Zinc sorption by permanganate treated pine chips

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ABSTRACT

The sorption equilibria and kinetics of zinc from aqueous solution on both untreated and permanganate treated pine chips were investigated. The sorption kinetics were best described by pseudo-second-order equation and the sorption isotherms were well fitted by a Langmuir model for both untreated and treated pine chips. Zinc sorption increased from $1.2\,\mathrm{mg\,g^{-1}}$ in untreated samples to $3.9\,\mathrm{mg\,g^{-1}}$ for the treated pine chips. Analysis shows that the carboxylic content increased after oxidative treatment of wood sorbents. This was responsible for the improved sorption of zinc onto the pine chips. The permanganate-wood reaction rate in batch experiments was biphasic first-order with an initial rate (0–25 min) and then a slower rate (25–807 min). The initial rates were approximately 3 times greater than the later stage rates. The reaction rates was also particle size dependent with the rate for 4.75 mm pine chips, 11–19% less than that of the 1.18 mm pine chips. Rate limiting mechanisms included intra-particle mechanism of MnO_4^{-} interaction with pine chips is complex and consisting of surface external mass transfer as well as intra-particle diffusion. Rate-limiting reactions in the column caused the shape of the breakthrough curve to exhibit tailing.

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Introduction

Zinc and other heavy metals can be introduced into the water environment from metal plating, mining operations, alloy processing and sewage sludge. Dissolved zinc can have a significant adverse impact on the environment and human health [1,2]. Various methods such as reverse osmosis, ion exchange, coagulation and sorption can be applied for the removal of dissolved metals from aqueous solution. Among these methods, sorption is the most widely used and is effective when well-designed [3,4]. Wood has potential as a sorbent due to its physico-chemical characteristics, low-cost and widespread availability. Wood contains lignin, cellulose and hemicellulose which can be utilized to sorb a variety of organic compounds [5,6] and heavy metals [7]. In recent years, agricultural by-products (e.g. wood, pine bark, sawdust, compost and leaves) have been widely used as bio-sorbents for metal removal [8,9]. The direct use of these bio-sorbents is often limited due to their low sorption capacity. Therefore, cost-effective chemical treatments are needed to improve the sorbent capacity of wood materials.

Woody biomass can be treated with permanganate to enhance the sorption capacity. Studies found that the oxidation of lignocellulosic material with permanganate had a rapid initial reaction as well as increasing the carboxylic group content [10,11]. Jolly et al. [12] oxidized a lignocellulosic substrate by permanganate at pH~2 and improved the binding capacity of the material for Cu by 32% and Zn by 41%. Infrared (IR) results indicated that oxidation of the lignin created carboxylic (COOH) groups. While the impact of permanganate treatment on sorption has been studied using different types of woody biomass, there is little work on the reaction kinetics between wood and permanganate. This knowledge is needed for the design and optimization of permanganate treatment of wood.

The aim of this study is to evaluate the capacity and performance of permanganate treated pine chips in the removal of zinc from aqueous solution as well as to examine the reactivity and kinetics between wood chips (pine) and permanganate. The reactivity between wood and permanganate were further investigated under dynamic conditions using column studies. The Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to investigate the surface functionalization of untreated and treated pine chips. It is expected such information will give insight into aqueous metal removal by modified pine chips and provide the basis for further development

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of modified wood sorbents engineered for improved sorption using complex wastewaters.

Experimental methodology

Pine chip material preparation and characterization

The pine chips (Superior Pine Chip) were supplied by Soilco Pty Ltd., Australia. The pine chips were sieved such that 4.75 mm material passed through a 6.5 mm sieve but was retained over a 4.75 mm mesh sieve and 1.18 mm passed through a 2.36 mm mesh sieve but was retained over a 1.18 mm mesh sieve. Visible contamination from pine bark fragments were removed prior to processing. All samples were washed with distilled water and dried in an oven at 50 °C for 48 h, then stored in an airtight desiccator at room temperature (22 °C) until use. All weights reported in the paper are as dry matter.

Lignin, cellulose, and hemicellulose contents were determined using methods for Acid Detergent Fibre, Acid Detergent Lignin-Neutral Detergent Fibre [13]. Total carbon and nitrogen content for all solid materials were determined in duplicate using a TRU-SPEC carbon nitrogen determinator. The cation exchange capacity (CEC) of the pine chips was measured using saturated ammonium extractants at pH 7 [14]. The specific surface areas and pore characteristics of solid phase media were measured using Brunauer–Emmett–Teller (BET/N_2) (Micromeritics Tristar). Measured pine chips surface area and pore volume data (Table 1) are similar to other reported values for wood [15,16] and the CEC is consistent for pine [17]. The variability between the size fractions in-terms of C/N ratio, particle size and pore width is likely due to sample variability and may represent some bark attached to the pine chips. It should be noted that the particles are highly elongate as a result of the grinding and sieving process [18].

Batch oxidation experiment

About 5 g of untreated pine chips were reacted at pH~2 in a 300 mL amber colour glass bottle with 250 mL of ~61 mM MnO_4^- and mixed in an orbital shaker at 150 rpm at 22 °C. An aliquot (~0.15 mL) of liquid samples were withdrawn at preselected time intervals and analysed for residual permanganate. All experiments were carried out in duplicate. The maximum deviation at absorbance 525 nm from the mean on any sample was less than 2%.

Column oxidative experiment

The columns were constructed in PVC pipe class 18 and sealing by a PVC cap at the end of the column using Silastic. All columns were packed by mixing 66 g of pine chips (4.75 mm) and 1665 g of 0.6 mm glass beads (~20–25% v v^{-1} pine) with a bed depth of approximately 54 cm long by 5.3 cm internal diameter (I.D.) and bulk density 1.5 g cm^{-3}. Both ends of the column were packed by a

layer of 1.5 cm of glass bead (3 mm) to ensure uniform flow. These glass beads (3 mm) are separated by plastic mesh at either ends. The inlet solutions were pumped from a 25 L plastic container at a constant flow rate and at a constant hydraulic head using peristaltic pump (Masterflex Model 7553-85) into the column under up flow directions. The control column was packed with glass bead and showed no evidence for the consumption of $KMnO_4$ due to contact with the column apparatus. Before start-up, the column was operated for approximately 12–24 h by passing distilled water until a steady flow, as well as stable conductivity and colour occurred.

A chloride tracer test was carried out to determine the column pore volume. This was undertaken both before the MnO_4^- injection and after MnO_4^- injection. The column was initially flushed with distilled water at flow rate ~5 mL min^{-1} for 24 h. The tracer solution (KCl, ~72 mg L^{-1}) was prepared and pumped through the column at a flow rate of ~5 mL min^{-1}. This test was used to determine the pore volume of the column and to compare the tracer and permanganate breakthrough curves. The effective porosity for the column filtration media was calculated from the total internal column volume (1232 mL) and the pore volume with relative concentration (C/C_o) at 0.5 which is one pore volume. Therefore, one pore volume in the column is equal to 525 and 517 mL for pre and post MnO_4^- injection tracer, with a corresponding porosity 0.43 and 0.42, respectively, at flow rate 5 mL min^{-1}. Thus the effective pore volume as determined by the tracer test is used in normalizing the accumulated effective volume of permanganate breakthrough curves. The tracer test was then followed by distilled water flush. All experiments were carried out at 22 °C.

The permanganate treatment of the pine chips was undertaken in-situ by injecting an aqueous solution (pH~2) of $KMnO_4$ ~61 mM at a flow rate ~5 mL min^{-1} into the column after the distilled water flushing. During oxidant injection, effluent samples (20 mL) were collected from the outlet of the column at various times for MnO_4^- analysis. Injection was continued until the concentration of $KMnO_4$ measured in the effluent changed less than 2% of the previous reading. This indicated steady state. Then the columns were drained and flushed with distilled water until MnO_4^- was no longer detected in the effluent. The breakthrough curve for oxidation of $KMnO_4$ onto the pine chips was obtained by plotting C (effluent concentration) divided by C_o (influent concentration) against number of column pore volumes. The effective column pore volume was determined by a chloride tracer test. The total quantity of permanganate consumed in the column was calculated from the area above the breakthrough curve (outlet $KMnO_4$ concentration, C/C_o versus time) multiplied by the flow rate. The consumption capacity of the pine chips were calculated from the mass consumed in the column divided by the mass of the pine chips (66 g) in the column.

Batch zinc sorption experiment

Batch sorption studies were conducted by placing 100 mL of a known concentration of zinc solution with a known weight of untreated and treated pine chips (1.18 mm size) in separate 250 mL Erlenmeyer flasks. For the batch kinetic tests these flasks were then shaken at 150 rpm for a specified time period and then analysed for residual concentration of Zn(II). Batch equilibrium sorption experiments were carried out by contacting ~0.2 g of pine chips with different initial concentrations of zinc aqueous solution (1–40 mg L^{-1}) at pH (~5) in separate flasks. The flasks were shaken for 72 h at room temperature (22 °C). All experiments of Zn(II) sorption were carried out in triplicate and the maximum deviation of residual concentration of zinc from the mean was less than 3%. Before analysis, all samples from each flask were decanted and filtered through a 0.2 μm Whatman filter paper.

Table 1
Physico-chemical properties of pine.

Parameters	Pine chips	
Particle size (mm)	1.18	4.75
BET surface area (m^2 g^{-1})	0.45	0.79
Pore width (nm)	10.0	15.6
Total carbon (mg g^{-1})	98.9	95.6
CEC (cmol kg^{-1})	6.2	6.2
Nitrogen (mg g^{-1})	0.23	0.16
Lignin (%)	23	23
Cellulose (%)	57	57
Hemicellulose (%)	14	14