Electrochemical and Photochemical Oxidation of Cationic Dyes: A Comparative Study

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Abstract: This study reports on comparative performance of electro-Fenton and photo-Fenton processes in the mineralization of three cationic dyes: BB41, BR46 and BY28. Primary objective was to determine the optimal conditions for both processes. It has been shown that the mineralization rate by electro-Fenton process depends on operating parameters such as applied current density, catalyst concentration, pH, etc. It was also observed that dyes degradation by hydroxyl radicals follows pseudo first-order reaction kinetics. Under the optimal operating conditions ($[Fe^{3+}] = 0.2$ mM, $j = 3$ mA cm^{-2}, and pH = 3), electro-Fenton process leads to an almost mineralization of dyes solutions reaching 93, 86 and 77% of TOC abatement for BB41, BR46 and BY28 respectively. The dye mineralization rate during photo-Fenton (UV/Fe^{3+}/H$_2$O$_2$) process is a function of reagent doses, and their concentration ratio R = [H$_2$O$_2$]/[Fe^{3+}]. Thus, mineralization rates obtained are around 95, 93 and 85% for BB41, BR46 and BY28 respectively for a treatment time of 5 h with a ratio R = 10 and [Fe^{3+}] = 0.2 mM. The mineralization of a mixture of the three cationic dyes was also studied in a second step. Results showed that both photo-Fenton and electro-Fenton processes are able to reach almost complete mineralization rates. Finally the electro-Fenton process is considered the more efficient and interesting technique due to its environmentally friendly character with low energy consumption and no use of chemical reagents.

Keywords: Electro-Fenton, Photo-Fenton, Advanced oxidation, Cationic dyes, Mineralization, TOC.

1. INTRODUCTION

In recent years, there has been a great interest for so-called advanced oxidation processes (AOPs) which constitute an attractive alternative to treating wastewater containing toxic and/or persistent pollutants. They are based on the *in-situ* generation of a powerful non specific oxidizing agent, the hydroxyl radical ($^•$OH) which is able to oxidize a broad range of organic pollutants quickly and non-selectively [1-7]. There are several methods for generating $^•$OH; among them, Fenton based oxidation processes [8-15] are the most popular ones. These processes are based on electron transfer between hydrogen peroxide (H$_2$O$_2$) and ferrous iron ion (Fe^{2+}) according to the reaction (1) (Fenton's reaction). In the case of the use of another M^{z+1}/M^{z+} homogeneous redox couple such as Cu^{2+}/Cu$^+$, Co^{3+}/Co^{2+} etc., instead of Fe^{3+}/Fe^{2+} couple, the process is called "Fenton-like process".

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^•OH + OH^- \qquad (1)$$
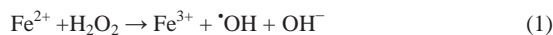
The oxidation power of H$_2$O$_2$ is enhanced in the presence of ferrous ion because Fenton's reaction leads to the formation of a very powerful oxidizing agent, the $^•$OH. This reaction requires large quantities of both reagents: H$_2$O$_2$ and iron (II) salt. On the other hand, the ferric iron generated from the Fenton's reaction precipitates in the form of insoluble Fe(OH)$_3$ salt, which constitutes the process sludge. In fact, the Fenton's reaction can be catalyzed in the presence of excess of H$_2$O$_2$:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^• \qquad (2)$$

$$Fe^{3+} + HO_2^• \rightarrow Fe^{2+} + O_2 + H^+ \qquad (3)$$
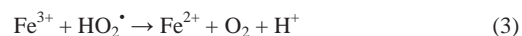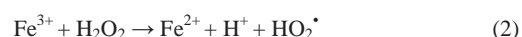
But the reaction kinetics, and consequently regeneration of Fe^{2+} is very slow through reactions (2) and (3). In addition in this system a large part of $^•$OH generated from reaction (1) can be consumed by wasting reactions (4) and (5) due to the enhancement of the reaction rates at high H$_2$O$_2$ and/or Fe^{2+} concentrations:

$$Fe^{2+} + {}^•OH \rightarrow Fe^{3+} + OH^- \qquad k = 7.5 \times 10^9 \text{ M}^{-1}\text{ s}^{-1} \qquad (4)$$

$$H_2O_2 + {}^•OH \rightarrow HO_2^• + H_2O \qquad k = 2.7 \times 10^7 \text{ M}^{-1}\text{ s}^{-1} \qquad (5)$$

The high values of rate constants of reactions (4) and (5) indicate that they can compete with the pollutant under treatment for $^•$OH leading to a decrease of the process efficiency, in particular when H$_2$O$_2$ and/or Fe^{2+} concentrations are important. In order to minimize the chemical reagent amount and consequently to avoid wasting reactions and process sludge formation, conventional Fenton process can be supported electrochemically (electro-Fenton process) [1,3,11-18] or photochemically (photo-Fenton process) [3,5,7, 19-22]. The photo-Fenton and electro-Fenton oxidations have recently emerged as very promising technologies because of their high efficiency and cost-effectiveness compared with other AOPs [23-30].

In the electro-Fenton process, the $^•$OH are produced in the bulk of the polluted solution using the electrogenerated Fenton's reagent (reaction 1) where H$_2$O$_2$ is supplied in situ from the two-electron reduction of dissolved O$_2$ (reaction (6)) and Fe^{2+} is continually regenerated from Fe^{3+} reduction (reaction (7)), which is initially added to the solution at a catalytic amount (i.e., 10^{-4} M) [1,15-18].