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Removal of toxic pollutants from pulp mill effluents by electrocoagulation

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ABSTRACT

This study investigated the effect of electrocoagulation treatment on toxic pollutant removal from pulp mill effluents. Synthetic wastewaters containing wood rosin and copper or pure resin acids were used to investigate the removal of resin acids and copper by electrocoagulation. Removal of pollutants by electrocoagulation was also tested with real debarking effluent. In this study, statistical experimental design and partial least squares modeling were used to investigate the effect of initial pH, current (current density) and treatment time. Electrocoagulation and subsequent filtration removed resin acids and copper from the synthetic wastewaters with high efficiency. Toxicity to algae (*Pseudokirchneriella subcapita*) was completely eliminated by the treatment, however reduction of bacterial toxicity (*Vibrio fischeri*) was more limited. While the initial EC_{50} value for bacteria in debarking effluent was around 8–14 vol%, toxicity was approximately halved by electrocoagulation. Toxicity removal from the debarking effluents was associated with color removal.

1. Introduction

Pulp and paper mills generate large amounts of wastewater in their manufacturing processes. Pollutants are produced during the wood debarking, digesting, pulp washing, pulp bleaching and papermaking processes. Effluents often contain high amounts of toxic chemicals which originate from raw materials, such as resin acids and tannins, or are produced during the manufacturing processes, such as chlorinated organic compounds. These pollutants can cause long-term toxic effects on animal life, such as respiratory stress, toxicity, mutagenicity and genotoxicity [1].

Soil, dirt and bark are removed from the wood raw material during the wood preparation stages [2]. Debarking can be carried out by means of wet processes [3]. Wet processes usually circulate water in order to reduce water consumption and produce lower effluent levels. Wet debarking processes remove large amounts of organic matter from the wood and transfer them into the circulating water. The effluents are highly colored due to their tannin content, which contributes to up to 50% of the COD of debarking wastewater [4]. The effluents are known to exhibit toxicity to bacteria and fish due to their interaction with enzymes [4–7].

Debarking waters also contain a high concentration of resin acids, which are weak hydrophobic acids. Commonly found resin acids in pulping wastewaters include isopimaric, sandacopimaric, levopimaric, abietic, dehydroabietic, neoabietic and palustric acids [1,8–10,14]. According to Peng et al., resin acid toxicity is strongly affected by wastewater pH which has an effect on the solubility of the resin acids [8]. Their toxicity correlates inversely with their solubility, the least soluble being the most toxic. According to the results of Peng et al. and Wilson et al. [8,11], in pulp and paper mill wastewaters isopimaric acid is the most toxic resin acid, although it is not the most prevalent. In studies with rainbow trout, acute lethal concentrations (LC_{50}) of individual resin acids have been found to be in the range of 0.4–1.1 mg/l [12–14]. Oikari et al. reported the minimum effective concentration of dehydroabietic acid to be as low as 20 μg/l [15].

Aerobic and anaerobic biological processes are able to remove resin acids from the effluent streams [1,9,10,17,18]. However, discharged residue can still be toxic to aquatic organisms [9,10]. Debarking effluents also cause problems in wastewater treatment due to their toxicity to microbes in the treatment process. Tannins have been found to be effective inhibitors of methanogens, which may in turn inhibit anaerobic biological treatment processes [4,19]. Oligomeric tannins have highest toxicity as they can form strong hydrogen bonds with proteins [6,20].

Chemical coagulation has been proposed as a treatment for toxic mechanical pulping effluents and bleaching filtrates [21,22]. Resin acids are poorly water soluble, in particular under acidic conditions, and are present as colloids, which could be destabilized by chemical coagulants. Stephenson et al. studied toxicity removal

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and metal salt recovery of a mechanical pulping effluent [21]. According to their results, chemical coagulation eliminated toxicity efficiently. Toxicity was completely eliminated from four-times diluted effluent at a ferric chloride dose of 5 g/l. Ferrous chloride was more effective than ferrous sulfate in decreasing Microtox toxicity. However, coagulants, especially ferrous sulfate, were themselves toxic at high concentration. It is possible that sulfate anions of the coagulant contributed to toxicity to some extent.

Electrocoagulation (EC) is an evolving technology which can be used to remove various chemical species of pollutants in effluents [23,24]. The EC cell consists of electrodes and an AC or DC power source. Anodes can be constructed from iron or aluminum, whereas the cathode material can also be inert, such as titanium. When sufficient external current flows in the cell, the iron anodes dissolve according to Eq. (1) producing iron cations ($n = 2$ for ferrous and 3 for ferric ions) which are further hydrolyzed according to Eq. (2), where m is the amount of hydroxyl anions bound with metal ions. According to this, the degree of hydrolysis depends on the pH of the solution.

$$Fe_{(s)} \rightarrow Fe^{n+}_{aq} + ne^- \quad (1)$$

$$Fe^{n+}_{(aq)} + mOH^- \leftrightarrow Fe(OH)^{(n-m)+}_n \quad (2)$$

Iron cations and hydrolyzed species cause destabilization of the particles or chemical aggregates in the solution [23,24]. It is probable that EC mainly removes impurities that are in colloidal form, as in chemical coagulation, and the main mechanisms of particle removal are the same for electrocoagulation and inorganic chemical coagulants: double layer compression, adsorption destabilization, bridging and precipitation [16]. However, there are significant differences between chemical coagulation and electrocoagulation, such as:

- No anions, such as sulfate or chloride, are added together with metal cations and hydroxides during electrocoagulation.
- Hydrogen produced at the cathode induces flotation that can separate agglomerated particles from water.
- Water pH increases during electrocoagulation, whereas typical iron and aluminum coagulants decrease water pH.

Electrocoagulation can also remove toxic pollutants from effluents. Toxicity caused by Cr(VI) [25–27], dyes [28–31], olive mill wastewater pollutants [32–34] and poultry manure wastewater pollutants [35] have been successfully removed by EC. Polyphenolic substances are mainly responsible for the toxic effects of olive mill wastewaters. According to the findings of Khoufi et al., EC and subsequent sedimentation decreased the inhibition of *Vibrio fischeri* luminescence by 66%, and further increased the biotransformation of pollutants in the subsequent anaerobic treatment [32]. Yetilmezsoy et al. used EC with anaerobic sludge blanket treated poultry manure wastewaters [35]. According to their results, 90% of chemical oxygen demand (COD) and 92% of residual color were removed during the treatment. They tested the toxicity with guppy fish (*Lebistes reticulates*), revealing no mortality or behavioral changes after 48 h exposure to the EC treated wastewater.

Chowwanapoonpohn et al. studied the recovery of tannins from tree bark by EC [36]. They first elutriated tannins from the bark with water, treated this solution with electrocoagulation, dissolved the coagulum in hydrochloric acid, extracted the tannins with 1-butanol, and evaporated the solution. The procedure increased tannin enrichment by 0–48% when compared to simple aqueous extraction and evaporation. However, the effect of EC treatment on the toxicity of debarking effluents has not been studied. High removal of organic matter in the EC process could enable reuse of water in the debarking process. Reducing the amount of toxic compounds going to the biological wastewater plant could enhance the stability of the biological wastewater treatment operation and decrease pollution of the receiving water body.

In this study, the effect of EC treatment on the removal of toxic components from pulp mill effluents was investigated. Synthetic wastewaters containing softwood rosin and copper or exclusively pure resin acids were used to investigate the removal of resin acids and copper by EC. Toxic pollutant removal by EC was also assessed for debarking effluents. Statistical experimental designs and partial least squares modeling were used to investigate the effect of initial pH, current (current density) and treatment time on pollutant removal.

2. Experimental

2.1. Test solutions

Synthetic wastewaters were used in order to analytically study the removal of resin acids and a metal pollutant (Cu) and their toxicity by electrocoagulation. These solutions contained Polish wood rosin (Hercules Corporation, Wilmington, DE, USA) and copper nitrate $Cu(NO_3)_2$. The main components of the Polish wood rosin are shown in Table 1. Additional tests were conducted using pure dehydroabietic acid (DHAA) and isopimaric acid (IPA) (purity 99.0%, Helix Biotechnologies, Canada).

Filtered Finnish oligotrophic lake water (Lake Palosjärvi, Toivakka) was used to dilute the mother solutions to final test concentrations. Lake water was used to obtain a realistic background, such as salts and metals concentration, for the electrocoagulation tests. Solution pHs were adjusted to 5, 7 or 9 using 0.5 M sulfuric acid or sodium hydroxide. To ensure adequate conductivity of the synthetic wastewaters, 20 ml of 0.5 M sodium sulfate (purity 99%, Merck) solution was added to the water.

Debarking effluent was collected from a Finnish pulp and paper mill and stored in a cold room. The effluent had a high organic matter content and dark color, and was filtered through a coarse sieve (0.2 mm mesh size) to remove bark fragments and needles prior to electrochemical treatment.

2.2. Electrochemical treatment

Electrochemical treatment was conducted in a standard 1000 ml glass beaker. For synthetic wastewaters, a volume of 600 ml was used during electrocoagulation treatment. The corresponding volume for debarking effluents was 400 ml. The electrochemical cell construction consisted of four iron electrodes which were connected to the power supply using a monopolar arrangement (Fig. 1). The plate dimensions were 70×50 mm and the iron electrode surface area 70 cm^2 per plate (double-sided), totaling an anode surface area of 140 cm^2. The distance between anodes and cathodes was 10 mm. A laboratory DC power source

Table 1
Breakdown of resin acids content of the Polish wood rosin (Hercules Corporation, USA) used in this study.

Resin acid	% (w/w)
Pimaric acid	8.0
Sandaracopimaric acid	1.7
Isopimaric acid	3.1
Palustric acid	20.7
Dehydroabietic acid	30.6
Abietic acid	22.4
Neoabietic acid	5.3
Levopimaric acid	8.2