

# Influence of ionic strength in the adsorption and during photocatalysis of reactive black 5 azo dye on TiO<sub>2</sub> coated on non woven paper with SiO<sub>2</sub> as a binder

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## Abstract

Reactive black 5 (RB5), an azo dye, was degraded by using UV-irradiated TiO<sub>2</sub> coated on non woven paper with SiO<sub>2</sub> as a binder. The adsorption capacity of the photocatalyst was studied at natural pH, superior to pH<sub>pzc</sub> of the binder, for various ionic strengths. Different salts such as NaCl, KCl, CaCl<sub>2</sub>, LiCl, Ca(NO<sub>3</sub>)<sub>2</sub> were used to increase the ionic strength. The presence of salt increased the adsorption capacity. The electrostatic interactions between dye and oxide surface charges (TiO<sub>2</sub>/SiO<sub>2</sub>) is very important in the adsorption phenomena. The effect of the ionic strength of the solution on photocatalyst degradation was studied. The rate of degradation was increased by the presence of salts in the range of the experimental conditions. The increase of the initial decolorization rate was observed in the following order: Ca<sup>2+</sup> > K<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup>. Experiments with different anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) had shown that nitrate was an indifferent electrolyte for the adsorption and photodegradation of the dye on SiO<sub>2</sub>/TiO<sub>2</sub>. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Photocatalysis; Water treatment; Azo dye; RB5

## 1. Introduction

Tannery factories are important users of dyes, and an important source of release of pollutants, especially in countries which are leading leather producers like China and North African countries. The discharge of highly colored wastewater into the ecosystem involves aesthetic pollution (even a small amount of dye is clearly apparent), and environmental problems such as the perturbation of aquatic life (some azo dyes and degradation products are highly carcinogenic [1]). Photocatalysis has been considered as a cost effective alternative for the purification of dye-containing wastewater [2,3]. Recent studies have demonstrated that photocatalysis can be used to mineralize organic compounds or degrade dyes [4–12] using TiO<sub>2</sub> under UV irradiation. Photocatalysis does not require expensive oxidants and can be carried out at mild temperature and pressure and these are the main advantages in comparison with other oxidation

processes. However, the obligation to separate the small TiO<sub>2</sub> particles from the suspension after treatment limits development of the process. Alternatively, the catalyst may be immobilized onto a suitable solid inert material, which eliminates the catalyst removal step [13–15]. As a consequence the specific area of catalyst decreases [16–17]. TiO<sub>2</sub> could be immobilized on a non woven paper with SiO<sub>2</sub> used as a binder.

The oxide surfaces of TiO<sub>2</sub> and SiO<sub>2</sub> in water are amphoteric and could be positively charged, negatively charged or neutral depending on the pH of the solution. For below the pH of zero charge (pH<sub>pzc</sub>), the oxide net surface charge is positive and above pH<sub>pzc</sub> the net surface charge is negative. Bandara et al. [18], had shown that adsorption of azo dye (Orange I, Orange II, Orange G) on the oxide surface could be attributed to reaction due to the electrostatic attraction between sulfonic moiety of the azo dye and positive charges of the oxide. They demonstrated that the sulfonic group of the dye participate to the adsorption mechanism for pH inferior to the pH<sub>pzc</sub> of the oxide and above the pK<sub>a</sub> of the sulfonic group (pK<sub>a</sub> ~ 1). In previous work [27] the authors had suggested that electrostatic attraction leads to the observed adsorption of RY 145 and RB5 azo dyes on SiO<sub>2</sub>/TiO<sub>2</sub>.

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Conversely, the adsorption at basic pH was prevented by repulsive electrostatic forces between  $-\phi-SO_3^-$  and  $TiO^-/SiO^-$  which were predominant in this range of pH.

In textile wastewater, a certain quantity of inorganic salts is present with dyes. As an example, NaCl, is used to promote

the transfer of dyestuff to the fabric and  $Na_2CO_3$  is used to produce covalent bonds between dyestuff and fabric [19]. Thus, a study of the effect of inorganic salts on dye photocatalytic was carried out. Table 1 lists studies dealing with the influence of inorganic salts on the photocatalysis degradation rate of organic

Table 1  
Experimental conditions for the study of the influence of inorganic salts on the photocatalyst degradation rate

Ions	Salt concentration (M)	Compounds	TiO <sub>2</sub>		pH range	Observations	References
Cl <sup>-</sup> /Na <sup>+</sup>	0–0.8	Benzamide parahydroxy benzoic	P25	S	5 < pH < 6 < pH <sub>pzc</sub>	Decrease of $r_o$ with increasing concentration of salt	[20]
Cl <sup>-</sup> /Na <sup>+</sup>	0.06	Ethanol, aniline, salicylic acid	P25	F	pH = 4.1 < pH <sub>pzc</sub>	Decrease of $r_o$ with increasing concentration of salt	[21]
Cl <sup>-</sup> /Na <sup>+</sup>	0.01	Omethyl benzoic acid	P25, Janssen	S	pH = 3 < pH <sub>pzc</sub>	Inhibitive effect on the reaction rate	[22]
Cl <sup>-</sup> /Na <sup>+</sup>	0.02	Methylene blue (cationic dye)	P25, PC500	F	pH = 7 to basic pH	Inhibitive effect on the reaction rate	[13]
Cl <sup>-</sup> /Ca <sup>2+</sup> , Mg <sup>2+</sup> , Zn <sup>2+</sup> , Ni <sup>+</sup> , Mn <sup>2+</sup> , Cr <sup>3+</sup> , Co <sup>2+</sup> , Fe <sup>3+</sup>	(0.28–1.1)·10 <sup>-3</sup>	Phenol	P25	S	4.1 < pH < 6.8*	(*) indication on the evolution of initial pH in relation with Cr <sup>3+</sup> concentration	[23]
F <sup>-</sup> /Na <sup>+</sup>	0.001–0.2	CBX (cationic dye), MX-5B (anionic dye)	P25	S	pH <sub>pzc</sub> < 8 < pH < 10.8	Decrease of $r_o$ with increasing concentration of salt	[7]
CO <sub>3</sub> <sup>2-</sup> /Na <sup>+</sup>	0.02	Methylene blue (cationic dye)	P25, PC500	F	pH = 7 to basic pH	Promoting effect on $r_o$ at basic pH	[13]
CO <sub>3</sub> <sup>2-</sup> /Na <sup>+</sup>	2.10 <sup>-3</sup>	Astrazone orange G (cationic dye)	Anatase	S	pH = 3.5	Promoting effect on $r_o$ at acid pH	[24]
SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	0.1–0.2	CBX (cationic dye), MX-5B (anionic dye)	P25	S	pH <sub>pzc</sub> < 8 < pH < 10.8	Increase of $r_o$ for CBX Decrease of $r_o$ for MX-5B	[7]
SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	0–0.1	Ethanol, aniline, salicylic acid	P25	F	pH = 4.1 < pH <sub>pzc</sub>	Decrease of $r_o$ with increasing concentration of salt	[21]
SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	1.7 × 10 <sup>-3</sup>	Astrazone orange G (cationic dye)	Anatase	S	pH = 3.5	Inhibitive effect to the reaction rate	[24]
SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	0.01	Omethyl benzoic acid	P25, Janssen	S	pH = 3 < pH <sub>pzc</sub>	Inhibitive effect to the reaction rate	[22]
NO <sub>3</sub> <sup>-</sup> /Na <sup>+</sup>	0.1	Ethanol, aniline, salicylic acid	P25	F	pH = 4.1 < pH <sub>pzc</sub>	No significant decrease of $r_o$	[21]
NO <sub>3</sub> <sup>-</sup> /Na <sup>+</sup>	2.3 × 10 <sup>-3</sup>	Astrazone orange G (cationic dye)	Anatase	S	pH = 3.5	Inhibitive effect to the reaction rate	[24]
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> /Na <sup>+</sup>	0–0.1	Ethanol, aniline, salicylic acid	P25	F	pH = 4.1 < pH <sub>pzc</sub>	Decrease of $r_o$ with increasing concentration of salt	[21]
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> /Na <sup>+</sup>	0–0.1	CBX (cationic dye), MX-5B (anionic dye)	P25	S	pH <sub>pzc</sub> < 8 < pH < 10.8	– pH 10.8 decrease of $r_o$ – pH 2.4 increase of degradation rate with an optimum concentration of salt	[7]

The letter S: TiO<sub>2</sub> used in suspension; F: TiO<sub>2</sub> fixed onto a support. P25 was purchased from Degussa (anatase/rutile) PC500 from Millenium (anatase), TiO<sub>2</sub> from Janssen (anatase).

compounds. It is noteworthy that, the initial pH studied was often below the  $\text{pH}_{\text{pzc}}$  of  $\text{TiO}_2$  and most of the researchers focused their research only on the effects of the inorganic anions. As a consequence, all the experiments were realized with sodium as the cation. Only Hu et al. [7] and Guillard et al. [13] carried out experiments with pH above  $\text{pH}_{\text{pzc}}$  and they found promoting or inhibiting effects on the photocatalysis degradation rate caused by the addition of inorganic salts. When ionic compounds are in solution they can influence electrostatic interactions between the oxide surface and the dye. The ionic strength was reported as an important parameter for the adsorption of dye on oxide surface [25]. Changing ionic strength will change the concentration of both cations and anions. So it was interesting to investigate the role of the positive ions during photocatalysis of the dye on  $\text{TiO}_2/\text{SiO}_2$  since the influence of the anions had been widely studied.

The aim of this study was to analyze the influence of inorganic salts on the photocatalytic dye removal using  $\text{TiO}_2$  coated on a non woven paper with  $\text{SiO}_2$  as a binder and pH conditions above  $\text{pH}_{\text{pzc}}$  of  $\text{SiO}_2$ .

## 2. Experimental

### 2.1. Chemicals

The dye, RB5, was purchased from the Moroccan textile industry and used without further purification. The molecular structure of the dye is given in Fig. 1. The salts NaCl, KCl,  $\text{CaCl}_2$ , LiCl and  $\text{Ca}(\text{NO}_3)_2$  (purity >98%) were obtained from Prolabo (France) and used without further purification. The ionic strength  $I$  of the solution is calculated with the Eq. (1):

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (1)$$

$C_i$ , concentration of charged species in solution ( $\text{mol L}^{-1}$ );  $Z_i$ , electric charge.

The water used in the experiments was obtained after purification through reverse osmosis (organic carbon =  $0.2 \text{ mg L}^{-1}$ ,  $\text{Cl}^- = 0.05 \text{ mg L}^{-1}$ ,  $\text{NO}_3^- = 0.07 \text{ mg L}^{-1}$ ).

### 2.2. Photocatalyst characteristics

The photocatalyst was PC-500 Titania from Millennium Inorganic Chemicals (anatase >99%; specific surface area > $320 \text{ m}^2 \text{ g}^{-1}$ ; mean crystallite size: 5–10 nm, characteristics from Millennium Chemicals company). Titania PC-500 was coated on non woven paper (natural cellulose fiber, 2 mm thick) using a binder. The binder was an aqueous dispersion of colloidal  $\text{SiO}_2$  ( $700 \text{ m}^2 \text{ g}^{-1}$ ). The cellulose fiber was coated with a

mixture of  $\text{TiO}_2$  and  $\text{SiO}_2$  ( $\text{TiO}_2/\text{SiO}_2$  mass ratio: 1) using a size press. The  $\text{TiO}_2$  surface loading determined after washing was  $25 \text{ g m}^{-2}$ . A detailed description of the photocatalytic material is given in Thevenet et al. [26].

### 2.3. Photoreactor and light source

Irradiation was performed in a cylindrical batch reactor ( $V_t = 700 \text{ ml}$ ,  $\varnothing = 10 \text{ cm}$ ) which was described in detail in previous studies [27] and will be briefly described here. A 25W low-pressure fluorescent lamp (Philips PL-L 24W/10/4P,  $\lambda_{\text{max}} = 365 \text{ nm}$ ) was placed vertically in a plugging tube. The radiant flux of the lamp was measured by means of a chemical actinometer (potassium ferrioxalate). The actinometer was irradiated under similar conditions as the experimental conditions used during the study. The incident photon flux,  $P_0$ , was estimated at about  $(3.64 \pm 0.07) 10^{-6} \text{ Einstein s}^{-1}$ .

### 2.4. Adsorption experiment

The adsorption isotherm of the dye on non woven paper coated with  $\text{TiO}_2$  was determined, in the dark, by mixing a 250 ml aliquot of aqueous dye solution for different initial concentrations,  $C_0$ , at constant pH (natural pH of the dye = 5.8) with addition of different salts. In all experiments the solution was in contact with 506 mg of  $\text{TiO}_2$  and 506 mg of  $\text{SiO}_2$  ( $1.875 \times 10^{-2} \text{ m}^2$  photocatalyst material). The temperature during the experiments was  $21 \pm 2 \text{ }^\circ\text{C}$ . The adsorption experiments with  $\text{TiO}_2$  alone in suspension was carried out in the same conditions.

### 2.5. Analyses

In a typical experiment, at scheduled times, 5 mL samples were taken from the reactor using a 10 mL syringe and then filtered through a Millipore filter ( $0.45 \mu\text{m}$ ) to stop particle entering the optical detection cell. The reaction was followed by UV–vis spectra using a Cary 50 (190–1100 nm) spectrophotometer. The kinetics of the reaction were obtained measuring the absorbance at  $\lambda = 597 \text{ nm}$  for RB5, at constant pH.

### 2.6. Photocatalytic degradation

In a typical experiment, the non woven paper coated with  $\text{TiO}_2$  was fixed on the inner wall of the photoreactor ( $3.7510^{-2} \text{ m}^2 = 1.01 \text{ g}$  of  $\text{TiO}_2$ ). Five hundred milliliters of RB5 solution of various concentrations were introduced into the photoreactor. The pH of the solution was the natural pH of the dye = 5.8. After adsorption equilibrium was carried out in the

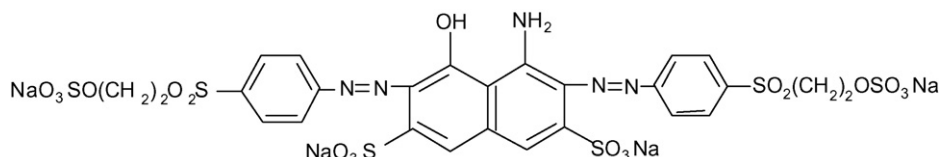


Fig. 1. Reactive black 5 (RB5) chemical structures. RB5 class: diazo; reactive group: sulfatoethylsulfone;  $\lambda_{\text{max}}$ (visible): 597 nm; molecular weight:  $991.8 \text{ g mol}^{-1}$ .

dark, the light was turned on to irradiate the solution and the first sample was taken ( $t = 0$ ).

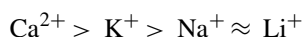
### 3. Results and discussion

#### 3.1. Effect of ionic strength on adsorption of RB5

##### 3.1.1. Influence of the cations on adsorption capacity

Dye adsorption depends strongly on electrostatic parameters such as oxide surface charge, pH, and ionic strength. In this paper the effects of the addition of LiCl, NaCl, KCl and CaCl<sub>2</sub> are studied at the natural pH of the dye (5.8) above  $\text{pH}_{\text{pzc}}$  of the SiO<sub>2</sub>, in order to highlight the effect of different cations on dye adsorption. The anions are expected to have no influence because of repulsive interactions.

Fig. 2 shows the amount of RB5 adsorbed on SiO<sub>2</sub>/TiO<sub>2</sub> and TiO<sub>2</sub> alone in suspension, for different ionic strengths. The amount of RB5 adsorbed on the TiO<sub>2</sub> alone in suspension is higher than the amount adsorbed on TiO<sub>2</sub> coated. This result is consistent with a decrease of specific area when TiO<sub>2</sub> is immobilized [16,17]. For experiments with TiO<sub>2</sub> alone in suspension when CaCl<sub>2</sub> was added, the amount of RB5 adsorbed on the oxide reached a maximum for ionic strength of 0.02 mol L<sup>-1</sup> and then decrease to be closed to the initial value for higher ionic strength. On the other hand, the amount of RB5 adsorbed decreased when KCl was added. This result highlight that the interactions between the TiO<sub>2</sub> surface and the cations are different and specific to the nature of the cations [29]. For adsorption experiments carried out on SiO<sub>2</sub>/TiO<sub>2</sub>, the effect of the addition of salts is an increase in the adsorption. In the range of concentration tested, in all cases the amount adsorbed reached a plateau. The amount of dye adsorbed on catalyst, at the plateau, varied in the following order:



If the  $\text{pH}_{\text{pzc}}$  of SiO<sub>2</sub> and TiO<sub>2</sub> are independent of each other, it could be assumed that at the experimental pH (5.8), the net surface charge of SiO<sub>2</sub> is negative ( $\text{pH}_{\text{pzc}} = 2.5$ ) and the net surface charge of TiO<sub>2</sub> is positive (with lot of neutral site;  $\text{pH}_{\text{pzc}} = 6.2$ ).

Since the amount of RB5 adsorbed on TiO<sub>2</sub> alone in suspension was increased when CaCl<sub>2</sub> was in solution, it could

be assumed that a part of the amount of RB5 adsorbed on SiO<sub>2</sub>/TiO<sub>2</sub>, in presence of CaCl, is also adsorbed on TiO<sub>2</sub> surface. In a different way, when KCl is added, the amount of the dye adsorbed on SiO<sub>2</sub>/TiO<sub>2</sub> is improved whereas a decrease of the amount of RB5 adsorbed on TiO<sub>2</sub> alone in suspension was observed (Fig. 2). Hence, it can be assumed that potassium neutralized the negatives sites of SiO<sub>2</sub> and diminished the electrostatic repulsion, then the dye could be closer to surface of TiO<sub>2</sub> and SiO<sub>2</sub> and adsorption could occur.

It can be stated that there are interactions between oxide surface, cations and the dye whatever the cation is, two phenomena could be considered:

- The addition of salts, hence the increase of the ionic strength, hindered the electrostatic repulsive effects by a compression of the electric double layer (EDL) as argued by Guillard et al. [13] and Hoogeven et al. [28]. Following this reasoning, the better efficiency of Ca<sup>2+</sup> to improve adsorption is in relation with the high valency in comparison with the monovalent ion, as cations with a strong electrostatic field (multicharged) are the most efficient at compressing the EDL. However, this assumption does not explain the difference observed between the three monovalent ions. Indeed, when the type of ion, at a given valency, has a significant effect on the adsorption of a substrate on an oxide, the ion must have a specific interaction with either the substrate or the oxide [29], unlike in the EDL theory.
- The addition of cations allows the neutralization of the negative sites of SiO<sub>2</sub> and hence the electrostatic repulsion barrier is hindered and non-electrostatic interactions between dye and neutral site can occur. These non-electrostatic interactions could be low energetic H-Bonds, or Van Der Waals short interactions. In this case there is no competition between dye and the negative accompanying ion.

These assumptions can explain the adsorption of dye versus different cations and ionic strengths, but it is difficult to predict what the effects will be. In our experimental conditions it is difficult to estimate the ratio of the dye adsorbed only on TiO<sub>2</sub>, since the dye is both adsorbed on TiO<sub>2</sub> and SiO<sub>2</sub>. However, if the enhancement of the amount of dye adsorbed on the oxide involves an increase of the initial degradation rate, it would prove that a part of the dye adsorbed on TiO<sub>2</sub> increases when the ionic strength increases because the higher the amount adsorbed on TiO<sub>2</sub> the higher the initial degradation rate.

##### 3.1.2. Influence of the anions

Above  $\text{pH}_{\text{pzc}}$ , the main electrostatic interactions between oxide surface site and ionic compounds occur with cations because the net oxide surface is negative. As suggested previously, firstly the anions are expected to not influence the adsorption capacity of the solid if the net surface is considered homogeneously negative charged. Nevertheless, if the heterogeneity of the surface is taken into consideration (distribution of positive, negative, and neutral sites), electrostatic interactions, implying positive surface sites and anionic compounds, could take place. In this case, anions could compete with the

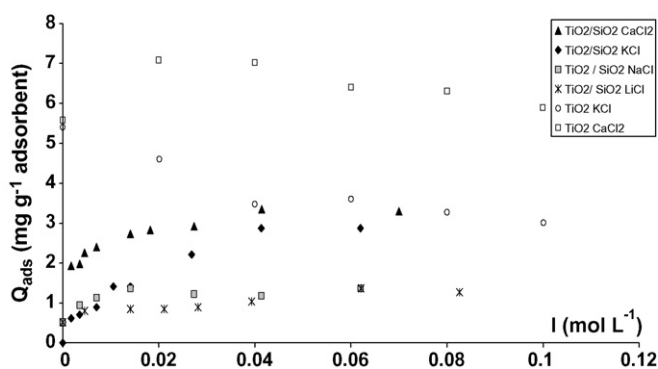


Fig. 2. Influence of the ionic strength of the solution for different cations on the amount of RB5 adsorbed onto photocatalyst material,  $C_0 = 40 \text{ mg L}^{-1}$ ,  $T = 21 \pm 2 \text{ }^\circ\text{C}$ .

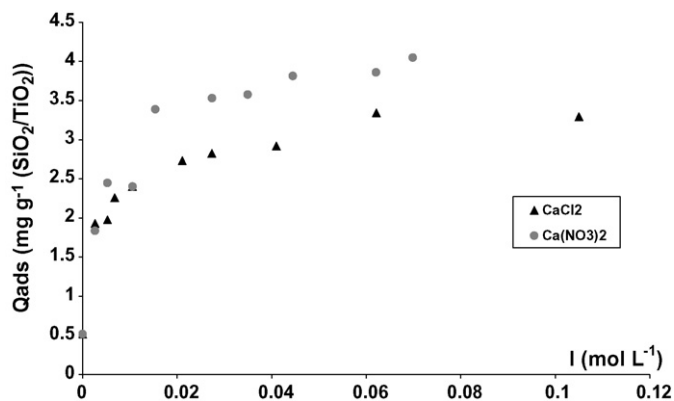


Fig. 3. Influence of the ionic strength of chloride and nitrate on the amounts of RB5 adsorbed onto photocatalyst material,  $C_0 = 40 \text{ mg L}^{-1}$ ,  $T = 21 \pm 2^\circ \text{C}$ .

dye, which is why we studied the influence of the nature of the accompanying anion on the adsorption of the dye on the catalyst support. Fig. 3 shows the amount of dye adsorbed on the catalyst for different concentrations of  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$ . It appears clearly that the amount of dye adsorbed is lower when  $\text{CaCl}_2$  is added in solution, rather than when  $\text{Ca}(\text{NO}_3)_2$  is added. This result emphasizes that the nature of the anion should be considered even if the ratio of positive sites is very low ( $\text{pH} > \text{pH}_{\text{pzc}}$ ). The less inhibiting effect of nitrate ion on adsorption capacity is consistent with the work of Bohmer et al. [30], which stated that nitrate was an indifferent electrolyte for the study of the

adsorption of PAA on  $\text{TiO}_2$  for pH above  $\text{pH}_{\text{pzc}}$ . So the chloride ion could compete with the dye when electrostatic interactions occur even if the phenomenon does not predominate compared to the beneficial effect on adsorption observed with the cations since the amount of negative and neutral sites are predominant in comparison with the amount of positive sites.

### 3.2. Photocatalytic degradation rate

#### 3.2.1. Influence of the ionic strength of different cations

Fig. 4a–d show the degradation of RB5 dye versus time for KCl, NaCl, LiCl and  $\text{CaCl}_2$  salts. In these experiments, the addition of salt increases the initial degradation rate, and decreases the time necessary to bleach the solution. In the case where  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Li}^+$  were added, the degradation rate increases progressively with increasing salt concentration in the solution and then reaches a limit degradation rate for salt concentration superior to  $1 \text{ g L}^{-1}$ . When  $\text{CaCl}_2$  salt is used, whatever the concentration is, the degradation curves versus time are very close. An enhancement of the degradation rate appears since the concentration of  $\text{CaCl}_2$  is equal to  $0.13 \text{ g L}^{-1}$ . These results indicate that the addition of salts for the pH tested do not diminish the kinetics of photocatalyst degradation of the dye, contrary to the results already observed by several authors [7,20–22,24]. The increase in the degradation rate when salt is added in solution can be correlated with the increase in the amount of dye adsorbed on  $\text{TiO}_2$ , since several authors [13,27] had proved that an increase of adsorption increases the photocatalytic degradation rate.

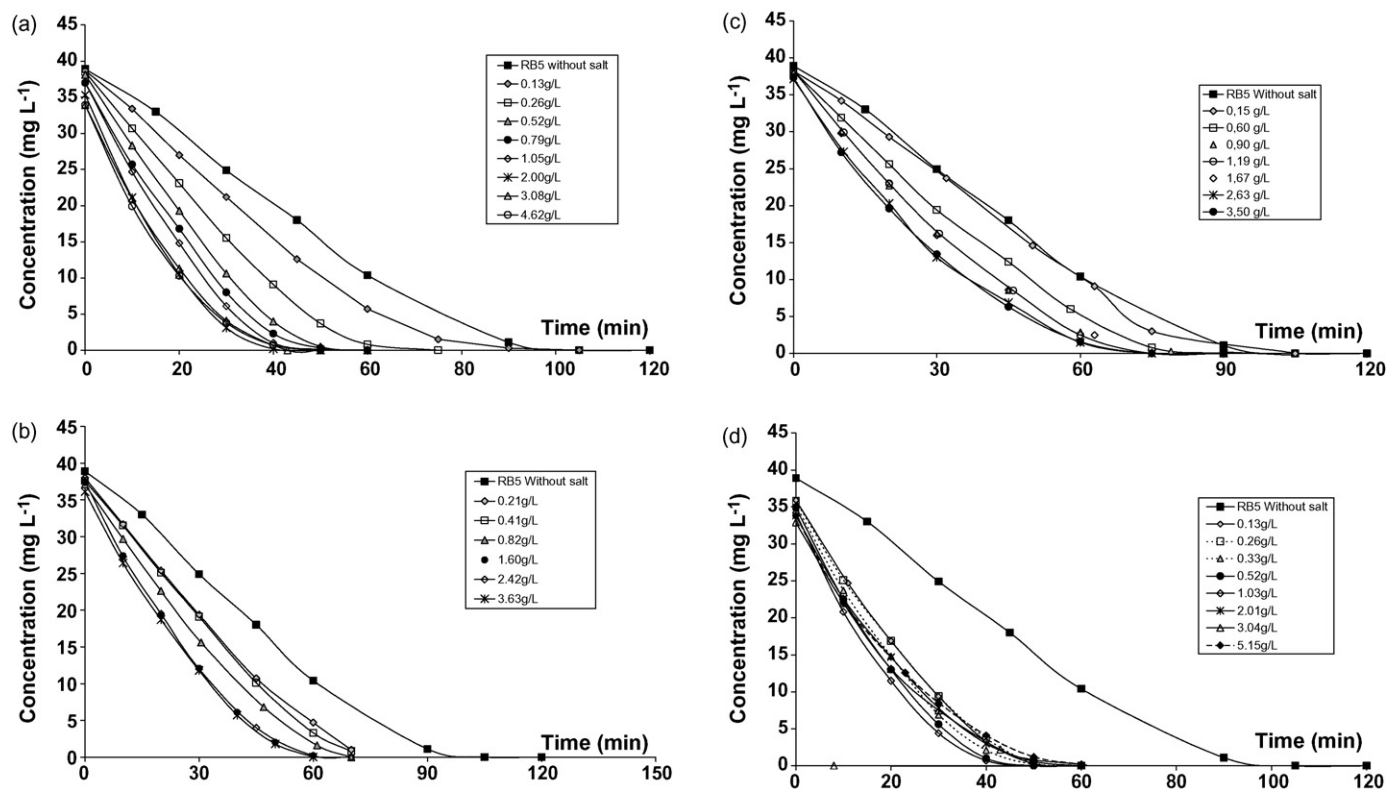


Fig. 4. (a) Effect of KCl concentration on the RB5 decolorization kinetics at natural pH. (b) Effect of NaCl concentration on the RB5 decolorization kinetics at natural pH. (c) Effect of LiCl concentration on the RB5 decolorization kinetics at natural pH. (d) Effect of  $\text{CaCl}_2$  concentration on the RB5 decolorization kinetics at natural pH.

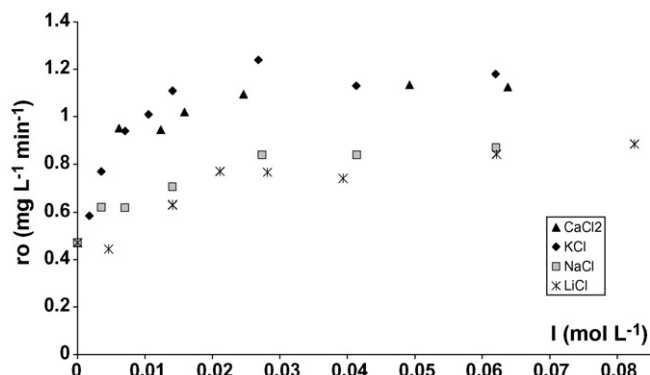


Fig. 5. Influence of ionic strength ( $I$ ) on the initial decolorization rate of RB5 for different cations,  $C_0 = 40$  ppm, natural pH.

The study of the initial degradation rate versus ionic strength ( $I$ ), shown in Fig. 5 indicates that for an ionic strength inferior to  $0.02 \text{ mol L}^{-1}$ , the sequence of the initial degradation rate versus the different cations is in accordance with the sequence of the amount of dye adsorbed when the respective cations are added in the solution:  $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ \approx \text{Li}^+$ . For ionic strengths superior to  $0.02 \text{ mol L}^{-1}$  the value of  $r_0(\text{Ca}^{2+})$  was close to the value obtained with  $\text{K}^+$ . The direct reaction of  $\text{Ca}^{2+}$  and the  $\text{TiO}_2$  surface is excluded as argued by Brezova et al. [23] whereas the scavenging effect of anions has been widely documented.

There are two fractions adsorbed on the photocatalyst material: the fraction adsorbed on the  $\text{TiO}_2$  which underwent decolorization under UV irradiation and the fraction adsorbed on the silica binder the colour of which slightly remains after decolorization of the solution. The adsorbed molecules on  $\text{SiO}_2$ , are far from the catalyst surface. The probability of reacting with radicals or with the  $\text{h}^+/\text{e}^-$  on the photocatalytic surface is reduced. A slow diffusion transport of the dye adsorbed on  $\text{SiO}_2$  (non photo reactive) to the  $\text{TiO}_2$  might occur, so degradation is slow.

The nature of the accompanying anion influenced the amount of dye adsorbed; it could also be implicated in the radical reaction by scavenging the hydroxyl radical even if the net benefit of the cations is predominant for the apparent degradation rate compared to the case of photocatalysis without salts.

### 3.2.2. Influence of the ionic strength for different accompanying ions

The trend of the initial degradation rate of dye in the presence of  $\text{Ca}(\text{NO}_3)_2$  is monotonic with increasing salt concentrations (Fig. 6) in correlation with the amount of dye adsorbed (Fig. 3). The nitrate should not react with hydroxyl radicals near the oxide surface or form radicals which are reactive enough to not decrease the initial rate. Even a lower amount was adsorbed on oxides at the plateau when  $\text{CaCl}_2$  was in solution, the maximum value of  $r_0$  was close to the one reached when  $\text{Ca}(\text{NO}_3)_2$  was in solution. These results was surprisingly since less of dye was adsorbed and the chloride have a scavenging effect and therefore should decrease the oxidation rate. To explain this result, it could be assumed that the higher amount adsorbed on  $\text{TiO}_2/\text{SiO}_2$ , when nitrate are in solution, was mainly adsorb on  $\text{SiO}_2$ , and

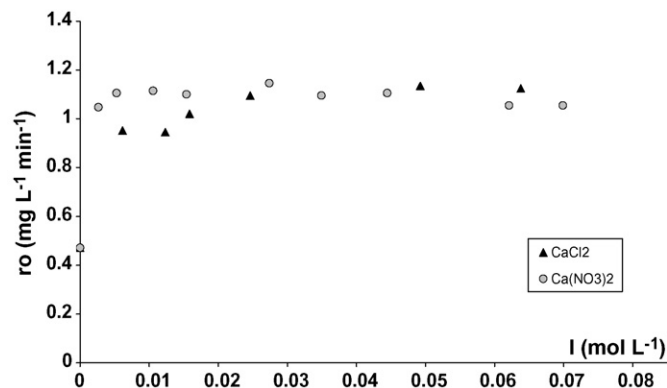


Fig. 6. Influence of ionic strength ( $I$ ) on the initial decolorization rate of RB5 ( $r_0$ ) in the presence of  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  salts,  $C_0 = 40 \text{ mg L}^{-1}$ , natural pH.

then this part of dye adsorbed on silica binder did not participate to degradation reaction.

## 4. Conclusion

The results of our study showed that the degradation of RB5 azo dye, carried out using coated  $\text{TiO}_2$  paper fibers, was strongly influenced by the ionic strength of the solution. It has been proved that above  $\text{pH}_{\text{pzc}}$  of  $\text{SiO}_2$ , the cations of the solution increased the amount of dye adsorbed onto the photocatalyst support. The contraction of EDL by the ionic compounds, the neutralization of negative sites by the cations were proposed to illustrate the electrostatic interactions between oxide surface and the dye. This study highlights the importance of the heterogeneity of the charge distribution at the oxide surface and is one of the reasons for the complexity of the phenomena. In correlation with the enhancement of the amount of dye adsorbed onto the catalyst support, an increase of the initial decolorization rate was observed in the following order:  $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+ \approx \text{Li}^+$ . To complete these results, experiments were carried out with different anions, even if they should had few influence on the degradation rate. However, the nature of the anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) could be important since the comparison of the amount of dye adsorbed and the decolorization rate showed that nitrate was an indifferent electrolyte and the distribution of the amount of dye adsorbed on  $\text{TiO}_2/\text{SiO}_2$  could be different according to the nature of the accompanying anion.

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