ENHANCING THE FENTON PROCESS BY UV LIGHT APPLIED IN TEXTILE WASTEWATER TREATMENT

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Abstract

Nowadays, an efficient wastewater management involves the use of advanced treatment technologies able to decompose hardly biodegradable compounds with reasonable costs at the lowest possible environmental impact. In our work we used one of the most efficient advanced wastewater treatment, the Fenton reaction and its photo-assisted version. The hydrogen peroxide was the oxidizer; despite its relatively high cost, its high activity in oxidizing of a large variety of organic persistent pollutants in the presence of Fe³⁺ ions as catalyst, makes it an alternative which is worth to be considered even in practical medium scale systems. The Fenton and photo-Fenton oxidation were performed using a model dye, the xanthene-type Rhodamine 6G, widely used in a series of biotechnology applications, but having major drawbacks when released in natural water flows, mainly mutagen and carcinogen effects. Therefore, a parametric case study was performed in order to define the optimal operating parameters (the pH value, the hydrogen peroxide concentration and the iron catalyst concentration). The oxidative degradation of Rhodamine 6G by Fenton reaction was more effective when combined with UV irradiation. Each parameter of the oxidative treatment is essential for the color and TOC removal. The optimal values found for the total color degradation and mineralization of the dye were as follows: 16 ppm Fe³⁺, 100 ppm H₂O₂ and pH of 4.5.

Key words: advanced wastewater treatment, advanced oxidation process, photo-Fenton, Rhodamine 6G, UV irradiation

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1. Introduction

The importance paid to an efficient wastewater management is a real label for a civilized, sustainable-oriented society. The complexity of the wastewater composition had increased a lot in the latest decades, due to the multiplication of the human activities (or the dramatic increase of their scales) requiring water as raw material: washing agent, steam production, heating and cooling agent. Up to an extent, the long-term kinds of water use are well-known and consequently, the water quality management and the corresponding decontamination treatments have entered to a routine. The big problem nowadays is the accumulation of organic stable and toxic compounds in the wastewater (dyes, pesticides, surfactants), refractory to the biologically degradation treatments, generating a chemical composition hard to define in details and even more difficult to establish a versatile strategy to get rid of (Caliman et al., 2008; Papić et al., 2014; Yazdanbakhsh et al., 2014; Zaharia and Suteu, 2012). On another part, the reuse of domestic or industrial wastewater after the treatments is not enough

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POPs is the hydrogen peroxide, H₂O₂ (Zaharia et al., 2009, water (Amilcar et al., 2009, 2012). and then finally mineralized to carbon dioxide and molecules are splitted gradually in smaller molecules and the oxygen participate together. The POP reaction medium. This reactive species is able to \( \cdot \) order to increase the efficiency of the HO ions as catalysts together with hydrogen peroxide, in the Fenton reaction involves the use of ferric or ferrous temperature recommend it as a “green oxidizer”. The polluting nature and high efficiency even at ambient 2009). Despite its relatively high price, its non-polluting nature and high efficiency even at ambient 3 and 4 (Amilcar et al., 2009). Sometimes a combined homogeneous-heterogeneous procedure is applied, using a solid as the Fe³⁺ source, by the partial dissolution of its framework, under the influence of the reaction medium; this strategy also allows applying higher pH values (around 7) for the reaction (Barona et al., 2015). The synthetic, non-degradable dyes are among the top pollutants due to their property to absorb light according to their structure. Even if not necessarily toxic, the fore-mentioned behavior leads to the modification of the aquatic environment for different living creatures and aesthetic pollution (Secula et al., 2008). The amount of iron required in this type of homogenous catalysis, could be controlled by anodic dissolution or an iron electrode, when the process is namely electro-Fenton (Petrescu et al., 2009; Priambodo et al., 2011). The presence of UV irradiation accelerates even more the process. Moreover, the UV light promotes the oxidation of Fe³⁺ to Fe⁴⁺, while generating HO⁻ radicals and acidifying the reaction medium (Eq. 1).

\[
Fe^{3+} + H_2O \rightarrow Fe^{2+} + HO^- + H^+ \tag{1}
\]

In brief, due to its high efficiency, the photo-Fenton reaction can be considered one of the most convenient, environmentally friendly and efficient method for the oxidation of POPs. (Almicar et al., 2012; Ruales-Lonfat et al., 2015; Sayid Abdullah et al., 2014). There are literature data (Chong et al., 2010) indicating the use of solar light as the UV radiation source (Muthuvel et al., 2012, 2014) or combining the photo-oxidation with electrochemical processes (Priambodo et al., 2011).

Rhodamine 6G is an intense and persistent xanthene dye, with intense pink color and green fluorescence, widely used as a tracer dye in hydrological studies as well as in laboratory investigations involved in biotechnology and genetic by microscopy, fluorescence, ELISA, etc. Its very high stability, persistence and color intensity even at concentrations around 1 ppm in solution makes it an interesting species to be studied in the oxidative mineralization (Lutic et al., 2012; Lutic et al., 2014; Zaleschi, 2014).

In this study, we investigated the degradation of dye Rhodamin 6G by the Fenton system, while UV irradiation is applied. The Fenton reaction is cited in literature as a reliable method to allow the decomposition or mineralization of several dyes (Muthuvel et al., 2012; Muthuvel et al., 2014; Peng-Sheng et al., 2009; Zaharia et al., 2014a)
2. Experimental part

The UV-vis spectrum of R6G shows a main maximum absorption peak at about 525 nm and a lower intensity peak located around 244 nm (Fig. 1). The position of the main peak is preserved constant during the photodegradation, so its intensity is trusted for the dye concentration measuring.

The experimental setup of the photo-Fenton process is displayed in Fig. 2. (Betianu et al., 2008; Lutic et al., 2012). The reactor (4) is a glass vessel of 0.5 L, covered with a lid (1), accommodating a central quartz tube (3) serving to insert an UV lamp (2). The dye solution was exposed to UV in the space between the reactor and the central tube.

The dye solution was magnetically agitated on a stirring plate (6) at about 400 rpm using a magnetic range (5). The runs were performed at ambient temperature (296 - 298K). The initial dye solution concentration was 30 ppm. Dye samples were taken at due time durations from the photoreactor and the concentration was measured by spectrophotometric measurements, on a Shimadzu UV-1700 apparatus. The Total Carbon Content (TOC) values on selected samples were measured on a SHIMADZU Total Organic Carbon Analyzer 5000A.

Ferric chloride, sulfuric acid and natrium hydroxide solutions (0.1 N) of analytical purity from Merck were used respectively as a source of Fe$^{3+}$ ions and for the pH setting at the desired values.

3. Results and discussion

3.1. Individual roles of the oxidation and irradiation on process effectiveness

According to a standard procedure, when investigating several factors which could give a synergetic effect on a reaction, their individual role must be highlighted before concluding (Lutic et al., 2012; Rein, 2001; Zaharia et al., 2014b). Therefore, blank experiments were performed as follows:

- if no oxidant (H$_2$O$_2$) was used and 16 mg/L Fe$^{3+}$ was mixed in the dye solution, the decolorizing after 60 min of exposure to light reached only around 14%; this is the photolysis degree with no oxidizer;
- when 100 ppm H$_2$O$_2$ was added but no catalyst (Fe$^{3+}$) was introduced in the system, the conversion was below 10% in the first 30 min and finally reached around 20% after 1 hour; this is the pure role of the oxidizer;
- when only the Fenton reagents were used, without illumination, the conversion was around 11%; we concluded that the light role was essential for the degradation of the dye;

The second and third blank experiments correlated show that the addition of Fe$^{3+}$ has a certain inhibition effect on the decolorizing.

Broad limits were taken for all the parameters to be studied, 27 - 173 ppm H$_2$O$_2$, 0.3-30.6 ppm Fe$^{3+}$ and pH 2.3 - 4.7.

3.2. Influence of pH value on the dye removal

This is a key parameter for the removal of organic pollutants by Fenton reaction, especially due to the iron ions solubility, but also to the activation of the dye molecule and generation of HO· radicals. The influence of the pH was investigated in reaction systems containing 100 ppm H$_2$O$_2$ and 16 ppm Fe$^{3+}$. We must outline that at ambient temperature, the spontaneous hydrogen peroxide decomposition occurs at an appreciable extent, so it is convenient to find the proper conditions able to remove the dye within some tens of minutes.

The time dependence of the decolorizing extent is displayed in Fig. 3. The results show that Fenton reaction is highly favored by the pH value of 3.5. The dye removal is extremely fast, since it had been removed almost totally within some minutes. Neither lower nor higher values of the pH worked better, but the pH value of 4.7 was much better than the low 2.3. It is important information, since usually wastewaters have pH values close to neutral and a fast reaction requires the pH adjustments. This set of experiments let us conclude that a pH value comprised between 3.5 - 4.5 is reasonable for an eventual practical application, since for both values the time reaction comprised between 15-20 minutes gave high decolorizing degrees.

A better way to express the degradation of a dye by Fenton reaction is measuring the remains of total organic matter by TOC determination, since
Decolorizing is the first step in the degradation, but the final target is to mineralize as much as possible the organic matter from the wastewater.

Table 1 presents some data illustrating the removal dye degree in terms of TOC. The high pH values seem to have a net more favorable effect on the dye removal, since at pH of 4.7 the mineralization degree reaches over 66% after one hour of reaction.

![Time, min](image)

**Fig. 3.** The pH value influence on photo Fenton reaction advancement in terms of decolorizing

### Table 1. Dye degradation extent calculated from TOC data at different pH values

<table>
<thead>
<tr>
<th>Time, min / pH value</th>
<th>2.3</th>
<th>4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.8</td>
<td>34.3</td>
</tr>
<tr>
<td>60</td>
<td>36.96</td>
<td>66.32</td>
</tr>
</tbody>
</table>

3.3. Influence of the H2O2 concentration on the performance of dye degradation

In order to investigate the influence of the oxidizer concentration on the process, in this series of experiments, the pH value of 3.5 was chosen and the Fe3+ concentration was kept also at 16 ppm. As expected, the hydrogen peroxide concentration has a strong influence on the performance of the reaction.

The high values of the oxidizer concentrations involved an extremely fast decolorizing photo Fenton process, almost instantaneous, when the H2O2 concentration value was 173 ppm. In fact, a lot more interesting from a practical perspective is the behavior when only 27 ppm H2O2 was added in the system. At a thus low concentration, the total decolorizing occurs in about 10 minutes. It indicates that the presence of H2O2 is necessary in the initial step of the oxidation, for the initiation of HO· radicals production and for this purpose 27 ppm is enough. Later on, the reaction continues on the expense of the radicals propagated in the system and after 10 minutes the decolorizing is almost complete (Fig. 4).

The TOC values for some selected points are shown in Table 2. In this case, the behavior is very different. The presence of high amounts of H2O2 determines the mineralization up to 70% during the first 30 minutes, and then the mineralization degree does not grow any more in a significant extent.

For the low concentrations of the H2O2, the mineralization is slower and weaker. It shows that the breakage of the chromophore chemical bondings can occur at low concentrations of the oxidizer, but the fragments resulted from the split of the entire dye molecule are transformed to carbon dioxide only in the presence of high hydrogen peroxide content. So, we could say that the photo-induced process is strictly necessary to initiate the bulk molecule split, while the oxidizer is very active for the mineralization of the smaller fragments.

![Time, min](image)

**Fig. 4.** The effect of H2O2 concentration on photo Fenton reaction – decolorizing

### Table 2. Dye degradation extent calculated from TOC data at different oxidizer concentrations

<table>
<thead>
<tr>
<th>Time, min / H2O2 concentration</th>
<th>27</th>
<th>173</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>18.86</td>
<td>66.70</td>
</tr>
<tr>
<td>60</td>
<td>31.47</td>
<td>69.59</td>
</tr>
</tbody>
</table>

3.4. The influence of the Fe3+ concentration on dye removal efficiency

Three values of Fe3+ concentrations were tested in the R6G degradation, namely 1.5, 16 and 30.6 ppm. These experiments were run at hydrogen peroxide concentration 100 ppm and pH value of 3.5 (the corresponding saturation concentration of the Fe3+ ions is 70.8 ppm).

Even at the very low concentration values of Fe3+, the Fenton system is working, although the decolorizing is very slow. An increase of the Fe3+ ions concentration to 16 ppm gives a spectacular decolorizing rate, since a reaction time of 5 minutes arises a 98% conversion degree (Fig. 5).

4. Conclusions

This research studied the performance of the Fenton system during UV irradiation on the degradation of Rhodamin 6G dye. The essential role of all components in the reaction medium was highlighted first: the oxidizer, the catalyst and the UV irradiation.
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A parametric study allowed defining the optimal set of working conditions judged from the point of view of dye decolorizing and its total mineralizing. The role of the oxidizer was rather to be an efficient initiator of the dye degradation, since its use at a low concentration of 27 ppm leads to the total decolorizing in several tens of minutes, while the high degrees of mineralizing required higher concentrations of oxidizer (around 100 ppm). The Fe³⁺ ions concentrations necessary for a high yield of the reaction were around 16 ppm and the pH value ranging between 3.5 and 4.7.

The possibility to enhance the performance of Fenton oxidation process of Rhodamin 6G dye in water solution in the presence of UV irradiation was proved and quantified.

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