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Application of intensified Fenton oxidation to the treatment of sawmill wastewater

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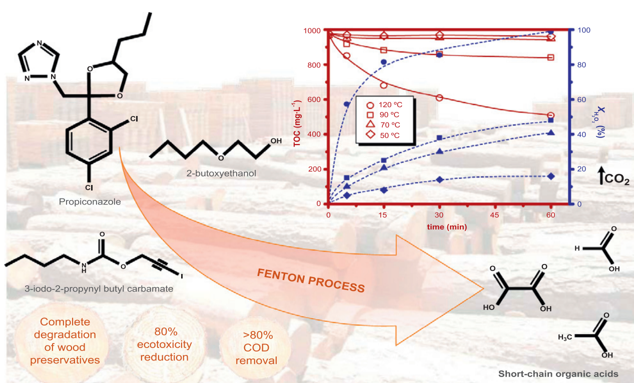
HIGHLIGHTS

- The intensified Fenton process represents a cost-effective alternative for sawmill wastewater treatment.
- Increasing temperature to 120 °C and feeding H_2O_2 in 3 additions improved the H_2O_2 consumption efficiency.
- High COD (≈80%) and TOC (≈70%) removal were achieved after 1 h reaction time.
- Fungicides were completely removed obtaining short-chain organic acids as main products.

GRAPHICAL ABSTRACT



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ABSTRACT

The application of the Fenton process for the treatment of sawmill wastewater has been investigated. The sawmill wastewater was characterized by a moderate COD load (≈3 g L^{-1}), high ecotoxicity (≈40 toxicity units) and almost negligible BOD/COD ratio (5×10^{-3}) due to the presence of different fungicides such as propiconazole and 3-iodo-2-propynyl butyl carbamate, being the wastewater classified as non-biodegradable. The effect of the key Fenton variables (temperature (50–120 °C), catalyst concentration (25–100 mg L^{-1} Fe^{3+}), H_2O_2 dose (1 and 2 times the stoichiometric dose) and the mode of H_2O_2 addition) on COD reduction and mineralization was investigated in order to fulfill the allowable local limits for industrial wastewater discharge and achieve an efficient consumption of H_2O_2 in short reaction times (1 h). Increasing the temperature clearly improved the oxidation rate and mineralization degree, achieving 60% COD reduction and 50% mineralization at 120 °C after 1 h with the stoichiometric H_2O_2 dose and 25 mg L^{-1} Fe^{3+}. The distribution of H_2O_2 in multiple additions throughout the reaction time was clearly beneficial avoiding competitive scavenging reactions and thus, achieving higher efficiencies of H_2O_2 consumption ($X_{COD} \approx 80\%$). The main by-products were non-toxic short-chain organic acids (acetic, oxalic and formic). Thus, the application of the Fenton process allowed reaching the local limits for industrial wastewater discharge into local sewer system at a relatively low cost.

1. Introduction

Wood is an important natural resource widely used as raw material for cellulose pulp, furniture and tools, among others. Sawmills generate relatively low amounts of wastewater (Taylor

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et al., 1996; Hedmark and Scholz, 2008). However, they represent an environmental concern due to the presence of wood preservatives against fungi and wood-boring insects since those chemicals are harmful highly toxic substances. Propiconazole and 3-iodo-2-propynyl butyl carbamate (IPBC) are wood preservatives widely used in the wood processing industry (EPA, 1997, 2006; Lebkowska et al., 2003). They are registered by the EPA due to their high toxicity to several water-living organisms, like fish (LC_{50} rainbow trout = 0.85 mg L^{-1} and 0.072 mg L^{-1} for propiconazole and IPBC, respectively) or crustacean like *Daphnia magna* (EC_{50} = 4.8 mg L^{-1} and 0.956 mg L^{-1} for propiconazole and IPBC, respectively) as well as their high persistency in the environment (EPA, 1997, 2006). Thus, the discharge of sawmill wastewater involves serious environmental problems.

Sawmills are in general relatively small facilities, being the liquid residues usually managed as hazardous wastes at a fairly high cost (≈150 € m^{-3}). Effective reduction of the organic load of those effluents by conventional biological processes is not likely due to their high toxicity and very low BOD/COD ratio (Taylor et al., 1996; Lebkowska et al., 2003). In fact, the treatment of sawmill wastewaters by means of biological treatments has been scarcely investigated in the literature (Hedmark and Scholz, 2008). Vidal and Diez (2005) studied the anaerobic degradation of different sawmill wastewaters using an Upflow Anaerobic Slugde Blanket system. The authors concluded that the toxicity of the wastewater caused strong inhibition of methanogenic bacteria. Thus, continuous anaerobic biodegradation of the sawmill effluent exhibited only low COD reductions (between 10% and 30%) without significant color decrease. In this context, the potential application of advanced oxidation processes (AOPs) can be analyzed for the sake of developing possible solutions. The Fenton process is a well-established AOP technology based on the catalytic decomposition of H_2O_2 by means of iron salts at acid pH, giving rise to hydroxyl radicals, strong and non-selective oxidant. This technology has been successfully applied for the treatment of highly polluted wastewaters such as cosmetics (Bautista et al., 2007; Pliego et al., 2012), olive-mill (Rivas et al., 2001; Lucas and Peres, 2009), chemicals (Pliego et al., 2012), pulp and paper (Pérez et al., 2002), power plant (Pliego et al., 2013) or textile (Pérez et al., 2002; Rodrigues et al., 2009), among others (Bautista et al., 2008). It has gained increasing attention due to the simplicity of design and setup, safe operation, high efficiency and the use of readily availability reagents. However, so far the only work dealing with the application of the Fenton process to the treatment of sawmill wastewater is that reported by Vlyssides et al. (2008). In that contribution, the authors worked at ambient temperature (20 °C) using an extremely high iron dose (5.5 g L^{-1} Fe^{2+}). In fact, most of the COD removal was attributed to the flocculation of organic matter during the neutralization step due to the precipitation of ferric hydroxide accompanied by the addition of a weak anionic polyelectrolyte. A significant COD reduction (≈70%) was achieved but associated to the formation of high amounts of sludge which represents an important drawback.

The intensification of the Fenton process addressed to achieve a more efficient use of H_2O_2 at low iron concentrations represents an important challenge nowadays. A decrease of the iron dose is important since it reduces the amount of $Fe(OH)_3$ sludge and also improves the efficiency of H_2O_2 through a better control of competitive scavenging reactions. A demonstrated solution for reducing parasitic H_2O_2-consuming reactions consists of distributing the overall dose of H_2O_2 in different successive additions or as a continuous feed throughout the reaction time (Zazo et al., 2009; Martins et al., 2010; Inchaurrondo et al., 2012). Thus, the way of feeding H_2O_2 must be strongly considered in the application of the Fenton process. Zazo et al. (2011) demonstrated that increasing the temperature also led to a more efficient consumption of H_2O_2 in the Fenton oxidation of phenol upon enhanced generation of $^{\cdot}OH$ radicals at low iron concentration. Therefore, the increase of temperature can be considered as a way of intensification of the conventional Fenton process.

The current study attempts to explore the feasibility of treating a real industrial sawmill wastewater by Fenton oxidation. The main purpose is to establish the optimal operating conditions allowing to fulfill the local limits for industrial wastewater discharge into the municipal sewer system. Thus, experiments were performed addressed to learn on the effect of temperature, iron concentration, hydrogen peroxide dose and the way of H_2O_2 feeding on the evolution of COD and TOC with the aim of achieving an efficient use of H_2O_2 at low iron concentrations in short reaction times. Particular attention is paid to the breakdown of highly toxic wood preservatives present in the wastewater and follow-up of the reaction byproducts and the ecotoxicity of the resulting effluents. The study also includes a preliminary estimation of the main operating costs for the application of the Fenton process to sawmill wastewater.

2. Materials and methods

2.1. Fenton experiments

Fenton experiments were carried out for 1 h (unless otherwise indicated) in a batch stainless steel pressurized reactor (BR-300, BERGHOF) with a 500 mL PTFE insert reaction vessel equipped with backpressure and temperature controllers. The stirring velocity was maintained at 200 rpm. The reactor was initially loaded with 200 mL of the raw wastewater. When the temperature was equilibrated, 5 mL of hydrogen peroxide solution and 5 mL of $Fe(NO_3)_3$ aqueous solution of adjusted concentrations were injected. The effect of temperature was tested within the 50–120 °C range (50, 70, 90 and 120 °C) since increasing the temperature has demonstrated to improve the efficiency of H_2O_2 consumption which is the major component of cost in Fenton process (Pignatello et al., 2006; Sievers, 2011; Pliego et al., 2012). Moreover, the exothermic character of the oxidation process (an increase of 5–10 °C was observed working at 120 °C) and the recovery of heat from the treated off-stream allows saving energy. The Fe^{3+} dose was varied in the range of 25–100 mg L^{-1}. The H_2O_2 doses tested correspond to 100 and 200% of the theoretical stoichiometric amount relative to COD (2.125 g H_2O_2 g^{-1} COD) (Lucas and Peres, 2009). In the experiments where the H_2O_2 dose was distributed in several steps, a first addition was initially done corresponding to 50% of the overall amount and the rest was fed in two subsequent additions (25% each) injected when the measured H_2O_2 concentration was negligible. The initial pH value was adjusted to 3 with nitric acid. Each run was carried out by triplicate being the standard deviation less than 5% in all cases. Blank experiments with the wastewater in absence of H_2O_2 and Fe^{3+} were also performed at all the temperatures tested.

2.2. Analytical methods

Samples were periodically withdrawn from the reactor (0, 5, 15, 30 and 60 min) and immediately analyzed. TOC was measured with a TOC analyzer (Shimadzu, mod. TOC, VSCH) and the H_2O_2 concentration was determined by colorimetric titration following the titanium sulfate method (Eisenberg, 1943) using an UV 1603 Shimazdu UV/Vis spectrophotometer. COD measurements were performed by the closed reflux colorimetric method using an UV/Vis spectrophotometer in accordance with a standard method using potassium dichromate as oxidant (APHA, 2012). Short-chain organic acids were analyzed by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A