Photocatalytic degradation of salicylic acid on fixed TiO_2 - kinetic studies

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ABSTRACT. The photocatalytic activity of TiO_2 deposits (Degussa-P25 and Sachtleben-Hombikat) has been studied using salicylic acid as a model water pollutant and an UV-fluorescent lamp as a light source. Both catalysts have shown very similar properties towards the photocatalytic degradation of salicylic acid. Special attention has been given to the effect of the light flux absorption and of the pollutant adsorption. Moderate mass-transfer limitation has been found. Specific parameters of the phenomenon have then been determined for the two catalysts and a simple general expression of the rate of photocatalytic degradation has been derived.

1. INTRODUCTION

The photocatalytic treatment of water pollutants has been widely developed during the last decade (for example [1, 2]). The main interest of such a method is the complete mineralisation of pollutants in the presence of titanium dioxide and UV irradiation. Suspended TiO_2 provides an efficient photocatalytic activity but the photocatalyst has to be removed from the purified water by a separation process. This can be avoided by using an immobilised titanium dioxide deposit film. Studies have been carried out on various topics ranging from fundamental aspects (for example [3]) to engineering using suspension [4]. In the present study, a photocatalyst has been immobilised on a flat support and has been tested on a bench-scale reactor in order to assess the parameters dictating the kinetics of a pollutant degradation and the efficiency of the deposit, keeping in view the operative aspects in photocatalytic engineering. Salicylic acid was chosen as a usual model pollutant for such a study [5, 6, 7, 8, 9].

2. EXPERIMENTAL

Titania Degussa-P25 (P25) and Sachtleben-[Hombikat UV-100] (HK) were obtained from the manufacturers, salicylic acid (SA) was reagent grade and used without further purification. De-ionised water was used for the solutions. The titania samples were deposited on a flat glass plate according to the following procedure. The clean plate was treated with dilute nitric acid, then washed and dried. A suspension of TiO_2 of $4\text{ g}\cdot\text{L}^{-1}$ at pH about 6 was stirred and sonicated then poured on the plate and the excess removed. The wetted plate was dried at 100°C for 1 hr then fired at 450°C for 4 hrs. After rinsing under running distilled water in order to remove loose particles, the amount of deposit was determined by weighing the dried plate before and after the deposition. This amount is given in the following as a "specific mass"

expressed in $\text{mg}\cdot\text{cm}^{-2}$. The corresponding thickness was determined from profilometry measurements to be of about $16\text{ }\mu\text{m}\cdot(\text{mg}\cdot\text{cm}^{-2})^{-1}$ for HK deposits. Thick layers were prepared by repeating the same procedure and using a suspension of higher concentration.

Light absorption by the deposits was monitored with a Perkin-Elmer Lambda2 spectrophotometer equipped with an integrating sphere. The raw spectra were corrected on the basis of the absence of absorption in the visible range.

Optical microscopy was performed on a Zeiss microscope and electron microscopy on a Jeol T330A apparatus. Optical profilometry was performed on a UBM profilometer equipped with a Microfocus probe.

The photocatalytic workbench has already been described [10]. It consists of a parallelepiped reactor with the catalyst on a flat glass plate $4\times 50\text{ cm}^2$ on the bottom, irradiated by a parallel UV fluorescent lamp (Mazda, 6 W, 56 cm long, emitting around 365 nm) and the aqueous solution running freely on to the plate. The concentration of the salicylic acid was measured with an HPLC chromatograph equipped with a Shimadzu SPD-6A spectrophotometric detector. A Lichrosob column was used and elution was carried out using a mixture of methanol and water.

3. ADSORPTION EQUILIBRIUM AND KINETICS

The SA adsorption isotherms have been monitored on deposited titania at room temperature (ca 21°C) using the experimental set-up described above, in the absence of irradiation (*cf.* Figure 1). The value of the pH is known to have an influence on the SA adsorption [11]. Under the experimental conditions, the pH was found to be about 4.5. An apparent Langmuir model is followed as shown by the linear variation of $1/Q$ vs $1/C$ where Q is the specific adsorbed quantity and C the SA concentration. From these plots the maximum specific adsorbed quantity Q_{max} and the adsorption constant K_L were determined (see Table 1). Accordingly, the ad-

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sorbed quantity is given by the Langmuir relationship:

$$Q = Q_{\max} \frac{K_L C}{1 + K_L C} \quad (1)$$

Figure 1. Isotherms of salicylic acid adsorption on titania deposits- Filled squares: P25 ($\mu = 0.22 \text{ mg} \cdot \text{cm}^{-2}$); empty squares: HK ($\mu = 0.54 \text{ mg} \cdot \text{cm}^{-2}$).

Figure 2. Adsorption of salicylic acid on P25 in suspension (lozenges), on plain deposit (empty circles), on fired deposit (filled circles), $C = 0.067 \pm 0.02 \text{ mmol} \cdot \text{L}^{-1}$.

The specific adsorbed quantities on deposited or suspended titania have been compared and found to be nearly identical as shown in Figure 2 (an initial SA concentration of $0.070 \text{ mmol} \cdot \text{L}^{-1}$ was always used but the equilibrium concentration varied slightly depending on the amount of catalyst). This means that the deposition does not hamper the access of pollutant to the catalyst. Titania samples are indeed aggregates of elementary crystals [12] and the deposition of these aggregates is not expected to alter the adsorption. The comparison

of the adsorbed quantity on fired or non-fired samples in Figure 2 shows that firing slightly reduced the adsorption as has already been observed [5]. Similar results were obtained on HK although the firing did not alter the adsorption. On the whole, the samples used for photocatalytic degradation of SA (deposited and fired) can be considered as having about the same adsorption power as suspended samples.

Table 1. Parameters in the adsorption and the kinetics of photocatalytic degradation of salicylic acid on deposited P25 and HK titania samples.

sample	P25	HK
LIGHT ABSORPTION		
$A_{\max}$	0.7	0.6
$\alpha \text{ (cm}^2 \cdot \text{mg}^{-1}\text{)}$	5.2	5.7
ADSORPTION		
specific area ($\text{m}^2 \cdot \text{g}^{-1}$)	43 [12]	190 [14]
$Q_{\max} \text{ (mmol} \cdot \text{g}^{-1}\text{)}$	0.095	0.105
$K_L \text{ (L} \cdot \text{mmol}^{-1}\text{)}$	4.4	24
$k_{\text{ads}} \text{ (min}^{-1}\text{)}$	≈ 0.2	≈ 0.12
fraction of occupied surface	0.4	0.09
KINETICS		
$K_{LH} \text{ (L} \cdot \text{mmol}^{-1}\text{, mean value)}$	25	35
$k_{\text{deg}} \text{ (g} \cdot \text{min}^{-1/2} \cdot \text{mE}^{-1/2} \cdot \text{cm}^{-1}\text{)}$	$7.9 \cdot 10^{-4}$	$5.1 \cdot 10^{-4}$

The kinetics of adsorption was studied by monitoring the decrease in the concentration with time of contact. The increase in the adsorbed quantity was fitted by the classical relationship in equation (2) where $Q(t)$ is the current adsorbed quantity and Q_e the adsorbed quantity at equilibrium [12] (assuming a nearly constant concentration during the adsorption):

$$Q(t) = Q_e \cdot [1 - \exp(-k_{\text{ads}} t)] \quad (2)$$

The adsorption rate constant k_{ads} was determined from the semilogarithmic plot of $[Q_e - Q]$ versus the time t . Considering the relatively short time of adsorption, this rate constant could not be obtained with good accuracy. It ranked from 0.1 to 0.4 min^{-1} for fired P25, with an average value of 0.20 min^{-1} . A somewhat lower value of 0.12 min^{-1} was found for the adsorption on HK. In addition, the rate constant of adsorption k_{ads} was found to be comparable with the value of 0.12 min^{-1} observed in suspension [12]. This confirms that the access of salicylic acid to the solid is not altered by the deposition process.

The adsorption properties on P25 and HK are slightly different. The constant of adsorption K_L is higher on HK but the specific maximum adsorbed quantities $Q_{\max}$ are similar. The fraction of occupied surface at maximum adsorption can be obtained from the specific area and the estimated area occupied by a single molecule of SA (about 0.32 nm^2). As shown in Table 1, the adsorption by an HK surface is much smaller than that of a P25 surface. HK is mostly anatase [14] whereas P25 is about 3/4 anatase and 1/4 rutile [13], this could suggest

higher adsorption properties of the rutile form but different preparation conditions are probably the origin of the differences in surface properties. There are indeed several varieties of surface sites according to the surroundings of titanium and oxygen surface ions [11]. It is not possible to correlate the observed adsorption properties with the surface structure but on the whole, the HK surface appears more specific, with stronger adsorption sites.

4. PHOTOCATALYTIC DEGRADATION OF SALICYLIC ACID

The photocatalytic process has been followed by monitoring the rate of disappearance of SA. Although the phenomenon takes place within the catalyst layer, it can be considered as a support-surface phenomenon in photocatalytic engineering. Due to the strong absorption of the light by the catalyst, only a thin coat is required. The activity within the three-dimensional thin layer of catalyst can therefore be considered as a pseudo activity of the catalyst impregnated support surface, which is the required parameter in the design of the reactor. The rate of the reaction r is then defined as being the quantity of SA disappeared per unit time and active support area, expressed in $\text{mmol} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$.

As will be pointed out later, the layer thickness intervenes in the phenomenon but from a practical point of view, this thickness will only be considered as a parameter of the pseudo-bidimensional process. Note that, for practical reasons, the thickness of the layer will be represented here by the "surface specific mass" μ ($\text{mg} \cdot \text{cm}^{-2}$) of the deposit in preference to the actual thickness (μm), to which it is proportional.

Degradation experiments have been carried out after allowing the system to equilibrate during about 1 h in the dark. The true initial concentration before adsorption decreases then to an equilibrium value C , which is the initial concentration for the degradation process. The pH of the solution was typically of about 4.5.

The influence of the initial SA concentration C , light flux F_0 and deposit surface specific mass μ have been studied. In these experiments, the rate has been determined over an extent of degradation of about 0.2.

4.1. Influence of the SA concentration. The variations of the rate of photocatalytic degradation r with the concentration C are represented in Figure 3. These variations are similar to those of the Langmuir isotherm, which suggests that the rate r is proportional to the surface coverage θ . This is the well-known Langmuir-Hinshelwood mechanism. This latter results from the assumption that the attack of the adsorbed pollutant molecule by a surface reactive species (OH radical, hole) is much slower than the rate of disappearance of the reactive species. The rate is then expressed as:

$$r = k_{LH} \cdot \theta = k_{LH} \cdot \frac{K_{LH}C}{1 + K_{LH}C}, \quad (3)$$

where k_{LH} ($\text{mmol} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$) is an apparent kinetic rate constant per unit support area. This rate constant is a function of various parameters, especially the deposit thickness μ , the light flux F_0 and the water flow rate D . The adsorption constant K_{LH} would be identical to K_L if the Langmuir model were strictly followed, i.e. assuming a single type of site. The constant K_{LH} can be determined by plotting $1/r$ against $1/C$. As can be seen in Table 1, the value for K_{LH} is higher than K_L , especially for P25. The value of $25 \text{ L} \cdot \text{mmol}^{-1}$ is comparable with that of about $60 \text{ L} \cdot \text{mmol}^{-1}$ already reported for a similar catalyst [9]. There is no doubt that the adsorption sites do not all participate in the photocatalytic degradation process. This could be understood by considering that the Langmuir adsorption model, although satisfactory, represents an average adsorption process on a variety of sites, those of high adsorption constant being the most active in the photocatalytic degradation, as has already been suggested [10]. Alternatively, it can be argued that the irradiated catalyst possesses different adsorption properties.

Figure 3. Influence of the concentration C on the rate r of photocatalytic degradation of salicylic acid. Filled squares: P25 ($\mu = 0.22 \text{ mg} \cdot \text{cm}^{-2}$); empty squares: HK ($\mu = 0.55 \text{ mg} \cdot \text{cm}^{-2}$); flow rate $600 \text{ mL} \cdot \text{min}^{-1}$, irradiation flux $F_0 = 4.3 \cdot 10^{-4} \text{ mE} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$.

This discrepancy between adsorption and photocatalytic degradation can also be checked by plotting the rate r against the surface coverage $\theta = Q/Q_{\text{max}}$ as shown in Figure 4. For HK there is no noticeable discrepancy as r is nearly proportional to θ , but for P25 the discrepancy is obvious. Considering that K_{LH} takes a similar value for P25 and HK, the whole effect can be pictured as the existence of an adsorption site of high efficiency for photocatalytic activity, which exists in a high proportion on the HK surface whereas it represents a small proportion on the P25 surface.

From a practical point of view, in the design of

a photoreactor, the apparent *LH* mechanism, although approximate, proves here to be a good model for relating the photocatalytic degradation rate to the pollutant concentration.

Figure 4. Variation of the photocatalytic rate of SA degradation against the surface coverage. Symbols and conditions as in Figure 3.

4.2. Influence of the light flux. The light flux F_0 has been varied by changing the distance d between the catalyst plate and the parallel fluorescent lamp. When using a light point source and irradiating the catalyst with a small solid angle, the flux would be proportional to $1/d^2$. Under the present conditions the source is extended and the solid angle of irradiation is important so that this usual law is not obeyed. The relative variation of F_0 was computed assuming a simple emission model (isotropic emission by the lamp surface). Under our conditions of a fluorescent lamp of length 56 cm and a parallel rectangular plate of $4 \times 50 \text{ cm}^2$, F_0 was found to be practically proportional to $1/d$ in the range of d [4.4–44 cm]. This calculation compared satisfactorily with actinometric measurements, using uranyl-oxalate. The average value of F_0 under the standard experimental conditions ($d = 8.5 \text{ cm}$) was found to be $4.3 \cdot 10^{-4} \text{ mE} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$.

The variation of r with F_0 for given conditions of concentration and deposit thickness have been determined for P25. They are given in Figure 5 which shows that r is proportional to $F_0^{1/2}$.

The effect of the irradiation has been confirmed by an alternative experiment where the amount of absorbed light is varied by changing the deposit thickness at constant light flux. The absorbed energy is then proportional to the fraction of absorption A , measured using an integrating sphere (see below). As shown in Figure 6, the rate r is practically proportional to $A^{1/2}$ both for P25 and HK, in agreement with the preceding experiment.

Both experiments show that the rate of reaction is proportional to the square root of the light absorption. This implies that the reactive species (OH

radicals or free charges) resulting from the light absorption disappear mainly through a bimolecular annihilation process, possibly the electron-hole recombination as has already been suggested [15, 16, 17].

Figure 5. Influence of the light flux F_0 on the rate of photocatalytic degradation of salicylic acid r . P25 deposit; $\mu = 0.22 \text{ mg} \cdot \text{cm}^{-2}$, flow rate $D = 110 \text{ mL} \cdot \text{min}^{-1}$, $C = 0.07 \text{ mmol} \cdot \text{L}^{-1}$.

Figure 6. Variation of the rate of photocatalytic degradation of salicylic acid r with the fraction of absorption A of the deposit. Symbols and conditions as in Figure 3.

4.3. Light absorption properties. The deposit thickness, or surface specific mass μ ($\text{mg} \cdot \text{cm}^{-2}$) as defined above, did not alter the mass specific adsorption but it played an important role in the photocatalytic degradation as shown in Figure 7. The limiting value of r results from a limiting value in the light absorption: the incident flux is maintained constant but the fraction of absorption A increases towards a limiting value A_{max} . The effect of the specific deposited mass is then redundant

with the effect of light absorption described above.

The variation of the absorption with the specific deposited mass has been followed with the aid of an integrating sphere. The fractions of transmission T and reflection R have been measured and A has been deduced from the energy balance ($R + A + T = 1$). The variations of these parameters are satisfactorily represented by an apparent exponential law analogous to the classical Beer-Lambert law for non turbid media:

$$A = A_{\max} \cdot [1 - \exp(-\alpha\mu)]. \quad (4)$$

The values of the parameters $A_{\max}$ and α for both catalytic deposits are given in Table 1. The HK deposit exhibits a slightly higher reflection ($1 - A_{\max}$) compared to that of the P25 deposits (0.4 and 0.3, respectively). The absorption coefficient α reflects both the actual absorption properties of the bulk of the crystals and the inner scattering dictated by the surface of the crystals. Note that P25 and HK deposits possess very similar absorption coefficients α although they differ slightly in their crystallographic structure. The value of α of about $5.5 \text{ cm}^2 \cdot \text{mg}^{-1}$ at 365 nm can be compared with those of the equivalent parameter κ determined in suspension. A similar value has been reported [4] at shorter wavelengths, around 340 nm for P25 and 310 nm for HK, whereas the absorption is very low around 365 nm. This discrepancy could be due to very different conditions of measurement (dry thin deposit or aqueous suspension).

Figure 7. Influence of the deposit specific mass μ on the rate of photocatalytic degradation of salicylic acid r . Filled squares: P25; empty squares: HK; flow rate $D = 600 \text{ mL} \cdot \text{min}^{-1}$, irradiation flux $F_0 = 4.3 \cdot 10^{-4} \text{ mE} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$, $C = 0.07 \text{ mmol} \cdot \text{L}^{-1}$.

4.4. Transfer processes. Transfer processes take place both outside the deposit (external transfer) and inside the deposit (internal transfer) and have to be considered separately.

Changing the flow rate D of the circulating solution will only modify the external transfer process. As

shown in Figure 8, there is a slight effect of D on the rate r of photocatalytic degradation, which means that an external transfer limitation intervenes, at least at low flow rate. However, under the standard conditions of the present study, at the maximum flow rate, the rate r is nearly independent of D , that is the external transfer is fast and has practically no effect on the kinetics. In addition, in our experimental set-up where the flow velocity is proportional to D , the transfer coefficient can be assumed [18] to be proportional to $D^{4/5}$. Thus, increasing D from 110 to $600 \text{ mL} \cdot \text{min}^{-1}$ would multiply the rate by a factor of about 4 if it were dictated by the external transfer although the experimental increase is only 18%, which corroborates the principle of a minor effect of the external transfer on the kinetics.

Figure 8. Influence of the flow rate D on the rate of photocatalytic degradation of salicylic acid r . P25 deposit, $\mu = 0.22 \text{ mg} \cdot \text{cm}^{-2}$, $C = 0.07 \text{ mmol} \cdot \text{L}^{-1}$, irradiation flux $F_0 = 4.3 \cdot 10^{-4} \text{ mE} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$.

The effect of an internal transfer has also been analysed by changing the geometry of the irradiation system as shown in Figure 9. In addition to the conventional setting of the lamp above the solution ("catalyst side" irradiation), the lamp could be positioned under the reactor ("glass side" irradiation) owing to a transparent reactor bottom and catalyst support. The irradiation flux was kept practically identical by allowing the same distance between the lamp axis and the deposit. In addition to these two conditions a third condition was experimented using two lamps simultaneously, one above and one under the reactor ("both sides" irradiation).

The effect of the deposit thickness μ has been studied under these three irradiation conditions and the results are plotted on Figure 10 and Figure 11.

As shown in these figures, the rate r_C under "catalyst side" irradiation increases to a limiting value corresponding to a limiting value in absorbed light energy as observed in titania suspensions [19]. In the "glass side"

irradiation, the light flux impinges on the lower side of the deposit whereas the pollutant molecules enter the deposit from the upper side. Under these conditions, the internal transfer takes place over a much larger distance than it does under “catalyst side” irradiation as is shown schematically in Figure 9. This should lead to a rate r_G smaller than r_C , particularly at high thickness when light absorption takes place within a fraction of the deposit thickness. However, although very thick deposits were tested (actually outside a sensible range for practical use), no effect was observed for HK and only a slight decrease in r was observed for P25.

Figure 9. Schematic irradiation conditions “catalyst side”, “glass side” and “both sides” and expected effect on the internal transfer.

Figure 10. Influence of the catalyst thickness μ on the rate of photocatalytic degradation of salicylic acid on P25 deposits. Rates r_C , r_G , r_{CG} under irradiation of “catalyst side”, “glass side”, and “both sides”, respectively, ($D = 110 \text{ mL} \cdot \text{min}^{-1}$, $C = 0.07 \text{ mmol} \cdot \text{L}^{-1}$, $F_0 = 4.3 \cdot 10^{-4} \text{ mE} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$). Comparison of r_{CG} with the values of r_{OVER} and r_{SEP} for perfectly overlapping or separate irradiations.

Therefore, it could be understood from these experiments that the internal transfer has little influence

on the kinetics, especially for HK samples. The rate of mass-transfer is therefore faster than the rate of degradation. However it can be noted that the rate of adsorption was found to be only about twice that of photocatalytic degradation, (due to the difficulty in measuring the rate of adsorption, this comparison was carried out on the average of several experiments at various deposit thickness). The rate of degradation is necessarily smaller than the rate of adsorption, but in the present case, it is not negligible so that a moderate diffusional limitation could be expected.

Figure 11. Influence of the catalyst thickness μ on the rate of photocatalytic degradation of salicylic acid on HK deposits (symbols and conditions as in Figure 10).

Actually, some limitation takes place under “both sides” irradiation. The rate r_{CG} under these conditions (with two lamps) is lower than the sum of the rates r_C and r_G (with only one of the lamps). At small thickness, there is a total overlap of the light absorption and taking into account a rate proportional to the square root of the absorbed light as seen above, the global rate should be equal to $r_{OVER} = [r_C^2 + r_G^2]^{1/2}$. On the contrary, at high thickness of the deposit, when there are separate irradiations, the global rate should be equal to $r_{SEP} = [r_C + r_G]$. Both rates r_{OVER} and r_{SEP} have been plotted in Figure 10 and Figure 11. According to the values of α given in Table 1, about 90% of the absorption takes place within a deposit of $0.4 \text{ mg} \cdot \text{cm}^{-2}$ and therefore the value r_{SEP} would be expected for r_{CG} for deposits of more than $0.8 \text{ mg} \cdot \text{cm}^{-2}$.

Accordingly, at small thickness r_{CG} is equal to r_{OVER} . However, at high thickness r_{CG} evolves from the “overlap” condition to the “separate” condition, but the limiting value of r_{SEP} is not reached, even at $2 \text{ mg} \cdot \text{cm}^{-2}$ where there is a quasi total absorption within 25% of the deposit depth, ensuring complete separation of “glass” and “catalyst” irradiations. This could be understood as a diffusional limitation effect, as the consumption of reactant in the top layer would hamper the access to the

bottom layer. The diffusional effect is more apparent in double irradiation as the rate of reactant consumption is twice as large as it is when using a single irradiation. It can be noted that the effect is less important for HK samples where no effect was observed in single irradiation.

The effect of the mass-transfer phenomenon can be estimated by the Weisz modulus [20, 21] (modified Thiele modulus):

$$\varphi = \frac{r_{\text{app}} \cdot L^2}{D_{\text{eff}} C}, \quad (5)$$

where r_{app} is the apparent volumetric rate (rate per unit of deposit volume), L the characteristic dimension of the catalyst, D_{eff} the effective diffusion coefficient and C the concentration in the solution (actually this ought to be the concentration at the deposit surface, but in the absence of external mass-transfer limitation, this is practically equal to C).

The Weisz modulus has been estimated for severe conditions (deposit specific mass of $0.75 < \text{mg} \cdot \text{cm}^{-2}$, rate of $13 \mu\text{mol} \cdot \text{m}^{-2} \cdot \text{min}^{-1}$). Assuming a thickness of the deposit of about $12 \cdot 10^{-6} \text{ m}$, a value of r_{app} was $4.2 \cdot 10^{-2} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3}$. As the deposit is in the shape of a slab, L is equal to the thickness. The diffusion coefficient of the reactant in water can be estimated to $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ on the basis of known coefficients [22] for comparable molecules and assuming typical values of 0.5 for porosity and 3 for the tortuosity factor, a value of $1.6 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ has been obtained for D_{eff} . The typical value of $0.07 \text{ mol} \cdot \text{m}^{-3}$ was given to C_s . Under these conditions, the Weisz modulus was about 0.7. The efficiency η of the catalyst is defined as the ratio of the actual rate to the maximum rate in absence of diffusional limitation. This efficiency was then determined, according to the classical diffusional model [20], to be about 0.8. This represents a moderate effect of mass-transfer as observed. This agreement is satisfactory, but still, the classical diffusional model corresponds to a first order kinetics whereas according to the Langmuir-Hinshelwood mechanism, the apparent order is actually lower than 1 in the range of concentration considered. In addition, the irradiation is not uniform, and neither is the catalyst activity, which also differs from the conditions in the classical model.

The small difference between the rates determined by irradiation on “catalyst side” or “glass side” can also be related to the structure of the deposit. The suspension used to build it consists of aggregates of elementary crystals [12] but the deposit is not a uniform tight packing of these aggregates: many cracks can be found under observation in optical and electron microscopy and smaller cracks on the micrometric scale, although not visible, are likely to take place, due to the shrinking of the wet deposit during drying and firing. The deposit can then be pictured as a being composed of associations of aggregates, inducing some mass transfer limitation, separated by relatively wide cracks where mass transfer is very fast. Under these conditions, mass

transfer within the aggregates would partly hamper the kinetics of degradation, as already suggested in suspensions [12] but this effect would not depend much on the deposit thickness as a fast mass transfer would take place through the cracks.

4.5. Expression for the rate of photocatalytic degradation. Taking into account the influence of the various parameters, the rate of photocatalytic degradation of salicylic acid on a thin deposited titania layer can be expressed as:

$$r = k_{\text{deg}} \cdot \sqrt{F_0 \cdot A_{\text{max}} \cdot [1 - \exp(-\alpha \cdot \mu)]} \cdot Q_{\text{max}} \cdot \frac{K_{\text{LH}} \cdot C}{1 + K_{\text{LH}} \cdot C}. \quad (6)$$

In this relationship, the apparent rate constant k_{deg} depends on non explicit parameters such as temperature and pH for example.

This master relationship includes:

- i) intrinsic parameters of the deposit (P25 or HK) as given in Table 1: A_{max} , α ,
- ii) intrinsic parameters of the [titania-reactant] system as given in Table 1: k_{deg} , Q_{max} and K_{LH} ,
- ii) working condition parameters: F_0 (irradiation flux), μ (deposit thickness) and C (reactant concentration).

Such a relationship is believed to be relevant for the design of a photoreactor using thin titania deposits. The value of k_{deg} is given in Table 1. It is higher for P25, but there are more active sites on HK so that there is little difference in the properties of these two samples towards the photocatalytic degradation of SA as these two effects compensate as shown in Figure 6. A slightly lower reflection of P25 leads to a higher maximum rate for thick deposits than for HK but the quantum yield (ratio of r to $A \cdot F_0$) is identical for both samples.

It is noteworthy that slicing a given deposit into smaller deposits will increase the total rate. For example, using two parallel separate half-layers of thickness $\mu/2$ instead of a single layer of thickness μ will increase the total rate by a factor up to $\sqrt{2}$. This effect is due to the dependence of the rate on the local volumetric absorbed intensity as discussed above. Such a property suggests the use of a succession of several separate thin deposits instead of using the same total specific mass in a single thick deposit [23]. Note that mass transfer limitation would suggest this design but in the present case, where mass transfer is not a limiting factor, this suggestion arises from the light absorption phenomenon.

5. CONCLUSION

The photocatalytic degradation of salicylic acid on deposited commercial titania samples has been studied with special attention to the effect of the deposit thickness, the pollutant concentration and the irradiation flux. This allows us to suggest a global relationship for the rate of the reaction as a function of the working conditions (irradiation, deposit thickness, concen-

tration) and intrinsic parameters of the system, which have been determined. Both catalysts have been found to possess different adsorption and activity properties although these cancel out so that they have practically identical photocatalytic properties towards the present reactant. External mass transfer can easily be cancelled at a rather small flow rate. Increasing the deposit thickness had little effect on the extent of internal mass transfer limitation. This analysis of the effect of deposit thickness suggests that several separate thin deposits should be used in the design of a photocatalytic reactor instead of a single layer.

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NOMENCLATURE

Roman letters:

A : fraction of absorption of light by the deposit.

$A_{\max}$: limiting value of A .

C : salicylic acid concentration ($\text{mmol}\cdot\text{L}^{-1}$).

d : distance between the fluorescent lamp and the deposit.

D : flow rate of the circulating solution ($\text{mL}\cdot\text{min}^{-1}$).

D_{eff} : effective diffusion coefficient in the catalyst deposit (m^2s^{-1}).

F_0 : light flux ($\text{mE}\cdot\text{cm}^{-2}\text{s}^{-1}$).

HK: Sachtleben Hombikat UV-100 titania sample.

k_{ads} : kinetic constant of adsorption (min^{-1}).

k_{deg} : intrinsic apparent kinetic rate constant ($\text{g}\cdot\text{min}^{-1/2}\cdot\text{mE}^{-1/2}\cdot\text{cm}^{-1}$).

k_{LH} : apparent kinetic rate constant ($\text{mmol}\cdot\text{min}^{-1}\text{cm}^{-2}$).

K_L : adsorption constant (from Langmuir isotherm, $\text{L}\cdot\text{mmol}^{-1}$).

K_{LH} : adsorption constant (from Langmuir-Hinshelwood kinetics, $\text{L}\cdot\text{mmol}^{-1}$).

L : deposit thickness (m).

P25: Degussa P25 titania sample.

Q : specific adsorbed quantity ($\text{mmol}\cdot\text{g}^{-1}$).

Q_e : specific adsorbed quantity at equilibrium ($\text{mmol}\cdot\text{g}^{-1}$).

$Q_{\max}$: maximum specific adsorbed quantity ($\text{mmol}\cdot\text{g}^{-1}$).

r : surface specific rate of photocatalytic degradation ($\text{mmol}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$) (relative to the support surface).

r_{app} : apparent volumetric rate ($\text{mol}\cdot\text{s}^{-1}\text{m}^{-3}$).

r_C, r_G, r_{CG} : experimental values of r for "catalyst side", "glass side" and "both sides" irradiations, respectively.

$r_{\text{OVER}}, r_{\text{SEP}}$: calculated values of r with total overlap or no overlap of "catalyst side" and "glass side" irradiations, respectively.

R : fraction of reflection of light by the deposit.

SA: salicylic acid.

T : fraction of transmission of light by the deposit.

Greek letters:

α : apparent extinction coefficient ($\text{cm}^2\cdot\text{mg}^{-1}$).

φ : Weisz modulus (modified Thiele modulus).

μ : deposit surface specific mass ($\text{mg}\cdot\text{cm}^{-2}$).

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