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Electro-Fenton decoloration of dyes in a continuous reactor: A promising technology in colored wastewater treatment

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ABSTRACT

This study focuses on the application of Electro-Fenton technique for the remediation of wastewater contaminated with synthetic dyes. A bubble reactor was designed to develop this treatment operating in continuous mode. In order to increase the efficiency of Electro-Fenton treatment, the effect of key parameters (iron dosage and pH) that play an important role in this process was investigated for Lissamine Green B decoloration in batch mode. Operating at the optimal conditions, determined for Lissamine Green B, several dyes (Methyl Orange, Reactive Black 5 and Fuchsin Acid) were decolorized by using Electro-Fenton process. A first-order kinetic model was used to simulate the experimental results operating at different pH, and iron concentration of 150 mg L^{-1}. This kinetic model for Lissamine Green, Methyl Orange and Reactive Black 5 was successfully used in the progression of the process from batch to continuous mode. About 80% color removal was achieved for Lissamine Green and Methyl Orange with a residence time of 21 h. The decoloration for Reactive Black 5 was lower, reached a value around 60% at the same residence time. Nevertheless in all assays a good agreement between experimental results and proposed model in a continuous bubble reactor was detected. In addition a continuous treatment with a mixture of dyes was carried out. Operating with a residence time of 21 h the obtained decoloration was close to 43% which is squared with a TOC reduction around 46%. Therefore, the results provide fundamental knowledge for the treatment of a real wastewater stream.

1. Introduction

Synthetic dyes are used to color many different products such as textiles, paper, cosmetics and drugs [1]. The discharge of these colored compounds in the environment causes considerable non-aesthetic pollution and serious health-risk factors [2]. Conventional wastewater treatment plants cannot degrade the majority of these pollutants and generating large volumes of sludge, thus causing secondary loading of environmental pollutants [3,4].

Advanced oxidation processes (AOPs) offer effective and rapid alternative treatments for various contaminants. The AOPs are based on the *in situ* generation of hydroxyl radicals (•OH), a highly powerful oxidizing agent, and are effective in treatment of persistent organic pollutants aqueous solutions until their overall mineralization [5]. Among these AOPs, the Fenton reaction with hydrogen peroxide and transitional metals, especially the ferrous ion, in an acidic aqueous system has been investigated in numerous studies [6]. However, this system generally offers effective contaminant removal only at high rates of hydrogen peroxide and soluble iron consumption due to the stoichiometric reaction [7].

Currently, some research groups have reported Electro-Fenton oxidation offering significant advantages as well as solving problems, without requirement for special equipment, and high efficiency in organic pollutants removal [8–10]. Electro-Fenton process consists of treating wastewater *in situ* with H_2O_2 electrogenerated in the presence of catalytic amounts of Fe(II) [11]. According to Fenton's reaction (Eq. (1)), hydroxyl radicals (•OH) are formed. These radicals are high oxidant species, they attack most organic molecules with rate constants usually in the order of 10^6–10^9 L mol^{-1} s^{-1} [12]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \quad (1)$$

This new hybrid technology employs the electricity which is a clean energy source so the overall process does not create secondary pollutants and is compatible with the environment [13].

Furthermore, *in situ* generation of H_2O_2 avoids the need for transport and storage of this hazardous substance, offers safer operation by virtue of providing diluted H_2O_2 solutions, enhances the mixing of solution [11].

There are many reports on Electro-Fenton process application for the degradation of phenol [14], aniline [15] and azo dyes [10,16]. Nevertheless to our knowledge there is no application of this hybrid

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technology in continuous mode. Industrial activities constantly produce colored wastewaters that need to be treated. Therefore, it is necessary to validate an adequate technique to remediate colored streams continuously.

The aim of this work is to design an Electro-Fenton bubble reactor to treat colored effluents in continuous mode at bench scale. In order to analyze the technique capacity, different dye solutions are used as model samples. The influence of several key parameters that play an important role in the Electro-Fenton process were investigated. In a first stage the electrode material, iron dosage and pH were evaluated to determine the best treatment conditions. From the kinetic studies in batch mode a bubble continuous reactor could be simulated. Finally, the Electro-Fenton bubble reactor was used to validate the treatment of different dyes in continuous flow.

2. Materials and methods

2.1. Dyes solutions

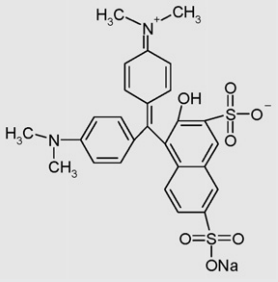
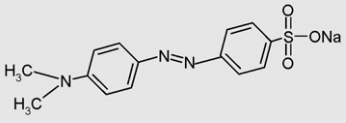
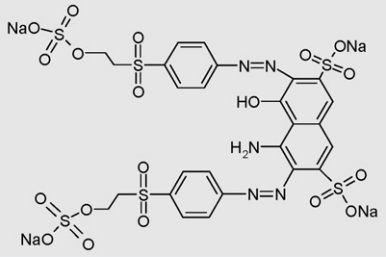
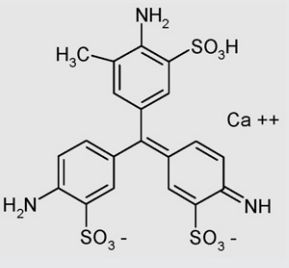
In this work several dye solutions were used to evaluate the Electro-Fenton treatment. The dyes characteristics and their concentrations are described in Table 1. Sodium sulfate 0.01 M was used as inert electrolyte, furthermore the presence of this compound is well-known in the wastewater from dyeing processes [17]. When a mixture of dyes was used the electrolyte concentration was raised proportionally (0.04 M).

2.2. Electro-Fenton bubble reactor

A glass cylindrical reactor with two electrode bars connected to a direct current (DC) power supply was used (Fig. 1). The Electro-Fenton bubble reactor had working volume of 0.675 L, and was operated in batch mode with total reflux or continuous mode (at 5.5, 16 and 21 h of residence time). The cathode and anode bars were placed 30 mm and 270 mm above the bottom of the cell, respectively. The distance between electrodes bars was fixed at 240.4 mm. Steel or graphite bars were employed. Each bar was 100 mm high with a diameter of 6.35 mm for graphite and 10 mm for stainless steel, resulting in a total contact surface area of 1.27 cm^2 to graphite and 3.14 cm^2 to stainless steel. A constant potential difference (15 V) was applied with a power supply (HP model 3662) and the process was monitored with a multimetre (Fluke 175).

In the Electro-Fenton process H_2O_2 is produced electrochemically via oxygen reduction on the cathode. For this purpose, continuous saturation of air at atmospheric pressure was ensured by bubbling compressed air near the cathode at about 1 L min^{-1}, starting 10 min before electrolysis to reach a stationary O_2 concentration [18]. Iron dosage was added as $FeSO_4{\cdot}7H_2O$ at different

Table 1
Dye class, chemical structures, wavelength at maximum absorbance and concentration used of the different dyes employed.

Dye	Type	C.I.	Structure	λ_{max} (nm)	Concentration (mg L^{-1})
Lissamine Green B (LGB)	Diphenylnaphthyl-methane	44,090		633	8.5
Methyl Orange (MO)	Mono-azo	13,025		466	1.5
Reactive Black 5 (RB5)	Di-azo	20,505		597	70
Fuchsin Acid (FA)	Triarylmethane	42,685		546	15