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Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load

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Abstract

The examination of the effectiveness of the chemical oxidation using Fenton's reagent (H_2O_2/Fe^{2+}) for the reduction of the organic content of wastewater generated from a textile industry has been studied. The experimental results indicate that the oxidation process leads to a reduction in the chemical oxygen demand (COD) concentration up to 45%. Moreover, the reduction is reasonably fast at the first stages of the process, since the COD concentration is decreased up to 45% within four hours and further treatment time does not add up to the overall decrease in the COD concentration (48% reduction within six hours). The maximum color removal achieved was 71.5%. In addition, the alterations observed in the organic matter during the development of the process, as indicated by the ratios of COD/TOC and BOD/COD and the oxidation state, show that a great part of the organic substances, which are not completely mineralized, are subjected to structural changes to intermediate organic by-products.

Keywords: Advanced chemical oxidation; Fenton's reaction; Organic load; Textile wastewater

1. Introduction

Conventional biotreatment methods are not effective for the most of the synthetic dyestuffs due to the complex polyaromatic structure and recalcitrant nature of dyes. Textile wastewaters exhibit low BOD to chemical oxygen demand (COD) ratios (ca. 0.1) indicating the non-biodegradable nature of dyes.

Advanced oxidation processes (AOPs) have been proven particularly effective for the treatment of a wide variety of wastewater containing refractory organic contaminants. These methods include among others, the use of UV, O_3, H_2O_2, TiO_2 and their combinations [1–6], photocatalysis [7–9], sonolysis [10–13] and supercritical oxidation [14–16]. These methods employ chemical, photochemical, sonochemical or radiolytic techniques to bring about chemical degradation of pollutants.

The common feature of these techniques is the generation of free hydroxyl radicals (·OH), which are very reactive since they have a high oxidation potential. The oxidation potential of the hydrogen peroxide has been reported to be 1.9 V [17] while the oxidation potential for the hydroxyl radicals is approximately 2.8 V. Using H_2O_2, the production of hydroxyl radicals is enhanced by the presence and action of ferrous ion (Fe^{2+}), as a catalyst. In this case, hydrogen peroxide is decomposed to hydroxyl radical and hydroxyl ion, while ferrous ion is transformed into ferric ion. This reaction is known as Fenton's reaction:

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

The Fenton's reaction is complex and it involves individual elementary reactions between initial reactants and generated radicals. A mechanism that describes the entire process includes the following reactions [18–20]:

Hydroxyl radicals might react with ferrous ions leading to the production of hydroxyl and ferric ions:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (2)$$

Hydroxyl radicals can react with hydrogen peroxide to form hydroperoxyl radicals and may also combine with each other to produce hydrogen peroxide:

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (3)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (4)$$

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Also, ferrous ion and radicals are formed during the following reactions:

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \quad (5)$$

$$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (6)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \quad (7)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (8)$$

The Fenton's reaction takes place in pH values ranging between 3 and 3.5. In these pH values, the formation of the free hydroxyl radicals is activated. In addition, the low pH values inhibit the formation and precipitation of the insoluble ferric hydroxide, $Fe(OH)_3$.

Moreover, the reaction rate in reactions (5) and (6) is lower than that in reaction (1). As a result, ferrous iron is consumed quickly and reproduced slowly.Several researchers examined the applicability of the Fenton reaction process for the treatment of wastewater generated at textile and dye industries.

Perkowski and Kos [21] investigated the applicability of Fenton reagent for the treatment of textile dyeing wastewater. The optimum conditions and efficiency of the method were determined, taking as an example three types of wastewater produced while dyeing cotton, polyacrylonitrile, and polyester. Two types of iron(II) salt were used: sulphate ($FeSO_4 \times 7H_2O$) and chloride ($FeCl_2 \times 4H_2O$). To adjust the pH of the wastewater, a 1% solution of calcium oxide (CaO) was used. The process of pollutant decomposition which took place in the wastewater under the influence of hydrogen peroxide alone at different concentrations was investigated. When the Fenton reagent was used both for iron sulphate and iron(II) chloride, the optimum doses of the two salts and hydrogen peroxide were determined. It was found that the tested dyeing wastewater showed high susceptibility to treatment using a combined action of ferrous salts and hydrogen peroxide. The main parameters of wastewater, that is the color threshold number, chemical oxygen demand, and anionic surfactants, were greatly reduced. Investigations of the wastewater after treatment showed a remarkable increase in susceptibility to biodegradation.

The efficiency and cost-effectiveness of H_2O_2/UV for the complete decolorization and mineralization of wastewater containing high concentrations of the textile dye Reactive Black 5 was examined by El-Deim et al. [22]. Oxidation until decolorization removed 200–300 mg/g of the dissolved organic carbon (DOC). Biodegradable compounds were formed, so that DOC removal could potentially be increased by 30% in a following biological stage. It was found that in order to attain 800 mg/g overall mineralization, 500 mg/g of the DOC had to be oxidized in the H_2O_2/UV stage.

The aim of the study performed by Solmaz et al. [23] was to compare the performance of coagulation, Fenton's oxidation (Fe^{2+}/H_2O_2) and ozonation for the removal of COD and color from biologically pre-treated textile wastewater. $FeSO_4$ and $FeCl_3$ were used as coagulants at varying doses and varying color removal efficiency was measured. For the Fenton process, COD and color removal efficiencies were found to be 78 and 95% and 64 and 71% for the Fenton-like process (Fe^{3+}/H_2O_2). Ozonation resulted in 43% COD and 97% color removal whereas these rates increased to 54 and 99% when 5 mg/l hydrogen peroxide was added to the wastewater before ozonation at the same dose.

Reuse of effluent obtained from the biological wastewater treatment plant of a textile dyeing facility has been investigated by Gonder and Barlas [24]. Effluent has been further treated by Fenton process, chemical precipitation, adsorption and demineralisation, respectively. Optimum molar ratio of ferrous sulfate to hydrogen peroxide ($FeSO_4/H_2O_2$) was determined to be 0.025 (0.25/10). Under these circumstances the wastewater COD has been decreased by 39%.

In a study carried out by Azbar et al. [25], a comparison of various advanced oxidation processes (AOPs) (O_3, O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, Fe^{2+}/H_2O_2) and chemical treatment methods using $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3$ and $FeSO_4$ for the COD and color removal from a polyester and acetate fibre dyeing effluent was undertaken. AOPs showed a superior performance compared to conventional chemical treatment. For the latter the maximum achievable color and COD removal for the textile effluent used in this study was 50 and 60%, respectively. Although O_3/H_2O_2/UV combination among other AOPs methods studied was found to give the best result (99% removal for COD and 96% removal for color), the use of Fe^{2+}/H_2O_2 gave a satisfactory COD and color removal performance (90% removal) and the method was proved to be economically the most viable choice for the acetate and polyester fibre dyeing effluent.

The research undertaken by Bae et al. [26] evaluated quantitatively the predominant reactions in a large-scale Fenton process that treated dyeing wastewaters and suggested an economical and effective treatment process. Through plant analysis, it was found that a great part of the COD was removed by ferric coagulation. The comparative evaluation of Fenton oxidation and ferric coagulation revealed that ferric coagulation was the predominant mechanism to remove COD. In Fenton oxidation, the removal efficiency of COD was 67.7% and in ferric coagulation, 60.8%. A combined process with iron coagulation/precipitation and Fenton oxidation reduced the hydrogen peroxide dosage by over 40% compared to a conventional dosage.

Finally, the oxidative treatment characteristics of biotreated textile-dyeing wastewater and typical chemicals such as desizing, scouring, dispersing, and swelling agents used in the textile-dyeing process by advanced oxidation processes were experimentally studied by Lim et al. [27]. The refractory organic matters remained in the effluent of biological treatment process were degraded to CO_2 by combined ozonation with and without hydrogen peroxide. As a result, AOPs, followed by biological treatment were proposed for the treatment of the refractory organics of the wastewater from the textile-dyeing process. On the other hand, the refractory chemicals contained in the scouring and swelling agent were not mineralized and their biodegradability was not improved by applying AOPs.