

# An investigation of the photocatalytic efficiencies of TiO<sub>2</sub> powders on the decolourisation of humic acids

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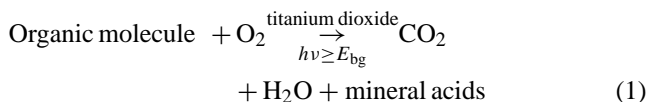
## Abstract

Photocatalytic efficiencies of two commercial titania brands, Degussa P-25 and Hombikat UV-100 were discussed in relation to the degradation of humic acid in aqueous solutions. Decolourisation rate of humic acid (Colour<sub>436</sub>, m<sup>-1</sup>) for Degussa P-25 was found to be higher than the rate achieved by using Hombikat UV-100 specimen, both in terms of pseudo-first-order and Langmuir–Hinshelwood kinetics. The adsorption isotherms exhibited different trends and the application of the Freundlich adsorption model revealed  $K_F$  values 0.549 for Degussa P-25, and 0.293 for Hombikat UV-100 indicating higher adsorption capacity of Degussa P-25 for humic acid under neutral pH conditions. This observation was also consistent with the intrinsic photocatalytic activities calculated as 0.196 m<sup>-1</sup> min<sup>-1</sup> m<sup>-2</sup> for Degussa P-25 and 0.0269 m<sup>-1</sup> min<sup>-1</sup> m<sup>-2</sup> for Hombikat UV-100. The higher surface area of Hombikat UV-100 did not render higher adsorption capacity values leading to higher degradation rates. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Adsorption; Humic acid; Photocatalytic decolourisation; Titanium dioxide

## 1. Introduction

The last decades brought increased attention to the photocatalytic degradation of organic compounds on semiconductor surfaces as an alternative method to mineralising a wide range of organic pollutants in water completely to CO<sub>2</sub> [1–3]. It is known that upon UV irradiation, TiO<sub>2</sub> particles generate electron–hole pairs ( $e_{CB}^-/h_{VB}^+$ ) in the bulk semiconductor which can migrate to the surface to form oxidising species (HOO•, O<sub>2</sub>•<sup>-</sup> and then •OH radicals) via reacting with preadsorbed O<sub>2</sub>. These radical species possess a potential to oxidise organic molecules at the TiO<sub>2</sub> surface. Although the main pathway of photomineralisation may easily be summarised by the reaction below (1), the detailed mechanisms of the photocatalytic oxidation processes at the TiO<sub>2</sub> surface keep to be elusive, particularly about the initial steps involved in the reactions of HOO•, O<sub>2</sub>•<sup>-</sup> and •OH radicals with the organic compounds:



On account of its stability, non-toxicity and low energy band-gap, TiO<sub>2</sub> is accepted to be one of the most suitable semiconducting materials for photocatalysis. Recently, various titania samples have been tested for the mineralisation of organics in aqueous and non-aqueous media and the differences in the photocatalytic activity values have been described as a function of their structure [4,5]. The quantum yields and the relative photonic efficiencies of the photodegradation of various organic substrates, namely substituted phenols, in air-equilibrated aqueous solutions for various TiO<sub>2</sub> particles were reported by Serpone [6]. Later studies also cover comparative investigations on the photocatalytic efficiencies of TiO<sub>2</sub> powders; among which mostly Degussa P-25 and Hombikat UV-100 have been investigated [5,7–14].

The presence of natural organic matter, mainly humic substances in surface waters, constitutes the main route for the absorbance of solar energy in aquatic systems through which a series of photophysical and photochemical processes occur. Humic acids comprise one of the most widely investigated groups of humic substances. Imparting aesthetically undesirable colour, forming complexes with metal ions, acting as precursors for the formation of potentially hazardous trihalomethanes, solubilising pesticides, and hydrocarbons; these naturally occurring aggregates are the culprits in drinking water supplies the consequences of which may lead to the deterioration of human health.

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Humic acids consist of a skeleton of alkyl/aromatic units cross-linked by a variety of functional groups such as carboxylic, phenolic and alcoholic hydroxyls, ketone and quinone groups [15]. Possessing various functional groups, many of which are depicted as model compounds in photocatalytic oxidation studies, one can perceive humic acids as a unified system of compounds, rather than organic clusters. Recently, the destruction of humic acids has become an important task and TiO<sub>2</sub> catalysed photodegradation of humic acids has been subject to many research projects [16–20]. The collective parameters most commonly used for characterisation of humic acids are TOC (total organic carbon), UV<sub>254</sub> (UV absorption measured at 254 nm) and Colour<sub>436</sub> (visible absorption at 436 nm). Colour<sub>436</sub> expresses the colour forming moieties that are the chromophoric groups containing conjugated double bond systems (delocalised electrons) and heteroatoms with lone pair of electrons like O, N and S.

The objective of the present research was to investigate the photocatalytic decolourisation efficiencies of the two commercial titanium dioxide samples: Degussa P-25 and Hombikat UV-100 in aqueous solution using humic acid as the model compound of natural organic matter. The adsorption properties of humic acid onto TiO<sub>2</sub> specimens were also studied.

## 2. Experimental section

### 2.1. Materials

Two different TiO<sub>2</sub> brands: Degussa P-25 and Hombikat UV-100 were obtained from ISFH, Germany. The detailed descriptions of the manufacturer's data were given in Table 1, with the complementary remarks of Tahiri et al. [5]. Commercial humic acid was supplied from Roth, Germany.

Stock humic acid solution (1000 mg l<sup>-1</sup>) was prepared according to the procedure outlined by Urano et al. [21]. Appropriate dilutions were made using distilled deionised water.

#### 2.1.1. Photoreactor

Photochemical experiments were performed in a 50 ml cylindrical Pyrex reaction vessel with a diameter of 7.5 cm and a height of 3.5 cm. The photoreactor was enclosed by a mirror casing and the whole system was placed in a box, the inner walls of which were covered with Al foil. A 125 W black light fluorescent (BLF) lamp emitting radiation between 300 and 420 nm with a maximum at 350 nm was used as the light source. The intensity of the incident light was measured by ferrioxalate actinometry as described by Hachard and Parker [22] and was found as  $2.84 \times 10^{-6}$  einstein min<sup>-1</sup>. The reaction vessel was illuminated from the top and continuous stirring of the suspension was provided by means of a magnetic stirrer.

### 2.2. Experimental

#### 2.2.1. Photocatalytic degradation

Bench scale experiments were performed under neutral pH conditions (pH 6.7). The slurry containing 10 mg l<sup>-1</sup> humic acid solution (Colour<sub>436</sub>, C<sub>0</sub>: 7.0 m<sup>-1</sup>) and 0.25 mg ml<sup>-1</sup> TiO<sub>2</sub> was sonicated to ensure a homogeneous mixture and then irradiated for certain reaction periods. Prior to the analysis, TiO<sub>2</sub> was removed from the suspension by filtration (Millipore, Millex 25 HA, 0.45 μm membrane filter). The clear solution was analysed with Shimadzu UV 160A double beam spectrophotometer for colour decolourisation at 436 nm wavelength (Colour<sub>436</sub>, m<sup>-1</sup>). No degradation was observed when the experiments were conducted in the dark or in the absence of the TiO<sub>2</sub> specimens. For the assessment of the Langmuir–

Table 1  
Physicochemical properties of TiO<sub>2</sub> specimens: Degussa P-25 and Hombikat UV-100

Property	Degussa P-25	Hombikat UV-100
Physical state	White powder	White powder
Composition (%)	≈80 (anatase) ≈20 (rutile)	100 (anatase)
Density (g ml <sup>-1</sup> )	3.8	3.9
BET surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	≈55	>250 (=189 [5])
Average primary particle size (nm)	≈30	<10
pH in aqueous solution	3–4	≈6
Contents		
SiO <sub>2</sub> (%)	<0.2	–
Al <sub>2</sub> O <sub>3</sub> (%)	<0.3	–
Fe <sub>2</sub> O <sub>3</sub> (%)	<0.01	–
TiO <sub>2</sub> (%)	>97	>99
HCl (%)	<0.3	–
Calcining losses (%)	<2 (1000 °C)	9 (850 °C)
Porosity	Non-porous	Porous (mesopores, ~5.6 nm in diameter)
Volatiles (%)	–	8 (105 °C)

<sup>a</sup> In kinetic calculations, BET surface area of Hombikat UV-100 was taken as 250 m<sup>2</sup> g<sup>-1</sup> although Tahiri et al. [5] reported as 189 m<sup>2</sup> g<sup>-1</sup>.

Hinshelwood (L–H) kinetic studies, the humic acid range was chosen as 10–50 mg l<sup>-1</sup>. Under the specified experimental conditions, the variability between replicate experiments was approximately 5%. All of the photocatalytic reactions were carried out at room temperature.

### 2.2.2. Batch adsorption experiments

Batch adsorption tests were carried out overnight in the dark, in a continuously shaking water bath at 25 ± 1 °C. Preliminary adsorption experiments showed that the equilibration was reached in 16 h, however, no major deviation was observed in a 24 h period. The span of the titanium dioxide concentration in an adsorption isotherm was chosen in the range of an order of magnitude (0.1–1.0 mg ml<sup>-1</sup>). This concentration range was also found to be the photocatalytically active range since the use of higher concentrations (≥5 mg ml<sup>-1</sup>) resulted in opaque solutions rendering inefficient light absorption conditions for photocatalytic degradation studies. The concentration of humic acid was kept constant at 10 mg l<sup>-1</sup> (Colour<sub>436</sub>, C<sub>0</sub>: 7.0 m<sup>-1</sup>). Following the termination of the adsorption experiments, clear solutions were obtained by filtration as explained above and the Colour<sub>436</sub> values were recorded in terms of absorbance values at 436 nm. Under the conditions given above, the difference between two replicates was ≤5%.

## 3. Results and discussion

### 3.1. The kinetics of photocatalytic degradation

The photodegradation kinetics of many organic compounds in TiO<sub>2</sub> suspensions under UV illumination has often been modelled to the L–H equation (Eq. (2)) which also covers the adsorption properties of the substrate on the photocatalyst surface [23–25]:

$$R = -\frac{dC}{dt} = \frac{k_{L-H}K_{ads}C_0}{1 + K_{ads}C_0} \quad (2)$$

$k_{L-H}$  is the reaction rate constant, m<sup>-1</sup> min<sup>-1</sup>;  $K_{ads}$  the adsorption coefficient of the reactant on TiO<sub>2</sub> particles, m;  $C$  the concentration of the solute, Colour<sub>436</sub>, m<sup>-1</sup>;  $C_0$  the initial concentration of the solute, Colour<sub>436</sub>, m<sup>-1</sup>.

Integration of Eq. (2) yields the following equation:

$$\ln\left(\frac{C_0}{C}\right) + K(C_0 - C) = k_{L-H}K_{ads}t \quad (3)$$

Then, the half-life,  $t_{1/2}$  (min) is derived as

$$t_{1/2} = \left(\frac{0.693}{k_{L-H}K_{ads}}\right) + \left(\frac{0.5}{k_{L-H}}\right)C_0 \quad (4)$$

Therefore, a plot of  $t_{1/2}$  versus  $C_0$  should give a straight line with a slope of  $0.5/k_{L-H}$  and intercept of  $0.693/k_{L-H}K_{ads}$  through which the coefficients  $k_{L-H}$  and  $K_{ads}$  can be calculated.

When the initial concentration  $C_0$  is small, Eq. (3) alters to Eq. (5), which expresses a pseudo-first-order reaction as

$$\ln\left(\frac{C_0}{C}\right) = k_{L-H}K_{ads}t = kt \quad \text{or} \quad C_t = C_0 e^{-kt} \quad (5)$$

yielding half-life,  $t_{1/2}$  (min)

$$t_{1/2} = \frac{0.693}{k} \quad (6)$$

$k$  is the pseudo-first-order reaction rate constant,  $k = k_{L-H}K_{ads}$ , min<sup>-1</sup>.

L–H rate law successfully explains the kinetics of the reactions occurring while both species are adsorbed, a free radical species reacts with the adsorbed substrate or a surface bound radical reacts with a free substrate in solution. The values of  $k_{L-H}$  and  $K_{ads}$  are used to explain the coefficients defining the rate determining reaction events and pre-equilibrium adsorption within an adsorbed monolayer at the oxide surface and the aqueous solution interface. The effect of light intensity is incorporated in  $k_{L-H}$  and  $K_{ads}$  specifically expresses the equilibrium constant for fast adsorption–desorption processes between surface monolayer and bulk solution.

The disappearance of the colour of humic acid as a function of the irradiation time was observed to follow an exponential decay form as depicted in Fig. 1. The first feature to be pointed out is the decolourisation profile in the presence of Degussa P-25 which was quite different than the Hombikat UV-100 sample for the first 20 min of irradiation time. The non-stabilised photoadsorption–photodesorption processes taking place may explain the presence of a plateau during the early stages of irradiation. A similar induction period of 20 min was also observed for TOC removal in the photocatalytic degradation of phenol for both of the specimens at pH 3. The absence of this period in the presence of Hombikat UV-100 may be explained by the poor adsorption characteristics of humic acid onto the TiO<sub>2</sub> specimen. The total conversion after 60 min was about 70% for Degussa P-25 and 50% for Hombikat UV-100. Further irradiation for 90 min resulted in 90% removal for Degussa P-25, whereas

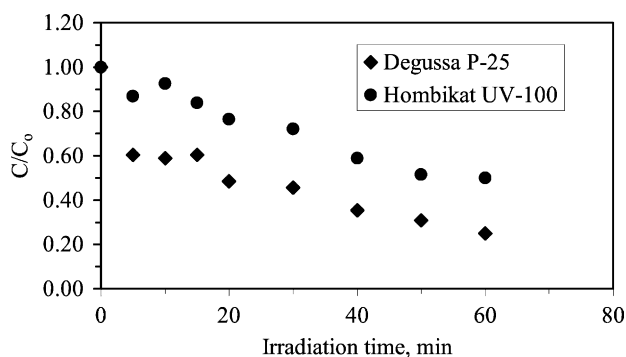


Fig. 1. Photocatalytic decolourisation of humic acid (Colour<sub>436</sub>) as a function of irradiation time (humic acid concentration: 10 mg l<sup>-1</sup>, photocatalyst mass concentration: 0.25 mg ml<sup>-1</sup>).

Table 2  
Pseudo-first-order kinetic parameters

Specimen	Rate ( $\text{m}^{-1} \text{min}^{-1}$ )	$k$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min)	$R^2$
Degussa P-25	0.135	$1.93 \times 10^{-2}$	36	0.96
Hombikat UV-100	0.0840	$1.20 \times 10^{-2}$	58	0.98

Hombikat UV-100 specimen exhibited a slower rate of decolourisation with only 70% removal in 100 min.

Data presented in this form allowed the assessment of decolourisation as a first-order kinetic relationship, and linear regression revealed the coefficients given in Table 2 for the  $\text{TiO}_2$  specimens. In the presence of Hombikat UV-100 approximately 40% decrease was observed in the reaction rate constant resulting in a pseudo-first-order reaction rate of  $0.135 \text{ m}^{-1} \text{ min}^{-1}$  for Degussa P-25 and  $0.0840 \text{ m}^{-1} \text{ min}^{-1}$  for Hombikat UV-100. The half-life values were calculated as 36 and 58 min for Degussa P-25 and Hombikat UV-100, respectively.

From a general comparative point of view, it could be seen that the pseudo-first-order reaction rate constants reported in literature for simpler compounds such as salicylic acid, benzoic acid and phenol, representing the functional groups of humic acid, were found to be within the same order of magnitude [1–5]. But it should be noted that the reaction kinetics of humic acid was expressed in terms of the removal of colour forming moieties.

It is also common practice to compare photocatalyst activities based on catalyst surface area “intrinsic photocatalytic activity,  $\text{m}^{-1} \text{ min}^{-1} \text{ m}^{-2}$ ” and catalyst mass “specific photocatalytic activity,  $\text{m}^{-1} \text{ min}^{-1} \text{ g}^{-1}$ ”. In order to eliminate the Brunauer–Emmett–Teller (BET) surface area factor, and make the comparisons on a relative basis, intrinsic and specific photocatalytic activities for both  $\text{TiO}_2$  species were also calculated (Table 3). The comparison of the ratio of the pseudo-first-order kinetic rates (presented as photocatalytic activity in Table 3) and the specific photocatalytic activities with the intrinsic photocatalytic activities for both samples, showed that the proportion in the rates increased almost five times favouring Degussa P-25. From another point of view, it could be said that the areal rates revealed a 50% increase for Degussa P-25, and a 68% decrease for Hombikat UV-100. This finding corroborated those of Sclafani and Herrmann [4] that normalising the rate with respect to the surface area did not bring about similar intrinsic photocatalytic activities. The results showed that the actual photocatalytic rate did not necessarily require the dependency on the BET surface area of the catalyst but rather to the available

or active sites or centres taking place in the course of the reaction. Therefore, properties of the  $\text{TiO}_2$  specimens like pore size, anatase versus rutile forms, and crystal structure also play important roles in the photocatalytic efficiencies.

The photocatalytic removal rates obtained according to the first-order kinetic model showed that Degussa P-25 was more efficient than Hombikat UV-100 in the photocatalytic decolourisation of humic acid which was consistent with the findings of many other recent studies [5,8–14]. Degussa P-25 was found to be more efficient than Hombikat UV-100 specimen for the photocatalytic oxidation of simple organic compounds such as phenol, 4-nitrophenol, 4-chlorophenol, salicylic acid and also for cylindrospermopsin—a cyanotoxin. The related kinetic data were reported in terms of apparent first-order rate model and no detailed information was given on the adsorptive properties of the substrates and L–H kinetic models. On the other hand, Hombikat UV-100 specimen expressed better efficiency for the gas phase photocatalytic oxidation of formaldehyde to carbon dioxide [11] and on the photoreduction of toxic/heavy metals such as Ag(I), Pb(II), Hg(II), Ni(II), Cu(II), Cr(VI), Fe(III) and Fe(II) [9,12]. Both specimens exhibited equal performances for TOC abatement for the photocatalytic degradation of landfill leachate in a batch reactor at pH 3 [7].

In this study, the L–H kinetics were evaluated for the decolourisation of humic acid in the concentration range of  $10\text{--}50 \text{ mg l}^{-1}$  ( $\text{Colour}_{436}$ ,  $C_0$ :  $7.0\text{--}35.6 \text{ m}^{-1}$ ). Increasing humic acid concentration by fivefold reflected as a decrease in pseudo-first-order reaction rate by an order of magnitude with respect to their lowest  $k$  values. Upon linearisation of the half-life values calculated according to Eq. (6) versus  $C_0$  ( $\text{Colour}_{436}$ ) of humic acid solutions, the reactivity constant  $k_{\text{L-H}}$  values were found as  $4.99 \times 10^{-2}$  and  $2.86 \times 10^{-2} \text{ m}^{-1} \text{ min}^{-1}$  for Degussa P-25 and Hombikat UV-100, respectively. The tendency of humic acid to be adsorbed by the two titania specimens were reflected by the  $K_{\text{ads}}$  values which were calculated as 0.332 m for Degussa P-25 and 0.219 m for Hombikat UV-100. The half-life  $t_{1/2}$  values were found to be considerably higher than the half-life values obtained by the application of the pseudo-first-order kinetic model for  $10 \text{ mg l}^{-1}$  humic acid. For comparison

Table 3  
Comparison of photocatalytic activities of titanium dioxide specimens

Specimen	Photocatalytic activity ( $\text{m}^{-1} \text{ min}^{-1}$ )	Intrinsic photocatalytic activity ( $\text{m}^{-1} \text{ min}^{-1} \text{ m}^{-2}$ )	Specific photocatalytic activity ( $\text{m}^{-1} \text{ min}^{-1} \text{ g}^{-1}$ )
Degussa P-25 ( $55 \text{ m}^2 \text{ g}^{-1}$ )	0.135	0.196	10.8
Hombikat UV-100 ( $250 \text{ m}^2 \text{ g}^{-1}$ )	0.0840	0.0269	6.72

Table 4  
L–H kinetic parameters<sup>a</sup>

Specimen	Rate (m <sup>-1</sup> min <sup>-1</sup> ) <sup>b</sup>	k <sub>L–H</sub> (m <sup>-1</sup> min <sup>-1</sup> )	K <sub>ads</sub> (m)	t <sub>1/2</sub> (min) <sup>b</sup>	R <sup>2</sup>
Degussa P-25	3.49 × 10 <sup>-2</sup>	4.99 × 10 <sup>-2</sup>	0.332	112	0.96
Hombikat UV-100	1.70 × 10 <sup>-2</sup>	2.86 × 10 <sup>-2</sup>	0.219	233	0.97

<sup>a</sup> Humic acid range: 10–50 mg l<sup>-1</sup>.

<sup>b</sup> Rate and half-life, t<sub>1/2</sub> were calculated for 10 mg l<sup>-1</sup> humic acid.

purposes the L–H rate (m<sup>-1</sup> min<sup>-1</sup>) and half-life, t<sub>1/2</sub> (min<sup>-1</sup>) values were presented in Table 4 for 10 mg l<sup>-1</sup> humic acid. In case of the presence of the highest humic acid concentration (50 mg l<sup>-1</sup>, C<sub>0</sub> = 35.6 m<sup>-1</sup>), the L–H decolourisation rate was found to be 4.60 × 10<sup>-2</sup> and 2.51 × 10<sup>-2</sup> m<sup>-1</sup> min<sup>-1</sup> for TiO<sub>2</sub> specimens as Degussa P-25 and Hombikat UV-100, respectively.

The L–H rate constant k<sub>L–H</sub> and the adsorption constant K<sub>ads</sub> are only valid at the initial stages of the photocatalytic degradation process. During the later stages intermediates (C<sub>i</sub>) are formed and the related kinetic terms (∑ KC<sub>i</sub>) must also be included in the L–H equation. Therefore, the kinetic data obtained for the early stages of the degradation should express the initial rate. Moreover, evaluation of the kinetic data excluding the early stages of irradiation (induction period, 20 min) for the Degussa P-25 specimen did not display any significant change in the decolourisation rate (<5%).

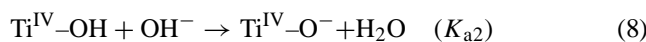
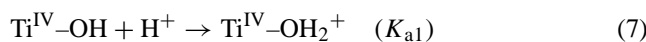
As an approximation, L–H rate equation (Eq. (2)) renders a simple pseudo-first-order kinetic equation (Eq. (5)) by which k values could be deduced using the k = k<sub>L–H</sub>K<sub>ads</sub> expression. The calculated k values (k<sub>cal</sub>, min<sup>-1</sup>) were found as 1.66 × 10<sup>-2</sup> and 6.26 × 10<sup>-3</sup> for Degussa P-25 and Hombikat UV-100, respectively. Comparison of these values with the pseudo-first-order rate constants showed that k<sub>cal</sub> was quite close to the reported value of k for Degussa P-25, whereas one-half the value was calculated for Hombikat UV-100 (Table 2). Since k<sub>L–H</sub> covers the effect of light intensity, a significant contribution should be assessed for the higher efficiency of Degussa P-25 than Hombikat UV-100. Contradictory results were reported for the light absorbing characteristics of Hombikat UV-100 [12,13].

### 3.2. The adsorption of humic acid by TiO<sub>2</sub> specimens

The adsorption of molecules onto a surface is a necessary prerequisite to any surface mediated chemical process. Therefore, the mechanism of binding of humic acids to the TiO<sub>2</sub> surface has to be addressed in order to improve the understanding of photocatalytic degradation. It is known that the initial adsorption kinetics of humic acids on solid surfaces is rather a complex process that depends on the nature of the surface and the solution conditions [26].

Trials to assess the adsorption kinetics of humic acid onto TiO<sub>2</sub> failed since a very fast adsorption process was observed for both of the specimens. Therefore, it was not possible to follow the attachment of molecules in such a short time scale. This was expected since attachment should be fast on

hydrophilic surfaces if electrostatic repulsion is considered as negligible. Considering the pH<sub>zpc</sub> of anatase TiO<sub>2</sub> (both for Degussa P-25 and Hombikat UV-100) as pH 6.3–6.6 and the pH of the reaction medium (pH 6.7), the role of electrostatic attractions should be considered as significant during the course of the adsorption process. At pH values close to the pH<sub>zpc</sub>, the surface of TiO<sub>2</sub> is equally positively and negatively charged according to the following equations:



By using Eqs. (7) and (8), the pH<sub>zpc</sub> of TiO<sub>2</sub> can be calculated as pH<sub>zpc</sub> = (pK<sub>a1</sub> + pK<sub>a2</sub>)/2.

Under neutral pH conditions, humic acid should be considered as an anion that is partially charged due to the deprotonation of the carboxylic groups present at the periphery of the molecules. Then, the surface-OH<sub>2</sub><sup>+</sup> and -OH groups might exchange with the anionic groups of humic acid through ligand exchange mechanism. In an aqueous solution Ti cations can bond to oxygen atoms of water molecules. If salicylate ions are present in solution the ability of their oxygen atoms to form chelate structures leads to the replacement of the solvent by organic ligand. The presence of such surface complexes between goethite and salicylate was identified by CIR-FTIR techniques and by analogy, depending on the adsorption experiments, a similar presentation of a surface complex formed by salicylate ions with Ti cations at the centre was reported [27]. Since salicylate ions comprise one major functional group of humic acid, similar binding mechanisms on the surface can be predicted.

Although the referred adsorption isotherm model should be chosen as “Langmuir” bearing the fact that the L–H kinetics are merely the substitution of photocatalytic degradation rate factor into the Langmuir equation; the isotherms found for 10 mg l<sup>-1</sup> humic acid in the photocatalytically active range of TiO<sub>2</sub> (0.1–1.0 mg ml<sup>-1</sup>), yielded patterns quite different for the two specimens (Fig. 2). It could easily be seen from Fig. 2 that Degussa P-25 showed an early stage of an S-type isotherm. The lack of an adsorption maximum might express surface unsaturation, which would further lead to an adsorbate–adsorbate interaction. Due to the heterogeneity of adsorbate having components with different affinities for the surface, multiple binding between adsorbed molecules and the oxide surface was also expected. This case was verified by expanding the surface area range out of the studied 0.1–1.0 mg ml<sup>-1</sup> TiO<sub>2</sub> dose then the adsorption isotherm exhibited a full trend of a multistage adsorption

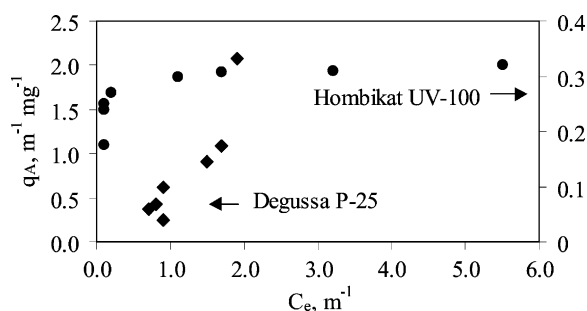


Fig. 2. Adsorption profiles of humic acid (Colour<sub>436</sub>) on TiO<sub>2</sub> specimens, Degussa P-25 and Hombikat UV-100.

isotherm [28]. On the other hand, the equilibrium isotherm obtained for Hombikat UV-100, displayed a Langmuirian type curve describing strong chemical interaction between the adsorbate and the adsorbent. This condition was usually produced either by surface complexation or by significant van der Waals interactions in the adsorption process [29]. Therefore, a simple Langmuir equation assuming the presence of only one type surface site could not be applied satisfactorily to both data obtained for Degussa P-25 and Hombikat UV-100 specimens.

In this study, the adsorption effects of humic acid on the two titania surfaces were interpreted in terms of Freundlich adsorption isotherm model depending on a heterogeneous surface with a continuous distribution of adsorption sites. The Freundlich adsorption model can be explained by the following equation:

$$q_A = K_F C_e^{1/n} \quad (9)$$

$q_A$  is the amount of solute adsorbed per unit weight of adsorbent, m<sup>-1</sup> mg<sup>-1</sup>;  $K_F$  the adsorption capacity;  $C_e$  the equilibrium concentration, m<sup>-1</sup>;  $1/n$  the adsorption intensity.

By the linearisation of Eq. (9) (via plotting  $\log q_A$  against  $\log C_e$ ), the two parameters of the Freundlich equation,  $q_A$  and  $1/n$  could be estimated from the intercept and the slope of the straight line, respectively. The results revealed  $K_F$  values 0.549 for Degussa P-25 and 0.293 for Hombikat UV-100 indicating higher adsorption capacity of Degussa P-25 for humic acid under neutral conditions. Considering  $1/n$  values were merely the empirical linearisation constants of the curvilinear plots covering the concentration effects of the adsorption process; this occurrence on Hombikat UV-100 successfully explained the low adsorption intensity value ( $1/n$ : 0.07), since the trend was not curvilinear once the adsorption maxima was reached. The increasing trend for Degussa P-25 justified the high  $1/n$  value (1.67). Furthermore, mixed crystalline nature of Degussa P-25 (80% anatase, 20% rutile) affected the binding mechanism of humic acid in such a way that adsorption constants increased as well as photocatalytic activity rates. The conflict between the surface areas and the contrary adsorption coefficients ( $K_F$  and  $1/n$ ) might refer to the fact that as the amount of humic acids bound to Hombikat UV-100 increases, the accessibil-

ity of active sites on the surface could be limited as a result of steric blockage by humic macromolecules. Similar results were also reported for the surface coverage (molecules per nm<sup>2</sup>) of Degussa P-25 being higher than Hombikat UV-100 by a factor of  $\cong 4$  for 4-chlorophenol [10]. The amount of humic acid (Colour<sub>436</sub>) adsorbed on Degussa P-25 was three times higher than the amount adsorbed on Hombikat UV-100 for the TiO<sub>2</sub> loading of 0.25 mg ml<sup>-1</sup> that was used in the photocatalytic decolourisation experiments.

It was expected that  $K_{ads}$  derived from L–H kinetic model should be equal to  $K$  values obtained by dark adsorption experiments provided that the surface characteristics remain unchanged upon the light irradiation. However, the adsorption constants calculated separately from L–H and Freundlich/Langmuir equations were quite different from each other. There have been several studies reporting that  $K_{ads}$  determined by the application of the L–H kinetic model was larger than  $K_F$  (Freundlich adsorption coefficient) or  $K_L$  (Langmuir adsorption coefficient) values deduced from the dark adsorption isotherms [30–32]. In contrast to the reported results of others, in this study, the Freundlich,  $K_F$  values were found to be larger than the  $K_{ads}$  values determined from the L–H equation. As an explanation to this behaviour, alteration of the adsorption sites due to the light induced changes in the electronic properties of the TiO<sub>2</sub> surface could be suggested [30]. Also, Liu et al. [33] stated that the Langmuir adsorption coefficients were higher than the  $K_{ads}$  values found from the L–H equation. The reason for this difference was explained by the photodesorption and/or photoadsorption and by the photoreaction of the substrate on the TiO<sub>2</sub> surface.

Under neutral pH conditions of the reaction medium, humic acid was likely to assume more extended (linear) conformations because of the hydrophilicity of the polar functional groups and the mutual repulsion of the ionised groups. Surface layers formed during adsorption process must extend in a direction normal to the surface for distances corresponding to several molecular diameters. Due to the huge molecular size of humic acids, rearrangements in the adsorbed layer either by conformational changes or by exchange of the adsorbed humic acid molecule with the newly arriving ones of larger mass, and desorption of the former photoreacted fractions lead to extreme surface heterogeneity forming microinterfaces within the adsorbed layer. This case lowers the probability of the reactivity of photogenerated holes through direct charge transfer thereby resulting in lowered photocatalytic oxidation rates. Since TiO<sub>2</sub> surface was hydrophilic and should be considered as not favourable for the adsorption of hydrophobic organic compounds, the aromatic moieties of humic acid should extend to the bulk of the solution, controlling the diffusion of the photoreacted species entrapped in the interstitial water regions. Therefore, the overall removal efficiency diminished depending on the strength of the inter- and intra-molecular attractions.

Having examined the quantum yields and the photonic efficiencies for various TiO<sub>2</sub> particles, Serpone [6] explained

the variations in rate due to several reasons like: (1) differences in the crystalline structure of the titania; (2) differences in sizes and shapes of the particles, which might affect the extent of light scattered; (3) differences in the density of the OH<sup>-</sup> groups on the particle surface and in the number of water molecules hydrating the surface; (4) differences in the number and the nature of trap sites both in the lattice and at the surface and finally; (5) the adsorption/desorption characteristics of each surface. In a recent study on the degradation of 4-chlorophenol to investigate the photocatalytic efficiencies of different industrial TiO<sub>2</sub> catalysts including Degussa P-25 and Hombikat UV-100, the influences of particle size, structure or active site density and the surface area of the catalyst were emphasised [10]. It was concluded that for lower surface area, the decrease in the readsorption rate of intermediate products resulted in a decrease in the photodegradation rate. On the other hand, for higher surface area catalysts due to a very low coverage, a lower rate of TOC disappearance was observed. With its moderate surface area (50 m<sup>2</sup> g<sup>-1</sup>) Degussa P-25 was found to be more efficient than Hombikat UV-100 (surface area, 250 m<sup>2</sup> g<sup>-1</sup>) [10]. In relation to the surface area effect, it was reported that the mesoporous texture improved the performance of TiO<sub>2</sub> photocatalyst provided that a high degree of crystallinity was attained leading to better photoreactivity [11]. Materials with high surface area could adsorb a large amount of organic molecules. On the other hand, high surface area powders were usually associated with a large amount of crystalline defects that favours the recombination of electrons and positive holes leading to a poor performance in photoactivity. Due to the presence of mesopores, mass transport could be relatively slow and the intermediate products formed might be confined in such restricted spaces, being able to back-react with active species favouring a net electron-hole recombination.

Considering the presented results, these findings might address some explanations about the different photocatalytic activities of the two titania specimens, namely Degussa P-25 and Hombikat UV-100. Furthermore, the difference in the crystal structures might bring about different binding mechanisms of the humic molecule onto the surface and might cause hindrance of the interface. For Hombikat UV-100, the results especially supported this verdict, since all the gathered data favoured Degussa P-25 as a successful adsorbent and photocatalyst, although none of its qualifications would reveal itself as an appropriate specimen. Therefore, photocatalytic degradation and adsorption coefficients might yield some unexpected results. The presence of mesopores on the Hombikat UV-100 surface could also influence the process efficiency, on the other hand, Degussa P-25 specimen exhibited a non-porous structure.

#### 4. Conclusions

The photocatalytic degradation efficiencies of the two commercial titania samples, Degussa P-25 and Hombikat

UV-100, were investigated in aqueous solution using humic acid. Decolourisation rate of humic acid (Colour<sub>436</sub>, m<sup>-1</sup>) by photocatalytic oxidation both in terms of pseudo-first-order and L-H kinetics was found to be more efficient in the presence of Degussa P-25 than the corresponding Hombikat UV-100 specimen. The results of the adsorption experiments as explained by Freundlich constants revealed higher  $K_F$  values for Degussa P-25 indicating higher adsorption capacity for humic acid at pH 6.7. This was also observed as an increase in the surface oriented reaction rate of humic acid onto titanium dioxide Degussa P-25 (Table 3). This occurrence could not be validated by the higher surface area of Hombikat UV-100 that was expected to render higher adsorption capacity values leading to higher degradation rates. The results showed that the actual photocatalytic rate did not necessarily require the dependency on the BET catalyst surface area. Therefore, morphological and crystallographical properties of TiO<sub>2</sub> might play important roles in the photocatalytic efficiencies.

The agreement in the adsorption parameters and the rate coefficients showed that there was to a certain extent dependency between the adsorption characteristics and the photocatalytic decolourisation rates. Hombikat UV-100 did not portray any effective degradation profile, as expected from its higher surface area. L-H and pseudo-first-order kinetic constants showed that Degussa P-25 was a better photocatalyst. This condition was in accordance with the findings from the adsorption constants. The probable reason for this occurrence could be the unified crystal characteristics of Degussa P-25. Regarding the complexity of the humic acid molecule, the photocatalytic degradation process still remains as an elusive mechanism to be investigated.

The initial adsorption kinetics of humic acids is a rather complex process which could be significantly modified by the reactive properties of humic acids in the presence of an oxide surface depending on the nature of the surface and the solution conditions. Further work is required to elucidate the adsorptive properties of humic acid onto TiO<sub>2</sub>.

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