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Treatment of effluents from wool dyeing process by photo-Fenton at solar pilot plant

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ABSTRACT

The decolourization and mineralization of simulated wastewaters from wool dyeing tanks were investigated by Fenton and photo-Fenton processes. Yellow, red and blue dyebaths with azo-type and anthraquinone dyes and additives were selected as colored effluents. Photo-Fenton reaction was much more efficient than the respective dark reaction under identical experimental conditions. The effect of H_2O_2 and Fe(II) dosage and fractional or initial addition of these reagents on the photo-mineralization processes were studied and the optimal conditions found. Experiments at a pilot plant based on compound parabolic collectors (CPCs) confirmed that, under optimal conditions, 100% of color removal was obtained requiring low accumulated energy. No toxic effects on marine bacteria *Vibrio fischeri* were observed at the end of photo-Fenton treatment for all studied effluents. High concentrations of sodium acetate are used as additive in the wool dying process. HPLC and TOC analysis of the effluents after photo-Fenton process confirmed that the remaining organic carbon is due to the presence of acetates. The obtained results showed the feasibility of photo-Fenton process to achieve suitable water qualities for internal reuse.

Introduction

The textile industry consumes large volumes of water in dyeing and finishing operations. In textile dyebaths, the degree of dye fixation is never complete resulting in dye-containing effluents [1]. Textile wastewaters cause significant problems for the environment. These wastewaters are highly polluted as a result of suspended solids (SS), high chemical oxygen demand values (COD), high biochemical oxygen demand values (BOD), heat, acidity, basicity and various soluble substances.

Most textile effluents are of non-biodegradable nature. Direct biological treatment of colored effluents is not effective [2]. Consequently, physical or chemical treatments have to be used to completely degrade the dye, or to produce a partial degradation solution amenable to a secondary biological treatment. Other methods such as coagulation/flocculation, activated carbon adsorption and reverse osmosis can only transfer the contaminants from one phase to another, leaving the problem essentially unsolved [3]. Therefore, the application of advanced oxidation processes (AOPs) is an interesting alternative for the treatment of textile wastewaters. These processes generate OH radicals, which have high oxidative power and obtain general organic pollutant abatement [4,5]. The most frequently used AOPs for wastewater containing high levels of total organic carbon include H_2O_2/UVC systems, Fenton and photo-Fenton reactions [6]. Some of the techniques involved require consumption of high energy photons generated by artificial light, with the consequent economic cost being too high for practical applications. However, the photo-Fenton reaction can be driven with low energy photons in the UVA-VIS region of the spectrum. Thus, photo-Fenton processes are a potentially low cost AOP that can be run under solar irradiation.

Fenton and photo-Fenton processes are AOPs in which oxidant species are generated from hydrogen peroxide and Fe(II) as a catalytic couple. In the Fenton reaction, ferrous salts react with hydrogen peroxide to generate hydroxyl radicals as follows (reaction (1)):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \qquad (1)$$

Then, Fe(III) can be reduced by reaction with excess H_2O_2 to form ferrous ion again as well as additional radicals (reaction (2)). This is the so-called Fenton-like reaction. Its reaction rate is slower

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than reaction (1).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\bullet} + H^+ \quad (2)$$

Degradation rates are significantly increased by incorporating UV–visible radiation into the process. This is then known as a photo-Fenton process, which becomes photocatalytic, since the ion Fe(II) oxidized to Fe(III) in the Fenton reaction is reduced again to Fe(II) by action of the radiation. When light is used, the regeneration of Fe(II) is produced by the combination of the following steps [7–11].

$$Fe^{3+} + H_2O \rightarrow [Fe(HO)]^{2+} + H^+ \quad (3)$$

$$[Fe(HO)]^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad (4)$$

The photo-Fenton reaction also enhances the reaction rate of oxidant production through the involvement of high valence Fe intermediates responsible for the direct attack on organic matter [12,13]. Absorption of visible light by the complex formed between Fe(III) and H_2O_2 seems to be the cause of the formation of such high valence Fe-based oxidants.

Previous studies have shown that Fenton and photo-Fenton processes are suitable for the treatment of synthetic and real textile wastewater [14–18]. However, none of these studies have evaluated the potential use of these processes on wastewaters from wool dying industries. Since acidic conditions are necessary to fix dyes to wool, organic acids such as citric acid are used as additives in wool dyeing. The final pH of these colored solutions is around 4. The acid nature of the effluents is a advantage since optimal Fenton and photo-Fenton processes require $pH < 3$ in order to prevent the iron precipitate in $Fe(OH)_3$. Thus, high amount of acid reagent to adjust the pH of the process is not necessary. The main goal of this work is to evaluate if photo-Fenton technology by using solar plant is a suitable technology for the decolourization, detoxification and mineralization of wastewaters from wool dying industries. The first step was the optimization of the processing conditions for acidic textile effluents at laboratory scale with UV light.

Experimental

Preparation of dyestuff solutions

Three synthetic dyestuff wastewaters were prepared following the recipe supplied by Pro Chemical and Dye Company. Lanaset Sun Yellow 180, Lanaset Scarlet 380 and Lanaset Royal Blue 483 were used as yellow, red and blue dyes, respectively. The yellow dye contains a mix of azo-dyes, scarlet 380 and Royal Blue 483 are mono-azo metal complex and anthraquinone dyes, respectively. These dyes were combined with other additives in order to improve dye adsorption to the wool. These additives were: citric acid, sodium acetate, Glauber salt ($Na_2SO_4 \cdot 10H_2O$), a wetting scouring detergent Synthrapol®, consisting of water, isopropanol and the detergent itself, a combination of ethoxylated and sulfated aliphatic alcohols and a leveling agent Albegal® SET, a mixture of ethoxylated and partially modified nitrogen containing fatty and alcoholic derivatives. The concentration of dyes and additives are shown in Table 1.

The organic contribution of the yellow, red or blue dye to the initial total organic carbon of the synthetic effluent is 116, 211 and 163 mg L^{-1}, respectively. In addition, the additives albegal set and synthrapol each contribute 66 and 40 mg L^{-1} to the initial value of total organic carbon, respectively. Initial physical–chemical characteristics of the dye solutions are shown in Table 2.

Table 1
Composition of synthetic dyestuff wastewater.

Components	Concentration (mg L^{-1})
Dye	621
Citric acid	1240
Sodium acetate	1240
Glauber salt ($Na_2SO_4 \cdot 10H_2O$)	2340
Albegal® SET	300
Synthrapol®	50

Chemicals

Hydrogen peroxide (Panreac 30%, w/w) and ferrous sulphate, $FeSO_4 \cdot 7H_2O$, (Panreac, 98%) were used as Fenton and photo-Fenton reagents. For pH adjustment, sulphuric acid (Panreac, 95–97%) and sodium hydroxide solutions (Panreac, 97%) were used. All synthetic effluents were prepared with potable water. The physical–chemical parameters of this water are shown in Table 3.

Reactor and light sources at laboratory

All experiments were carried out in a 250 cm^3 Pyrex cylindrical reactor at laboratory scale. The reaction mixture inside the vessel consisting of 200 mL of textile effluent and Fenton reagent was continuously stirred with a magnetic bar. The experiments were conducted at 25 °C and pH was adjusted to 3.0. A 60 W Solarium Philips HB175 equipped with four 15 W Philips CLEO fluorescent tubes with emission spectrum from 300 to 400 nm (maximum around 365 nm) (9 mW cm^{-2}) was used as light source in the photo-Fenton experiments. The incident light flux has been obtained by using a optomer Graseby Optronics model S370 optical power meter with a Hamamatsu photodiode that capture the incident light between 200 and 400 nm. The photodiode is placed instead of the cylindrical reactor and the light output of the fluorescence tubes is measured.

Solar pilot plant

All the solar experiments were carried out in a photo-reactor composed by one CPC module (total irradiated surface 0.248 m^2) inclined at 28° N (local latitude of Las Palmas de Gran Canaria), four borosilicate glass tubes (inner diameter, 30.6 mm; length, 750 mm) connected in series, one tank and one recirculation pump. The total volume of water in the reactor was 5 L and the total irradiated volume was 1.8 L. The water flow was 6 L min^{-1} throughout the run using a Pan World NH-5PX-D pump. The solution pH was measured with a MultiMeter 44 supplied by Crison Instruments. Solar ultraviolet radiation was measured with a UV-A radiometer (Acadus 85-PLS) mounted on the experimental pilot plant at the same angle as the CPC. The radiometer provides the incident instantaneous UV-A radiation per area unit (W m^{-2}) and, with an LS-3200 integrator, the accumulated energy $E(t)$ received by the total irradiated surface of the photoreactor (in W h). The relationship between the experiment duration time (t),

Table 2
Initial physical–chemical characteristics of synthetic textile wastewaters.

Dye solution	Yellow	Red	Blue
pH	4.29	4.29	4.26
TOC (mg L^{-1})	1070	1150	973
COD (mg L^{-1})	2388	2328	2089
BOD_5 (mg L^{-1})	805	820	870
BOD_5/COD	0.34	0.35	0.41
Toxicity (% INH)	33.18	48.88	31.38
Suspended solids (mg L^{-1})	35–90	35–90	35–90
Color number (CN)	0.0008	0.8368	1.7747