

Adsorption properties of TiO_2 related to the photocatalytic degradation of organic contaminants in water

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Abstract

The purpose of this study was to correlate the photocatalytic degradation of water contaminants with the adsorption phenomena, taking both the equilibrium state and kinetics into consideration. 1,2-Dichloroethane (DCE) was chosen as a test pollutant. The adsorption isotherm was found to follow the Langmuir model. The kinetics of adsorption were studied and interpreted as a mass transfer process. The kinetics of photocatalytic degradation were analysed with special attention given to the influence of the reactant concentration. A kinetic model is proposed, which includes mass transfer, leading to an apparent Langmuir–Hinshelwood equation for the degradation rate, even when the kinetics are controlled by mass transfer. The experimental results show an agreement with the model at concentrations above 0.5 mmol l^{-1} , but at lower concentrations the rate is lower than expected, possibly due to a loss of DCE or hydroxyl radicals.

Keywords: Adsorption; Photocatalytic degradation; Organic contaminants

1. Introduction

Heterogeneous photocatalysis on TiO_2 is a promising method for the elimination of toxic and bioresistant organic and inorganic compounds from wastewater by their transformation into harmless species [1–3]. In the last decade, the mechanism of heterogeneous photocatalysis of TiO_2 has been the subject of numerous publications. It is agreed that the main step of degradation is the formation of highly reactive OH^\cdot radicals on the irradiated semiconductor, although the direct oxidation of the product by electron vacancies has also been suggested, especially in the case of ZnO [4], but also for TiO_2 [5,6]. There is also some debate about whether the OH^\cdot radical and/or the pollutant react as adsorbed species, as summarized in Ref. [7]. However, the most commonly suggested mechanism is the reaction between adsorbed species, leading to the classical Langmuir–Hinshelwood rate expression [8]. Few investigations have been published which consider the actual adsorption of the organic contaminants on TiO_2 . Moreover, the effect of this phenomenon on the kinetics of photocatalytic degradation has been overlooked, although it has been reported [9–11] that a contact time

(about 1 h or more) must be allowed prior to irradiation in order to reach the adsorption equilibrium. As the photocatalytic degradation is particularly effective on halocarbons, this study was carried out using 1,2-dichloroethane (DCE) as a test substance. The adsorption of DCE on titania powder was studied with particular attention given to the effect of this process on the kinetics of the photocatalytic degradation reaction.

2. Experimental procedures

2.1. Materials

The titanium dioxide (Degussa P25) was mainly anatase. According to the manufacturer's specifications [12], the elementary particle in dry powder form was approximately spherical in shape and the particle size was approximately 20 nm. The specific surface area, as measured from N_2 adsorption at 77 K, was $44 \text{ m}^2 \text{ g}^{-1}$, in agreement with the manufacturer's specification. The size distribution of the particles suspended in water was measured by laser diffraction on a Malvern Mastersizer apparatus; the average suspended particle size was $5 \mu\text{m}$. The pollutant (DCE) was a laboratory reagent and was used without further purification. The water

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used for all solutions and slurries was ion exchanged prior to use.

2.2. Adsorption measurements

Experiments on adsorption–desorption of DCE on TiO_2 were carried out in a 600 ml Pyrex vessel equipped with a magnetic stirring bar. As DCE is volatile, the vessel was completely filled and sealed so as to be free of any gaseous phase. Adsorption was followed by measurement of the DCE concentration in the aqueous phase.

2.3. Photodegradation apparatus

The reactions were carried out in a flow photoreactor made of Pyrex and Teflon. The catalyst slurry was circulated through a 220 ml cylindrical reactor and a 600 ml sampling vessel equipped with a magnetic stirring bar using a polypropylene centrifugal pump (maximum flow, 300 ml min^{-1}). The reactor inner radius was 1.0 cm. Six 18 W medium-pressure mercury fluorescent lamps (Mazda TFWN18) provided the illumination. They were positioned parallel to the reactor axis, in a hexagonal arrangement. The wavelength domain of irradiation was continuous from approximately 350 to 390 nm and no additional light filtering was used. The temperature of the reactor was maintained constant at 20°C using an air circulation system. A load of catalyst of $W=0.6 \text{ g l}^{-1}$ was used as it led to the best photodegradation rate in the present apparatus. As in the adsorption experiments, the whole apparatus was kept free of gaseous phase. The suspension was air saturated before sealing, and the amount of dissolved oxygen was not sufficient to allow complete photo-oxidation of the reactant. Kinetic studies are therefore restricted to a small degree of reaction.

2.4. Measurement of DCE concentration in the aqueous phase

Aliquots of 0.1 ml were withdrawn with a syringe through a rubber septum, and then filtered using a $0.1 \mu\text{m}$ membrane filter in order to remove the TiO_2 particles. The DCE concentrations in the filtered samples were then measured using a Hewlett-Packard model 5890 gas chromatograph equipped with a flame ionization detector. Samples of $0.5 \mu\text{l}$ were injected directly onto a 2 m stainless steel column containing 30% SE30 on Chromosorb. The peak areas on the chromatograms were converted to DCE concentration using a linear calibration curve. A slight adsorption on the filter (around 5%) was taken into account in this calibration.

3. Results and discussion

3.1. Adsorption of DCE on TiO_2

Adsorption equilibrium

The time evolution of the adsorption of DCE on titania is shown in Fig. 1 for various initial concentrations C_i in DCE, where Q is the specific adsorbed quantity (mmol g^{-1}) at contact time t , determined from the decrease in the concentration in the aqueous phase.

The saturation time was found to be about 60 min. The extent of adsorption then remained practically constant even for an extended period of contact (4 h). Therefore the plateau can be considered to be the state of adsorption equilibrium. In addition, the reversibility of the adsorption process was verified by following the release of DCE after dilution (as has already been observed for organic acids in Ref. [10]).

Adsorption isotherm

From the limiting values in Fig. 1, the adsorption isotherm $Q_a(C_e)$ can be plotted (see inset in Fig. 2), where Q_a is the specific adsorbed quantity of DCE and C_e is the solute concentration, both at equilibrium. The conventional linear transform of the Langmuir isotherm

$$\frac{C_e}{Q_a} = \frac{1}{KQ_{\max}} + \frac{1}{Q_{\max}} C_e \quad (1)$$

where Q_{\max} is the specific number of adsorption sites accessible to DCE molecules on the TiO_2 surface and K is the adsorption constant, is a satisfactory linear plot (Fig. 2) giving $Q_{\max}=0.18 \text{ mmol g}^{-1}$ and $K=2.5 \text{ l mmol}^{-1}$.

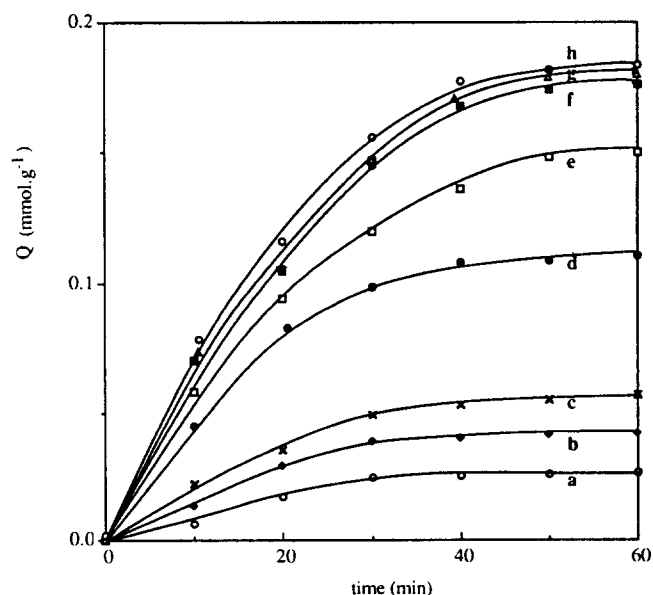


Fig. 1. Time evolution of the adsorption of DCE on TiO_2 for various initial concentrations (mmol l^{-1}) of the adsorbate (catalyst load, 0.6 g l^{-1} ; temperature, 20°C ; pH 5.7): a, 0.05; b, 0.10; c, 0.20; d, 0.50; e, 0.80; f, 1.20; g, 1.50; h, 2.00.

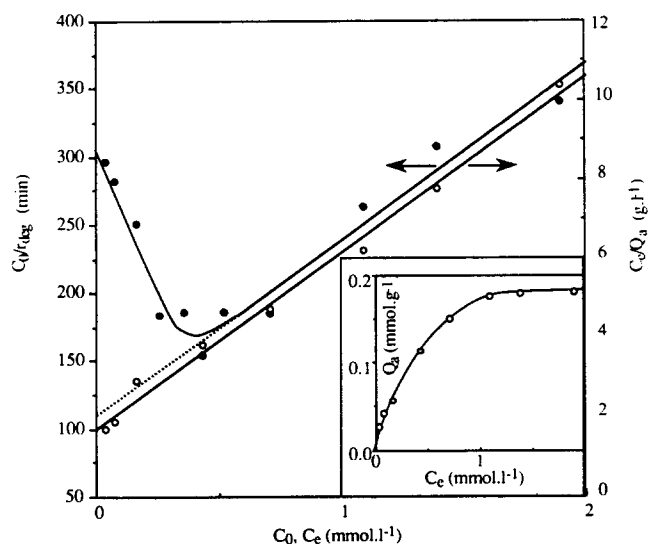


Fig. 2. Comparison of the variations of C_e/Q_a and C_0/r_{deg} vs. C_e or C_0 (conditions as in Fig. 1). Inset: corresponding adsorption isotherm.

The adsorption of DCE onto TiO_2 appears to be a surprisingly efficient process. Little is known about the adsorption of reactants subjected to photodegradation on TiO_2 , especially the adsorption constants. These are usually derived from photodegradation kinetic studies assuming a Langmuir law. However, experiments carried out simultaneously on adsorption and photodegradation show that adsorption constants obtained from adsorption and kinetic experiments may disagree [11]. The mechanism of adsorption of DCE is not clear. Suggested adsorption processes on TiO_2 and other oxides include the formation of surface complexes and/or covalent bonds with ions [13–16], or the formation of hydrogen bonds with polar molecules [17]; however, none of these processes takes place in the present case. As all the valencies of the carbon atoms are filled and the breaking of a molecular bond would require considerable energy, the bond is presumably physical in nature. The DCE dipole moment is small, but an ion–molecule interaction could take place, taking the polarizability of the molecule into account.

Assuming that a complete monolayer is formed at total adsorption, Q_{max} is equal to $A_{sp}/N_A A^0$, where A_{sp} is the specific surface area of the solid, N_A is Avogadro's number and A^0 is the average area per adsorbate molecule. The experimental value of Q_{max} and a specific surface area of the solid of $44 \text{ m}^2 \text{ g}^{-1}$ give a value of 0.40 nm^2 for A^0 . This value is larger than the area of 0.28 nm^2 estimated using the usual space-filling model of a compact arrangement of spheres in the liquid and adsorbed phases. This could be due to the presence of several H_2O molecules attached to the DCE molecule. Alternatively, the potential sites may not all be accessible to DCE and only about 70% of the monolayer may be attained.

Adsorption kinetics

The kinetics of adsorption of DCE on titanium dioxide, following contact at time $t=0$, are shown in Fig. 1. The adsorption data in Fig. 1 were analysed using a model found to describe the adsorption of a variety of ions on TiO_2 [18,19]

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

where Q is the specific quantity adsorbed at time t and k_{ads} is a kinetic constant.

The variation of the adsorption is plotted in Fig. 3 following the linear form of Eq. (3)

$$\ln(Q_a - Q) = \ln Q_a - k_{ads}t \quad (3)$$

Satisfactory linear plots are obtained at least for concentrations up to 0.8 mmol l^{-1} , thus corroborating the validity of this first-order rate law. The corresponding values of the adsorption kinetic constant k_{ads} for various initial DCE concentrations (at time $t=0$) are given in Table 1. The values of k_{ads} corresponding to the highest DCE concentrations are subject to some error. It should

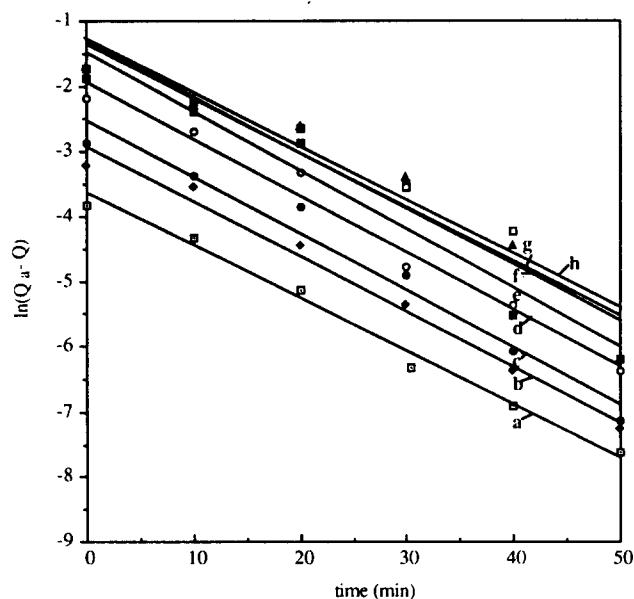


Fig. 3. Linear transform of the kinetic law for the adsorption of DCE on TiO_2 (conditions and labelling as in Fig. 1).

Table 1
Adsorption kinetic constant k_{ads} for various initial concentrations of DCE (C_i) (catalyst load, 0.6 g l^{-1} ; temperature, $20 \text{ }^\circ\text{C}$; pH 5.7)

C_i (mmol l^{-1})	k_{ads} (min^{-1})
0.05	0.0815
0.10	0.0846
0.20	0.0871
0.50	0.0871
0.80	0.0803
1.20	0.0836
1.50	0.0855

be noted that the kinetic constant k_{ads} is nearly constant at 0.085 min^{-1} over most of the concentration range studied.

Taking the derivative of Eq. (3) gives, after rearrangement

$$\frac{dQ}{dt} = k_{\text{ads}}(Q_a - Q) \quad (4)$$

which shows that the adsorption flux is proportional to the deviation of Q from the equilibrium value Q_a . This can be considered to be the master equation describing the adsorption kinetics.

Although the adsorption isotherm agrees with a Langmuir model, this is not the case for the adsorption kinetics. In the case of the Langmuir model (elementary processes of adsorption and desorption and no mass transfer limitation), it is easily shown that, assuming a constant concentration of the adsorbate, Eq. (3) will be obeyed with

$$k_{\text{ads}} = k_d(1 + KC_e) \quad (5)$$

where k_d represents the apparent rate constant of the elementary process of desorption.

Since in our experiments the amount of DCE adsorbed is less than 20% of the total initial amount, the solution concentration does not vary greatly and Eq. (5) is a good approximation. The experimental value is therefore expected to vary significantly as KC_e varies in the range under study (from 0.26 to 3.9). This is not the case, and the nearly constant value of k_{ads} suggests that the kinetics are controlled by other phenomena such as transport processes.

It should be noted that in Eqs. (3) and (4) the term Q_a contains the expression of the Langmuir isotherm. However, the kinetics are not those of the Langmuir model.

It is interesting to compare the experimental rate of adsorption with the rate of mass transfer from the bulk of the solution to the elementary particles of TiO_2 (diffusive external mass transfer). The rate of this mass transfer is given by

$$r_{\text{ext}} = (6.10^4)k_{\text{ext}}(C - C_s)A_{\text{sp}}W \text{ (mmol l}^{-1} \text{ min}^{-1}) \quad (6)$$

where the factor $50/3$ accounts for the units chosen for the various parameters. k_{ext} (m s^{-1}) is the rate constant of mass transfer, C is the bulk-concentration of the solute, C_s is the local concentration at the particle surface, A_{sp} is the specific surface area of the solid and W is the catalyst load. The rate constant k_{ext} takes its lowest value for a motionless spherical particle in a stagnant fluid: $k_{\text{ext}} = D/R$, where D is the molecular diffusion coefficient of the solute and R is the radius of the particle. For an estimation of r_{ext} , the elementary TiO_2 particle can be compared to a spherical crystal with a radius of about 10^{-8} m. A common value of $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ can be assumed for a small molecule

such as DCE in water, giving a value of k_{ext} of 0.1 m s^{-1} .

The actual initial rate of adsorption, in the presence of the DCE concentration C_i , can be deduced from Eq. (4)

$$r_{\text{ads}} = k_{\text{ads}}Q_{\text{max}} \frac{KC_i}{1 + KC_i} W \text{ (mmol l}^{-1} \text{ min}^{-1}) \quad (7)$$

Therefore the maximum relative difference between C and C_s arises at the initial time and low concentration, when the DCE concentration is equal to C_i , with

$$\frac{C_s}{C_i} = 1 - 0.4 \times 10^{-10} \quad (8)$$

This ratio is very close to unity, whereas it would be equal to zero in the case of a rate-limiting transport process. This shows that the “external” transport process plays a negligible part in the kinetics of adsorption in our case, which is in agreement with previous estimations and experiment [20–22].

The rate-limiting process is not likely to arise from adsorption or desorption as the adsorption probably has a physical nature, with a low activation energy. However, the rate limitation may arise from an internal mass transfer process. The elementary TiO_2 particle is a non-porous crystal: taking into account a crystal density of 3.8 g cm^{-3} , spherical crystals with a diameter of 18 nm would have a measured specific surface area of $44 \text{ m}^2 \text{ g}^{-1}$, which agrees well with the size of the particles observed using a transmission electron micrograph [12]. However, the particle size in aqueous suspension was found to be $5 \text{ }\mu\text{m}$. This suggests that an aggregation of the elementary particles takes place in the aqueous suspension. Thus diffusion within these aggregates may be the rate-controlling process.

It is of interest to compare the kinetics of adsorption with those of a rate-limiting internal mass transfer within an equivalent porous solid. A thorough study has been given in Ref. [23], but in the simplest case, assuming a diffusion coefficient within the pores close to that in aqueous solution (that is if the pores are large enough), i.e. about $10^{-9} \text{ m}^2 \text{ s}^{-1}$; the experimental half-time of adsorption (about 8 min) corresponds to an aggregate diameter of approximately 3 mm. As the particles in suspension are much smaller (a few micrometres), the “pore” diameter must be small enough to ensure a very small diffusion coefficient. In fact, this diameter is likely to compare with the size of the elementary particles (about 20 nm). Assuming an aggregate diameter of $5 \text{ }\mu\text{m}$, the diffusion coefficient should have a value of about $10^{-16} \text{ m}^2 \text{ s}^{-1}$, a value which is of the same order of magnitude as the diffusion coefficient in microporous solids such as zeolites. However, it is possible that the actual diffusion coefficient is larger, but that other phenomena, such as a high

organization of the first three layers of water molecules in the vicinity of the surface [24,25], slow down the kinetics.

3.2. Photocatalytic degradation

Photocatalytic nature of the degradation

A preliminary experiment shown in Fig. 4 demonstrates the photocatalytic nature of the degradation process. In this experiment, four runs were carried out: (a) with no destructive agent; (b) with UV only; (c) with TiO₂ only; (d) with UV and TiO₂.

In all runs, the reactive mixture was maintained for a period of 20 min in the dark, and magnetic stirring was performed in the photocatalytic reactor to ensure perfect mixing and adsorption in the presence of the catalyst. The DCE concentration was then at the “initial” value C_0 . The relative decrease in concentration C/C_0 was then followed under the four conditions described above.

Apart from the trivial adsorption process, practically no decrease in concentration was observed under the first three conditions. Only the treatment of DCE in the presence of titanium dioxide and UV illumination efficiently eliminates the organic contaminant from water, thus indicating the photocatalytic nature of the process.

The period of 20 min in the dark described above has been included in the procedure for all the experiments. It should be noted that the adsorption equilibrium is not totally complete after this period, but is well advanced (about 83% of the adsorption at equi-

librium). When measuring the rate of degradation, the decrease in DCE concentration due to a small adsorption following time “zero” can be neglected when compared with the photocatalytic degradation.

Photodegradation kinetics

The relative decrease in the DCE concentration C/C_0 with irradiation time as shown in Fig. 4 was followed for various initial DCE concentrations. The experimental decay of C/C_0 appears to agree with pseudo-first-order kinetics. This is convenient for deriving the value of the rate r_{deg} (mmol l⁻¹ min⁻¹) of the photodegradation reaction at the initial time, by plotting $\ln(C/C_0)$ vs. time over a range of 50 min.

Many investigations have been carried out on photocatalytic degradation, but few have included an analysis of the adsorption at equilibrium. Moreover, the kinetics of adsorption are usually not taken into account, although the decrease in concentration “in the dark”, due to adsorption, has sometimes been reported [9,10].

It is of interest to compare the kinetics of adsorption with the kinetics of photodegradation. For example, with an initial concentration of DCE of 0.5 mmol l⁻¹, the rate of photodegradation is 3.2×10^{-3} mmol l⁻¹ min⁻¹. In the limiting case, where the irradiation is sufficiently high to eliminate readily all the adsorbed reactant (that is $Q=0$), the rate of the reaction will be equal to the rate of adsorption from a fresh solution, i.e.

$$r = r_{\text{ads}} = k_{\text{ads}} Q_{\text{max}} W \frac{KC_0}{1 + KC_0} = 5.4 \times 10^{-3} \text{ mmol l}^{-1} \text{ min}^{-1} \quad (9)$$

This limiting rate is only about twice as large as the experimental photodegradation rate. This shows that mass transfer phenomena partly control the photodegradation kinetics. Under our experimental conditions, the actual kinetics probably arise from competition between physical and chemical processes.

A simple mechanism taking chemical and transfer processes into account can be proposed.

A commonly used “chemical” mechanism is assumed here. Irradiation generates holes, which lead to the formation of highly reactive OH[•] radicals on the surface. These react at the surface with adsorbed reactant molecules, which then quickly undergo complete degradation through the formation of intermediates that are present in low steady state concentration, such as vinyl chloride [26] and chloroacetic acid [27].

These OH[•] radicals are produced with a quantum yield ϕ , which is a function of the light flux [7,15,28]. The rate of formation of the OH[•] radicals is then ϕI_a where I_a is the absorbed intensity (meinstein l⁻¹ min⁻¹). The reaction of OH[•] radicals with the reactant competes with other modes of disappearance, especially recom-

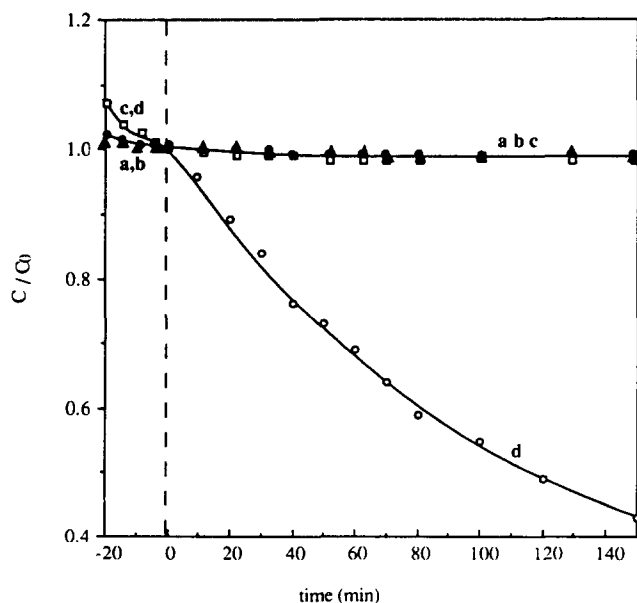


Fig. 4. Illustration of the photocatalytic process (0.05 mmol l⁻¹ DCE, 20 °C, pH 5.7): a, no catalyst or UV; b, UV only; c, catalyst only; d, catalyst plus UV.

bination to give H_2O_2 (although the latter may ultimately give new OH^\cdot radicals); therefore ϕ depends on I_a [15].

The rate of the reaction of OH^\cdot radicals with the adsorbed reactant is proportional to the surface coverage θ , i.e. if the OH^\cdot radical appears close to an adsorbed DCE molecule, it will react with it, otherwise it will be lost. If this process of attack of the reactant by OH^\cdot is of minor importance, the reaction rate will be equal to $\phi\phi_p I_a \theta$, with a proportionality factor ϕ_p , which is dependent on the local concentration of OH^\cdot and therefore on I_a . A rate proportional to $I_a^{1/2}$ can be observed as a consequence of the variation of $\phi\phi_p$ with I_a [29–31]. As we are dealing here with the effect of the DCE concentration, $\phi\phi_p$ is assumed to be constant.

The evolution with time of the coverage θ and the solution concentration C results from both the photodegradation as described above and the mass transfer expressed in Eq. (4). Thus θ and C obey the following differential system

$$\begin{cases} \frac{d\theta}{dt} = -(\phi\phi_p I_a / Q_{\max} W)\theta + k_{\text{ads}} \left(\frac{KC}{1+KC} - \theta \right) & (10a) \\ \frac{dC}{dt} = -k_{\text{ads}} Q_{\max} W \left(\frac{KC}{1+KC} - \theta \right) & (10b) \end{cases}$$

where Q_{\max} is the number of sites per unit catalyst weight and W is the mass of catalyst per unit volume. It should be noted that the Langmuir isotherm intervenes in Eq. (10a, 10b).

The physical meaning of this system (Eq. (10a, 10b)) is that the overall disappearance of the reactant takes place with the rate $\phi\phi_p I_a \theta$, but the value of the actual coverage θ is lower than the equilibrium value, thus inducing a flow of reactant towards the reactive surface.

Two limiting cases can be considered, i.e. when the chemical kinetics or mass transfer is the rate-limiting process.

If the chemical kinetics are rate limiting ($\phi\phi_p I_a \ll k_{\text{ads}} Q_{\max} W$), the adsorption phenomenon is practically at equilibrium and the solution is

$$r_{\text{deg(chemical)}} = -\phi\phi_p I_a \left(\frac{KC}{1+KC} \right) \quad (11a)$$

If mass transfer is the rate-limiting process ($k_{\text{ads}} Q_{\max} W \ll \phi\phi_p I_a$), the surface coverage is practically equal to zero and the solution becomes

$$r_{\text{deg(mass transfer)}} = -k_{\text{ads}} Q_{\max} W \left(\frac{KC}{1+KC} \right) \quad (11b)$$

which is the experimental law for adsorption as described above.

The solution of Eq. (11a, 11b) is not simple in the general case. However, an approximate solution can be derived by assuming a quasi-stationary state for the

adsorbed species, i.e. $(d\theta/dt) = 0$. Such an assumption is fully valid on two conditions: (a) if the amount of adsorbed DCE is very small compared with the amount of DCE in solution (in the present case, up to 20% may be adsorbed); (b) if the stationary state is attained in a very short time with respect to the observation time scale.

Considering an initial time at which the adsorption is at equilibrium (after “dark adsorption”), we obtain the approximate solution during the irradiation

$$\begin{aligned} r_{\text{deg}} &= -\frac{dC}{dt} = -\frac{k_{\text{ads}} Q_{\max} W \phi\phi_p I_a}{k_{\text{ads}} Q_{\max} W + \phi\phi_p I_a} \left(\frac{KC_0}{1+KC_0} \right) \\ &= k_{\text{deg}} \left(\frac{KC_0}{1+KC_0} \right) \end{aligned} \quad (12)$$

which is an intermediate solution between the two limiting cases given above. It should be noted that an adsorption equilibrium is no longer assumed during the irradiation, as the surface coverage is given by the following equation

$$\theta = \left(\frac{KC}{1+KC} \right) \left(\frac{k_{\text{ads}} Q_{\max} W}{k_{\text{ads}} Q_{\max} W + \phi\phi_p I_a} \right) \quad (13)$$

The validity of the approximation has been checked by comparing the approximate solution with a true numerical solution. A good fit of the DCE photodegradation was obtained taking a value of about $0.01 \text{ mmol l}^{-1} \text{ min}^{-1}$ for the kinetic factor $\phi\phi_p I_a$. Under these conditions, the stationary state is attained in about 10 min. As a consequence, the value of the approximate rate over the first 50 min of irradiation is slightly higher than the true rate by less than 10%. In the present experimental conditions, the approximation is acceptable. The main feature of this model is that the rate of reactant disappearance is the product of an apparent rate constant k_{deg} and the Langmuir term, whatever the controlling phenomenon. Thus experiments reported to behave according to a Langmuir–Hinshelwood “chemical” mechanism could actually be partly or totally controlled by mass transfer phenomena.

The validity of the model in the present case can be checked by plotting the linear equation (at constant catalyst load and irradiation flux)

$$\frac{C_0}{r_{\text{deg}}} = \frac{1}{k_{\text{deg}} K} + \frac{1}{k_{\text{deg}}} C_0 \quad (14)$$

This “kinetics” plot is shown in Fig. 2. It is satisfactory over most of the concentration range. The variations in C_e/Q_a vs. C_e (see Eq. (1)) are plotted on the same figure so as to compare the effect of the concentration on the rate of degradation and the initial surface coverage. It should be noted that C_e and Q_a correspond to equilibrium conditions (adsorption isotherm), whereas C_0 and r_{deg} correspond to the initial time of

irradiation, after 20 min of contact, where equilibrium is almost reached.

In the region of larger values of C_0 ($C_0 > 0.5$ mmol l^{-1}), the plot of C_0/r_{deg} vs. C_0 is approximately linear. The adsorption and kinetics plots compare well in this concentration range. In both the kinetics and adsorption plots, the ratio of the intercept to the slope gives the adsorption constant K . There is good agreement in the value of K in both experiments.

However, in the range of lowest values of C_0 , the curve exhibits upward curvature. Previous experiments on DCE [7,26] agree with a linear plot, but the concentration range lies above 0.5 mmol l^{-1} , which is, in the present case, the limit of linearity. In most studies, a good linearity is obtained for reactants such as chlorohydrocarbons or organic acids. However, a similar effect has been found for phenol [32], where a maximum is obtained in the variation of the apparent first-order rate constant of degradation, which is simply the reciprocal of the ratio C_0/r_{deg} .

The experimental rate at low concentration is lower than the value expected by extrapolation from the domain of relatively high concentrations. This is an unexpected effect, as increasing the concentration is more likely to reduce the overall apparent rate constant rather than increase it.

Such an effect has previously been attributed to a limitation by mass transfer processes at decreasing concentrations [32], on the basis of a higher quantum yield of reactant consumption. However, in the present study, the limiting rate of adsorption has been measured and found to be approximately twice the rate of photodegradation in the upper range of concentration. This limiting rate, which follows a Langmuir law, is therefore much higher than the rate of photodegradation in the lower range of concentration and does not impede the overall kinetics.

A decrease in the apparent rate constant of photodegradation at low concentration may be due to depletion of one of the reactive species in the initial process, i.e. adsorbed DCE or the hydroxyl radical.

A possible explanation involves the alteration of the adsorption of DCE by irradiation. Photodesorption has already been suggested [11], a phenomenon which would be relatively more effective at low concentrations where the surface coverage is low. However, such a phenomenon seems dubious in the present case as the adsorption is very likely to be physical in nature.

If it is assumed that the adsorption equilibrium is obeyed during photodegradation, the rate is observed to be of apparent order 1.7 with respect to the coverage θ . This implies the occurrence of a bimolecular process involving two adsorbed DCE molecules, which can be ruled out. A more satisfactory explanation is the occurrence of a bimolecular process of disappearance of adsorbed OH^\bullet species [15]. Thus the apparent rate

constant of photodegradation can be expected to decrease at low coverage when more OH^\bullet radicals are present on the surface, whereas a conventional mechanism would apply over most of the concentration range.

4. Conclusions

The adsorption–desorption of DCE on TiO_2 in water has been studied. The adsorption obeys the Langmuir adsorption isotherm; the maximum coverage of the surface is about the value of half an ideal monolayer. The kinetics of adsorption obey the classical law for porous solids, which may be due to the formation of pseudo-porous aggregates of elementary solid particles. The degradation of DCE is a photocatalytic process. The influence of DCE concentration on the kinetics has been studied. The kinetics are partly determined by the mass transfer process, a process which should be taken into account when studying photocatalytic processes in suspensions. However, it is shown that, even if this physical process does take place, the classical Langmuir–Hinshelwood law is apparently obeyed. In the present case, the agreement with this law is satisfactory, but the classical mechanism is not followed at low concentrations, which may be due to the occurrence of photodesorption or a bimolecular process between two adsorbed hydroxyl radicals.

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Appendix: Nomenclature

A_{sp}	specific surface area ($m^2 g^{-1}$)
C	DCE concentration in the aqueous solution at time t (mmol l^{-1})
C_0	value of C after the preliminary adsorption period
C_e	value of C at adsorption equilibrium
C_i	initial value of C before adsorption
C_s	value of C close to the surface
D	molecular diffusion coefficient of DCE ($m^2 s^{-1}$)
DCE 1,2-dichloroethane	
I_a	absorbed light intensity (meinstein $l^{-1} min^{-1}$)
k_{ads}	adsorption kinetic constant (min^{-1})
k_{ext}	external mass transfer kinetic constant (ms^{-1})
k_{deg}	photodegradation apparent kinetic constant (mmol $l^{-1} min^{-1}$)
k_d	apparent desorption kinetic constant for a Langmuir model (mmol $l^{-1} min^{-1}$)

K	adsorption constant ($l \text{ mmol}^{-1}$)
Q	specific adsorbed quantity at time t (mmol g^{-1})
Q_a	value of Q at equilibrium
Q_{max}	value of Q at maximal adsorption
r_{ads}	rate of adsorption ($\text{mmol l}^{-1} \text{ min}^{-1}$)
r_{deg}	rate of photodegradation ($\text{mmol l}^{-1} \text{ min}^{-1}$)
r_{ext}	rate of external mass transfer ($\text{mmol l}^{-1} \text{ min}^{-1}$)
R	radius of an ideal spherical elementary TiO_2 particle (m)
t	time (min)
W	catalyst load (g l^{-1})

Greek symbols

θ	surface coverage
ϕ_p	proportion of OH^\bullet radical reacting with DCE
ϕ	quantum yield of OH^\bullet radical

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