Effect of adsorption on the photocatalysis performance of anthraquinone dye
Mehdi Ismail and Latifa Bousselmi

ABSTRACT

The adsorption and photocatalytic efficiency of several TiO$_2$ 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 ($q_{\text{ads}}$) were then determined. The expected correlation between specific surface and $q_{\text{max}}$ was verified. The addition of sulphate ions in the case of catalysts Degussa P25 and TiO$_2$-Ishihara ST01 was found to inhibit adsorption of RB2 on the TiO$_2$ 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

INTRODUCTION

Photocatalytic detoxification is a promising technology for destroying organic pollutants, and especially textile dyes. Titanium dioxide (TiO$_2$) 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 TiO$_2$ 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 SO$_4^{2-}$ 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 (λ_max = 619 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 curried 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; λ > 253 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 (C₀) 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

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Photocatalyst</th>
<th>Specific surface m²/g</th>
<th>TiO₂ allotropic phases</th>
<th>Crystal size (nm)</th>
<th>pH_{ZPC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degussa</td>
<td>P25</td>
<td>50</td>
<td>80% Anatase</td>
<td>30</td>
<td>6.6–5.9</td>
</tr>
<tr>
<td>Degussa</td>
<td>F618</td>
<td>130</td>
<td>20% Rutile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sachtleben Chemie</td>
<td>UV 100</td>
<td>250–270</td>
<td>90% TiO₂ (Anatase)</td>
<td>15–20</td>
<td>5.1</td>
</tr>
<tr>
<td>Millenium</td>
<td>PC 50</td>
<td>40–50</td>
<td>100% TiO₂ (Anatase)</td>
<td>9</td>
<td>5.7</td>
</tr>
<tr>
<td>Ishihara</td>
<td>ST 01</td>
<td>320</td>
<td>100% TiO₂ (Anatase)</td>
<td>20–30</td>
<td>4.07</td>
</tr>
<tr>
<td>Ishihara</td>
<td>ST 21</td>
<td>50</td>
<td>95% TiO₂ (Anatase)</td>
<td>7</td>
<td>6.35</td>
</tr>
<tr>
<td>Tayca</td>
<td>MT 100</td>
<td>293</td>
<td>95% TiO₂ (Anatase)</td>
<td>20</td>
<td>5.95</td>
</tr>
<tr>
<td>Tayca</td>
<td>TKP 101</td>
<td>290</td>
<td>92.8% TiO₂ (Anatase)</td>
<td>6</td>
<td>6.7</td>
</tr>
<tr>
<td>Tayca</td>
<td>TKP 105</td>
<td>254</td>
<td>84.2% TiO₂ (Anatase)</td>
<td>6</td>
<td>3.2</td>
</tr>
<tr>
<td>Tayca</td>
<td>TKP 05</td>
<td></td>
<td>90.5% TiO₂ (Anatase)</td>
<td>6</td>
<td>7.8</td>
</tr>
</tbody>
</table>
As the first criterion was not verified for some photocatalysts with high specific surface, for these cases, initial concentration of \(238 \, \text{m mole/L}\) 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 \(\mu\)m) to separate TiO\(_2\) particles, 0.45 \(\mu\)m 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\(_2\)O molecules at surface metal sites is followed by the dissociation of OH groups leading to coverage with chemically equivalent Titanuim hydroxyl groups (Ti-OH). The following two equilibria are then considered

\[
\text{Ti-OH} + \text{H}^+ \leftrightarrow \text{Ti-OH}^+ \quad K_1
\]

\[
\text{Ti-OH} + \text{OH}^- \leftrightarrow \text{TiO}^- + \text{H}_2\text{O} \quad K_2
\]

The zero point of charge pH\(_{ZPC}\) of TiO\(_2\) particles is defined as the pH at which the concentrations of
protonated and deprotonated surface groups are equal (Lakshmi et al. 1995):

\[ \text{pH}_{ZPC} = \frac{1}{2}(pK_1 + pK_2) \]  

(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.

### Table 2: Apparent pKa values and Single pKa values for unprotonated and protonated species

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

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

Figure 2: Log D function of pH curve of RB2.
Adsorption results

Acidic pH was set at 2.5, less than the pHZPC 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 (Ce). This behaviour are due to electrostatic attractions between the positively charged TiO2 (pH < pHZPC) 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 TiO2 (mg/g) at equilibrium (qe) were calculated from the following equation:

\[ q_e = \frac{C_i - C_e}{M} V \]

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 \( R^2 \). This was expected since Langmuir adsorption model was widely verified for textile azo and anthraquinonic dyes (Lachheb et al. 2002; Bouzaida et al. 2004; Muruganandham & Swaminathan 2004; Zayani et al. 2006, 2008).

\[ \frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_{\text{ads}}} \]

\( q_{\text{max}} \) is the maximum amount of adsorbed dye corresponding to monolayer coverage; \( K_{\text{ads}} \) is the Langmuir adsorption equilibrium constant. The \( q_{\text{max}} \) and \( K_{\text{ads}} \) 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 5(b)) corresponding to very high \( K_{\text{ads}} \). Such a value of \( K_{\text{ads}} \) 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 \( K_{\text{ads}} \) 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 (\( q_{\text{ads}} \)) with high initial concentration (476 \( \mu \)mole 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 \( q_{\text{max}} \) function of the TiO2 specific surface (SS) and pHZPC is indicated. Two groups are detected: one characterized by a SS less than 150 m²/g.

![Figure 3](image-url)

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

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>( q_{\text{max}} ) (10(^{-4}) mol g(^{-1}))</th>
<th>1/( K_{\text{ads}} ) (10(^{-4}) mol L(^{-1}))</th>
<th>( R^2 )</th>
<th>SA = ( q_{\text{max}}/SS ) (10(^{-4}) mol/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>82</td>
<td>0.0408</td>
<td>0.99</td>
<td>1.64</td>
</tr>
<tr>
<td>ST21</td>
<td>73</td>
<td>0.0026</td>
<td>0.99</td>
<td>1.46</td>
</tr>
<tr>
<td>F618</td>
<td>63</td>
<td>&lt; 10(^{-4})</td>
<td>0.97</td>
<td>0.48</td>
</tr>
<tr>
<td>PC50</td>
<td>58</td>
<td>0.1786</td>
<td>0.93</td>
<td>1.29</td>
</tr>
<tr>
<td>UV100</td>
<td>200</td>
<td>0.0047</td>
<td>0.99</td>
<td>0.77</td>
</tr>
<tr>
<td>MT100</td>
<td>208</td>
<td>&lt; 10(^{-4})</td>
<td>0.99</td>
<td>0.71</td>
</tr>
<tr>
<td>TKP101</td>
<td>106</td>
<td>&lt; 10(^{-4})</td>
<td>0.99</td>
<td>0.56</td>
</tr>
<tr>
<td>TKP103</td>
<td>220</td>
<td>0.0021</td>
<td>0.99</td>
<td>0.86</td>
</tr>
<tr>
<td>ST 01</td>
<td>222</td>
<td>&lt; 10(^{-4})</td>
<td>0.99</td>
<td>0.69</td>
</tr>
</tbody>
</table>

(G1) and the other by a SS greater than 250 m²/g (G2).
The general observed trend is that high specific surface leads to high $q_{\text{max}}$ 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 $q_{\text{max}}$ lower than expected. It has the lowest pH ZPC (SS = 290 m²/g and pHZPC = 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 TiO₂ 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, pHZPC 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 ± 0.17 µmole/m² and 0.76 ± 0.08 µmole/m² for G1 and G2, respectively (Table 3).

If assumed that the highest value of 1.64 µmole/m² 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 Ångstrom for TKP103 and UV100, respectively, close to RB2 molecule dimension. They both have similar $q_{\text{max}}$ 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 TiO₂ 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 TiO₂ 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 pHZPC. 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 µmole/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 µmole/L. However, no clear $C_{\text{eq}}$ decrease was observed with TKP101 and MT100 during photocatalysis. For the other photocatalysts, the evolution of $C_{\text{eq}}$ 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 ($k_{\text{app}}$) 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 TiO₂ was curried 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...
by UV–vis spectrometry). Indeed, the work of Bouzaida et al. (2004) on degradation of anthraquinonic dye confirmed this interference leading to lower $K_{\text{app}}$ (McCafferty 2009). Despite this observation, and independently of photocatalyst properties, high adsorption of RB2 pollutant on TiO$_2$ ($q_{\text{ads}}$) led to a higher apparent rate constant ($k_{\text{app}}$), as shown in Figure 5(b) (initial concentration of 119 µmol 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 $C_{\text{eq}}$ 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 µmole/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

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

*Determined differently by following discoloration of adsorbed dye $q_{\text{ads}} = (C_{\text{total}} - C_i) / C_{\text{TiO2}}$.

Figure 5 | (a) Dye discoloration and linear transform ln($C/C_0$) vs. time (P25, pH 2.5 and $C_i = 119$ µmole L$^{-1}$), (b) ($k_{\text{app}}$) vs. ($q_{\text{ads}}$) (pH 2.5 and $C_i = 119$ µmole L$^{-1}$).
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 TiO$_2$ 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 SO$_2^{2-}$ ions**

Progressive quantities of SO$_2^{2-}$ 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 TiO$_2$ surface was positively charged (TiOH$^+$) in acidic pH as the pH$_{ZPC}$ was 6.5 for P25 and 6.35 for ST01 (Table 1). After introducing SO$_2^{2-}$ 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 SO$_2^{2-}$ reaction with OH$^-$ produced sulphate radicals SO$_4$$^{2-}$ (oxidation potential of SO$_4$$^{2-}$: $E_0 = 2.6$ 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 SO$_2^{2-}$ 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 TiO$_2$ which led to preferential reaction with adsorbed OH$^-$ (l-OH)$^-$ and better monitoring of RB2 degradation by solution analysis. The reaction (R1) $l$-OH$^- + RB2 \rightarrow l$-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 $q_{\text{max}}$ and the specific surface, but pH$_{\text{zpc}}$ 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 $k_c$.

Sulphates hindered adsorption of RB2 on the photocatalysts in acidic conditions. They reacted with the TiOH$_2^+$ 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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