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Photocatalytic degradation of a mixture of two anionic dyes: Procion Red MX-5B and Remazol Black 5 (RB5)

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ABSTRACT

The photocatalytic degradation of a mixture of two anionic dyes, Remazol Black (RB5) and Red Procion MX-5B in presence of TiO_2 Degussa P-25 was investigated using wavelength higher than 290 nm. UV–vis spectroscopy was employed to monitor the amount of each dye in the mixture and to compare the degradation of both dyes individually and mixed.

The adsorption equilibrium of each dye, the influence of pH and the initial concentration of dyes on the kinetics of discoloration and mineralization were performed and compared to their kinetics when they are individually degraded. Although no complex was put in evidence between these two coloring agents using spectroscopy UV–vis, an important modification of the RB5 adsorption is noted in the mixture. However, the presence of RB5 has no effect on the MX-5B adsorption. This difference of behaviour can be explained by considering the modification of pH by increasing the initial concentration of MX-5B in the mixture. Above 15 μmol/L, both anionic dyes are in competition for the same site. Even if the adsorption of RB5 is modified, the disappearance rate of both dyes individually or mixed are similar at low concentration of dyes. At high concentration their disappearance rates in the mixture decrease in agreement with the number of available site. Besides the study of the discoloration, we studied the evolution of Total Organic Carbon (TOC), the formation of NH_4^+, NO_3^-, SO_4^{2-} of both dyes during their individual or mixed photocatalytic degradation are compared. The results suggest that the mechanisms of degradation are modified in the mixture.

1. Introduction

The release of colored wastewaters in the ecosystem is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life. For the majority of them, their half-lives under sunlight are greater than 2000 h [1] and their resistance to biological and even chemical degradation [2,3] makes them hazardous for the environment even at low concentration. As international environmental standards are becoming more stringent (ISO 14001, October 1996, EPA, CCL 3 lists, September 2009), technological systems for the removal of organic pollutants, such as dyes have been recently developed. But are often very costly methods, ineffective for complete degradation of some recalcitrant organic dyes or only transfer the contaminant from one phase to another in some cases.

Photocatalytic oxidation process based on UV-irradiated TiO_2 is a highly effective method for the degradation and mineralization of priority pollutants like pesticides, fungicides, herbicides, dyes, chlorophenol, organic acids but also microorganisms in water and wastewater. Several books and reviews have been devoted to this problem [4–8] and many publications deals with photocatalytic degradation of dyes. Only some of them were cited in this publication [9–24]. Upon adsorption of photons with energy larger than the bandgap of TiO_2 (wavelength lower than 388 nm), electrons in the valence band are excited to the conduction band, generating an electron–hole (e^-/h^+) pair. These pairs are able to initiate oxidation and reduction reactions at the TiO_2 surface. The photogenerated electrons could reduce the dye or react with electron acceptors such as O_2 reducing it to superoxide radical anion $O_2^{\bullet -}$ and hydroperoxide $HO_2^{\bullet -}$. The positive holes can oxidize the organic molecules adsorbed at the surface, directly or through the formation of $OH^\bullet$ radicals. The resulting $OH^\bullet$ radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of the dyes into intermediates which subsequently undergo a complete mineralization. On the other hand, the photogenerated electron can produce radical species such as superoxide $O_2^{\bullet -}$ and hydroperoxide $HO_2^{\bullet -}$. It is also important to note that he life-time of these electrons holes pairs (e-/h+) is some nanoseconds and

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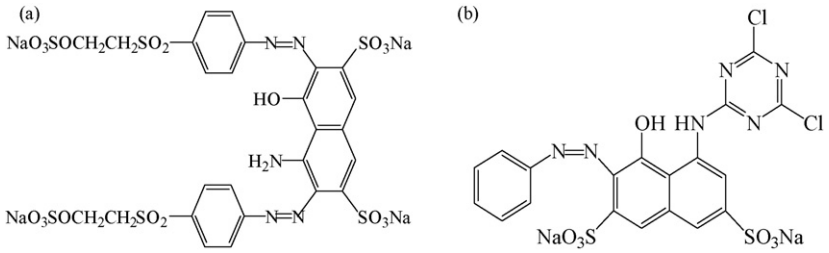

Fig. 1. Chemicals structures of the azo dyes: Remazol Black 5 (RB5); λ_{max} = 597 nm (a) and Procion MX-5B; λ_{max} = 538 nm (b).

that another pathway is to return to the valence band by releasing the energy in the form of heat. The quantum yields returns are generally some percents [25]. Moreover, some compounds containing a triazinic cycle cannot be mineralized. Several papers show that the triazinic cycle oxidizes mainly in cyanuric acid which is stable in aqueous solution, this compound being harmless for the environment [26–28].

The photocatalytic process also presents an interesting advantage for this type of pollution, actually, a direct mineralization of azo group in gaseous nitrogen occur, which constitutes an ideal case of environmental treatment, with the production of one of the constituents of the atmosphere [14,15]. However, if many papers describe the photodegradation of single component systems, much less are interested in mixtures. Robert et al. showed that in the case of a binary mixture (4-hydroxybenzoic acid and benzamide) it was possible to degrade one molecule without any concentration change in respect of the other molecule. With the appropriate modifications of two parameters (pH and TiO_2 concentration) it also appears to be possible to improve the selectivity [29]. Recently, Gora et al. have reported a kinetic analysis of the photocatalytic oxidation of a mixture of three herbicides [30]. At the same time, Gupta et al. have studied the photocatalytic degradation of a mixture of an anionic azo dye (methyl red) and a cationic triphenylmethane dye (crystal violet) in aqueous suspensions using Ag^+ doped TiO_2 [31].

In this present work, a mixture of two anionic azo dyes (Remazol Black and Procion Red MX-5B previously studied in single component systems [17]) is photodegraded in the presence of TiO_2-P25 in the goal to determine if the kinetic of decoloration or mineralization of carbon and heteroatoms can be estimated from the degradation of dyes taken separately. In a first time, we will determine a method to measure the amount of each dye in the mixture. Then, we will compare the degradation of the two dyes individually and mixed by investigating the effect of the initial dyes concentrations on kinetics of decoloration and mineralization.

2. Experimental and modelling details

2.1. Dyes

The two dyes, Remazol Black 5 (55% purity) and Procion Red MX-5B (50% purity) were purchased from Sigma–Aldrich and used without further purification. Their structure are presented in Fig. 1. Solutions were prepared in ultra-pure water obtained from a Millipore waters Milli-Q equipment.

2.2. Photocatalyst

The photocatalyst used was Titania Degussa P-25 which is made of anatase (80%) and rutile (20%) under the shape of non-porous particles with a surface area of 50 m^2/g and mean crystallite sizes of ca. 30 nm.

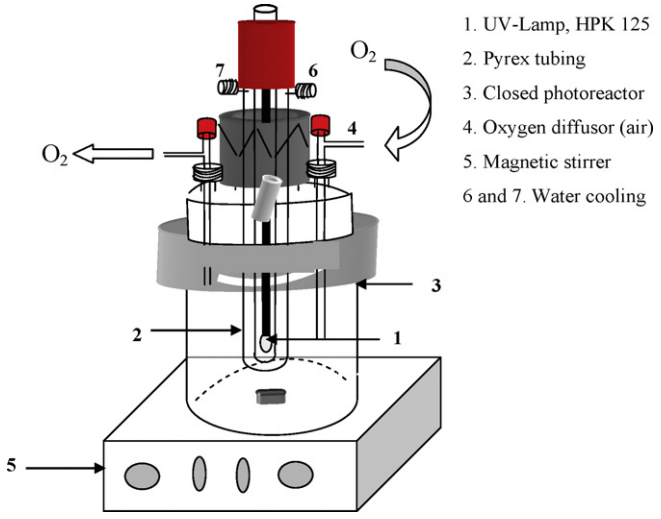

Fig. 2. Laboratory slurry photoreator for dyes elimination.

2.3. Photoreactor and light source

Irradiation was performed in a 1 L cylindrical glass reactor. Irradiation was provided by a 125 W UV-lamp Philips HPK placed in a plugging tube. A Pyrex cylindrical jacket located around the plugging tube contained circulating water to absorb IR radiation and avoid heating of the solution.

The radiant flux reaching the exposed inner part of the reactor was measured using a VLX-3W radiometer with 2 detectors CX-365 (355–375) and CX-312 nm (280–320 nm) and estimated to be 6×10^{-6} Einstein s^{-1} (mol of photons per second). This value corresponds to the sum of the both values obtained with each cell. The values are measured at different place situated on the inner tube containing the lamp (Fig. 2).

2.4. Procedure

375 mg of Titania P25 was added to 750 mL of the aqueous solution of dye. The amount of TiO_2 (0.5 g/L) used has been adjusted for a full absorption of the incident photon flux.

2.5. Adsorption tests

The adsorption equilibrium of both dyes on TiO_2 was determined in the dark by using 750 mL of aqueous solution of dyes of various initial concentrations (5, 10.5, 21.5, and 42.5 μmol/L) at natural pH ($5.6 \leq pH \leq 6.6$; see Table 1), acidic pH (3) and basic pH (7.4), adjusted using sulfuric acid or sodium hydroxyde. After 60 min of mechanical stirring, the aqueous samples were filtered through 0.45 μm millipores discs to remove TiO_2 powder before analysing.

Table 1
Values of the pH of the initial solution of the both dyes and of their mixture at different initial concentrations of each dye.

C_0 (μmol/L)	2	5	10.55	21.1	42.2
pH RB5	5.60	5.60	5.61	5.61	5.66
pH MX-5B	5.7	5.95	6.05	6.37	6.66
pH mixture (50% RB5, 50% MX-5B)	5.82	5.93	6.24	6.43	6.66

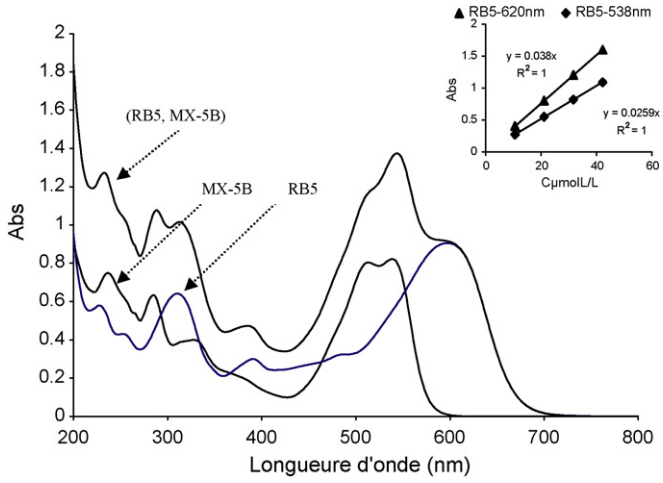

Fig. 3. UV–vis spectra of RB5, MX-5B, experimental mixture of the two dyes and theoretical mixture of dye considering the mathematical addition of UV–vis spectra of each dye.

2.6. Analyses

The decoloration of RB5 and MX-5B solutions was monitored by measuring absorbance with an UV–visible spectrophotometer Perkin Elmer at a wavelength of 597 and 538 nm, respectively. Total Organic Carbon (TOC) was determined by using a Bioritech (model 700) TOC analyser. The formation of inorganic ions was detected with a Dionex DX-120 ion-chromatograph equipped with a Ion-Pac AS14A 4 mm (length: 250 mm; inner diameter: 4 mm) for the anions (mobile phase: Na_2CO_3/$NaHCO_3$; flow rate: 1 mL/min) and with a Ion-Pac CS 12A (length: 250 mm; inner diameter: 4 mm) for the cations (mobile phase: H_2SO_4; flow rate: 1 mL/min).

3. Results and discussion

3.1. Calibration of both dyes in the mixture

Whatever the concentration of RB5 and MX-5B dyes, the absorbance of mixture is always equal to the sum of absorbance of each dye indicating that these both dyes are not linked by chemical or physical bond. In other word no complexes are formed. Taking into account the UV–vis spectra of the mixture and of each dye, it appears that only RB5 dye absorbs at wavelengths higher than 600 nm, allowing to measure its degradation, in the mixture, at 620 nm. The amount of MX-5B during the irradiation is then obtained at 538 nm by the subtraction of the absorption corresponding to the quantity of RB5 (Fig. 3).

3.2. Adsorption of a mixture of dyes

The adsorption equilibrium of RB5 and of MX-5B in a single component system have already been published by our in a previous work [17].

The adsorption equilibrium of RB5 individually taken is of L1 type according to the classification of Gilles et al. as already described in our previous work [17]. In the equimolar mixture (50% RB5, 50% MX-5B), over concentrations of 5 μmol/L the amount of RB5 adsorbed is largely decreased (Fig. 4).

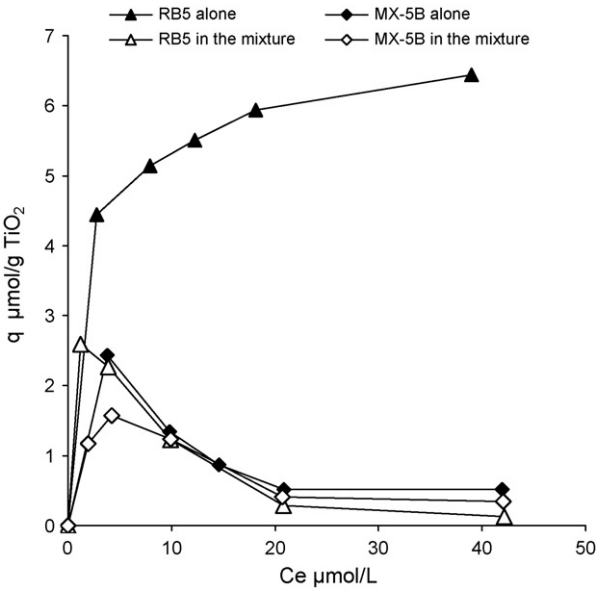

Fig. 4. Adsorption equilibrium of RB5 and of MX-5B individually taken or in an equimolar mixture (50% RB5, 50% MX-5B).

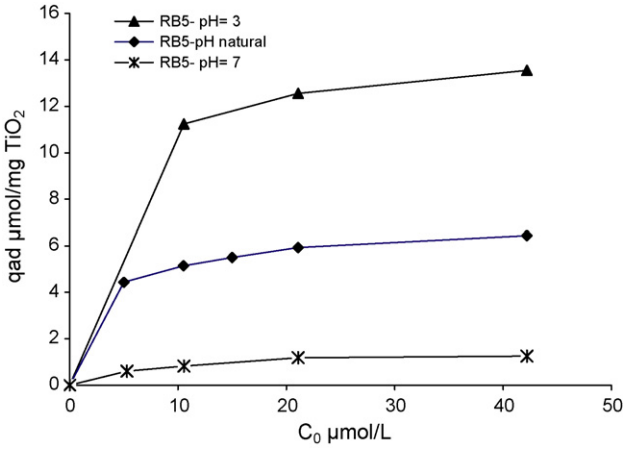

Fig. 5. Effect of the pH on the adsorption of RB5 taken individually. In inset is represented the maximum of RB5 adsorbed as a function of pH.

In a first approach, this diminution could be attributed to a competition between the adsorption of both dyes. Nevertheless, in the mixture, the amount of MX-5B adsorbed is not modified, only RB5 adsorption is changed (Fig. 4). According to the value of pH of individual and mixture dye solutions, the decrease of adsorption of RB5 could be explained by the modification of the pH enhanced by the addition of MX-5B. Effectively the pH of the solution takes about one unit to attempt a value of 6.6 (Table 1).

This is in agreement with the RB5 adsorption equilibrium obtained at different pH (Fig. 5). The higher adsorption at acid pH of RB5 is in agreement with amphoteric properties of TiO_2.

TiO_2 can be charge negatively or positively according to the pH of the environment (Eqs. (1) and (2)).

$$\text{pH} < \text{pcz}\,TiO_2: \quad \text{Ti-OH} + H^+ \rightarrow TiOH_2{}^+ \tag{1}$$

$$\text{pH} > \text{pcz}\,TiO_2: \quad \text{Ti-OH} + OH^- \rightarrow TiO^- + H_2O \tag{2}$$

pcz TiO_2 = 6.5.

At acidic pH (pH = 3), RB5 containing sulfonate groups ($SO_3{}^-$) is better adsorbed than at pH = 5.6–6.6 due to the positive charge of

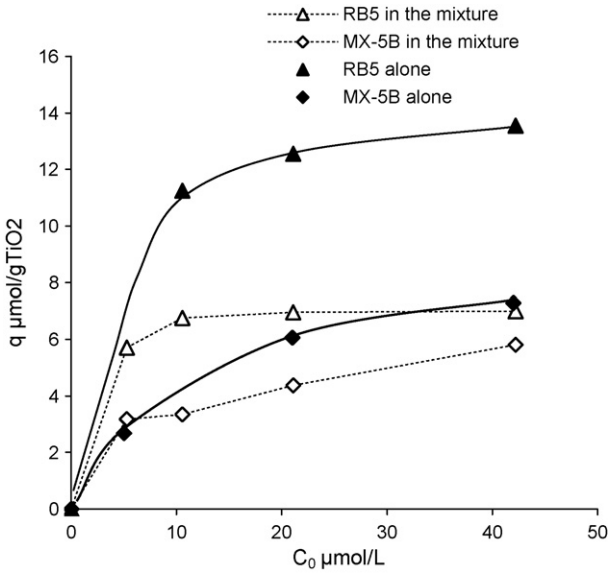

Fig. 6. Adsorption equilibrium at pH = 3 for RB5 and MX-5B taken individually and in an equimolar mixture (C_0 is the concentration of RB5 or MX-5B).

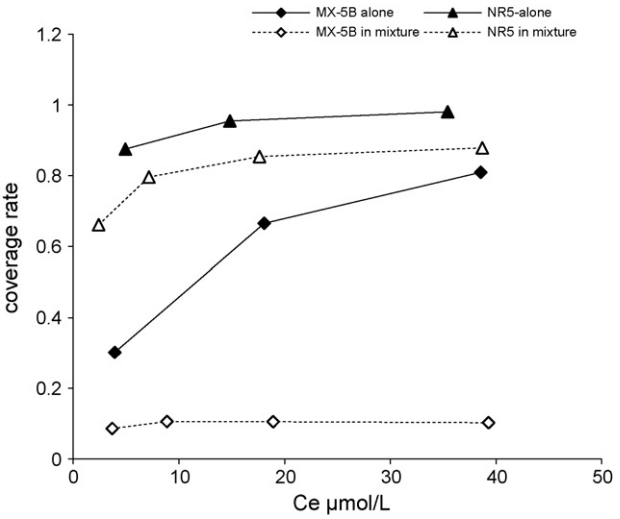

Fig. 7. Rate of recovery of the surface catalyst at pH = 3 by the two dyes taken individually or in mixture (C_0 is the concentration of RB5 or MX-5B).

the catalyst surface ($TiOH_2^+$). This pH effect is largely studied in the literature on different organic compounds [9,32–35].

Same behaviour is also observed for MX-5B (Fig. 6). Its adsorption taken individually or in equimolar mixture (50% RB5, 50% MX-5B) is considerably improved with regard to those obtained in natural pH ($5.8 \leq pH = 6.6 \leq 6.7$) and is of type L1 according to Giles's classification.

It is to be noticed that the adsorption of the RB5 in mixture is more important than that of the MX-5B. This can be attributed to the more important number of sulfonates groups in the RB5 molecule which increases the strengths of attraction between the sites of adsorption of TiO_2 and the dye. To confirm this result the rate of covering of the surface according to the concentration of both dyes taken individually and in mixture has been drawn using Eq. (3) (Fig. 7). It appears that the maximum of the surface of TiO_2 is covered by the molecules of RB5.

$$\theta = \frac{K_{ads} C_{eq}}{1 + K_{ads} C_{eq}} \quad (3)$$

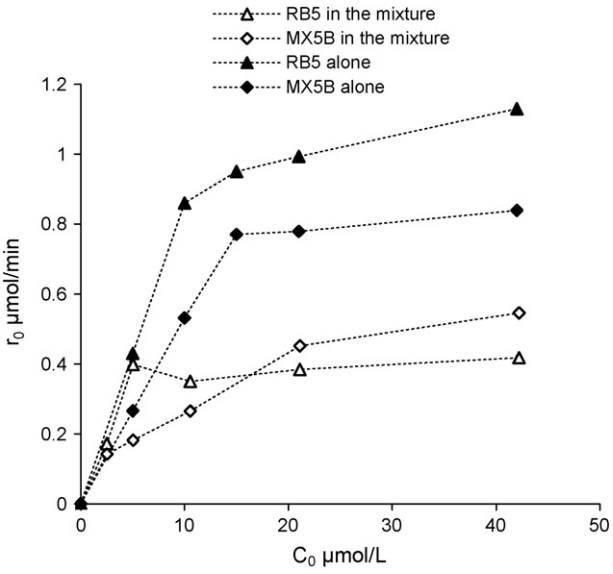

Fig. 8. Kinetic of decolorization of RB5 and of MX-5B taken individually and in mixture at natural pH (C_0 is the concentration of RB5 or MX-5B).

C_{eq} is the concentration of dye at equilibrium of adsorption.
K_{ads} is the Langmuir adsorption constant calculated taking the results at pH = 3.
θ corresponds to the ratio of the number of occupied sites to the number of total sites, or to the ratio of the amount of dye adsorbed to the maximum amount of dye that the surface can adsorb.

At basic pH (pH = 7.4 > pzc), the catalyst surface is negatively charged. TiO^- species are predominant and push away both dyes by electrostatic effect, so that the dye adsorption becomes no significant.

3.3. Photocatalytic degradation

The effect of the initial concentration on the kinetic of discoloration has been investigated by varying the concentration of the dyes in equimolar mixture at natural pH (pH = 6.6). The results are shown in Fig. 8.

It is found that at low concentrations ($C_0 \leq 3$ µmol/L) the initial kinetic of discoloration of the two dyes is the same whatever the dyes are taken individually or in mixture. This can be explained by the availability of the site of adsorption at the surface of the catalyst at low concentrations. Up to concentrations of 5 µmol/L the kinetic of decolorization of the two dyes is lower in mixture than in single component systems. For concentrations from 3 to 10 µmol/L the degradation of RB5 is faster than the one of MX-5B, this result is correlated to the quantity of RB5 adsorbed at the surface of TiO_2 (Fig. 4). At higher concentrations (>10 µmol/L), the augmentation of the pH in the solution is unfavourable to the RB5 adsorption and consequently the kinetic of discoloration of RB5 decreases towards the kinetic of discoloration of MX-5B. Moreover at high concentration the dyes are in competition for the adsorption at the surface of the catalyst. At pH < pzc of TiO_2 the degradation is in favour of RB5 whereas at pH > pzc the degradation of MX-5B is better.

3.4. Mineralization

3.4.1. TOC measurements

The mineralization of organic carbon of both dyes in single component systems or in equimolar mixture is investigated by the Total

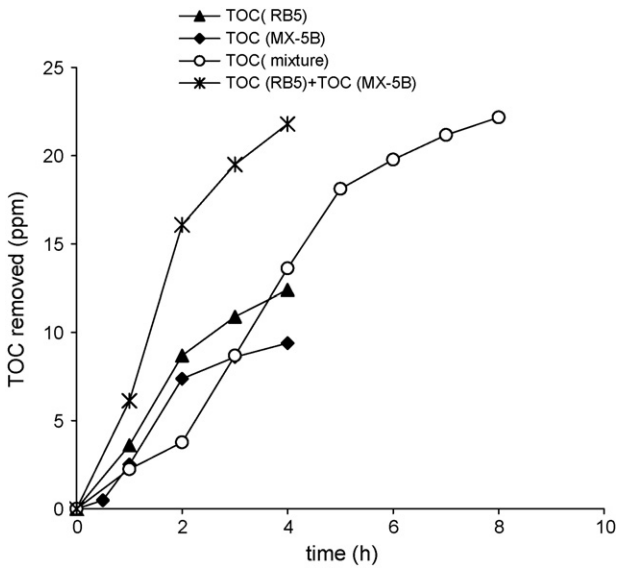

Fig. 9. Comparison of the amount of TOC disappeared during the degradation of the two dyes taken individually and in mixture ($C_{0\,RB5}$ = 42 μmol/L, $C_{0\,MX\text{-}5B}$ = 42 μmol/L).

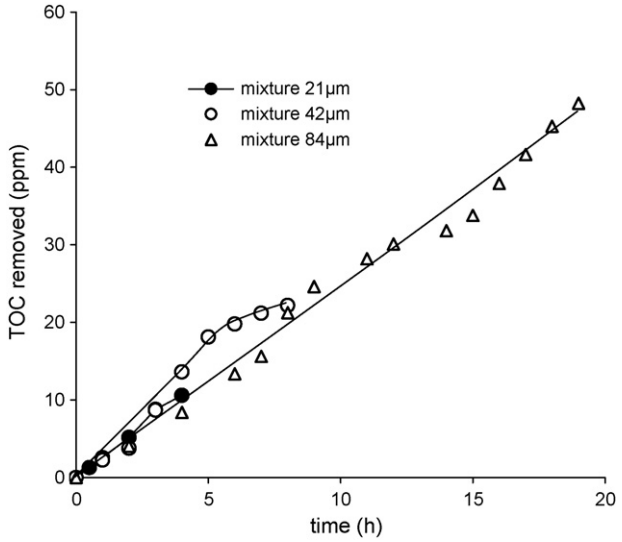

Fig. 10. Effect of the concentration on the mineralization of TOC during the degradation of the mixture (C_0 = 42 μmol/L for each dye).

Organic Carbon (TOC) measurement during the degradation of the solution at natural pH and for different concentrations (21, 42 and 84 μmol/L).

The kinetics of TOC disappearance versus irradiation time [TOC] = $f(t)$ are given in Figs. 9 and 10.

Fig. 9 shows that the TOC amount degraded in the mixture is not the result of the simple mathematic addition of the TOC degraded in single component systems. This behaviour can be explained considering the initial kinetics of TOC disappearance in equimolar mixtures 21, 42, and 84 μmol are similar (Fig. 10) which remain constant (about 2.6 ppm/h).

This result is in correlation with the adsorption equilibrium of the mixture (Fig. 4) which shows a saturation of the catalyst surface at concentrations above 5 μmol/L. After a total saturation of the active sites of the catalyst the quantity of organic substance degraded at the surface remains constant. It would be interesting to study the degradation of some mixtures of concentrations lower than 5 μmol/L but the sensibility

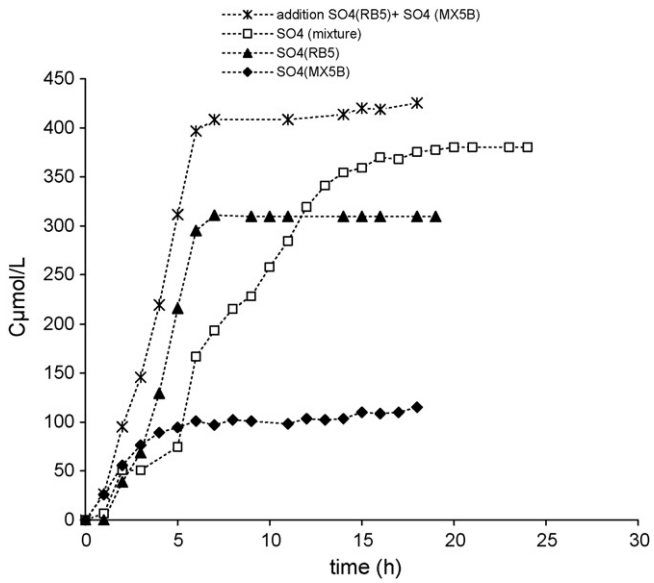

Fig. 11. Evolution of SO_4^{2-} in the photocatalytic degradation of the mixture of both dyes (C_0 = 42 μmol/L of each dye).

of the apparatus does not permit to obtain reliable measurements.

3.4.2. Mineralization of heteroatoms

The sulfonates and sulfones groups are mineralized into sulfate ions. The study of the sulfate concentration in aqueous solution versus time (Fig. 11) shows that sulfate ions are produced initially in the degradation of MX-5B and of the mixture and only after 1 h of irradiation in the case of RB5. At low concentration of dyes ($C_0 \leq 3$ μmol/L), there is the same amount of SO_4^{2-} formed in the mixture and this one calculated by the mathematical addition of sulfate formed for each dye degraded separately. At higher concentration, the amount of sulfate ions obtained in the degradation of the mixture does not result in the mathematic addition of the sulfate ions obtained in the degradation of each dye in single component system.

The mineralization of nitrogen atoms in the –N=N– azo-groups and amino groups is purchased by the measurement of NH_4^+ and NO_3^- ions appearance.

The fate of nitrogen strongly depends on its initial oxidation degree. If it present in the −3 state as in amino groups, nitrogen spontaneously evolves as NH_4^+ with the same degree of oxidation, before being subsequently and slowly oxidized into nitrates. In the –N=N– double bond both nitrogen atoms are already formally at the zero oxidation degree and the logical evolution is the formation of gaseous dinitrogen.

In the mixture, NH_4^+ ions are detected after 1 h of irradiation (Fig. 12a) whereas these ions are formed only after few minutes of irradiation in the case of the degradation of each dye. The amount of ammonium ions obtained in the degradation of the mixture does not result in the mathematic addition of the ammonium ions obtained in the degradation of each dye in single component system.

Same behaviour is observed in the formation of NO_3^- ions. There are formed slower in the mixture (Fig. 12b) and only appeared after 10 h of irradiation. After 24 h of irradiation, equilibrium is not still reached probably due to the slow oxidation of the amino group linked to the triazinic ring in MX-5B.

For neither of the ions, the formation in the mixture is the mathematical addition of the ones formed during the degradation of each dye because (1) the adsorption of these both dye is not similar at

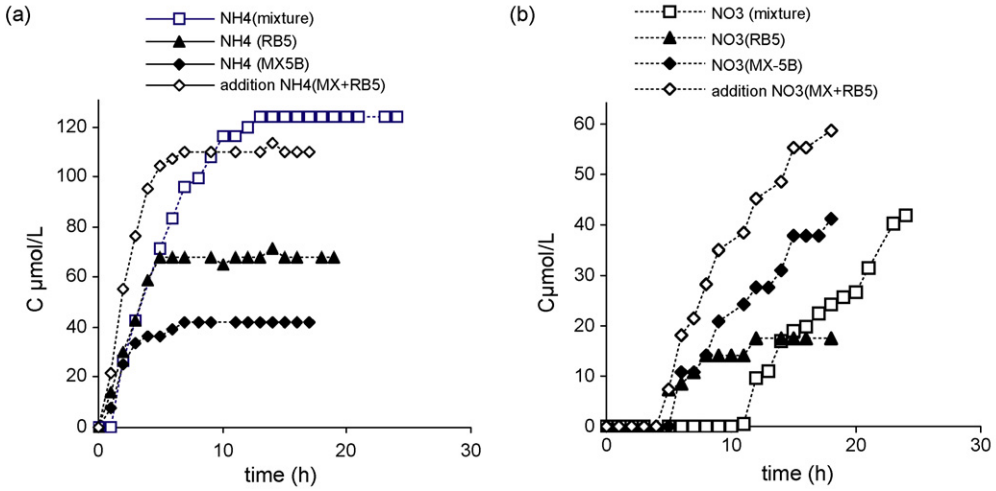

Fig. 12. Evolution of NH_4^+ (a) and NO_3^- (b) in the degradation of RB5 and MX-5B in equimolar mixture (C_0 = 42 μmol/L) or separately.

same concentration and (2) natural pH is not the same if dyes are mixed or not leading to a modification of degradation mechanisms.

4. Conclusions

Above the saturation of photocatalyst, adsorption and kinetic of discoloration and mineralization of RB5 and MX-5B dyes are modified if they are mixed. Whereas the presence of RB5 has no initial effect on the MX-5B adsorption, an important modification of the RB5 adsorption is noted in the mixture which is attributed to the increase of pH by increasing the initial concentration of MX-5B in the mixture. At high concentration (above 5–10 μml/L of each dye) both anionic dyes are in competition for the same site and their adsorption decrease.

At low coverage rate of TiO_2 surface, the disappearance rate of both dyes individually or together degraded are similar whereas at high concentration their disappearance rates in the mixture decrease in agreement with the number of available site. Considering the mineralization of carbon and heteroatoms, above the coverage rate of photocatalyst, the TOC removed, sulfate, ammonium and nitrate ions formed in the degradation of the mixture does not result in the mathematic addition of these compounds obtained in the degradation of each dye in single component system indicating a modification of the mechanism of degradation probably due to the saturation of photocatalyst surface but also to the natural pH slightly different in the mixture. We have also shown that above the saturation of the surface of catalyst, the initial kinetics of TOC disappearance remains similar.

These studies allowed us to better understand the kinetic of photocatalytic degradation of the mixture of both anionic dye, the Remazol Black 5 (RB5) and the Procion Red MX-5B and to show that in the real textile wastewater it will be difficult to forecast the kinetic of discoloration and mineralization. Other studied should be done using mixture of different dyes at different concentration and pH.

Acknowledgement

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References

[1] J.J. Porter, EPA Report-R2-73-058, Washington, DC, 1973.
[2] S. Dai, W. Song, T. Li, Y. Zhuang, Adv. Environ. Sci. 4 (1996) 1–9.
[3] J.G. Montaño, X. Domènech, J.A. García-Hortal, F. Torrades, J. Peral, J. Hazard. Mater. 154 (2008) 484–490.
[4] O. Legrini, E. Oliveros, A. Braun, Chem. Rev. 93 (1993) 671, Solar purification and potabilization of water containing dyes 431.
[5] D.M. Blake, Bibliography of Work on Photocatalytic Removal of Hazardous Compounds from Water and Air, NREL/TP-510-31319, National Renewable Energy Laboratory, Golden, CO, 2001.
[6] M. Kaneko, I. Okura (Eds.), Photocatalysis: Science and Technology, Springer, 2002.
[7] H. De Lasa, B. Serrano-Rosales (Eds.), Advances in Chemical Engineering, Photocatalytic Technologies, first edition, Academic Press, 2009, p. 36 (Hardcover).
[8] U.-I. Gaya, A.-H. Abdullah, J. Photchem. Photobiol. C: Photochem. Rev. 9 (2008) 1–12.
[9] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Appl. Catal. B: Environ. 31 (2001) 145–157.
[10] M. Vautier, C. Guillard, J.M. Herrmann, J. Catal. 201 (2001) 46–59.
[11] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Appl. Catal. B: Environ. 39 (2002) 75–90.
[12] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaluoi, J.-M. Herrmann, J. Photochem. Photobiol. A: Chem. 158 (2003) 27–36.
[13] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.M. Herrmann, Appl. Catal. B: Environ. 46 (2003) 319–332.
[14] M. Karkmaz, E. Puzenat, C. Guillard, J.-M. Herrmann, Appl. Catal. B: Environ. 51 (2004) 183–194.
[15] T.H. Bui, M. Karkmaz, E. Puzenat, C. Guillard, J.-M. Herrmann, Res. Chem. Intermed. 33 (2007) 421–431.
[16] P.-A. Pekakis, N.-P. Xekoukoulotakis, D. Mantzavinos, Water Res. 40 (2006) 1276–1286.
[17] K. Sahel, N. Pérol, H. Chermette, C. Bordes, Z. Derriche, C. Guillard, Appl. Catal. B: Environ. 77 (2007) 100–109.
[18] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B: Environ. 49 (2004) 1–14.
[19] A. Aguedach, S. Brosillon, J. Morvan, E.K. Lhadi, Appl. Catal. B: Environ. 57 (2005) 55–62.
[20] M.A. Rauf, S. Salman Ashraf, Chem. Eng. J. 151 (2009) 10–18.
[21] A.R. Khataee, M.N. Pons, O. Zahraa, J. Hazard. Mater. 168 (2009) 451–457.
[22] R.-B.-M. Bergamini, E.B. Azevedo, L.R. raddi de Araujo, Chem. Eng. J. 149 (2009) 215–220.
[23] F. Han, V.-S.-R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu, Appl. Catal. A: Gen. 359 (2009) 25–40.
[24] V.-A. Sakkas, Md.-A. Islam, C. Stalikas, T.-A. Albanis, J. Hazard. Mater. 175 (2010) 33–44.
[25] J. Rasaiah, J. Hubbard, R. Rubin, S.H. Lee, J. Phys. Chem. 94 (1990) 652.
[26] C. Hu, J.C. Yu, Z. Hao, P.K. Wong, Appl. Catal. B: Environ. 42 (2003) 47–55.
[27] E. Pelizzetti, V. Maurino, P. Piccinni, M. Vincenti, Coord. Chem. Rev. 125 (1993) 183–194.
[28] V. Maurino, C. Minero, E. Pelizzetti, N. Seprone, Fine Particles Science and Technology, 1996, pp. 707–715.
[29] D. Robert, A. Piscopo, J.V. Weber, Solar Energy 77 (2004) 553–558.
[30] A. Gora, B. Toepfer, V. Puddu, G.L. Puma, Appl. Catal. B: Environ. 65 (2006) 1–10.
[31] A.K. Gupta, A. Pal, C. Sahoo, Dyes Pigments 69 (2006) 224–232.
[32] A.P. Toor, A. Verma, C.K. Jotshi, P.K. Bajpai, V. Singh, Dyes Pigments 68 (2006) 53–60.
[33] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Chemosphere 46 (2002) 905–912.
[34] K. Soutsas, V. Karayannis, I. Poulios, A. Riga, K. Ntampegliotis, X. Spiliotis, G. Papapolymerou, Desalination 250 (2010) 345–350.
[35] C. Hu, J.C. Yu, Z. Hao, P.K. Wong, Appl. Catal. B: Environ. 46 (2003) 35–47.