**Photo Fenton degradation of an azo day color (Yellow Sun)**

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**Abstract:** The production of dyes and their use generates persistent effluent biorefractory non-biodegradable, highly colored, toxic, carcinogenic and mutagenic. It is in this context the advanced oxidation processes (AOPs) have emerged, they can treat the dyes in aqueous solution because they generate highly reactive species such as hydroxyl radicals (OH⁻). In this work, an azo dye (Yellow Sun), was treated by the photo-Fenton process using design of experiments. We could establish a mathematical model representative of the degradation of the dye with a deviation less than 10% with the experimental; the best yield 97, 68% is obtained with a hydrogen peroxide concentration 1 mmol L⁻¹, concentration of catalyst equal to 1 mmol L⁻¹ and a concentration of the dye 10 mg L⁻¹.

**Key words:** Advanced oxidation processes, hydroxyl radicals, photo-Fenton, yellow sun dye.

1. Introduction

Water is the main constituent of living beings and the essential element in any form of life. The increase in agro-industrial activities is putting increasing pressure on the world's freshwater reserves. Indeed, these activities generate a great diversity of chemicals that pour into the water cycle, living in peril the fragile natural balance that allowed life to develop on earth. Often chemicals in wastewater are difficult to biodegrade and the lack or inadequacy of treatment systems leads to their accumulation in the water cycle.

The protection of the environment has thus become a major economic and political issue. All countries are concerned with safeguarding freshwater resources, either because they lack water or because they pollute it (Daud et al., 2010).

Better production and less pollution are the challenges faced by manufacturers in any sector. Constraints in legislative and normative form are increasingly drastic (Ramirez et al., 2007).

Industries as diverse as chemicals, petrochemicals, food industry, textiles, paper and tanneries produce a wide variety of effluents, each of which requires new investigations and the development of specific processes.

Over the past decade, much research has focused on a new class of oxidation techniques: advanced oxidation (POA) processes. These technologies have already shown their potential in the treatment of toxic and "biologically recalcitrant" organic pollutants. These processes rely on the in situ formation of hydroxyl OH⁻ radicals which have a higher oxidizing power than conventional oxidants such as H₂O₂, Cl₂, ClO₂ or O₃. These radicals are capable of partially or totally mineralizing most organic and organometallic compounds. POAs include chemical oxidation processes in homogeneous phase: H₂O₂/ Fe (II) (Fenton's reagent), O₂/OH⁻ (ozonation), O₂/ H₂O₂ (peroxonation), etc.; Photochemical processes: UV alone, H₂O₂ / UV (photolysis of H₂O₂), O₃ / UV; H₂O₂/Fe (III) (homogeneous photocatalysis or photo-Fenton), TiO₂/UV (heterogeneous photocatalysis), etc.; Direct and indirect electrochemical processes (anodic oxidation, electro-Fenton), electrical processes (sonolysis, electron beam, etc.) and electrical discharge processes (corona discharge, wet air plasma) (Hammami et al., 2007).

As regards the Fenton reagent (Fe²⁺/ H₂O₂), these applications are limited and essentially concern the purification of industrial waste water. The main limitations of this system are the need the need to use large amounts of chemical reagents and the formation of process sludge in the form of ferric hydroxide. The use of UV irradiation makes it possible to increase the degradation efficiency significantly (Walling and Goosen, 1973; De Laat and Gallard, 1999).

The photo-Fenton process (Fe²⁺ / H₂O₂ / UV) is superior to the conventional Fenton process. This is in fact the photochemically assisted Fenton reaction where the contribution of UV radiation reduces ferric iron to ferrous iron, while producing the hydroxyl radical through the photolytic decomposition of hydrogen peroxide. This photo-reduction can thus reduce the doses of reagents to be used.

The objective of this study is to show the interest of the photo-Fenton process on the discoloration of a mono azo dye very used in agro-food: sun-yellow by applying the method of experimental plans and elaboration a reliable mathematical model describing the influence of the various parameters on the degradation efficiency.
2. Materials and methods

2.1 The chemicals product:

The solutions were prepared with distilled water. The different reagents used in this study are:

- Yellow Sun Dye;
- H₂SO₄ (purity 95-97%): Sigma Aldrich;
- Fe₂(SO₄)₃.5H₂O (98% purity): Fluka Guarantee;
- H₂O₂ (purity 33%): Scharfau

2.2 Materials relating to electrochemical treatment:

Degradation of the dye by the Photo-Fenton process was carried out in a glass reactor volume of 700 ml. Ultraviolet radiation (315-400 nm) is emitted by a Philips UVA lamp, type: PL-L 24W / 10 / 4P 1CT, Power: 24W.

The lamp is contained in a quartz tube immersed in the reaction liquid. This type of quartz is particularly transparent to ultraviolet rays. The reactor is covered with aluminum before the lamp is switched on, in order not to have an additional source of radiation from the sun and to protect our eyes because the UV is dangerous.

The solution is continuously stirred (350 rpm) to ensure homogeneity of the solution. The medium is adjusted to pH 3 with sulfuric acid (0.1M) in order to avoid the precipitation of ferric ions in the form of hydroxides. We worked at room temperature (24°C).

The samples taken are centrifuged at 4000 rpm on a Sigma 4-16S centrifuge and the supernatant is recovered for analysis.

We studied the oxidation of the Yellow Sun by the Photo-Fenton process in order to show the effectiveness of this process to degrade the Yellow sun, as well as the modeling of the process by a mathematical equation.

3. Results and discussion:

3.1 Establishment of the calibration curve:

Before drawing the yellow sun calibration curve, it is first necessary to search for the maximum wavelength of the latter, for which a solution of 100 mg L⁻¹ of the dye was prepared and analyzed by spectrophotometer (UV -1700 Pharma Spec SHIMADZU). The results obtained are shown in figure 1.

From the curves, we note that λ_max is equal to 481 nm. Subsequently, this value will be set for absorbance reading.

3.2 The plot of the calibration curve

The aqueous solution of the dye was prepared by dissolving the powder in distilled water. This procedure consists in preparing first a concentrating stock solution (100 mg L⁻¹), from which we prepare, by successive dilutions, a series of different concentrations (solutions 10; 20; 30; 40; 50; 60; 70; 80; 90 mg L⁻¹). The latter will be analyzed by UV-visible spectrophotometer.

The residual concentration of the dye will be determined from the equation Abs= 0.0226.X

X: is the concentration of the colorant

4. Modeling of yellow sun degradation

In order to diversify and enrich our working methods in the field of experimentation, we applied the experimental design method to the parametric study of the Yellow Sun dye degradation by Fenton photo.

The main objective is to develop a reliable mathematical model describing the influence of different parameters on the degradation efficiency of the dye from an aqueous phase and to determine the optimum conditions.

We considered the influence of the hydrogen peroxide concentration, the concentration of the catalyst (Fe²⁺) and the concentration of the dye. The fields of study of these three parameters are summarized in Table 1.

Table 1. Values and levels of the operating parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Notation</th>
<th>Level (-1)</th>
<th>Level (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of H₂O₂ (mmol L⁻¹)</td>
<td>x₁</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Concentration of Fe²⁺ (mmol L⁻¹)</td>
<td>x₂</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Initial concentration of the dye (mg L⁻¹)</td>
<td>x₃</td>
<td>10</td>
<td>100</td>
</tr>
</tbody>
</table>

We have made a complete factorial plan 2³. 8 experiments realized in the domain of work (Table 2)

Table 2. 2³ Full Factorial Design Matrix: Coded Values of Parameters.

<table>
<thead>
<tr>
<th>Run N°</th>
<th>X₁</th>
<th>X₂</th>
<th>X₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>6</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
Figure 1. Representation of the absorbance as a function of the wavelength.

Figure 2. Comparison of experimental and predicted responses

According to the experimental design method, the answer Y is expressed in the general form (equation 1):

\[ Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 \]  

(1)

The coefficients \( b_i \) are determined from the relation:

\[ b_i = \frac{1}{j} X^T Y_i \]  

(2)

Taking into account the values of the different coefficients, the model corresponding to the studied system is written:

\[ Y = 75.859 - 7.251 x_1 - 13.769 x_3 - 4.021 x_2 x_3 - 2.966 x_1 x_2 x_3 \]  

(3)

5. Development of the final model

In order to be able to judge the importance of each coefficient and to establish a definitive model, a mathematical means is used, which consists in comparing the value of each coefficient with the average standard error (\( \sigma_E \)) following the equation (4). Only the coefficients with a value greater than \( \sigma_E \) are kept.

\[ \sigma_E = \sqrt{\frac{1}{j} \sigma_Y} \]  

(4)

Where \( \sigma_E^2 \) is the variance; \( \sigma_E = 2.581 \)

These results orient us towards the choice of a model whose parameters must be greater than or equal to 2.581. With this in mind, the new model will be:

\[ Y = 75.859 - 7.251 x_1 - 13.769 x_3 - 4.021 x_2 x_3 - 2.966 x_1 x_2 x_3 \]  

(5)

6. Verification of the validity of the model

We compared the experimental yields with those calculated from the equation of the established model (Equation 5) and calculated the difference between the two yields (according to equation 6), the results are summarized in the table 3.

\[ \text{Ecart (\%)} = \left| \frac{\eta_{exp} - \eta_{cal}}{\eta_{cal}} \right| \]  

(6)

\( \eta_{exp} \): Experimental yield.

\( \eta_{cal} \): Calculated yield using the model.

We note from Table 3 that the calculated and experimental values are almost equal and the difference is less than 10, implying that the model is well validated in the field of study, which is verified by Plot of both yields (figure 2). It is also noted that the best yield 97.68% is obtained for \( x_1 = -1, x_2 = +1, x_3 = -1 \) which correspond to a concentration of hydrogen peroxide equal to 1 mmol L\(^{-1}\), a catalyst concentration equal to 1 mmol L\(^{-1}\) and a concentration of the dye 10 mg L\(^{-1}\).
Table 3. Comparison of experimental and predicted responses.

<table>
<thead>
<tr>
<th>Run N°</th>
<th>Calculated yield (%)</th>
<th>Experimental yield (%)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.824</td>
<td>97.62</td>
<td>1.8742</td>
</tr>
<tr>
<td>2</td>
<td>75.390</td>
<td>77.73</td>
<td>3.1038</td>
</tr>
<tr>
<td>3</td>
<td>97.934</td>
<td>97.68</td>
<td>0.2593</td>
</tr>
<tr>
<td>4</td>
<td>89.364</td>
<td>85.48</td>
<td>4.3462</td>
</tr>
<tr>
<td>5</td>
<td>70.396</td>
<td>70.65</td>
<td>0.3608</td>
</tr>
<tr>
<td>6</td>
<td>61.826</td>
<td>65.71</td>
<td>6.2821</td>
</tr>
<tr>
<td>7</td>
<td>78.286</td>
<td>66.49</td>
<td>2.6301</td>
</tr>
<tr>
<td>8</td>
<td>47.852</td>
<td>45.51</td>
<td>4.8942</td>
</tr>
</tbody>
</table>

Conclusion

We were able to establish a very representative model of yellow sun dye degradation. This model was validated in the field of study with a very low error of less than 10%. The different cases studied made it possible to establish the optimal influential parameters:
- Low concentration of hydrogen peroxide.
- Low concentration of sun yellow, so from the practical point of view a dilution before can be a means of increasing the yield.
- An increase in the concentration of ferric sulphate is favorable.

In perspective, it would be interesting to test this model outside the field of study to validate it in a general way.

References


