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Decolorization and mineralization of yellow 5 (E102) by UV/Fe^{2+}/H_2O_2 process. Optimization of the operational conditions by response surface methodology

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ABSTRACT

In this study, the optimization and implementation of a homogeneous photo-Fenton process for the decolorization and mineralization of a wastewater containing highly concentrated yellow 5 (E102) dye, resulting from an industry placed in the suburbs of Medellin (Colombia), is presented. Response surface methodology was applied as a tool for the optimization of operational conditions such as initial dyestuff concentration, H_2O_2 concentration, and UV-radiation power (number of lamps). The decolorization, degradation and mineralization efficiencies were used as response variables. The following conditions were found to be optimal for decolorization and mineralization of yellow 5: UV radiation of 365 nm (4 W, one lamp), dye concentration of 200 mg/L, Fe^{2+} concentration of 1.0 mM, H_2O_2 concentration of 1.75 mL/L, treatment time of 180 min, Fe^{2+} concentration of 1 mM and pH = 3. Under these conditions (180 min), the photo-Fenton process allowed us to reach ca. 100% of color dye degradation, 99% of COD degradation, and 85% of mineralization (TOC). The scavenging effect of the Cl^- anion on the photodegradation process was also confirmed.

1. Introduction

Azo dyes are complex aromatic compounds characterized by both high stability and toxicity. Their practical application includes textile, pharmaceutical, cosmetic, and food industries. Their presence in wastewaters gives a strong coloration to the waterbodies, suppressing the photosynthesis processes [1]. The colorant's structures and attributes are very complex and variable. Many of them present organic origin, solubility in water, high resistance to the action of chemical agents as well as low biodegradability [2].

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One of the most consumed pigments by the textile industry is the yellow one, originating from the diazoacetoacetanilides group. Currently, the yellow 5 dye (E102 or tartrazine; molecular formula: $C_{16}H_9N_4O_9S_2Na_3$; $\lambda_{max} = 430$ nm) is one of the most employed due to its brightness, color, and favorable price [3,4]. Since the Colombian environmental legislations have become more rigorous for these kinds of pollutants, the mineralization of residual colorants started to be a challenge for both industrial and academic research groups. In general, conventional biological treatments are useless for their degradation, basically due to the formation of secondary compounds that in turn are more toxic than their parent substances [5]. Moreover, sedimentation, flocculation, and adsorptive methods are also ineffective for their efficient remotion [6–8]. Recently, a special interest has presented the so-called advanced oxidation processes (AOPs) [8,9]. They are based on the generation of highly reactive hydroxyl radicals as primary oxidants. The main advantages of their application are: simplicity of use, accessibility, and moderate cost [10]. Among the AOPs, Fenton's and photo-Fenton's type reactions are very promising [11,12]. The pollutant oxidation using Fenton's reagent is a homogeneous oxidation that occurs in the presence of H_2O_2 and ferrous ions mixtures. In an acidic environment, if H_2O_2 is added to an aqueous system containing an organic substrate and ferrous ions, a complex redox reaction occurs.

The ferrous ion initiates and accelerates the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, $^{\bullet}OH$, a powerful oxidation agent with an oxidation potential of 2.8 V. They are able to attack rapidly the organic substrates, causing their chemical decomposition by H-subtraction and addition to C = C unsaturated bonds.

Thus, numerous competing reactions involving Fe^{2+}, Fe^{3+}, H_2O_2, $^{\bullet}OH$, $HO^{\bullet}_2$ and other radicals derived from the substrate may take place. The $^{\bullet}OH$ radicals can be scavenged by reacting with Fe^{2+} or H_2O_2, leading to the formation of Fe^{3+} and $HO^{\bullet}_2$, respectively. Thus, the formed Fe^{3+} ions can react with H_2O_2, involving $^{\bullet}OH$ and $HO^{\bullet}_2$ radicals and resulting in the regeneration of Fe^{2+} ions. According to the literature [11], the addition of UV radiation to Fenton's process, known as photo-Fenton (H_2O_2/Fe^{2+}/UV), appears to be an interesting option for the decolorization of dyes due to its capacity to influence the direct formation of $^{\bullet}OH$ radicals. Thus, UV radiation can accelerate the mineralization process through the following pathways:

- the enhancement of Fe^{2+} regeneration from the additional photo-reduction of Fe^{3+} species [10–12];
- the photolysis of hydrogen peroxide [13];
- the photolysis of complexes of Fe^{3+} with some oxidation products, such as oxalic acid.

This work deals with the optimization and implementation of a photo-Fenton process for the decolorization and mineralization of a wastewater containing highly concentrated yellow 5 (E102) dye, resulting from an industry placed in the suburbs of Medellin (Colombia). Since decolorization can be achieved more easily than mineralization, the effect of different process variables (the initial dyestuff concentration, H_2O_2 concentration, and the UV-radiation power [number of lamps]) on color, COD, and TOC removal efficiencies was considered. However, most of the recently published studies [14–18] concerning the effect of these variables adopt rather a one-factor-at-a-time approach (one parameter was varied thereby keeping the others constant). Nevertheless, the process parameters may involve synergistic effects, due to complex interactions between the process variables. Therefore, the application of conventional optimization techniques can be inadequate, time consuming, and does not allow a precise process optimization. In order to overcome these drawbacks, the optimization can be based on statistical design tools. Thus, the response surface methodology (RSM) was applied as a tool for the optimization of yellow 5 degradation and mineralization by a homogeneous photo-Fenton (PF) process, at laboratory scale. This method permits us to assess the individual and interactive effects of several operating parameters (the initial dyestuff concentration, H_2O_2 concentration, and the UV-radiation power [number of lamps]) on the treatment efficiency (color, COD, and TOC removal). As far as we know, no similar study was performed for the treatment of yellow 5 dye using photo-Fenton process. The RSM is a statistical technique that allows establishing the relationships between several independent variables and one or more dependent ones, reducing the number of experimental trials, experimental errors and overall cost [19,20]. The optimization of the operational conditions by the RSM involved the following steps:

- the implementation of the statistically designed experiments;
- the estimation of the coefficients of a mathematical model using regression analysis;
- the prediction of the response;
- the verification of the adequacy of the model.

Among the available statistical design methods, a multilevel Box–Behnken experimental Design (BBD) was chosen for the purpose of response optimization [21,22]. The scavenging effect of the Cl^- anion on the photodegradation process was also investigated. Therefore, the decolorization and mineralization of yellow 5 by a homogeneous UV/Fenton process was optimized by the RSM-BBD method. Considering that in the case of yellow 3 dye [23] homogeneous UV/Fenton process (UV/Fe^{2+}/H_2O_2) was proved to be more efficient than the heterogeneous one, more acceptable for the environment, we have decided to apply the homogeneous variation to this process. Moreover, although the heterogeneous catalysts present usually higher reactivity and a reduced dependence on the pH of the solution in comparison to the homogeneous Fe catalysts, they also have higher rates of the side reaction of hydrogen peroxide decomposition into water and oxygen [24].

2. Materials and methods

2.1. Reagents

All reagents were of analytical grade: NaCl (99%), yellow 5 colorant (98%), $FeSO_4{\cdot}7H_2O$ (99%), H_2O_2 (30%),