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Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater

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ABSTRACT

Integrated processes have been proposed for high strength wastewaters such as pulp and paper wastewater. In this work, electrocoagulation (EC) followed by UV/oxidant system was studied for the removal of organic compounds from pulp and paper wastewater. EC process was optimized by Box–Behnken design. Under optimum conditions (natural pH, time = 33.7 min and current density = 5.55 mA/cm^2), about 61% COD removal was achieved. The obtained effluent was remediated by UV/persulfate (PS) and UV/peroxymonosulfate (PMS). The results showed that UV/PS had the best performance in natural pH (pH of electrocoagulated effluent i.e. pH = 8.2) while UV/PMS required pH adjusting since pH = 4.0 provided the best efficiency. The scavenging effect was observed in overdosing oxidant in UV/PS while in UV/PMS, increase in PMS dosage increased the removal efficiency. The partial oxidation parameter showed that with increase of time, total oxidation was the predominant mechanism compared to partial oxidation. EC process was not effective in case of biodegradability improvement whereas EC along with UV/oxidant could significantly increase biodegradability (BOD_5/COD ratio). In addition, the solar irradiation was tested as an alternative for UV source and the related results exhibited a negligible efficiency. Electrical energy consumption and current efficiency were also calculated.

1. Introduction

Pulp and paper industry is a major consumer of energy (fossil fuels and electricity), natural resources (water and wood) which has been considered as a serious polluter for the environment. An evidence of environmental impact of pulp and paper industry is given by the observation that one ton of pulp products requires 75–225 m^3 water (Eskelinen et al., 2010; Khansorthong and Hunsom, 2009). Wastewater generated from pulp and paper industry is very complex in case of constituents; hence it is almost impractical to characterize all components as for other industrial wastewaters. This wastewater has high organic content, dark color and toxic matters (Asha et al., 2014; Hermosilla et al., 2015). One of the impacts related to the discharge of dark color wastewater into receiving waters is the reducing photosynthetic activity of aquatic plants (Lucas et al., 2012). Moreover, the increase of high organic matter in water leads to decrease of dissolved oxygen concentration and disturbing life of the fishes and other organisms consequently (Lucas et al., 2012; Pokhrel and Viraraghavan, 2004). Several processes are available for removal of organic content from pulp and paper wastewater

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(Kamali and Khodaparast, 2015). Biological processes are highly depended on the wastewater quality and they cannot be applicable for non-biodegradable wastewaters with BOD_5/COD lower than 0.3 since the presence of toxic compounds affects microorganism growth and activity (Soloman et al., 2009). Chemical processes are efficient methods for degradation or separation of organic compounds which have been widely used for treatment of industrial wastewaters. However, sole application of chemical processes is not able to treat pulp and paper wastewater completely. Therefore, a combination of various chemical processes is necessary in order to obtain satisfactory results (Rodrigues et al., 2008; Yazdanbakhsh et al., 2015). Electrocoagulation (EC) is a versatile and efficient process which has been exerted for different industrial wastewaters (Ghanbari et al., 2014a; Khandegar and Saroha, 2013). In EC process, coagulant agents are electrochemically generated from sacrificial anode made from iron or aluminum. The generated metallic ions will produce hydroxide metals which have a strong capacity for coagulation or adsorption of pollutants (Ghanbari and Moradi, 2015; Moradi et al., 2016a).

$$\text{Anode}: \mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^- \quad (1)$$

$$\text{Cathode}: 2\mathrm{H_2O} + 2e^- \rightarrow 2\mathrm{OH}^- + \mathrm{H_2} \quad (2)$$

$$\mathrm{Fe}^{n+} + n\mathrm{OH}^- \rightarrow \mathrm{Fe(OH)}_n \quad (3)$$

EC can successfully remove colloids, suspended matters and some dissolved organics from wastewater. However, this process may be insufficient for treatment of high strength wastewaters such as pulp and paper wastewater. Hence, integrated processes can be a good strategy in treatment and management of high strength wastewaters. Nowadays, advanced oxidation processes (AOPs) based on sulfate radical have been considered for degradation of organic pollutants. Sulfate radical ($SO_4^{\bullet-}$) is a strong oxidant with redox potential (E^0 = 2.5–3.1 V) which has a more oxidation power in comparison with hydroxyl radical (E^0 = 1.8–2.7 V) (Anipsitakis and Dionysiou, 2004; Zhang et al., 2015). Sulfate radical can be generated by activation of persulfate (PS) and peroxymonosulfate (PMS) using transitional metals (Ghanbari et al., 2014b), UV irradiation (Ghanbari et al., 2016; Sharma et al., 2015), electrochemistry (Akbari et al., 2016) and heat (Antoniou et al., 2010). The residual transitional metals can be hazardous since they have negative effects on human health. Besides, UV irradiation is an environmentally friendly way for producing sulfate radical (Liu et al., 2013).

$$\mathrm{S_2O_8^{2-}} + \mathrm{UV} \rightarrow \mathrm{SO_4^{\bullet-}} + \mathrm{SO_4^{\bullet-}} \quad (4)$$

$$\mathrm{HSO_5^-} + \mathrm{UV} \rightarrow \mathrm{HO^\bullet} + \mathrm{SO_4^{\bullet-}} \quad (5)$$

The UV based processes are limited by high color and turbidity absorbing UV radiation and preventing activation of oxidant. Hence, application of a pretreatment process is necessary for effective performance of UV/PS or PMS for treatment of pulp and paper wastewater.

To the authors' knowledge, there is no previous study in the combination of electrocoagulation and UV/PS or UV/PMS technologies for pollutant degradation. Moreover, few studies have focused on real wastewater treatment by sulfate radical and no work has been conducted for treatment of pulp and paper wastewater based on sulfate radical. The main objectives of this study include: (1) optimization of EC process by Box–Behnken design for COD removal from pulp and paper wastewater; (2) study on the performance of UV/PS and UV/PMS systems in COD removal from electrocoagulated effluent; (3) determination of partial oxidation parameter and biodegradability index in UV/oxidant systems.

Table 1 – Some properties of pulp and paper wastewater.

Parameters	Unit	Values
COD (chemical oxygen demand)	mg/L	1537 ± 50
TOC (total organic carbon)	mg/L	421 ± 2
BOD_5 (5-day biochemical oxygen demand)	mg/L	410 ± 35
TSS (total suspended solids)	mg/L	280 ± 50
TDS (total dissolved solids)	mg/L	880 ± 20
Cl^-	mg/L	340 ± 8
pH	–	6.38 ± 0.05
Appearance	–	Dark

2. Materials and methods

2.1. *Wastewater sampling*

The wastewater was manually collected from Pars manufacturer which is located in Khuzestan province, Iran. The Pars manufacturer consumes a large volume of water for production of one ton of paper (250 m^3). This manufacturer produces 25,000 m^3 wastewater per day and the wastewater is being discharged to the Dez River without any treatment process. The collected sample was stored in plastic containers and was immediately transferred to the water laboratory and kept at 4 °C to minimize the biological reactions. Some characteristics of the sample were analyzed. Each parameter was analyzed three times and average values are presented in Table 1.

2.2. *Chemicals and reagents*

Sulfuric acid (98%), silver sulfate, mercury sulfate, sodium hydroxide were purchased from Merck Company. Ferrous ammonium sulfate was provided from Aldrich Inc. Sodium persulfate was purchased from Fluka Company. The Oxone ($KHSO_5$•0.5$KHSO_4$•0.5K_2SO_4) was provided from Sigma–Aldrich Inc. as a source of PMS. All solutions were prepared by deionized water.

2.3. *Design of experiments*

The Box–Behnken Design (BBD) for response surface methodology was used for optimization and evaluation of three main factors of EC. The effects of initial pH, current density and electrolysis time were evaluated on COD removal as response. The factors were coded before analyzing the regression. The actual variables were coded as 1, 0 and −1 for high level, central point, and low level respectively. The actual variables (X_i) were coded by Eq. (6) (Salahi et al., 2013).

$$X_i = \frac{x_i - x_0}{\Delta x} \quad (6)$$

where X_i is the dimensionless coded value of the independent variable, x_i is the uncoded value of the ith independent variable, x_0 is the ith uncoded independent variable at the center point, and Δx is the step change value. The coded and actual values of the factors are presented in Table 2. The levels of factors were selected based on both several preliminary tests and