Removal of Some Hazardous Dyes by Photodegradation in Presence of Yttrium Oxide

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Abstract - The photodegradation of Rhodamine B and Congo red dye solutions were studied in presence of yttrium oxide. The rate constant of the photodegradation process was calculated. The effects of pH values, sun light, UV lamps, the dye concentration, and the dose of Y₂O₃ on the rate of photodegradation were studied. Also the kinetic parameters by using Longmire equation were calculated. The carbon oxygen demand (COD) and the total organic carbon (TOC) were determined. The analysis of the obtained results indicate that photodegradation of the both dyes depend on the structure of the dyes, the function groups of the dyes, the pH value of the media, the dose of the catalyst and the concentration of the dyes.

Keywords: Photodegradation, Dyes mineralization, Rhodamine B, Congo red and yttrium oxide

I. INTRODUCTION

In generally, the industrial wastewater contains different containments of organic and inorganic materials by increasing the demand of the water, different trails were done to remove the pollutant materials from the wastewater. These trails including physical and chemical treatments such as coagulation, adsorption, electro chemical, photo chemical and chromatography techniques. Among these methods the adsorption and the photodegradation attended a special attention from different researchers. In the previous works, the authors used different materials to remove some toxic materials and some of hazardous dyes from wastewater, some of nature ores, semiconductor oxides and nanoparticles oxides were used. They found that the nanoparticles titanium oxides exhibit an excellent photodegradation during removing of some hazardous dyes from the wastewater. So that this work aimed to study the role of yttrium oxide as strong oxidizing agent's titanium oxide through photodegradation technique.

On the other hand, Rhodamine B (C₂₂H₉₂N₂O₃Cl) is widely used as a colour agent in different industrial such as textile and food, etc. Unforinitely, it is harmful if swallowed by the organisms and effect on their life and growing. Owing to the harmful effects of the Rhodamine B, different process were used to remove it from the wastewater. Also Congo red (C₂₇H₂₃N₂Na₂O₇S₂) was used in the dyeing process for different industries proposes, especially in pharmaceutical treatment where its colour changes with high acidity in early gastric cancers.

The wastewater containing Rhodamine B or Congo red are difficult to removed or biodegraded because they have high organic content and high color concentration. Moreover, both of them have also been known as a carcinogenic substances, so the removal of the both dyes effluent is very important for environmental and human health tasks. The literature survies refer to use of the adsorption process by active carbons which one of the abundant in this field and photodegradation processes. While the photodegradation process is more preferable than the adsorption process because the last one needs preparation, activation and regeneration. These treatment exhausted extra energy and need chemical and physical treatment before using. In this respect, this work was focused on the use of the photodegradation process to remove the dyes in presence of an active oxide (Y₂O₃).

The photodegradation pathway has been already established in our laboratories for three dyes namely Methylene Blue, indigo carmine and Methyl orange. In the present article, the photodegradation by a UV/Y₂O₃ treatment of some dyes having different chemical properties such as Congo red as azo dye and Rhodamine B as a fluorescence dye was the our target.

The photocatalytic oxidation using some semiconductors oxides is considered as an advanced process for removing the pollutants materials because it success in oxidation a wide different of the carcinogenic materials to harmless substances such as carbon dioxide and water. On the other hand using of sun light and UV light during the photodegradation process cleavage the conjugated chains of the dye as a result of its absorbed the lights. The effect of the pH, solar/UV light, the dose of the catalyst and photoluminescence were studied. Also, kinetic rate constant was calculated.

II. EXPERIMENTAL

2.1 Chemicals

Congo red used in this work was obtained from Judex Company England. Rhodamine B was obtained from BDH Company England. While yttrium oxide was obtained from Fluka company.

2.2 Photodegradation process

The photodegradation experiments were carried out in a batch type reactor with yttrium suspended in solutions containing the dye to be degraded. All the experiments were done at room temperature (25°C). The reaction vessel positioned at 8 cm a part from the light source. The light source was UVA light bulbs (40 w/cm², measured by YK-35 UV radiometer, Taiwan). The reactor contained a stirring rod supported by a magnetic stirrer to confirm homogeneity of the mixture throughout the reactor. For every single experiment, 100 ml of dye was added to a given weight of...
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yutrium (2 g/litre). The pH of dye solutions were adjusted by adding HCl or NaOH using IQ scientific experimental pH meter.

2.3 UV/Visible Measurements.
The change in spectra of the dye was measured spectrophotometrically using PerkinElmer UV.

2.4 Chemical Oxygen Demand Measurements.
The change in chemical oxygen demand (COD) measurements were followed up using Hanna COD Meter and Multiparameter Photometer Model HI 83099. The COD percentages of the investigated dyes were calculated by applying the following equation:

\[
\text{% COD} = 100 \times \frac{(C_0 - C_t)}{C_0}
\]

where \(C_0\) is the initial COD value of the investigated dye (Rhodamine B or Congo red) and \(C_t\) is the COD value at interval times of UV irradiation process.

2.5 Total Organic Carbon Measurements.
The change in the total organic carbon (TOC) at interval times of UV irradiation process was measured by the TOC analyzer, Model TOC-VCPH from Shimadzu Company.

2.6 Fluorescence Measurements.
Fluorescence of the dyes solutions were taken on a Shimadzu RF-5301PC spectrophotometer.

III. RESULT AND DISCUSSION

The main effective factors such as the pH values of the medium, the type of light source and the dose of the catalyst were studied.

3.1. pH effect on the photodegradation rate
Fig. 1 represents the variation of the rate constant of the photodegradation (K) with the pH values for the two dyes (Rhodamine B and Congo red). It is found that the values of the k remains constant in the acidic and slight neutral medium at pH (3.0 and 6.5) for the Rhodamine B and then increased rapidly in the basic medium up to pH 9.0. While in case of Congo red, the values of the degradation rate increases as the pH value increases. This means that the photodegradation of the rhodamine B has positive effect in the heterogeneous in basic medium while this positive effect observed as heterogeneous in all medium in case of Congo red. Table 1 represents the values of rate constant of photodegradation for the both dyes at different pH values. This table shows that the values of K for Congo red is always higher than that obtained for Rhodamine B in all pH ranges. This findings may due to their molecular weight and chemical structure, because of the molecular weight of Congo red (696.665 g/mol) is higher than Rhodamine B (479 g/mol) and the chemical structure of the Congo red is easily degradable than Rhodamine B.

3.2 Dye concentration effect
The photodegradation for the both dyes was also investigated at different concentrations. The results of this study were shown in Fig. 2. From this figure it may concluded that the rate of degradation was increased until \(4 \times 10^{-5}\) M for the Rhodamine B, then decreased as concentration increases, while for Congo red the rate of degradation was increased until \(3 \times 10^{-5}\) M and then also decreased with increasing of the dye concentration.
Figure 2. Variation of rate constant for the photodegradation of (a) Rhodamine B and (b) Congo red at different initial dye concentration.

3.3. Effect of Sun light/UV light

This study was carried with difference wavelength corresponding to the sun light and UV lamps used in presence of yttrium oxide as a catalyst. The photodegradation percentages of the dyes were recorded against the irradiation time in figure 3 and 4.

These figures in generally show that the photodegradation percentages increased with irradiation time for the two dyes. Also it is observed the irradiation with UV is more effective than the sun light. This findings may due to the power of the light source of UV lamps 40 W/cm while it is 4.2 W/cm for sun light.

Figure 3. Photodegradation % for Rhodamine B at pH=9 in presence of 2 g/L yttrium oxide

Figure 4. Photodegradation % for Congo red at pH=6.5 in presence of 2 g/L yttrium oxide

3.4. Kinetic study of the photodegradation process

A known amount (0.5 - 5.0 g/L) of yttrium oxide powder was added to the both dyes solution and their mixture were irradiated with the UV lamp. The Langmuir-Hinshelwood model was used to determine the photocatalytic performance of the dye using the equation:

$$\ln(C_0/C) = kt$$

where $C_0/C$ is the normalized dye concentration, $t$ is the reaction time, and $k$ is the photodegradation rate constant. (Fig. 5 and 6) depicts the kinetics of Rhodamine B and Congo red degradation by plotting the normalized concentration with time.

3.5 Effect of Dose of catalyst

The results indicate that for the both dyes the efficiency $C_0/C$ increased nearly in the same trends when the $Y_2O_3$ content increases from (0.5 - 5.0 g/L). By plotting $\ln(C_0/C)$ versus $t$, the linear relation obtained (Fig. 7 and 8), which indicates that all the reactions followed first-order kinetics.

Table 2 summarized the degradation rates for the both dyes in presence of different dose of the yttrium oxide and Fig. 9 represents the effect of dose of the $Y_2O_3$ on the rate of the photodegradation process for the two dyes, where it is observed from these results there is a slight difference in the behaviors in the photodegradation for the two dyes, this may due to their optical activity because of Congo red classified as azo dye while Rhodamine B as fluorescence dye.
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Table 2. Photodegradation rates for dyes at different yttrium content

<table>
<thead>
<tr>
<th></th>
<th>0.5 g/L</th>
<th>1 g/L</th>
<th>1.5 g/L</th>
<th>2 g/L</th>
<th>5 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine B</td>
<td>0.02 x 10^3</td>
<td>0.4 x 10^3</td>
<td>8.0 x 10^3</td>
<td>56 x 10^3</td>
<td>26 x 10^3</td>
</tr>
<tr>
<td>Congo red</td>
<td>0.07 x 10^3</td>
<td>0.2 x 10^3</td>
<td>6.6 x 10^3</td>
<td>60 x 10^3</td>
<td>31 x 10^3</td>
</tr>
</tbody>
</table>

Figure 6. Normalized concentration of photodegradation of Congo red with different Yttrium content

Figure 7. Kinetic reaction rates for photodegradation of Rhodamine B with different Yttrium content at pH = 9

Figure 8. Kinetic reaction rates for photodegradation of Congo red with different Yttrium content at pH = 6.5

Figure 9. Effect of dose of catalyst content on the photodegradation rates for the two dyes

3.6 Dyes mineralization

The total mineralization of the two dyes has been investigated by two techniques, the chemical oxygen demand (COD) and that of the total organic carbon (TOC), both of them being complementary depending on the detoxification water level.

3.6.1 Kinetics of COD analysis

The kinetics isotherms of COD disappearance are given in Fig. 10 and 11. For RhodamineB dye, it is shown that COD has totally disappeared in <4 h while it has disappeared in 3 h for Congo red dye.

Figure 10. COD disappearance for Rhodamine B at pH = 9
3.6.2 Kinetics of TOC analysis

The kinetics isotherms of TOC disappearance are given in Fig. 12 and 13. For Rhodamine dye, it is shown that TOC has totally disappeared in <4 h while it has disappeared in 3 h for Congo red. Both parameters (COD and TOC), which directly evaluate the pollution level of an aqueous solution, do not exhibit similar disappearance patterns. This could be accounted for by the influence of the different molecular structures of the dyes on their reactivity with OH• radicals which constitute the main oxidizing agents generated in UV-irradiated process. TOC analysis seems more accurate and appropriate for evaluating the decontamination of polluted waters containing organics from the toxicological point of view. These results indicate the dependence of the photodegradation on the structure and nature of the dyes.

Figure 11. COD disappearance for Congo red at pH=6.5

3.7 Photoluminescence (PL)

Both dyes reveal visible luminescence in green and yellow spectral range and efficient excitation of them occurs at an excitation wavelength of 504 and 553 nm for Congo red and Rhodamine B respectively. PL intensity attributed to the nature of the investigated dyes, PL intensity of Rhodamine B higher than that observed for Congo red. These expected results because of classification of these dyes, Rhodamine B as fluorescence dye and Congo red as azo dye. (Fig. 14).

IV. CONCLUSION

The analysis of the obtained results may conclude that:
1- Some of the pollutant materials such dyes could be removed by the photodegradation process for the wastewater.
2- Y2O3 owing to its oxidizing effects acclimates the photodegradation process.
3- There many factor effects on the photodegradation of the dyes such as their structure (Rhodamine B as a fluorescence dye and Congo red as azo dye) and...
concentration used, as well as the pH value of investigated media

REFERENCES


