

Effect of adsorption on the photocatalysis performance of anthraquinone dye

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ABSTRACT

The adsorption and photocatalytic efficiency of several TiO₂ suspended catalysts were compared to see how well they could degrade the organic pollutant anthraquinone dye Reactive Blue 2 (RB2). The adsorption of RB2 on catalysts follows the Langmuir model and adsorption capacity's influence on degradation performance has been established. Correlations between degradation kinetics and the amount of dye adsorbed (q_{ads}) were then determined. The expected correlation between specific surface and q_{max} was verified. The addition of sulphate ions in the case of catalysts Degussa P25 and TiO₂-Ishihara ST01 was found to inhibit adsorption of RB2 on the TiO₂ surfaces. The hindrance of adsorption in acidic conditions improved the efficiency of the photocatalytic degradation of ST01. No adsorption was observed in alkaline pH and the photodegradation kinetic was generally higher in this condition except for that seen in photocatalysts with a low recombination rate.

Key words | adsorption, anthraquinone dye, Langmuir model, photocatalytic degradation, recombination rate

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INTRODUCTION

Photocatalytic detoxification is a promising technology for destroying organic pollutants, and especially textile dyes. Titanium dioxide (TiO₂) is widely used as photocatalyst, since it is well known to be capable of oxidizing various pollutants, non-toxic, chemically stable, and commercially available (Ao *et al.* 2004, 2007; Ghezzar *et al.* 2007). However heterogeneous photocatalysis is very complex process. On one hand, it can involve a number of steps such as diffusion (Bousselmi *et al.* 2004), adsorption and oxidation influenced by experimental parameters (Lachheb *et al.* 2002). On the other hand, the relationship between TiO₂ properties and the photocatalytic reaction kinetic is a complex one that depends on several parameters such as competing adsorption between water and pollutants, light absorption and recombination rate of photoproduced charges linked to density of defects (Wiszniewski *et al.* 2002; Enriquez & Pichat 2006; Zayani *et al.* 2008). Numerous studies linked closely adsorption properties of

photocatalysts and pollutants to photocatalytic performance by applying the Langmuir–Hinshelwood model. This model can be used as a guideline to estimate treatment time (Arslan *et al.* 2000; Muruganandham & Swaminathan 2004; Son *et al.* 2004; Zayani *et al.* 2006; Gomathi *et al.* 2009).

The purpose of this study is to further investigate the relationship between adsorption and photocatalysis performance. This relationship depends on pollutant compounds; an anthraquinone dye (Reactive Blue 2, RB2) was herewith considered. Anthraquinonic dyes represent the second most important class of commercial dyes after azo-compounds and such type of textile dye was consequently widely investigated (Lachheb *et al.* 2002; Sauer *et al.* 2002; Ao *et al.* 2007; Ghezzar *et al.* 2007). Three different steps were taken in order to modify adsorption properties: (i) nine photocatalysts were tested, (ii) acidic, and alkaline pH were applied and (iii) competitive adsorption was introduced using SO₄²⁻ ions.

MATERIALS AND METHODS

Chemical and reagent products

Several types of TiO₂ were used in the photocatalytic degradation of RB2 in water. Suspensions were prepared at the optimal concentration amount of 1 g L⁻¹ (Lachheb *et al.* 2002; Sauer *et al.* 2002; Wiszniowski *et al.* 2002). The characteristics of the photocatalysts, taken from the manufacturer's data and the X-ray diffraction analysis (Philips, type PAN analytical (X Pert PRO-MPD)), are described in Table 1. The selected titanium dioxides had specific surfaces ranging from 50 to 320 m²/g and crystal sizes from 6 to 30 nm. The main crystallite phases of photocatalysts are presented in Table 1. However, the amorphous content in the titanium dioxide samples is not known and may play a significant role on adsorption and photocatalytic processes.

The organic pollutant was Reactive Blue 2 (RB2), an anthraquinone dye (Aldrich) with 60% purity, a blue colour ($\lambda_{\text{max}} = 619 \text{ nm}$) and the molecular formula presented in Figure 1. The maximum molecular diameter was approximately 20 Angstrom. Molar Volume was estimated at 419.4 ± 3.0 cm³, and the density at 1.845 ± 0.06 g/cm³. The SO₄²⁻ anions were introduced in Na₂SO₄ form.

Experimental

Adsorption tests

Batch adsorption experiments were carried under dark conditions at the temperature of 25 ± 1°C. During

adsorption tests, dye solutions (20 ml) with known amount of RB2 were adjusted to the desired pH then time was started simultaneously with the addition of TiO₂ powder (1 g L⁻¹). The suspension was agitated with a magnetic stirrer in the dark and samples were taken at different times during 2 to 3 h. The concentration of RB2 was varied from 30 to 476 μmole/L. The initial pH was adjusted to the required value (2.5 and 9.5) either by using HCl or KOH.

Photoreactor and light source

A cylindrical annular Pyrex photoreactor was used (total illuminated volume 1 L) with an external water jacket for temperature control. The light source was a high pressure mercury lamp (Cathodeon HPK 125 W; $\lambda > 253 \text{ nm}$) which was placed vertically into a plunging tube. The illuminated volume was equal to 1 litre. Before photocatalysis tests, suspensions of TiO₂ (1 g L⁻¹) in the dye solution were stirred 30 minutes in the dark at 25°C, a sufficient time to reach dye equilibrium concentration. The UV light was then switched on for 3 hours to monitor discoloration kinetics. Photocatalytic experiments were carried out at 25°C and at different pHs (2.5 and 9.5). An initial concentration (C_i) of 119 μmole/L was selected basing on two criteria. First we have to prevent total adsorption to have the possibility to follow photocatalytic degradation in the solution and secondly the absorbance versus concentration has to obey a linear Beer–Lambert relationship under operational conditions.

Table 1 | Characteristics of photocatalysts

Manufacturer	Photocatalyst	Specific surface m ² /g	TiO ₂ allotropic phases	Crystal size (nm)	pH _{zpc}
Degussa	P25	50	80% Anatase 20% Rutile	30	6.6–5.9
Degussa	F618	130	90% TiO ₂ (Anatase)	15–20	5.1
Sachtleben Chemie	UV 100	250–270	100% TiO ₂ (Anatase)	9	5.7
Millenium	PC 50	40–50	100% TiO ₂ (Anatase)	20–30	4.07
Ishihara	ST 01	320	95% TiO ₂ (Anatase)	7	6.35
Ishihara	ST 21	50	95% TiO ₂ (Anatase)	20	5.95
Tayca	MT 100	293	92.8% TiO ₂ (Anatase)	6	6.7
Tayca	TKP 101	290	84.2% TiO ₂ (Anatase)	6	3.2
Tayca	TKP 103	254	90.3% TiO ₂ (Anatase)	6	7.8

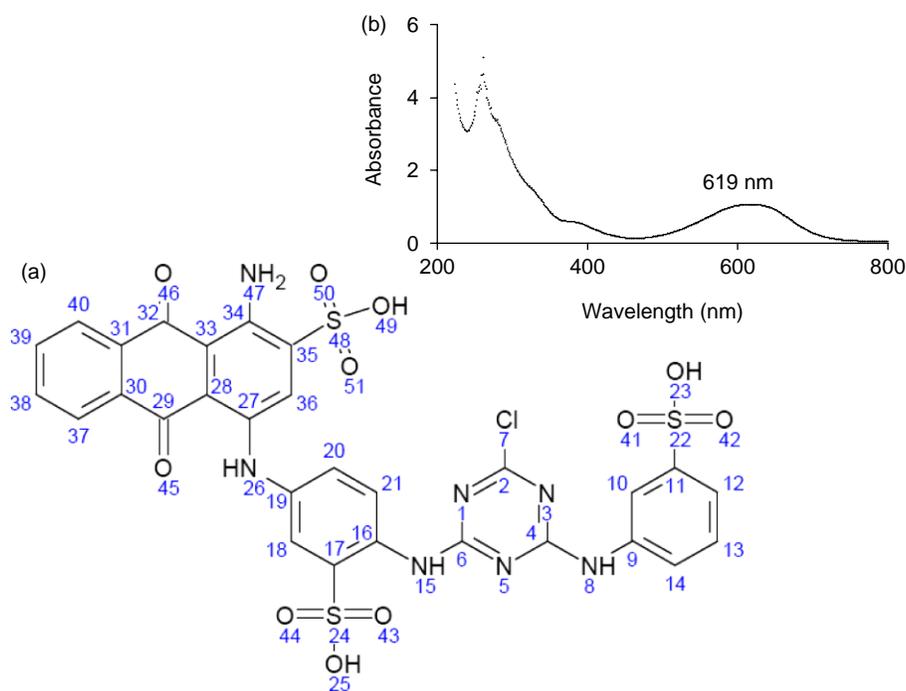


Figure 1 | (a): Molecular formula of RB2; (b): UV spectra of RB2.

As the first criterion was not verified for some photocatalysts with high specific surface, for these cases, initial concentration of 238 $\mu\text{mole/L}$ was applied for better monitoring of RB2 in solution during degradation. The maximum initial concentration is also limited by the solubility of RB2 at pH 2.5.

Analyses

Suspension samples taken at different irradiation times during adsorption and photocatalytic tests are instantly filtered through a Millipore syringe filter (0.45 μm) to separate TiO_2 particles, 0.45 μm pore size is below the TiO_2 agglomerations size estimated by SEM observation. The analysis of dye remaining in solution was done calorimetrically using UV-Visible spectrophotometer (*Thermospectronic UV1*). The wavelength of 619 nm, in the visible spectrum of RB2 (Figure 1), was selected to monitor the disappearance of the dye. The calibration graph of the absorbance versus concentration obeyed a linear Beer-Lambert relationship under operational conditions.

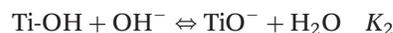
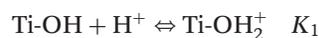
RESULTS AND DISCUSSION

Adsorption

In order to determine the effect of pH, three conditions were tested: acidic pH (2.5), neutral and alkaline pH (9.5). Adsorption of RB2 was not observed at neutral and alkaline pH, while it was very fast for acidic one. Such a result can be better understood taking into account both the surface state of titania and the ionization state of the dye.

Effect of pH on photocatalysts and RB2

The adsorption of H_2O molecules at surface metal sites is followed by the dissociation of OH groups leading to coverage with chemically equivalent Titanium hydroxyl groups (Ti-OH). The following two equilibria are then considered



The zero point of charge pH_{ZPC} of TiO_2 particles is defined as the pH at which the concentrations of

Table 2 | Apparent pKa values and Single pKa values for unprotonated and protonated species

Atom number	Atom	Approximated apparent pKa value		Acidic/basic		
		Unprotonated species	Error	Protonated species	Single pKa value	Error
5	N	2.65	0.1	MB	2.26	0.1
23	O	-0.99	0.3	A	-0.63	0.3
25	O	-1.14	0.5	A	-0.73	0.5
49	O	-1.22	0.2	MA	-1.2	0.2
47	N	-5.0	0.2	B	-4.24	0.2
1	N			B	-1.63	0.1
3	N			B	-1.41	0.1
26	N			B	-4.19	0.2
8	N			B	-0.29	0.5
15	N			B	-1.41	0.5

Notes: A, acid; B, basic; M, mild.

protonated and deprotonated surface groups are equal (Lakshmi *et al.* 1995):

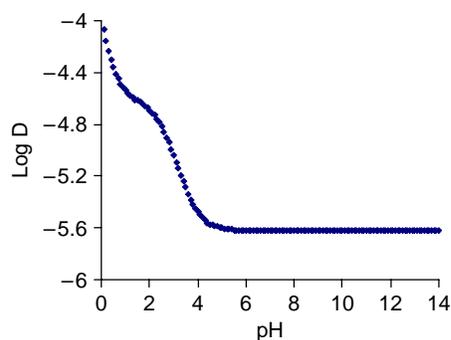
$$\text{pH}_{\text{zpc}} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) \quad (1)$$

As a consequence of this, catalyst surfaces are predominantly positively charged in pH 2.5 below their pH_{ZPC} (see Table 1) and negatively charged above.

On the other hand RB2 is an anionic dye bearing the three anionic sulfonate functions (cf. Figure 1(a)) (Sauer *et al.* 2002). It is conceivable then that at high pH values an electrostatic repulsion between TiO_2 and the dye occurs leading to the hindrance of adsorption. Similar observations were found for both the Acid Blue 25 anthraquinone anionic dye (Bouzaida *et al.* 2004) and for an azo dye having similar three sulphonate groups (Muruganandham & Swaminathan 2004).

Whereas, it is likely at high pH, the sulfonate groups of RB2 will be deprotonated, it is not at all clear that the various amine groups will not be protonated, especially at acidic pH. If they were protonated, then the dye overall would have a positive charge, rather a negative charge which will have a high effect on RB2 adsorption. It is necessary in this case to identify and attribute the various pKa transitions of RB2 dye, which are not readily available in the literature. Physical Property Prediction of RB2 was conducted using ACD/Labs pKa software ACD/Labs (2009),

a tool with capabilities for communicating information about molecular structures and properties. Table 2 is a summary of apparent pKa calculation and single pKa value for protonated species corresponding to specific atoms on RB2 molecule of Figure 1. Single pKa values for all possible dissociation centers, are calculated considering the rest of the molecule neutral. Only one nitrogen (number 5 of Figure 1) presents a positive value of apparent pKa. Figure 2 represents log D function of pH, calculated using ACD/Labs logD software ACD/Labs (2009), which varies according to the protogenic nature of the molecule: ability to donate a hydrogen ion (proton) in a chemical reaction. As expected RB2 presents acid behaviour and last deprotonation will be achieved at pH close to 2.3.

**Figure 2** | Log D function of pH curve of RB2.

Adsorption results

Acidic pH was set at 2.5, less than the pH_{ZPC} of all photocatalysts leading to positive charge of catalyst surfaces. At this pH, RB2 is expected to have a global negative charge. For all photocatalysis, adsorption is very fast during the two first minutes followed by constant concentration of the dye in the solution corresponding to the adsorption equilibrium concentration (C_e). This behaviour are due to electrostatic attractions between the positively charged TiO_2 ($\text{pH} < \text{pH}_{\text{zpc}}$) and an expected negatively charged dye anion. It was particularly noteworthy that the process showed an extraordinarily fast initial rate of adsorption corresponding to more than 90% of the equilibrium amount of the dye. This behaviour was obtained by Xiong *et al.* (2010) and considered as indicative of a fast initial external mass transfer step which is in agreement with well shaken adsorption system and fast chemical ion surface attachment (Belessi *et al.* 2009).

The adsorbed dye amount onto the TiO_2 (mg/g) at equilibrium (q_e) were calculated from the following equation:

$$q_e = \frac{C_i - C_e}{M} V \quad (2)$$

where C_i , C_e are the initial and equilibrium dye concentration in the dark, V the solution volume (L) and M the photocatalyst mass (g). Figure 3 represents an example of the evolution of q_e vs. C_e .

The two common adsorption isotherm models Langmuir and Freundlich are used to fit experimental results. Better fitting is obtained with Langmuir model using Equation (2) with good correlation coefficient R^2 (Table 3). This was expected since Langmuir adsorption model was widely verified for textile azo and anthraquinonic dyes

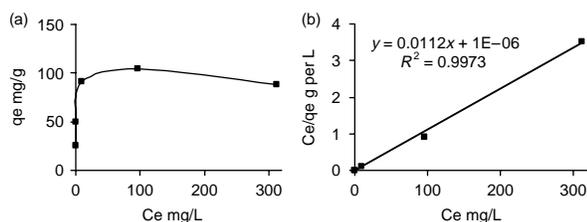


Figure 3 | (a) Adsorption isotherm obtained with TKP101, (b) corresponding Langmuir adsorption isotherm.

Table 3 | Adsorption constants of RB2 on different photocatalysts at pH 2.5

Photocatalyst	q_{max} ($10^{-6} \text{ mol g}^{-1}$)	$1/K_{\text{ads}}$ ($10^{-6} \text{ mol L}^{-1}$)	R^2	SA = q_{max}/SS (10^{-6} mol/m^2)
P25	82	0.0408	0.99	1.64
ST21	73	0.0026	0.99	1.46
F618	63	$< 10^{-4}$	0.97	0.48
PC50	58	0.1786	0.93	1.29
UV100	200	0.0047	0.99	0.77
MT100	208	$< 10^{-4}$	0.99	0.71
TKP101	106	$< 10^{-4}$	0.99	0.36
TKP103	220	0.0021	0.99	0.86
ST 01	222	$< 10^{-4}$	0.99	0.69

(Lachheb *et al.* 2002; Bouzaida *et al.* 2004; Muruganandham & Swaminathan 2004; Zayani *et al.* 2006, 2008).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}} \cdot K_{\text{ads}}} \quad (3)$$

q_{max} is the maximum amount of adsorbed dye corresponding to monolayer coverage; K_{ads} is the Langmuir adsorption equilibrium constant. The q_{max} and K_{ads} presented in Table 3 were calculated from the slope and intercept respectively. However, for some photocatalysts, the intercept value is very low (as observed in Figure 3(b)) corresponding to very high K_{ads} . Such a value of K_{ads} has to be used carefully since a very slight variation in the calculation of the ordinate at the origin can give rise to a significant variation of K_{ads} value (Bouzaida *et al.* 2004), only indication is presented in Table 3.

Also, it should be noted that irregular decrease in the amount of adsorbed dye (q_{ads}) with high initial concentration ($476 \mu\text{mol L}^{-1}$) was observed for some photocatalysts (an example is presented in Figure 3(a)). At this point, it should be mentioned that in addition to pH, which strongly influences adsorption, the coverage of the surface is significantly affected by the potential of the interface region. Thus the accumulation of the negatively charged ions of RB2 in this region causes the development of a negative charge, which may inhibit adsorption of the ions of the dye (Belessi *et al.* 2009) at high concentration.

Specific surface is the major parameter acting on adsorption. Figure 4 shows the q_{max} function of the TiO_2 specific surface (SS) and pH_{ZPC} is indicated. Two groups are detected: one characterized by a SS less than $150 \text{ m}^2/\text{g}$

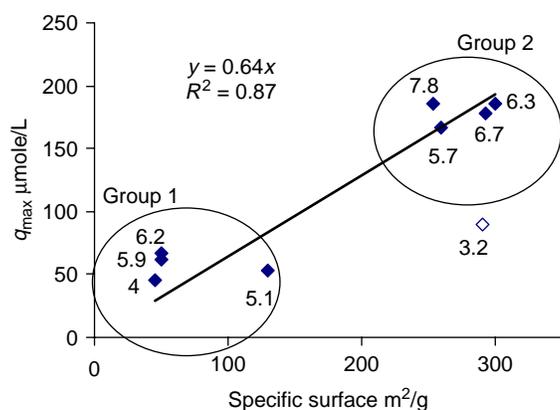


Figure 4 | q_{\max} function of specific surface at pH 2.5; pH_{ZPC} is indicated.

(G1) and the other by a SS greater than $250 \text{ m}^2/\text{g}$ (G2). The general observed trend is that high specific surface leads to high q_{\max} and correlation is obtained with correlation coefficient fairly large (Figure 4) if we consider the large variation of photocatalysts proprieties. However, the catalyst TKP101 in particular, had a q_{\max} lower than expected. It has the lowest pH_{ZPC} (SS = $290 \text{ m}^2/\text{g}$ and $\text{pH}_{\text{ZPC}} = 3.2$) nearest to the pH solution; the potential of zero charge is shown to be linear function of the pH_{ZPC} (McCafferty 2009). Also, when the pH approached pH_{ZPC} , the repulsive forces between TiO_2 particles decreased causing particle aggregation with influence on reactive surface area and impacting on the dye uptake (Belessi *et al.* 2009). For the other catalysts of G2, pH_{ZPC} was between 6.35 and 7.8, far from the pH solution.

For all of the other catalysts, specific adsorption (SA) of RB2 was characterised by an average of $1.46 \pm 0.17 \mu\text{mole}/\text{m}^2$ and $0.76 \pm 0.08 \mu\text{mole}/\text{m}^2$ for G1 and G2, respectively (Table 3).

If assumed that the highest value of $1.64 \mu\text{mole}/\text{m}^2$ obtained with P25 corresponds to one layer of recovery according to the Langmuir hypothesis, it appears that only 42 to 52% of the surface of G2 catalysts is available for RB2 adsorption. Three possibilities may explain this phenomenon: (i) first, catalyst particle agglomerations can be expected in the solution, especially with small particles, and/or (ii) secondly, the upper surface contains micropores which are not accessible to RB2. Micropore diameter was estimated by the SF Pore Diameter Method using Quantachrome at 34.7 and 33.8 Angstrom for TKP103 and UV100, respectively, close to RB2 molecule dimension. They both

have similar q_{\max} as well. The ST01 micropore has a maximum pore diameter of 15 nm (Zayani *et al.* 2006). The third possibility (iii) may be due to TiO_2 particles surrounded by several layers of well-organized, adsorbed water linked via hydrogen bonding to surface hydroxyl groups, hindered dye penetration. This layer is denser for TiO_2 samples not thermally treated, such as was the case for ST01 and UV100 (Zayani *et al.* 2006).

The high values of the adsorption constants mean that adsorption was very fast. No clear relationship was obtained either between adsorption constant and the specific surface (SS) or with the driving force pH_{ZPC} . However, the lowest adsorption kinetic constants were obtained first with PC50, and then followed by P25.

Photocatalysis

pH 2.5

The dye solution was magnetically stirred in the dark during 30 min before irradiating the reactor to make sure that adsorption equilibrium was reached. An initial concentration of RB2 (C_i) of $119 \mu\text{mole}/\text{L}$ was applied to all catalysts except MT100, TKP101, ST01 and TKP103 where a higher initial concentration was necessary to track RB2 degradation as all of the RB2 was adsorbed. In these four cases, C_i was $238 \mu\text{mole}/\text{L}$. However, no clear C_{eq} decrease was observed with TKP101 and MT100 during photocatalysis. For the other photocatalysts, the evolution of C_{eq} in the solution was monitored during reaction time (Figure 5(a)). Discoloration kinetics of RB2 at pH 2.5 followed an apparent first-order kinetic model. The apparent rate constant (k_{app}) was obtained by fitting the linear plot of $\ln(C/C_{\text{eq}})$ versus time (insertion in Figure 5(a), $C_{\text{eq}} = C_0 =$ concentration just before UV irradiation) and presented in Table 4.

Disappearance of RB2 without TiO_2 was carried to compare the efficiency of the photocatalytic degradation with that of direct photolysis. As expected, the direct photolysis is much slower than photocatalytic degradation since an apparent constant kinetic of 0.014 h^{-1} was obtained.

During photocatalytic experiments, intermediates are formed and may interfere in the determination of RB2 concentration based on bleaching of the solution (followed

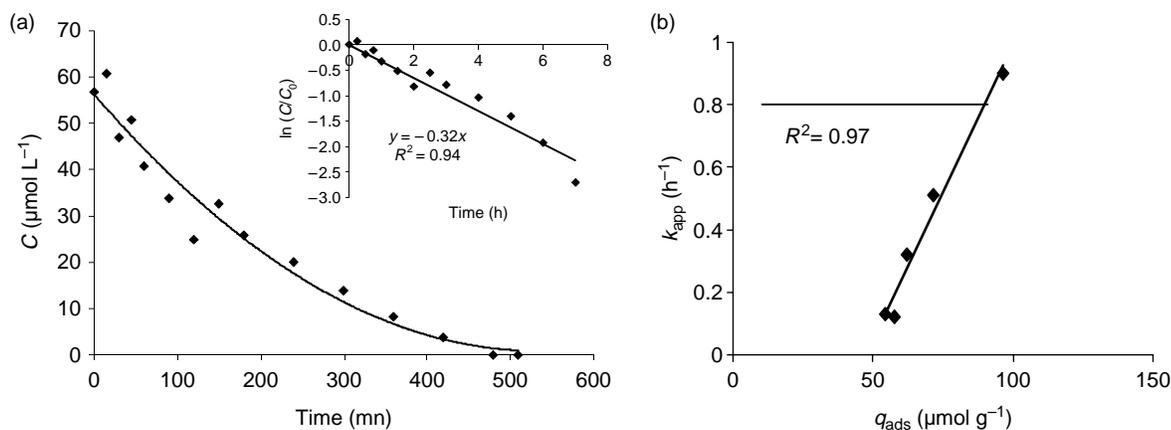


Figure 5 | (a) Dye discoloration and linear transform $\ln(C_0/C)$ vs. time (P25, pH 2.5 and $C_i = 119 \mu\text{mole L}^{-1}$), (b) (k_{app}) vs. (q_{ads}) (pH 2.5 and $C_i = 119 \mu\text{mole L}^{-1}$).

by UV-vis spectrometry). Indeed, the work of Bouzaida *et al.* (2004) on degradation of anthraquinonic dye confirmed this interference leading to lower K_{app} (McCafferty 2009). Despite this observation, and independently of photocatalyst properties, high adsorption of RB2 pollutant on TiO_2 (q_{ads}) led to a higher apparent rate constant (k_{app}), as shown in Figure 5(b) (initial concentration of $119 \mu\text{mol L}^{-1}$). At this point, it can be concluded that high adsorption is linked to high photocatalytic reaction. Availability of the dye at the photocatalyst interface is most important than UV absorption or screening effect of adsorbed dye on photocatalytic process in this case.

To understand the different behaviour observed in catalysts with a high SS, a different procedure was used.

The evolution of the adsorbed RB2 was monitored over time instead of C_{eq} since it is very low and initial concentration is limited by the solubility of RB2. An alkaline solution (pH 9) was used after sampling to desorb RB2 before UV-visible analysis. Two photocatalysts, MT100 and TKP101, were tested with a C_i of $119 \mu\text{mol/L}$. During the first hour of treatment, kinetics were very slow but increased thereafter. For comparison, a global first order kinetic constant was calculated and equal to 0.14 and 0.17 h^{-1} for MT100 and TKP101, with correlation coefficient fairly large ($R^2 = 0.84$) for both photocatalysts.

Zayani *et al.* (2008) used the ranking of the $k_{\text{app}}/q_{\text{ads}}$ values to express the detrimental effect of the recombination

Table 4 | Discoloration kinetic parameters, pH 2.5 and 9.5

Photocatalyst	pH = 2.5				pH = 9.5
	$C_{\text{initial}} (10^{-6} \text{ mol L}^{-1})$	$q_{\text{ads}} (10^{-6} \text{ mol g}^{-1})$	$k_{\text{app}} (\text{h}^{-1})$	$k_{\text{app}}/q_{\text{ads}} (10^{-2} \text{ g h}^{-1} \text{ mol}^{-1})$	$k_{\text{app}} (\text{h}^{-1})$
P25	119	62.2	0.32	51.4	0.52
ST21	119	54.3	0.13	23.9	0.18
F618	119	71.6	0.51	71.1	0.35
PC50	119	57.4	0.12	20.8	0.47
UV100	119	96.5	0.9	93.1	0.43
MT100	119	119	0.14*	11.7*	0.12
TKP101	119	119	0.17*	14.2*	0.1
TKP103	238	203.5	0.03	1.4	0.06
ST 01	238	193.3	0.14	7.2	0.15

*Determined differently by following discoloration of adsorbed dye $q_{\text{ads}} = (C_{\text{initial}} - C_0)/C_{\text{TiO}_2}$.

rate k_r on the photocatalytic activity. In this case, the ranking of k_r is UV100 < F618 < P25 < PC50 = ST21 < MT100 = TKP101 < ST01 < TKP103. This ranking may be linked to the degree of crystallinity of TiO₂ particles; ST01 and TKP101 photocatalysts exhibit on X-ray diffraction analysis low crystallinity compared to others photocatalysts such as P25 (not shown). Except UV100, all photocatalysts of G2 are behind photocatalysts of G1 in obtained ranking. The advantage of high adsorption on G2 group leading to the availability of RB2 molecules at the interface for photo degradation appears strongly decreased by the effect of recombination.

pH 9.5

Adsorption of RB2 was not observed at neutral or alkaline pH (9.5), however a high production of hydroxyl radicals OH· was expected due to the presence of OH⁻. Discoloration kinetics of RB2 at pH 9.5 followed an apparent first-order kinetic model. The apparent kinetic constant (k_{app}) increased for P25 to 0.52 h⁻¹ but only to 0.15 h⁻¹ for ST01 (Table 4). Similar behaviour was noted in the other photocatalysts, except UV100 and F618, which showed the highest degradation rate in acidic media and the lowest recombination rate k_r . In alkaline pH, oxidation of RB2 molecules by adsorbed OH· appears in general more efficient than direct oxidation by electron/hole pairs in acidic one. The two mechanisms are completely different and kinetics cannot be correlated.

Concerning MT100 and TKP101, the k_{app} obtained following the degradation of adsorbed RB2 was higher

than that determined at alkaline pH: 0.12 and 0.10 h⁻¹, respectively. In order to follow the discoloration of dye during high adsorption, it seemed more accurate to follow the disappearance of adsorbed dye than its concentration in solution, especially concerning the photocatalysts of group 2.

Effect of SO₄²⁻ ions

Progressive quantities of SO₄²⁻ were introduced during adsorption tests at acidic pH to decrease RB2 adsorption. Catalysts P25 (G1) and ST01 (G2) were considered for these experiments; both have similar pH_{ZPC}. At a concentration of sulphates greater than 100 mg/L, the amount adsorbed at equilibrium decreased considerably (Figure 6(a)); adsorption of RB2 is then inhibited. In fact, the TiO₂ surface was positively charged (TiOH₂⁺) in acidic pH as the pH_{ZPC} was 6.5 for P25 and 6.35 for ST01 (Table 1). After introducing SO₄²⁻ anions, they reacted with the positive sites leading to their own adsorption and hindering adsorption of RB2.

In the presence of sulphates, the discoloration of RB2, followed by solution analysis, was inhibited, as expected, for P25 of group 1 shown in Figure 4 (low SS), but was highly enhanced for ST01 of group 2 (high SS), as shown in Figure 6(b). This enhancement at pH 2.5 cannot be explained by saying that the SO₄²⁻ reaction with OH· produced sulphate radicals SO₄⁻ (oxidation potential of SO₄⁻: $E_0 = 2.6$ V, Evgenidou *et al.* 2005) less oxidative than hydroxyl radicals OH· (oxidation potential of OH·: 2.8 V, Rachel *et al.* 2002), but should be linked to less adsorbed

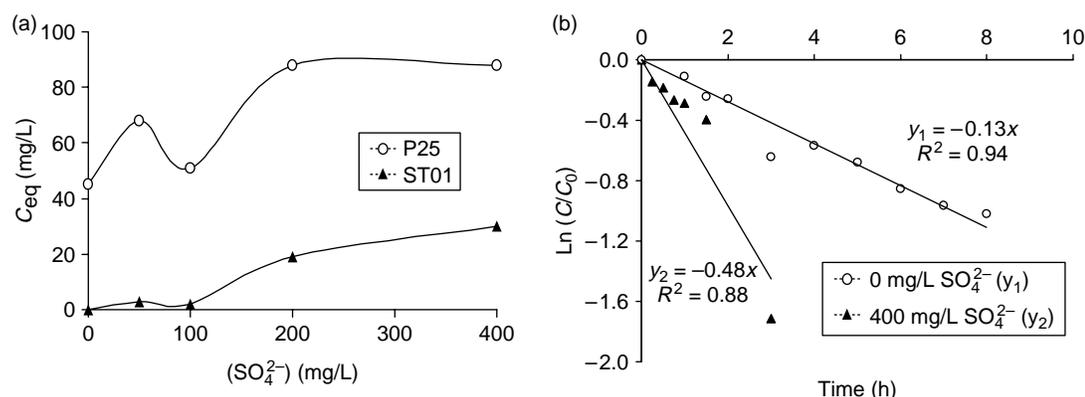


Figure 6 | Effect of SO₄²⁻ introduction on the adsorbed amount of RB2: (a) C_{eq} (mg/L) (30 nm of adsorption; pH 2.5) photocatalyst P25 and ST01; (b) discoloration kinetics for ST01.

RB2 on the TiO₂ which led to preferential reaction with adsorbed OH· (l-OH·) and better monitoring of RB2 degradation by solution analysis. The reaction (R1) $l\text{-OH}\cdot + \text{RB2} \rightarrow l\text{-products}$ appears more efficient. The reaction R1 may be preferred due to the presence of several layers of hydroxyl groups at the surface of ST01 which was not thermally treated (Zayani *et al.* 2008). For P25, less adsorbed RB2 decreases slowly the photocatalytic kinetic.

CONCLUSIONS

The adsorption of RB2 on the different photocatalysts followed the Langmuir model. A significant correlation was established between q_{max} and the specific surface, but pH_{zpc} may influence this correlation. Also photocatalytic activity is linked to the amount of adsorbed dye with large correlation coefficient at pH 2.5. There was no adsorption in alkaline pH due to the anionic aspect of RB2 in solution. However, photocatalysis performances were, in general, higher in alkaline pHs than in acidic ones due to the high production of OH·, except for UV100 and F618 which had the lowest recombination rates k_r .

Sulphates hindered adsorption of RB2 on the photocatalysts in acidic conditions. They reacted with the TiOH₂⁺ positive sites, increasing the free RB2 molecules (screen effect) which in turn reacted with OH· and increased photocatalytic discoloration, especially for those catalysts having a high adsorption capacity.

Finally, with the high adsorption of RB2 (as was the case of MT100 and TKP101), it seemed more accurate to follow the disappearance of adsorbed dye than its concentration in solution.

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