gain of the wood from the grafted citric acid for this treatment condition was 28.5% and resulted in a 236.6 % increase in Cu²⁺ ion sorption capacity (mg/g). At treatments longer than 2 h, decreases to Cu²⁺ ion sorption capacity and increases to 1,730 cm⁻¹ absorbance, may be due to ester cross-links formed between wood hydroxyls and free carboxyls of the bound citrate (see Figures 1 and 2).

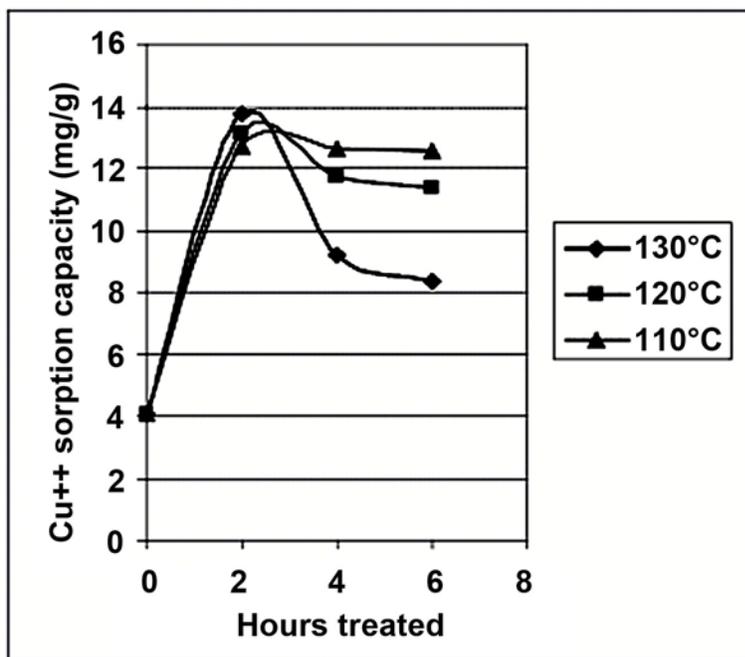


Figure 1. Cu²⁺ ion sorption capacity (mg/g) of citric acid treated aspen wood as a function of treatment time at 110°C, 120°C and 130°C using 0.01 M sodium acetate buffered standard with initial pH of 5.1. Y-axis values are an average of three replicates. The point at zero hours treated is untreated wood.

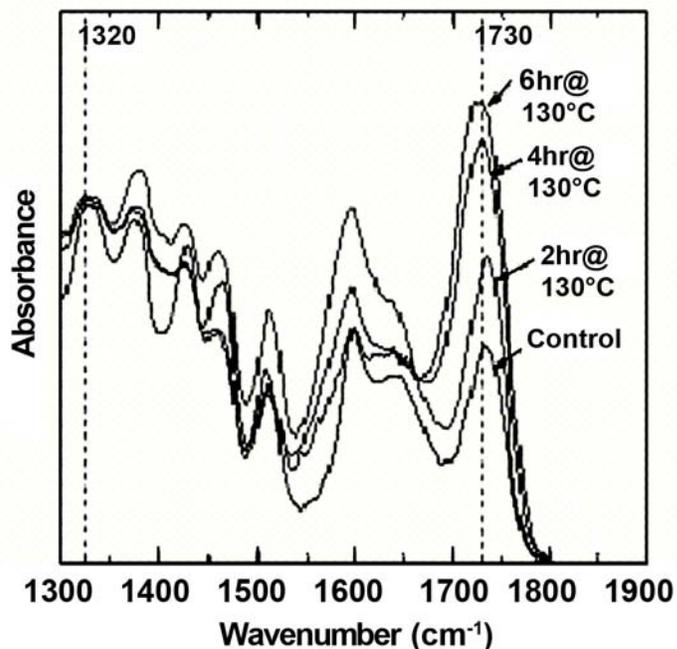


Figure 2. FTIR scans of $1,730\text{ cm}^{-1}$ (ester) carbonyl region with baselines normalized to 1320 cm^{-1} . Samples are treated with 0.1 M NaOH . Scans are of untreated (control) aspen wood and wood reacted with citric acid for 2, 4 and 6 hours at 130°C .

The results in Table 1 show the periodate/hypobromite method applied to southern pine wood. The greatest increase was with a 24 hour reaction at room temperature, 3% (w/v) sodium periodate reaction followed by a 24 hour at room temperature, 0.8% (w/v) Br_2 (as hypobromite) reaction. The total weight loss to the wood for this reaction was 12.6% and resulted in a 148.4% increase in Cu^{2+} ion sorption capacity (mg/g). Figure 3 shows increases to the carboxylate region with increasing concentration of periodate/hypobromite.

Table 1. Sodium periodate and sodium hypobromite treatments of southern pine wood.

Treatment ^{1,2}	(%) Change in Oxidant	(%) Weight Change after treatment	q _e Cu ²⁺ (mg/g)	Sorption pH range
Untreated			3.1	4.6-5.2
1% Periodate for 24hrs, 0.3% Br ₂ for 24 hrs	-29.2, -82.6	-1.9, -3.4	4.7	4.6-4.7
2% Periodate for 24hrs, 0.6% Br ₂ for 24 hrs	-29.2, -85.3	-2.6, -5.6	7.0	4.6-4.7
3% Periodate for 24hrs, 0.8% Br ₂ for 24 hrs	-18.1, -87.7	-2.5, -10.1	7.8	4.6-4.8

¹ % oxidant is w/v; ² q_e sorption values an average of 3 replicates.

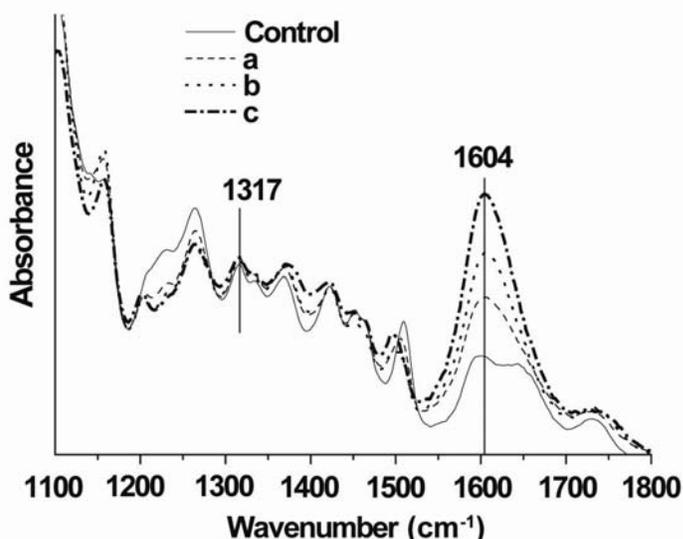


Figure 3. FTIR scans of 1,604 cm⁻¹ (carboxylate) carbonyl region with baselines normalized to 1,317 cm⁻¹. Scans are of untreated (control) southern pine wood and the following treatments: a = 1% Periodate for 24hrs, 0.3% Br₂ for 24 hrs; b = 2% Periodate for 24hrs, 0.6% Br₂ for 24 hrs; c = 3% Periodate for 24hrs, 0.8% Br₂ for 24 hrs.

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