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Sonication of pulp and paper effluent

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ABSTRACT

Final effluent from a pulp and paper kraft mill was exposed to power ultrasound at 357 kHz with the aim of reducing color, turbidity, and chemical oxygen demand (COD). Absorbance measurements showed a bleaching of the effluent at wavelengths above 250 nm, indicating loss of aromatic chromophores. Effluent turbidity also decreased. Surprisingly, there was no observable decrease in COD, within experimental error. This is attributed to the presence of bicarbonate and sulfate ions in the final effluent, which react with hydroxyl radicals and effectively block the oxidation of organics in the effluent. This was demonstrated by sonicating solutions of potassium hydrogen phthalate (KHP) containing chloride, bicarbonate, or sulfate ions, which are the major inorganic ions in the final effluent studied. A solution containing only 2.3 mM KHP showed a 19% reduction in COD after 6 h of sonication. An identical solution with 200 ppm chloride also showed a 19% COD reduction. However, solutions with 700 ppm sulfate and 400 ppm bicarbonate showed COD reductions of 11% and 3%, respectively.

1. Introduction

The pulp and paper industry is water-intensive [1] and the effluent can have an adverse impact on aquatic environments [2]. In Canada, pulp and paper effluent typically undergoes primary and secondary treatments. Primary treatment involves the settling out of solids. Secondary treatments include aeration and activated sludge reactors [2]. However, even after primary and secondary treatment, effluents contain residual pollutants.

Conventional pollutant factors associated with pulp and paper effluent are suspended solids, colour and turbidity, and organic enrichment loads [3]. In addition to aesthetic concerns, colour and turbidity can reduce light penetration into some receiving waters, which impedes the growth of vegetation. Organic enrichment loads are commonly measured by biochemical oxygen demand (BOD) and chemical oxygen demand (COD). COD is particularly useful as a measurement because it represents the fraction of organic compounds in the effluent that are difficult to degrade [4].

The chemical composition of pulp and paper effluent is complex and varies widely among mills [1]. There are hundreds of known compounds present [4] that include organic acids, phenolics, and a range of sulfur containing compounds [3]. These are lignin-derived compounds that arise from the pulping and bleaching processes.

There are increasing efforts to use sonication technology towards the destruction of pollutants associated with industrial waste water [5, 6]. These include an interest in hybrid technologies that couple ultrasound with hydrogen peroxide or ozone, for example [7]. Pulp and paper effluent is a possible target for the application of power ultrasound, with the aim of reducing the conventional pollution factors associated this effluent, namely colour, turbidity, and chemical oxygen demand (COD) [3]. The extreme microscopic mechanical agitation of power ultrasound in water is likely to pulverize suspended solids that are present in the effluent, thus reducing turbidity. Acoustic cavitation produces hydroxyl radicals that are expected to oxidize organic species, lowering COD and bleaching organic chromophores.

This paper gives the results of a laboratory study into the effectiveness of sonication in decreasing the colour (as measured by absorbance), turbidity, and COD of pulp and paper final effluent.

2. Experimental

2.1. Materials

$K_2Cr_2O_7$, concentrated sulfuric acid (A.C.S. Reagent grade), $Na_2SO_4 \cdot 10H_2O$, and NaCl were obtained from Fisher Scientific. $HgSO_4$ (98%) and potassium hydrogen phthalate (KHP) (99.95%) were obtained from Sigma–Aldrich. $NaHCO_3$ (analytical grade) was obtained from BDH. KHP was dried to constant weight at 110 °C. Other reagents were used as received. Distilled water was used for all analytical procedures.

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A 4-L grab sample of final effluent was provided by the Alberta Pacific Forest Industries Inc. kraft mill in Athabasca. This kraft mill primarily processes aspen and poplar. The effluent was shaken vigorously prior to sonication runs in order to re-suspend fine solids that had settled.

2.2. Ultrasound reactor

The ultrasound system used was a T&C Power Conversion, Inc. Model AB-1006 LF Amplifier/Generator coupled to an ELAC Nautik Ultrasonic Transducer USW 51 with a 500 mL laboratory reactor. The area of the signal transducer was 19.6 cm^2. All sonication runs were at 357 kHz, at powers of 2.4 W/cm^2 or 4.0 W/cm^2, as determined by calorimetry (see reference [8] for an example). For all runs, the temperature in the reactor was controlled to 20 ± 2 °C by circulating coolant through the water jacket of the reactor.

2.3. Analytical measurements

Absorbance spectra were obtained using an Ocean Optics USB4000 spectrometer and USB-ISS-UV/VIS tungsten/deuterium light source, using 10 mm pathlength cuvettes.

Turbidity was measured using an Oakton Instruments T-100 Turbidimeter. The instrument was calibrated using formazin standards that were prepared by the manufacturer. Turbidity values were recorded in nephelometric turbidity units (NTU).

COD measurements were conducted according to Standard Method 5220 D. Closed Reflux, Colorimetric Method [9]. Triplicate 2.5 mL aliquots of KHP standards or solution from the reactor were placed in borosilicate test tubes. 1.5 mL of dichromate digestion solution was added using an automatic pipette. 3.5 mL of conc. H_2SO_4 was added with a pipette. The tubes were sealed with screw-on bakelite caps with PTFE liners, and digested at 150 °C for 2 h. After cooling to room temperature, the absorbance at 420 nm was determined using a Novaspec LKB Biochrom Model 4049 spectrophotometer, using 2 mm pathlength glass cuvettes.

3. Results and discussion

3.1. Bleaching of final effluent

Fig. 1 shows the changes in absorbance spectra of final effluent that was sonicated for 25 h. There is a general decrease in absorbance above 250 nm, which suggests the destruction of residual aromatic chromophores that are a known component of lignins [10]. The increase in absorbance below 250 nm may be due to the higher concentrations of carbonyl and conjugated alkene chromophores [11] that are expected to form as intermediates toward full oxidation products.

3.2. Reduction in turbidity

The sample of final effluent in this study had low turbidity prior to sonication. It was observed that sonication decreased turbidity further, as shown in Fig. 2. The kinetics of turbidity loss was complex and it was not possible to fit the kinetic data to simple zero, first, or second order kinetics. However, the kinetics of turbidity loss was highly reproducible over several runs. The reduction in turbidity is consistent with the expected mechanical pulverization and ultimate dissolution of suspended solids under sonication.

3.3. Chemical oxygen demand

It was expected that COD would decrease over the course of sonication. This was not observed in several runs. Within the experimental error of approximately 5% for COD measurements for effluent samples, no change in COD was observed. For example, in one run the initial COD was 110 ppm and after 5 h of sonication

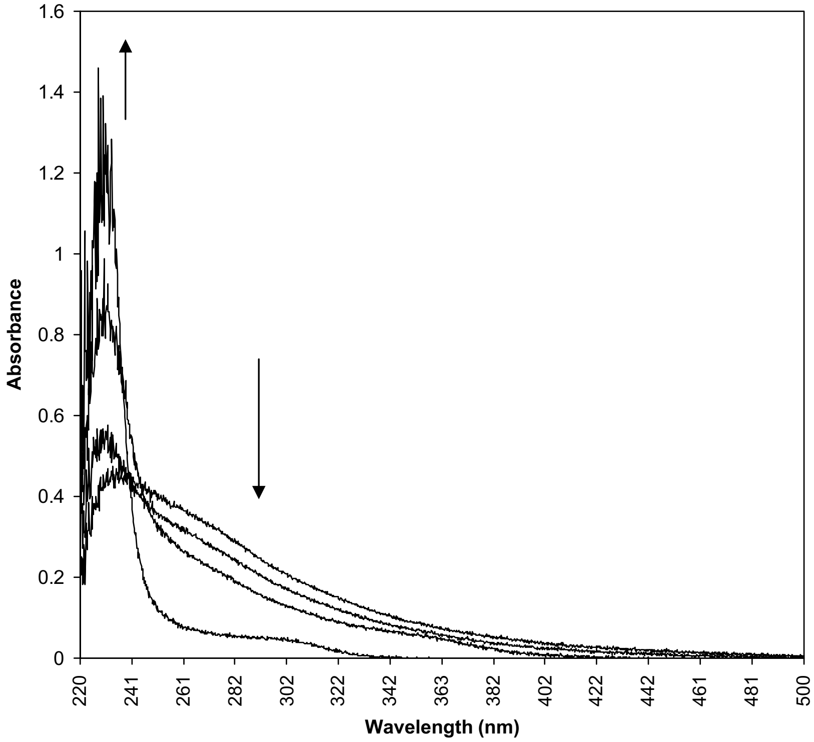

Fig. 1. Absorbance spectra of final effluent at 0, 1, 6, and 25 h of sonication at 4.0 W/cm^2 and 20 °C. Arrows indicate direction of absorbance changes.