Full Paper

Heterogeneous Photocatalytic Discoloration/Degradation of Rhodamine B with H₂O₂ and Spinel Copper Ferrite Magnetic Nanoparticles

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The discoloration/degradation of the artificial dye Rhodamine B (RhB) was investigated using advanced oxidation technologies. Aqueous solutions of RhB containing spinel copper ferrites ($CuFe_2O_4$) as a heterogeneous catalyst were exposed to UV irradiation/hydrogen peroxide. Under these experimental conditions the discoloration/degradation of RhB is strongly promoted by copper ferrites, reaching 95 % discoloration of the dye in 10 min and 97 % degradation in 200 min. The influence of the catalyst amount, H_2O_2 concentration, light source, and UV light intensity were studied. Optimum concentrations of H_2O_2 and catalyst dosage were found for the RhB degradation reaction. The catalyst had high magnetic sensitivity under an external magnetic field, which allowed its magnetic separation from water avoiding secondary pollution processes, and its recycling. A markedly synergetic effect of spinel copper ferrite and UV light irradiation was observed for the RhB discoloration/degradation with H_2O_2 as a green oxidant.

Introduction

Currently, an urgent need has arisen to preserve the enviroment by removing chemical pollutants originating from different human activities. Many industries, such as coal conversion, petroleum refining, iron and steel, textile, dyes, resins, plastics, and agrochemicals, discharge wastewater containing phenolic or aniline compounds.[1] Dyes are widely used in textile, printing, dyeing, dyestuff manufacturing, and food plants. The industrial discharge of effluents containing dyes influences the natural aspect of rivers and has a negative affect upon aquatic life causing serious environmental problems.[2–4] Water pollution is a serious problem that affects human's health due to the accumulation and transportation of pollutants in streams, rivers, lakes, and dams. To date, many different traditional treatments are being applied to industrial wastewaters, such as coagulation, flocculation, membrane separation (ultrafiltration, reverse osmosis), or elimination by activated carbon adsorption.[2] The major disadvantage of these methods is the transference of the pollutant from one phase to the other generating a secondary pollutant.[3,5] On the other hand, the biological treatment of effluents is not a complete solution to the problem because of the biological and chemical resistance of some dyes.[1] At present, catalysis appears to be even more important than before and constitutes one of the major sources of improvements in our society.

Among many options, the development of processes to transform the toxic and hazardous pollutants into harmless compounds is one of the most effective solutions. Advanced oxidation technologies (AOTs) are well recognized treatments for the discoloration/degradation of polluted waters as well as other non-biodegradable organic substances that represent an environmental danger. Hence, the resources of AOTs like UV/H_2O_2, Fenton, photo-Fenton, and photocatalytic processes could be a good option to treat and eliminate synthetic dyes.[2] These AOTs based on physicochemical processes can produce fundamental changes in the chemical structure of pollutants involving the generation of transient species with high oxidizing power, such as the hydroxyl radical ($OH^{\bullet}$) generated by the decomposition of water or H_2O_2 which is known as a green oxidant. Efficient radicals for the oxidation of organic matter can be generated by photochemical means, including solar light or other forms of energy such as sonochemistry. It was demonstrated that the combination of sonochemical or photochemical technologies, in the presence of $OH^{\bullet}$ and an adequate catalyst, markedly accelerated the degradation processes of organic pollutants.[6–10] Among the AOTs, the Fenton and photo-Fenton processes are very promising because of their advantages which include the use of inexpensive chemicals, ease of operation, and high oxidation performance. Nevertheless, the main disadvantage of these processes is the large amount of Fe^{II} salts added which can result in troublesome sludge problems.[11–14] In contrast, heterogeneous photocatalysis using a semiconductor photocatalyst has been considered as an effective technology for treating refractory organic compounds in water.[15] In this sense, TiO_2 has been the most widely used photocatalyst because of its

exceptional physical and chemical properties.[3,6] TiO_2 has high photostability and is highly resistant to chemical attack and photocorrosion. It is also a safe and low cost material with multiple applications in different industries. However, highly efficient catalysts are still needed.

The present work aims to study the discoloration/degradation of an aqueous solution of the organic dye Rhodamine B (RhB, Fig. 1) in the presence of H_2O_2 by heterogeneous photocatalysis. Magnetic spinel copper ferrites ($CuFe_2O_4$) obtained by different synthetic routes were used as photocatalysts.[16] The effect of different operating parameters such as the amount of photo-catalyst, H_2O_2 concentration, light intensity, radiation source, and reutilization of the photocatalyst on successive dye discol-oration experiments was also investigated.

Results and Discussion

The introduction of a catalyst is a well known method to drive the decomposition of H_2O_2 for the oxidation of organic con-taminants.[14] In this work, the photocatalytic degradation/ discoloration of RhB, as a typical dye pollutant, was investigated to assess the catalytic ability of copper ferrite particles ($CuFe_2O_4$) to activate H_2O_2. The heterogeneous catalysts used in the experiments have been prepared and conveniently characterized in a previous work.[16] The particles were obtained in nanometric sizes with a porous morphology by low cost wet-chemical syn-thetic methods. The presence of nanometric particles in copper ferrite was confirmed by transmission electron microscopy (TEM) analysis. Calculation of the average size and the size distribution of particles was carried out by counting particles in the TEM image and through the estimation from the mean sur-face diameter. According to this most particles are below 60 nm. A high amount of metal cations (Cu^{II} and Fe^{III}) are available on their surface because of the partially inverted spinel structure. In addition, a synergic effect between the metal cations in the nanoparticles is produced by the ferromagnetic ordering.[16]

The reaction integrates photolysis and heterogeneous cata-lysis in the presence of H_2O_2 and spinel copper ferrites prepared by different routes. Nanoparticles obtained from nitrate precur-sors were labelled NIT and those obtained by citric acid-aided processes, CIT.

The kinetic study was developed with an initial RhB concen-tration $\sim 2 \times 10^{-5}$ mol L^{-1} at ambient temperature and at the natural pH of the RhB solution (pH 6.2) varying the other experimental conditions (catalyst type and amount, concentra-tion of H_2O_2, irradiation source, and light intensity).

Adsorption Control Experiment

The amount q (mg g^{-1}) of dye adsorbed by a known amount of catalyst ($m = 0.02$ g), was calculated considering the initial concentration of RhB (C_0^{RhB} in mg L^{-1}) put into contact with the catalyst, the final concentration of RhB at equilibrium after 24 h in the darkness (C_e^{RhB}), the mass of catalyst (m), and the volume of the dye solution in the reactor ($V = 0.05$ L) (Eqn 1).[17]

$$q = (C_0^{RhB} - C_e^{RhB}) \times V/m \qquad (1)$$

The corresponding q values calculated for the adsorption control experiment reached ~ 0.233 mg RhB (g NIT)$^{-1}$ and 0.150 mg RhB (g CIT)$^{-1}$. These values represent insignificant adsorption of the dye onto the surface ($\sim 0.971\%$ on NIT and 0.626% on CIT). So, under the experimental conditions of the
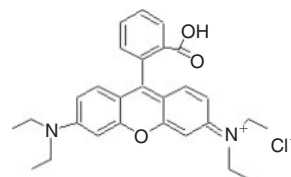

Fig. 1.   Chemical structure of Rhodamine B synthetic dye.

present work, the adsorption of the dye on the surface of the catalysts $CuFe_2O_4$ should be neglected.

Synergetic Effect Between the Photochemical and Catalytic Discoloration/Degradation of RhB

The discoloration of the solution of RhB was evaluated by the disappearance of the visible absorption band at 554 nm. The discoloration efficiency can be expressed as the percentage of discoloration (%**D**), considering the initial and the final absorbance values of the dye solution at a wavelength of 554 nm (A_0 and A_f, respectively) (Eqn 2, Table 1).

$$\%\textbf{D} = [(A_0 - A_f)/A_0] \times 100 \qquad (2)$$

In control experiments, it was confirmed that almost no discoloration of RhB was observed neither when the solution was irradiated by UV light (254 nm) only in the presence of copper ferrites without hydrogen peroxide added (Fig. 2, line 2, not more than 6.8 %**D**), nor in the simple catalytic system of H_2O_2/copper ferrites without UV irradiation (Fig. 2, line 1) even when the solution was left for extended periods of time.

Experiments 1 to 3 in Table 1 show that RhB reached $\sim 70\%$ discoloration in 10 min in the presence of H_2O_2 under UV irradiation without catalyst added (Fig. 2, line 3). Nevertheless, the degradation rate of RhB is highly accelerated when the solution is irradiated by UV light in the presence of H_2O_2 and NIT showing $\sim 97\%$ discoloration due to a synergetic effect (Fig. 2, line 4; Exp. 6a in Table 1). Changes in absorbance spectra of the photocatalytic discoloration of RhB at different intervals of time were attempted by monitoring changes in the absorbance of the dye at 554 nm (Fig. 3). The total disappear-ance of colour is coincident with the absence of absorption at 554 nm and was reached in a period of time close to 10 min, while the reduction of the band at wavelengths lower than 254 nm was reached in over 6 h. The global discoloration reaction followed a pseudo first order kinetic law up to at least three half lives of RhB discoloration. The corresponding appa-rent rate constant values (k_{ap} in s^{-1}) for RhB photocatalytic discoloration were determined in the presence of NIT or CIT nanoparticles with the UV lamp installed at 4 or 8 cm from the liquid surface (Table 1). Taking into account that the mineral-ization is typically slower than discoloration, the disappearance of the dye colour does not necessarily indicate a complete degradation of RhB or a marked decrease in toxicity. Neverthe-less, the decrease of absorbance at 254 nm after 200 min of photocatalytic degradation of RhB (t_4 in Fig. 3) was indicative of a nearly complete destruction of aromatic rings.[18] The corre-sponding degradation efficiency was 94.7 % (Eqn 2).

Under these experimental conditions (UV radiation/H_2O_2/ heterogeneous photocatalyst), copper ferrites may constitute a low cost alternative for the nearly complete discoloration/ degradation of RhB in times of industrial interest.[16]

Table 1. Pseudo-first order rate constant values (k_{ap}) for Rhodamine B photocatalytic discoloration under UV radiation and $[H_2O_2] = 83\ mmol\ L^{-1}$

NIT: $CuFe_2O_4$ prepared using nitrate precursors; CIT: $CuFe_2O_4$ prepared using citric acid precursors; %**D**: percentage discoloration reached in 600 s under UV (254 nm) irradiation unless otherwise indicated

Experiment	Catalyst amount [g L^{-1}]	h^A [cm]	k_{ap}^B ($\times 10^{-3}$) [s^{-1}]	%**D**
1	none	4	2.20	73.3
2	none	8	1.90	71.4
3	none	8	2.01	68.0
4	NIT-0.13	4	5.20	79.1
5	NIT-0.23	4	6.40	84.7
6a	NIT-0.44	4	11.4	97.1
6b	NIT-0.44	4	9.50	96.5^C
7	NIT-0.44	4	10.0	96.7
8	NIT-0.44	4	10.6	96.5
9	NIT-0.44	4	9.40	97.0
10	NIT-0.44	4	9.10	96.9
11	NIT-0.44	4	9.90	97.1
12	NIT-0.44	4	10.4	97.4
13	NIT-0.44	4	9.20	96.9
14	NIT-0.44	4	8.90	96.8
15	NIT-0.44	4	8.70	96.5
16	NIT-0.41	8	6.90	96.5
17	NIT-0.41	8	6.30	97.5
18	NIT-0.41	8	6.00	96.3
19	NIT-0.41	8	6.40	96.5
20	NIT-0.41	8	4.50	91.3
21	NIT-0.41	8	4.20	91.4
22	NIT-0.80	4	9.80	95.3
23	CIT-0.24	8	5.50	87.4 (390 s)^D
24	CIT-0.46	8	9.30 (1st)	98.8 (423 s)^D
25	CIT-0.46	8	8.60 (2nd)	95.9 (360 s)^D
26	CIT-0.46	8	5.80 (3rd)	82.0 (300 s)^D
27	CIT-0.46	8	6.90 (4th)	92.8 (390 s)^D
28	CIT-0.46	8	6.20 (5th)	93.0 (300 s)^D
29	CIT-0.46	8	6.70 (6th)	99.7 (870 s)^D
30	CIT-0.46	8	5.50 (7th)	85.3 (360 s)^D
31	CIT-0.88	8	9.50	94.0 (300 s)^D
32	CIT-0.92	8	7.80	93.7 (375 s)^D

^{A}Distance from the UV lamp to the surface of the Rhodamine B solution.
^{B}Values in brackets indicate the number of cycles of the catalyst. Pseudo first-order behaviour up to at least 300 s.
^{C}Under UV (366 nm) irradiation.
^{D}Irradiation time in brackets.

Reuse of Catalyst

Because of its magnetic properties, the catalyst can be easily extracted from the solution by sliding a magnet on the external glass reactor wall while the coloured solution is cleanly decanted and reused avoiding filtration or centrifugation processes.

The photocatalytic activity of $CuFe_2O_4$ prepared by citrate or nitrate (CIT or NIT), was confirmed by monitoring consecutive experiments of the discoloration of RhB solution (Table 1) under UV light radiation in the presence of H_2O_2 as a source of OH$^\bullet$ radicals (Eqn 3). The catalyst, previously separated from the solution by applying an external magnetic field, was washed with distilled water and dried at ambient temperature to be used a in new experiment. It was observed that the %**D** (Table 1) slightly decreased with increasing the number of regeneration cycles of the catalyst indicating a slight reduction in the activity of the $CuFe_2O_4$. Experiments 6a and 7 to 15 (Table 1) showed that over 96 % of RhB with NIT catalyst could be decolorized
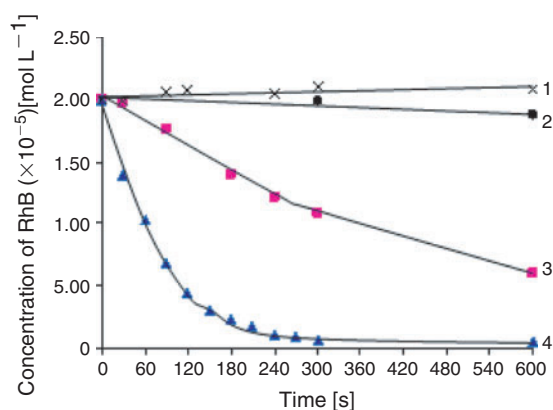
Fig. 2. Photocatalytic degradation of Rhodamine B (2×10^{-5} mol L^{-1}): (1) H_2O_2/NIT; (2) UV 254 nm/NIT; (3) UV 254 nm/H_2O_2; (4) UV 254 nm/H_2O_2/NIT. Other conditions: H_2O_2 initial concentration 83 mmol L^{-1}; 0.4 g L^{-1} NIT; 22 ± 2°C and pH 6.2 (NIT: $CuFe_2O_4$ nanoparticles obtained from nitrate precursors).
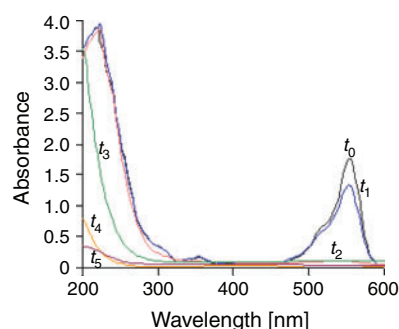
Fig. 3. UV-Visible spectra showing discoloration/degradation of Rhodamine B by UV 254 nm/H_2O_2/NIT. The scans were taken at $t_0 = 0$, $t_1 = 1$, $t_2 = 10$, $t_3 = 120$, $t_4 = 200$, and $t_5 = 390$ min after photocatalytic treatment (NIT: $CuFe_2O_4$ nanoparticles obtained from nitrate precursors).

even after 10 cycles. On the other hand, the reusability of CIT was also analyzed up to seven cycles (Experiments 24–30 in Table 1) reaching 91 % discoloration. These results suggested that NIT and CIT catalysts still present a good activity for the degradation of RhB after repeated use.

$$H_2O_2 \xrightarrow{h\nu} 2HO^\bullet \qquad (3)$$

In general, a slight decrease in the efficiency with the repetitive use of the catalyst might be caused by several factors: a reduction of the surface of the catalyst; the incomplete removal of residual products and reactants from active catalytic sites during washing and drying processes; only part of the magnetic nanoparticles might be rinsed during the discharge of supernatants when cleaning them; photocorrosion of the catalyst; and loss of Cu^{II} by dissolution. Further research is necessary to elucidate the causes of catalyst deactivation in order to diminish this problem and to develop an efficient regeneration procedure.

Effect of UV Light Intensity

The photocatalytic reaction rate depends largely on the radiation absorption of the photocatalyst. In general, an increase in the light intensity produces an increase in the degradation rate during photocatalysis.[19] The UV light intensity reaching the solution was varied by changing the distance (*h*) from the

Table 2. Total photonic flux (I_{total}) in the photoreactor at 254 nm at different distances (h) between the lamp and the surface of the RhB solution

R: correlation coefficient

h [cm]	I_{total} ($\times 10^{-4}$) [Einsteins s^{-1}]	R
4	17.04	0.996
8	5.24	0.992

UV lamp to the surface of the solution (Table 2).[13] The intensity of the UV light on the surface of the liquid, measured by chemical actinometry as the total photonic flux (I_{total}) diminishes when h increases (Table 2) (more details in the Experimental section).[20,21]

At a distance of 4 cm, the intensity of the UV light is 3.25 times more intense than at 8 cm (Table 2), so, the rate of hydroxyl radical formation from H_2O_2 (Eqn 3) increased, resulting in an increase in the rate of RhB discoloration. A comparison between Experiments 6a and 16 (Table 1) demonstrated that k_{ap} decreases ~39.5 % when the distance h is varied from 4 to 8 cm and the wavelength of the lamp is maintained at 254 nm during 300 s irradiation time. On the other hand, when the irradiation was maintained for 600 s the %D was practically independent of the distance h as can be seen by comparing Experiment 6a and 16 (Table 1), where the %D variation was lower than 1 %.

Effect of the Radiation Source

A comparison between Experiments 6a and 6b (Table 1) demonstrated that k_{ap} decreases ~17 % when the irradiation wavelength is varied from 254 to 366 nm and the irradiation time is maintained at 300 s; nevertheless, a nearly total discoloration (96.5–97 %) was reached in 600 s.

An experiment carried out on a sunny day ($\lambda > 310$ nm) showed that the discoloration of RhB needs long exposure times to reach a total discoloration of the solution, i.e. in 65 min the %D was close to 23.7. Nevertheless, taking into account that solar radiation is costless, its use associated with the elimination of dyes in waste waters could be a complementary alternative for industrial effluent treatments.

Effect of Initial Concentration of H_2O_2

The use of an oxidizing reagent such as H_2O_2 became necessary to accelerate the dye decomposition process. It is well known that the presence of H_2O_2 in solutions exposed to UV radiation of wavelength below 380 nm causes the generation of strong oxidizing hydroxyl radicals (HO$^\bullet$) (Eqn 3).[22] On the other hand, it has been shown that H_2O_2 can be activated in heterogeneous systems in the presence of insoluble catalysts containing Cu^{II}.[23,24]

The effect of the initial concentration of H_2O_2 on RhB photocatalytic discoloration/degradation rate in the presence of copper ferrite obtained by NIT route was investigated up to a concentration close to 206 mmol L^{-1} (Table 3). The UV 254 nm irradiation power was also kept constant maintaining a 4 cm distance (h) between the lamp and the surface of the liquid. As can be seen in Table 3, significant discoloration occurs in a reaction time close to 300 s even for low H_2O_2 concentrations (21 mmol L^{-1}). The discoloration efficiency increases up to 93–95 % while the initial concentration of H_2O_2 increases up to 83 mmol L^{-1}. It is assumed that a high concentration of HO$^\bullet$ radicals (Eqn 3) can be generated when increasing the

Table 3. Percentage discoloration (%D) of Rhodamine B in 300 s at different initial H_2O_2 concentrations

Other experimental conditions: 0.44 g L^{-1} NIT (CuFe$_2$O$_4$ prepared using nitrate precursors); distance form irradiation source = 4 cm

Conc. H_2O_2 [mmol L^{-1}]	%D
0	6.8[A]
21	53.5
41	75.3
83	93.3[B]
165	94.7
206	93.9[B]

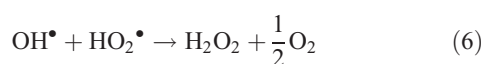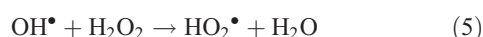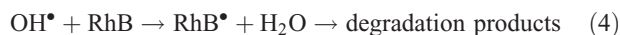[A]UV irradiation time ~600 s as represented in line 2 in Fig. 2.
[B]This value corresponds to Experiment 6a in Table 1.
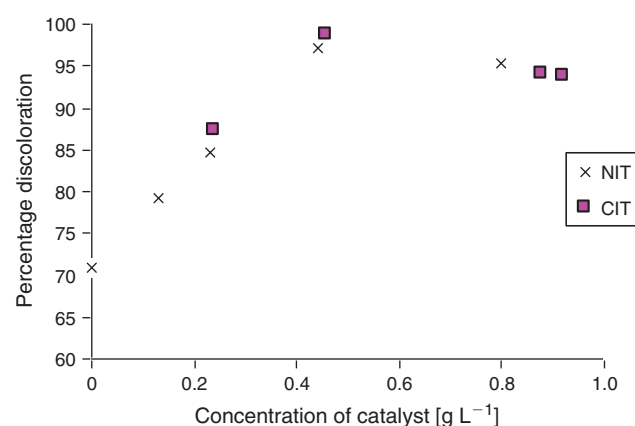
Fig. 4. Effect of CuFe$_2$O$_4$ magnetic nanoparticles' nature and loading on the percentage discoloration of Rhodamine B solutions. NIT: CuFe$_2$O$_4$ prepared using nitrate precursors, distance from lamp (h) = 4 cm. CIT: CuFe$_2$O$_4$ prepared using citric acid precursors, distance from lamp (h) = 8 cm.

concentration of H_2O_2, so the dye discoloration/degradation is accelerated and a complete discoloration of the solution can be reached according to Eqn 4. Nevertheless, a nearly constant level is reached after increasing the concentration of H_2O_2 from 83 to 206 mmol L^{-1}, probably attributable to the 'scavenging effect' (Eqns 5 and 6).[7,8,25] The active oxidizing OH$^\bullet$ radicals in solutions are consumed in parallel reactions instead of supporting the dye decomposition. Eqn 5 represents the self quenching of OH$^\bullet$ radicals, with formation of hydroperoxyl radicals (HO$_2^\bullet$) which have an oxidation potential much lower than that of OH$^\bullet$ radicals.[25]

$$OH^\bullet + RhB \rightarrow RhB^\bullet + H_2O \rightarrow \text{degradation products} \quad (4)$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2{}^\bullet + H_2O \quad (5)$$

$$OH^\bullet + HO_2{}^\bullet \rightarrow H_2O_2 + \frac{1}{2}O_2 \quad (6)$$

Nature of the Photocatalyst

Kinetic data included in Table 1 and Fig. 4 show that there is no great difference in catalytic effects by using either NIT or CIT ferrites. The technique for the preparation of NIT is easier than that to obtain CIT, because the metal complexation with citrate is not necessary; therefore, copper ferrites obtained by the NIT route might be used in future research.[16]

Effect of the Loading of CuFe₂O₄

Effect of the Loading of CuFe$_2$O$_4$

The amount of catalyst is an important parameter for the RhB discoloration. The effect of the CuFe$_2$O$_4$ dosage on the discoloration of RhB was studied by varying the amount of catalyst (NIT and CIT) from 0 to 0.92 g L^{-1} and keeping the initial H$_2$O$_2$ concentration (83 mmol L^{-1}), the distance from the UV lamp, and the reaction time (600 s) constant (Fig. 4). The percentage of photocatalytic discoloration of RhB (%*D*) and the apparent rate constant values (k_{ap}) with different amounts of the catalyst are shown in Table 1 (Experiments 4, 5, 6a, and 22 with NIT; Experiments 23, 24, 31, and 32 with CIT). The discoloration efficiency is strongly influenced by the concentration of the photocatalyst showing a proportional increase in photodegradation with catalyst loading. When the catalyst amount increased from 0 to 0.44 g L^{-1}, the k_{ap} value of RhB discoloration is greatly increased from 2.2×10^{-3} to 9.76×10^{-3} s^{-1}, with an increase of ~28 % in the discoloration percentage. The heterogeneous catalyst probably accelerates the decomposition of H$_2$O$_2$ (Eqn 3), resulting in an easier generation of strong oxidizing OH$^\bullet$ radical species.[26] Beyond the catalyst loading of 0.44 g L^{-1}, k_{ap} approaches an almost constant value showing evidence of an inhibition effect caused by unfavourable light scattering and reduction of light penetration into the solution with an excess of photocatalyst loading.[7,27] The same phenomenon has been reported in the literature as an inhibition effect by the presence of excessive quantities of a metallic species which are responsible for the scavenging of the hydroxyl radicals.[4,28] An amount of ~0.4 g L^{-1} of ferrites can be considered as the optimum catalyst concentration to ensure total absorption of efficient photons with a discoloration of RhB dye up to at least 93 %.

Conclusions

Aqueous RhB dye solutions can be discolored up to 70 % in the presence of UV/H$_2$O$_2$. The discoloration/degradation rate can be markedly improved when the decomposition of H$_2$O$_2$ into reactive radical species (OH$^\bullet$) is increased by the introduction of magnetic nanoparticles of spinel copper ferrites (CuFe$_2$O$_4$) as heterogeneous catalyst. Under the experimental conditions of this work, the RhB discoloration was nearly complete in only 10 min and the degradation in 200 min. The reusability of copper ferrite nanoparticles was demonstrated by recycling them in 6 to 10 consecutive experiments. A markedly synergetic effect of copper ferrospinels and light irradiation is observed for the degradation of RhB with H$_2$O$_2$ because of the positive interaction between photochemical effects and the catalyst. In this way, the use of copper ferrites obtained by wet-chemical methods from nitrate precursors or a citric acid-aided process becomes a promising approach for the removal of organic pollutants by photocatalytic oxidation in the presence of H$_2$O$_2$ and may constitute an alternative for total discoloration/degradation of the RhB dye.

Experimental

Dye

The synthetic dye [9-(2-carboxyphenyl)-6-diethylamine-3-xanthenylidene] diethylammonium chloride known as Rhodamine B (Merck, p.a., C$_{28}$H$_{31}$O$_3$N$_2$Cl, CI 45170, Basic violet 10, Fig. 1) was used without prior purification.

Hydrogen Peroxide

Hydrogen peroxide (60 %) was purchased from Anal Quim.

Adsorption Study

Samples of 50 mL of the RhB dye (2×10^{-5} mol L^{-1}) were put in contact with a known amount of the catalyst (NIT or CIT) to evaluate the extent of adsorption of RhB on CuFe$_2$O$_4$. After an initial time of 600 s under ultrasonic irradiation to reach the dispersion of the catalyst on the dye solution, the system was maintained for 24 h in the darkn at ambient temperature and at the natural pH of the solution (~6.2). An ultrasonic cleaner (Testlab tb04) was used for the adsorption control experiment. Samples of 3 mL of the supernatant solution were taken at given time intervals and the concentration of RhB was calcualted by measuring the absorbance at the maximum wavelength of the dye (554 nm) to establish the equilibrium of the adsorption–desorption process on the surface of the catalyst.

Light Intensity Determination: Chemical Actinometry

The UV-light intensity received by an aqueous solution of hydrogen peroxide (40 mmol L^{-1}) was determined by chemical actinometry at the natural pH of the solution (6.2).[20,21] An aliquot of 50 mL of H$_2$O$_2$ aqueous solution contained in a glass reactor (11 cm internal diameter) was irradiated for 300 min with a UV lamp at 254 nm. The exposed surface area of the solution was kept constant in all the experiments while the distance (*h*) between the solution surface and the lamp was varied from 4 to 8 cm.

The mass balance for H$_2$O$_2$ in the batch photoreactor yields the following ordinary differential equation (Eqn 7), where *V* is the reactor volume and *C* is the H$_2$O$_2$ concentration at time *t*.

$$V \times (\mathrm{d}C/\mathrm{d}t) = r_{\mathrm{phot}} \qquad (7)$$

The overall kinetic rate expression (r_{phot}) of the photolytic reaction can be represented by Eqn 8 where Φ_λ is the H$_2$O$_2$ quantum yield at a known wavelength (λ) and I_λ is the corresponding absorbed radiation.

$$r_{\mathrm{phot}} = -\sum \Phi_\lambda \times I_\lambda \times t \qquad (8)$$

Eqn 9 can be written when the integrated form of Eqn 7 is included in Eqn 8 considering that $C = C_0$ at $t = 0$.

$$V \times (C - C_0) = -\sum \Phi_\lambda \times I_\lambda \times t \qquad (9)$$

The number of moles can be written as $N = VC$, with *V* measured in L and *C* in mol L^{-1}, so Eqn 9 can be expressed in moles as it is shown in Eqn 10,

$$N_0 - N = \sum \Phi_\lambda \times I_\lambda \times t \qquad (10)$$

The total photonic flux (I_{total}) in the photoreactor can be calculated from the linear representation of Eqn 10 (Fig. 5) where $\Phi_\lambda \times I_\lambda$ represents the slope of the line. The H$_2$O$_2$ quantum yield at the selected wavelength (254 nm) is a known constant value ($\Phi_\lambda = 0.5$ mol Einsteins^{-1}).[21,29]

The kinetic parameters of the photolytic decomposition of H$_2$O$_2$ were determined by high performance liquid chromatography (HPLC) using a Hewlett Packard 1050 C series instrument, using a reverse-phase column ODS (Hypersil, 5 µm, 100×4.6 mm^2) and variable wavelength UV–visible detector ($\lambda = 216$ nm). Distilled water was used as the mobile phase at a pressure of 50 bar and at a constant flow (0.5 mL min^{-1}).
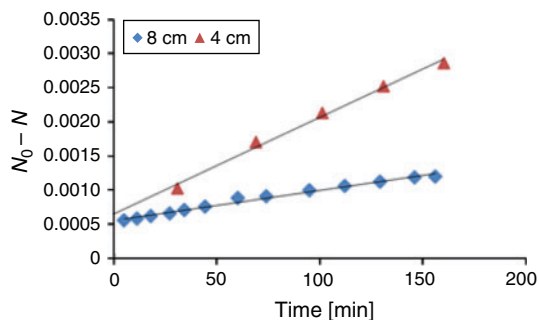
Fig. 5. Evolution of H_2O_2 concentration in actinometric assays (Eqn 10) at different distances (h) between the solution surface and the lamp.

Preparation of Samples and Discoloration/Degradation Procedures: Analytical Kinetic Methods

The stock dye solution (1×10^{-3} mol L^{-1}) was artificially prepared using distilled water. It is important to recognize that this dye solution does not exactly simulate wastewater from the dying of paper, silk or wool because it is likely that other constituents would be present.

Necessary dilutions of the stock solution were carried out to obtain dye solutions (2×10^{-5} mol L^{-1}) for discoloration/degradation studies. Different amounts of spinel copper ferrites used as catalyst (0–0.8 gr L^{-1}) were added to a known volume of RhB (50 mL) at ambient temperature and at the natural pH of the solution ($\sim$6.2). The photocatalytic discoloration/degradation experiments were carried out using a glass reactor (250 mL capacity) open to the air. The degradation of the RhB in the mixture irradiated with UV or solar light was started by rapid addition of a given amount of hydrogen peroxide necessary to reach an initial concentration varying from 0 to 206 mmol L^{-1}. The distance from the UV lamp to the liquid solution surface (h) was mostly kept constant at 4 cm or 8 cm during the experiment. The UV-source used in the present study was a Spectroline lamp (Model ENF-260 C/F, 230 V, 50 Hz, 17 Amp) that produces UV-C and UV-A light (254 and 365 nm) of high intensity. Some experiments were irradiated by direct solar light.

Irradiated solution samples (3 mL) were withdrawn at given times and their UV-vis spectra were recorded over the interval 222–600 nm. The characteristic wavelength of RhB in the visible region ($\lambda_{max} = 554$ nm) was used for discoloration studies. The UV-vis spectra of RhB solutions before and after discoloration/degradation and their change during catalytic discoloration were recorded using a spectrophotometer (Metrolab 1700). After completion of the measurement, the sample was returned to the glass reactor which was held under the UV lamp. The discoloration reaction was followed until the almost total disappearance of colour at room temperature and at the natural pH of the RhB solution. All experiments were performed at least in triplicate so that the values shown in the tables are averages. The degradation of intermediate reaction products which absorb light in the UV region needs at least 6.5 h under UV light exposure.

Acknowledgements

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