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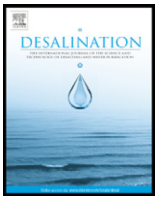

Optimization of TiO_2/Fe(III)/solar UV conditions for the removal of organic contaminants in pulp mill effluents

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ABSTRACT

Solar degradation of effluents of pulp mill industry containing toxic chemicals has been studied using TiO_2/Fe(III) (Degussa P25 TiO_2 was used as a catalyst). Effects of some operating parameters such as the initial oxidant and catalyst concentrations and circulation rates of wastewater on TOC, color and AOX removals were investigated using the Box–Wilson statistical experimental design method. The highest color, TOC and AOX removals of 78%, 64% and 68% were obtained at TiO_2 concentration of 188 mg/L and Fe (III) concentration of 0.5 mM, respectively.

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1. Introduction

Pulping processes utilize large amounts of water which reappear in form of an effluent. In a pulp and paper industry, the most significant sources of pollutions are wood preparation, pulping, pulp washing, screening, bleaching and coating operations. Among the various processing steps, pulping generates a high-strength wastewater containing toxic chemicals such as phenolics [1]. Three main groups of organic compounds present in a paper industry are, (a) starch degradation products, such as saccharides or carboxylic acids, (b) phenolic compounds arising from lignin and (c) other pollutants that may be present in the fresh waters such as surfactants [2]. Major pollutants present in the effluents of paper industry are suspended solids, chemical oxygen demand (COD), toxicity, color, adsorbable organic halogens (AOX) and high concentration of nutrients that cause eutrophication in receiving water [3,4]. Since some of the contaminants in pulp and paper industry effluents are non-biodegradable, conventional biological treatment processes are not sufficient for treatment. The extent of toxicity and color removal by conventional biological treatment vary depending on the pulping process used. In order to meet increasingly stringent discharge limits, pulp mills are forced to adopt technologically advanced treatment systems. Organic compounds such as chlorophenols are not fully degraded by biological processes which require advanced oxidation after biological treatment to reduce refractory organics and color of the pulp mill wastewater [5,6].

Advanced oxidation processes (AOPs) were developed and used as potentially powerful methods capable of transforming the pollutants into harmless substances [7]. AOPs are based on the generation of very reactive non-selective transient oxidizing species such as the hydroxyl radicals (•OH) which were identified as the dominant oxidizing species [8]. For effective oxidations of refractory organic compounds, the hydroxyl radicals must be generated continuously in situ through chemical or photochemical reactions due to their instability. Solar photocatalysis is an advanced oxidation process (AOP) that has been found to be efficient in the treatment of some industrial wastewaters [9,10]. It consists in the use of solar light to generate a highly oxidizing species, commonly the hydroxyl radical (•OH). Catalysts are needed in the process, being the Fenton reagent and titanium dioxide the two most widely employed [11].

Titanium dioxide is a solid semiconductor that upon light excitation generates electrons in the conduction band and holes in the valence band [12]. Also in this case the mechanism remains to be fully established: the holes could initiate oxidation of the substrate, generating its radical cation. Alternatively, hydroxyl radicals could be generated from water molecules [13]. As radiation with wavelengths shorter than 380 nm is absorbed by titanium dioxide, the UV fraction of sunlight can be employed in the process. Photocatalytic degradation of recalcitrant organic contaminants in the presence of TiO_2 has been recently investigated [14,15], since a large number of aliphatic and aromatic compounds can be mineralized by UV/TiO_2 treatment under suitable conditions. The prototype of a heterogeneous photocatalytic reaction is based on the irradiation of particles of the semiconductor TiO_2 in the presence of dissolved molecular oxygen (Eq. (1)). The TiO_2 particles are either suspended in water or immobilized on an appropriate support material. The generally accepted mechanism of

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TiO_2 photocatalysis includes redox reactions of adsorbed water and oxygen molecules or of other subsrates. The formation of the electron–hole pair (h_{vb}^{+}–e_{cb}^{-}) after excitation is followed by the oxidation of adsorbed water molecules by electron transfer to h_{vb}^{+} with formation of hydroxyl radicals and H^{+} (Eq. (1)). Oxygen molecules that are adsorbed at the reductive side of the TiO_2 particle serve as electron acceptors to form superoxide radical anions according to Eq. (2). These are protonated to yield hydroperoxyl radicals (Eq. (3)). Hydrogen peroxide and oxygen molecules are then formed by disproportionation of the intermediary hydroperoxyl radicals (Eq. (4)). Alternatively, adsorbed substrate molecules (R–X) may be oxidized directly by electron transfer at the h_{vb}^{+} side of the semiconductor particle (Eq. (5)) with formation of radical cations of the substrate. This mechanism depends strongly on the nature of R–X and on its electron donating properties [16].

$$TiO_2 + hv \rightarrow TiO_2\left(h_{vb}^{+} + e_{cb}^{-}\right)\begin{cases} h_{vb}^{+} + H_2O \rightarrow H^{+} + \cdot OH \\ e_{cb}^{-} + O_2 \rightarrow O_2^{\cdot -} \end{cases} \tag{1}$$

$$TiO_2(e_{cb}^{-}) + O_2 \rightarrow TiO_2 + O_2^{\bullet -}(\text{reduction}) \tag{2}$$

$$O_2^{\bullet -} + H^{+} \rightarrow HO_2^{\bullet}(\text{protonation}) \tag{3}$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2(\text{disproportionation}) \tag{4}$$

$$TiO_2(h_{vb}^{+}) + R{-}X \rightarrow TiO_2 + R{-}X^{\bullet +}(\text{oxidation}) \tag{5}$$

The major objective of this study is to investigate the performance of solar oxidation for color, TOC and AOX removal from paper mill effluent. For this reason, Fe(III)/TiO_2/solar UV treatment was employed. The Box–Wilson experimental design was used in order to investigate the effects of important process variables on color, total organic carbon and adsorbable organic halogens removal performance. The Box–Wilson experimental design is a response surface methodology used for evaluation of a dependent variable as functions of independent variables [17]. The Fe(III), TiO_2 concentrations and circulation velocity were considered as independent variables and color, TOC and AOX removal efficiencies were considered as dependent variables in the Box–Wilson statistical design method.

2. Materials and methods

2.1. Characterization of the pulp mill effluent

The pulp mill industry wastewater samples were obtained from a stabilization pond of a pulp and paper industry wastewater treatment plant located in Aliağa/Izmir, Turkey. Composition of the wastewater used in this study was analyzed before the experimental studies. The pH values of the effluent samples used in the experimental studies varied from 7.12 to 8.50. The COD concentrations of the samples varied from 608 mg/L to 1500 mg/L. The BOD concentrations of the samples were between 260 mg/L and 500 mg/L. The TOC concentrations of the samples varied from 206.2 mg/L to 303.2 mg/L and, the AOX concentrations of the samples were between 136 μg/L and 2864 μg/L. A low BOD/COD ratio of 0.33–0.42 indicated low biodegradability of the organic compounds present in the wastewater which require advanced treatment.

2.2. Materials

The Titanium dioxide (TiO_2) was used as oxidants in oxidation experiments. The powder form of the TiO_2 (P25) obtained from Degussa. The Iron sulphate ($Fe_2(SO_4)_3 \cdot 7H_2O$) was used as source of Fe(III), was analytical grade and obtained from Merck. A stock solution of 10 g/L Fe (III) was used to prepare the desired concentrations in the experiments after dilution. The Fe(III) stock solution was stored at a dark place to prevent the oxidation of Fe(III). Distilled water was used in cleaning and experimentation.

2.3. Photocatalytic reactor

All experiments were performed in a photocatalytic reactor with a total volume of 40 L. The photocatalytic reactor was operated as a batch process. The system consists of sun light collectors, water preparation tank, circulation pump and a control panel. The solar collector is mounted on a fixed platform tilted 37° (local latitude). The sun light collectors were made up of eight borosilicate glass cylindrical tubes 100 cm in length and 3 cm in diameter. The tubes were connected to each other in a series by polyethylene cylindrical parts. A circulating

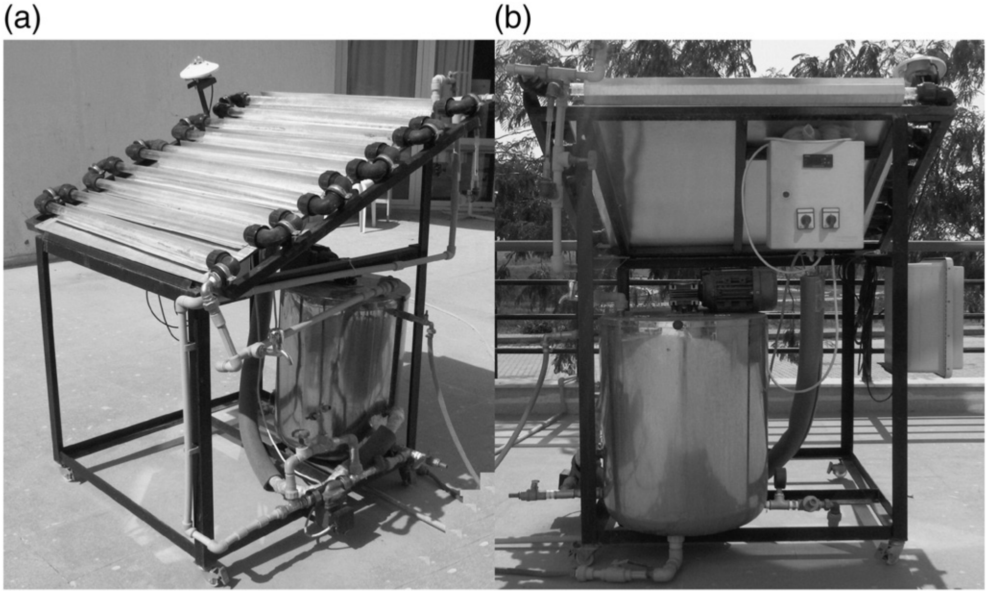

Fig. 1. (a) Front view of the pilot scale solar reactor. (b) Back view of the pilot scale solar reactor.

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