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

Hoda R. Galal, Walied A. A. Mohamed, Hanan A. Mousa, Ammar A. Labib, Adli A. Hanna

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 Y_2O_3 on the rate of photodegradation were studied. Also the kinetic parameters by using Longmireequation 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: Photodegradtion, 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[1, 2]. So that this work aimed to study the role of yttrium oxide as strong oxidizing agentas titanium oxide through photodegradationtechnique[3-9].

On the other hand, Rhodamine B ($C_{28}H_3N_2O_3Cl$) is widely used as a colour agent in different industrials such as textile and food, etc. Unfornelty, 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 ($C_{32}H_{22}N_6Na_2O_6S_2$) 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[10, 11].

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The wastewater containing Rhodamine B or Congo red are difficult to removed or biodegraded because they have high organic content and high color concentration[12-14]. 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[15].

The literature survies refer to use of the adsorption process by active carbons which one of the abundant in this field and photodegaradtion processes[16-18]. 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 (Y_2O_3).

The photodegradation pathway has been already established in our laboratories for three dyes namely Methylene Blue[19-21], indigo carmine[22-24] and Methyl orange[25]. In the present article, the photodegradation by a UV/Y_2O_3 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^{O}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:

$$\%\, COD = 100 \times \frac{(C_0 - C_t)}{C_0} (1)$$

where $C_0$is the initial COD value of the investigated dye (Rhodamine B or Congo red) and $C_t$is the CODvalue 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 processwas measured by the TOC analyzer, Model TOC-$V_{CPH}$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 inbasic medium while this positive effect observed as heterogeneous in all medium in case of Congo red.Table 1 represents thevalues 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 higherthan that obtained for Rhodamine B in all pH ranges. This findings may due to theirmolecular weightand chemical structure, because of the molecular weightof Congo red (696.665g/mol) is higher than Rhodamine B (479 g/mol) and the chemical structure of the Congo red is easily degradable than Rhodamine B.

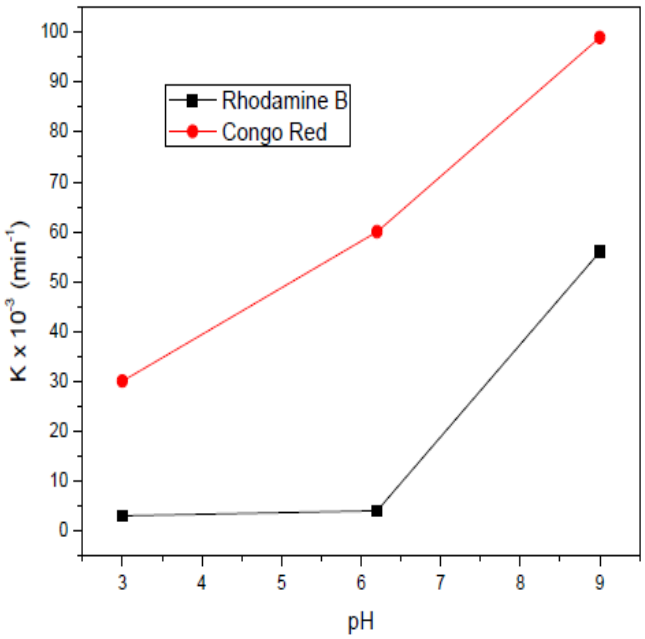


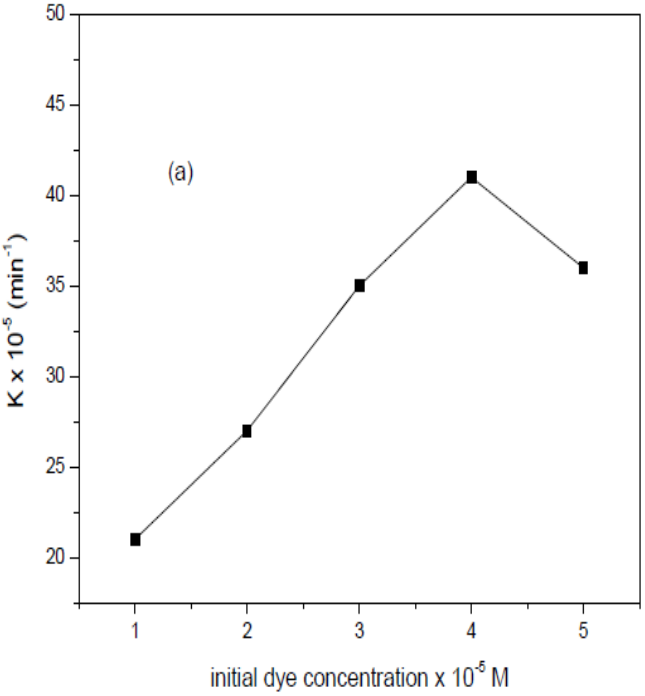
Figure 1.Variation of rate constant for the photodegradtion of Rhodamine B and Congo red at different pH values.

Table 1.Photodegradation rates for dyes

Dye	pH =3	pH =6.5	pH =9
Rhodamine B	**3×10^{-3}**	**4×10^{-3}**	**56×10^{-3}**
Congo red	**30×10^{-3}**	**60×10^{-3}**	**99×10^{-3}**

3.2 Dye concentration effect

The photodegradation for the both dyes was alsoinvestigated 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 4×10^{-5}M for the Rhodamine B, then decreasedas concentration increases, while for Congo red the rate of degradation was increased until 3×10^{-5}M and then also decreased with increasing of the dye concentration.



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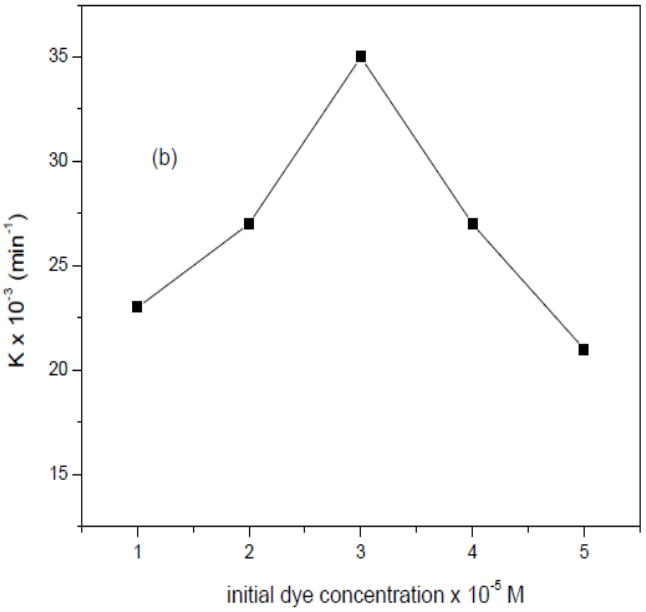

Figure 2. Variation of rate constant for the photodegradtion of (a) Rhodamine B and (b) Congo red at different initial dye concentration.

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.

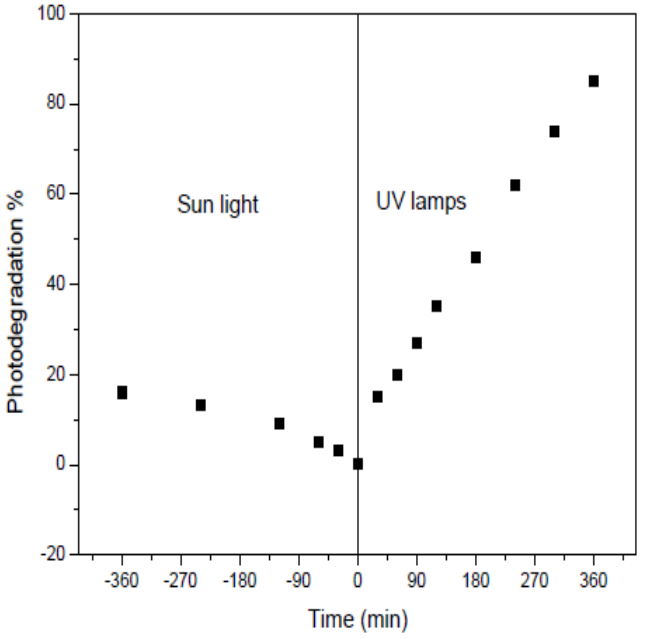

Figure 3. Photodegradation % for Rhodamine B at pH=9 in presence of 2 g/L yttrium oxide

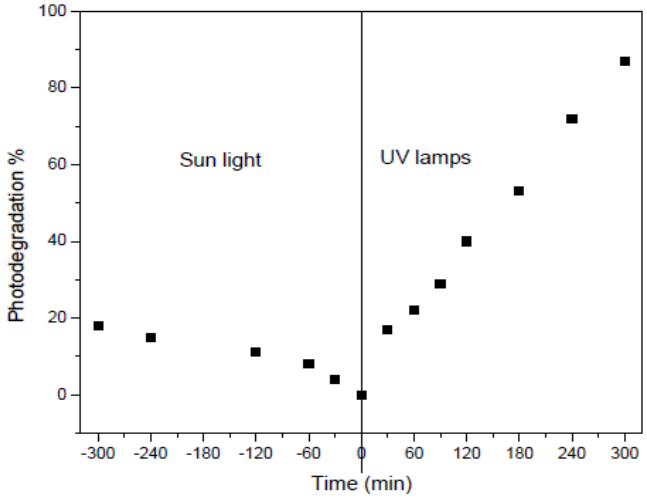

Figure 4. Photodegradation % for Congo red at pH=6.5 in presence of 2 g/L yttrium oxide

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 withthe UV lamp.The Langmuir-Hinshelwood model was used to determine the photocatalytic performance of the dye using the equation:

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

where *Co/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 *Co/C* increased nearly in the same trends when the Y_2O_3 content increases from (0.5 - 5.0 g/L). By plotting ln*Co/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

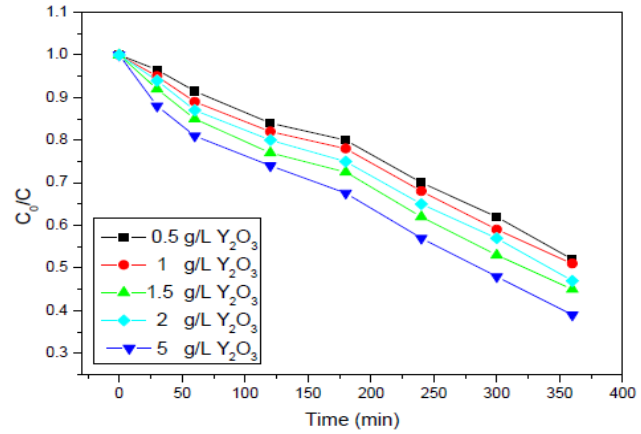

Figure 5. Normalized concentration of pfotodegradation of Rhodamine Bwith different Yttrium content

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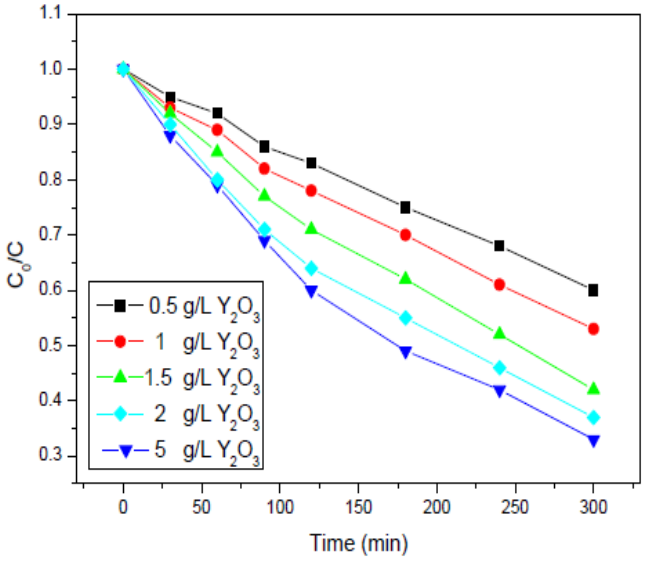

Figure6. Normalized concentration of photodegradation of Congo red with different Yttrium content

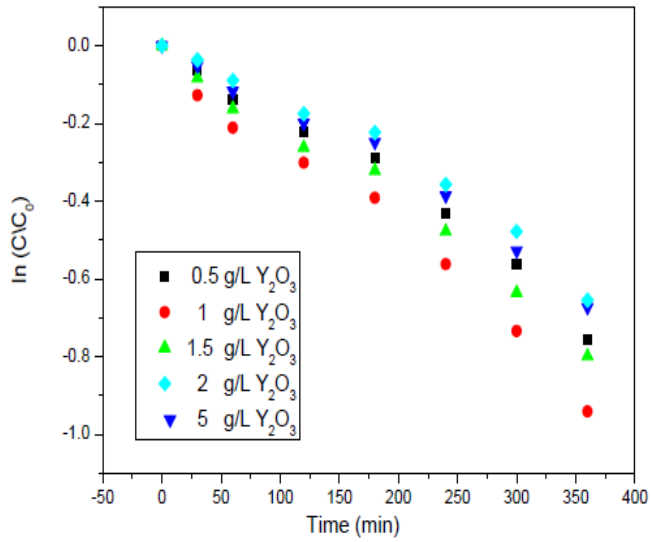

Figure7.Kinetic reaction rates for pfotodegradation of Rhodamine B with different Yttrium content at pH =9

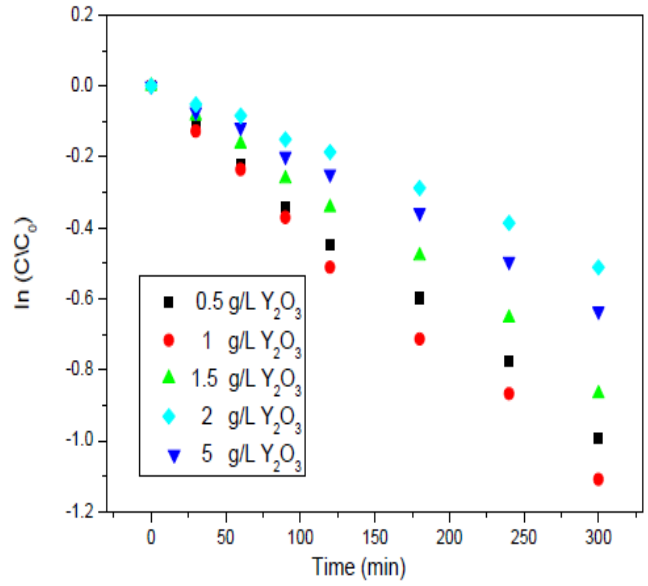

Figure8.Kinetic reaction rates for photodegradation of Congo red with different Yttrium content at pH =6.5

Table 2.Photodegradation rates for dyes at different yttrium content

Dye	0.5 g/L	1 g/L	1.5 g/L	2 g/L	5 g/L
Rhodamine B	0.02 × 10^{-3}	0.4 × 10^{-3}	8.0 × 10^{-3}	56 × 10^{-3}	26 × 10^{-3}
Congo red	0.07 × 10^{-3}	0.2 × 10^{-3}	6.6 × 10^{-3}	60 × 10^{-3}	31 × 10^{-3}

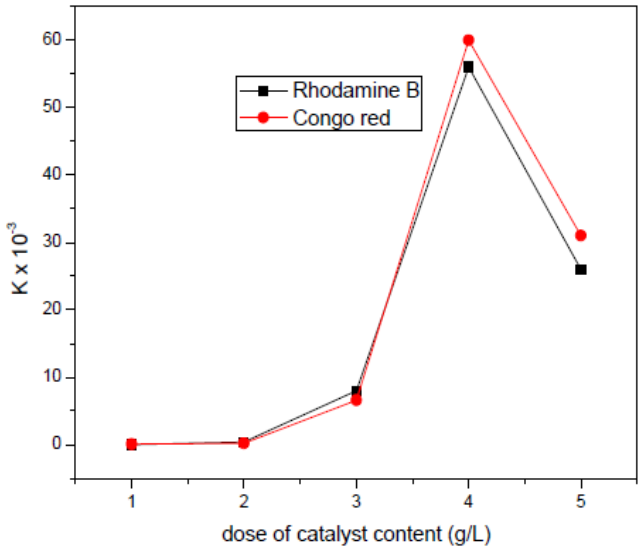

Figure 9.Effect of dose of catalyst content on the photodegradation rates for the two dyes

3.6 Dyes mineralization

The total mineralization of the twodyes 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 aregiven in Fig. 10 and 11. For RhodamineB dye, it is shown that CODhas totally disappeared in <4 h while it has disappeared in 3 h for Congo red dye.

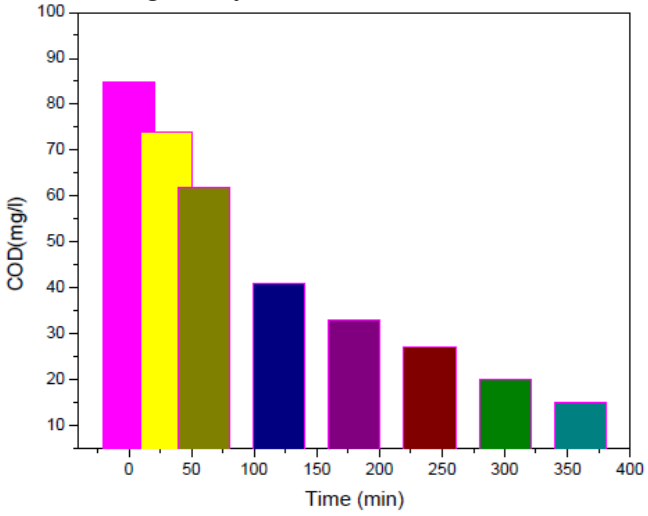

Figure 10. COD disappearance for Rhodamine B at pH=9

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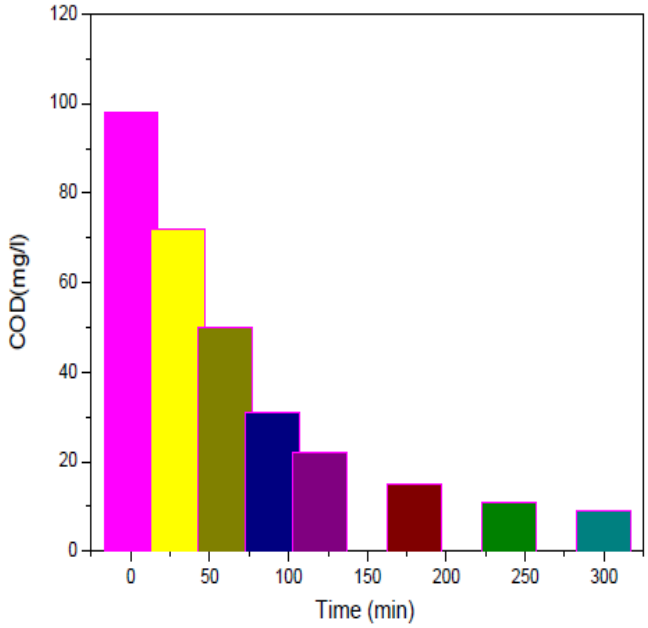

Figure11. COD disappearance for Congo red at pH=6.5

3.6.2 Kinetics of TOC analysis

The kinetics isotherms of TOC disappearance are given in Fig. 12 and 13. For Rhoda mine dye, it is shown that TOC has totally disappeared in <4 h while it has disappeared in 3 h for Congo red dye. 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 indicates the dependence of the photodegradation on the structure and nature of the dyes

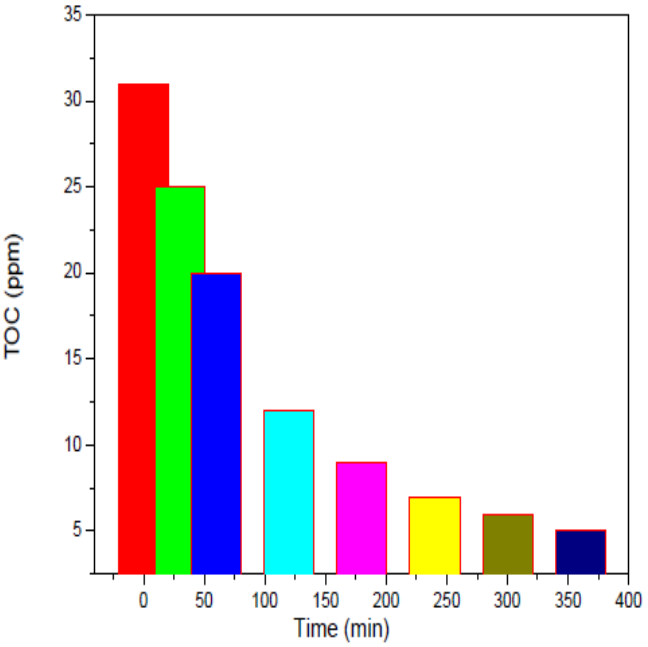

Figure12. TOC disappearance for Rhodamine B at pH=9

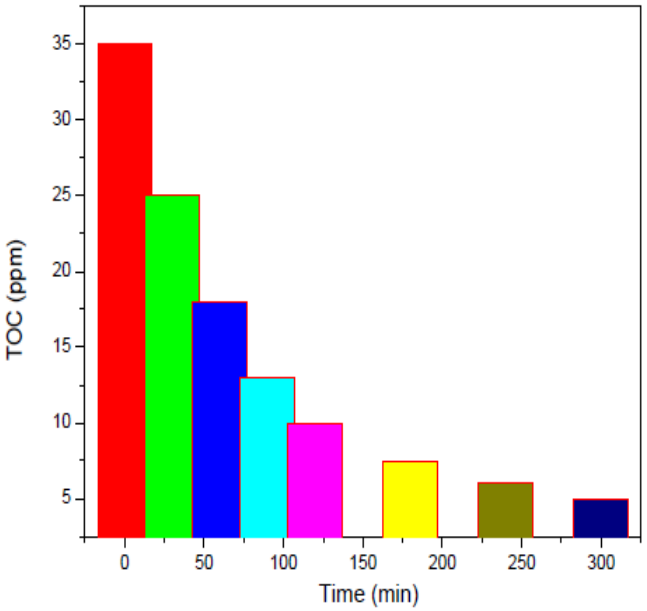

Figure 13.TOC disappearance for Congo red at pH=6.5

3.7Photoluminescence (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 Rhoda mine B higher than that observed for Congo red. These expected results because of classification of these dyes, Rhoda mine B as fluorescence dye and Congo red as azo dye. (Fig. 14).

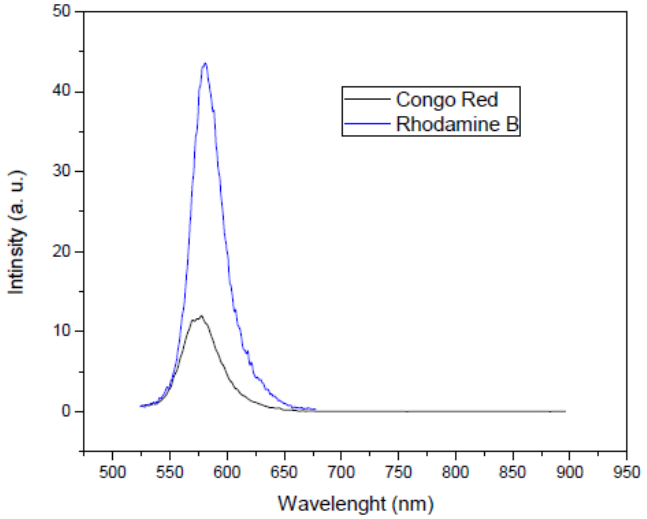

Figure 14. Photoluminescence spectra of Rhodamine B and Congo red

IV. CONCLUSION

The analysis of the obtained results may concluded 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 the

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concentration used, as well as the pH value of investigated media

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