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Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO_2 by inorganic ions

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Abstract

The effect of the inhibition of various adsorbed inorganic ions on the adsorption of dichloroethane (DCE) in a titanium dioxide aqueous suspension was studied. The adsorption of the ions was competitive with that of DCE and the adsorption kinetic constant k_a varied only slightly around a value of 0.08 min^{-1}. The kinetics of adsorption were controlled by DCE mass transfer, since the ion mass transfer was much more rapid. The affinity of the ions for TiO_2 and the competition with DCE for adsorption were in the order: $Cl^- < NO_3^- < [HCO_3^-, CO_3^{2-}] < SO_4^{2-} < [H_2PO_4^-, HPO_4^{2-}]$. The Langmuir model of adsorption was unsatisfactory for the whole set of experiments, thus suggesting a non-uniform surface. The photodegradation occurred on the surface according to an apparent Langmuir–Hinshelwood mechanism, and the inhibition of the ions for this reaction was in the order: $NO_3^- < Cl^- < HCO_3^-, CO_3^{2-} < SO_4^{2-} < H_2PO_4^-, HPO_4^{2-}$. The effect of inhibition on the photocatalytic degradation was about half that on the adsorption of DCE, which could be attributed to the surface heterogeneity and/or to a mass transfer phenomenon. © 1997 Elsevier Science S.A.

Keywords: Adsorption; 1,2-Dichloroethane; Inorganic ions; Kinetics; Photocatalysis; Titanium dioxide; Wastewater

1. Introduction

Owing to the interest in environmental protection, the mechanism of the heterogeneous photocatalysis of TiO_2 has been the subject of numerous studies, but the inhibition of the photocatalytic degradation of aqueous organic pollutants has seldom been investigated [1–5]. However, chloride ions are present in commercial titania and carbonate ions are present in aerated water. In addition, apart from being found in natural water, chloride, nitrate and phosphate ions may be present as reaction products in the degradation of organic compounds [6,7]. The aim of this work is to compare and correlate the adsorption phenomena of mineral additives with their inhibition of the photocatalytic degradation of water contaminants. KCl, KNO_3, K_2CO_3, K_2SO_4 and KH_2PO_4 were selected as additives and, following a previous study [8], 1,2-dichloroethane was used as test pollutant.

2. Experimental procedures

The titanium dioxide used, "TITANDIOXID P25" Degussa, was mainly anatase. According to the manufacturer's specifications [9], the elementary particle in dry powder was approximately spherical in shape and the particle size was approximately 20 nm. The specific surface area, as measured by N_2 adsorption at 77 K, was 44 $m^2\ g^{-1}$, in agreement with the manufacturer's specifications. The size distribution of the particles suspended in water was measured by laser diffraction on a Malvern Mastersizer apparatus, indicating an average suspended particle size of 5 μm. The test pollutant, 1,2-dichloroethane (DCE), was a laboratory reagent. K_2HPO_4, K_2SO_4, K_2CO_3, KNO_3 and KCl were of reagent grade and were used without further purification. The water for all solutions and slurries was deionized prior to use.

Experiments on the 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 filled completely and sealed to eliminate any gaseous phase. The adsorption and degradation were followed by measurement of the DCE concentration in the aqueous phase by gas chromatography.

The experimental set-up for the photocatalytic degradation has been described previously [8]. As in adsorption experiments, the whole set-up was kept free of any gaseous phase.

The measurement of the DCE concentration in the aqueous phase was carried out as follows. Samples of 0.1 ml were withdrawn with a syringe through a rubber septum and fil-

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tered using a 0.22 μm membrane filter in order to remove the TiO_2 particles. The DCE concentrations in the filtered samples were measured using a Hewlett-Packard gas chromatograph (model 5890) equipped with a flame ionization detector. Samples of 0.5 μl were injected directly into 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. Slight adsorption on the filter (around 5%) was taken into account in this calibration.

3. Results

3.1. Competitive adsorption

The competitive adsorption of DCE and various salts was studied by monitoring the DCE concentration in the aqueous phase following three distinct procedures:

1. simultaneous addition at time zero of DCE and salt to the TiO_2 suspension;
2. addition at time zero of DCE to a pre-equilibrated suspension containing salt;
3. addition at time zero of salt to a pre-equilibrated suspension containing DCE.

Pre-equilibration was carried out by allowing the suspension to equilibrate for about 1 h (found to be sufficient in view of the kinetics of adsorption shown later).

In all experiments, the load of TiO_2 was 0.6 g l^{-1} and the temperature was 20 °C. A value of about pH 6 was used, except for phosphate and carbonate solutions where it varied in the range pH 6–10 according to the salt concentration.

Adsorption kinetic curves, in which the specific adsorbed quantity Q is plotted against time, were plotted for the three procedures. The simultaneous addition of DCE and salt and the addition of DCE after salt lead to similar kinetics (Fig. 1(a)). The addition of salt after DCE shows the desorption of DCE (Fig. 1(b)). Equilibrium is practically reached in about 1 h, with the exception of the pre-adsorption of KH_2PO_4.

The three procedures lead to similar equilibrium states, as shown in Fig. 2. In Fig. 2, the specific quantity of adsorbed DCE at equilibrium (Q_e) following the three procedures is plotted for convenience against a reference value (Q_{er}) deduced from the analysis of the isotherms.

The isotherms obtained following simultaneous adsorption and DCE desorption are given in Figs. 3(a) and 3(b).

3.2. Inhibition of the photocatalytic degradation

The photocatalytic degradation of DCE in aerated suspensions was followed by monitoring the DCE concentration C in the aqueous phase. After simultaneous addition of DCE and salt to the suspension and equilibration, irradiation was carried out. The "initial" concentration of DCE was taken to be C_0. The effect of additives is shown in Figs. 4(a) and

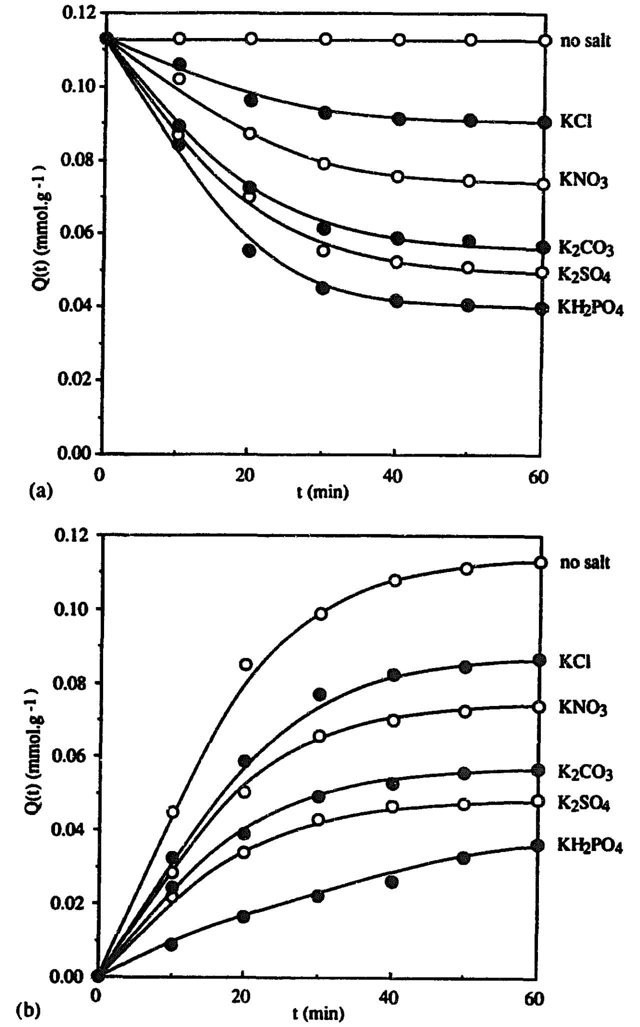

Fig. 1. (a) Kinetics of adsorption of DCE after equilibrated adsorption of salts; ($Q(t)$, specific adsorbed quantity of DCE; initial concentrations: [DCE] = 0.5 mmol l^{-1}; [salt] = 0.5 mmol l^{-1}). (b) Kinetics of desorption of equilibrated DCE by salts; ($Q(t)$, specific adsorbed quantity of DCE; initial concentrations: [DCE] = 0.5 mmol l^{-1}; [salt] = 0.5 mmol l^{-1}).

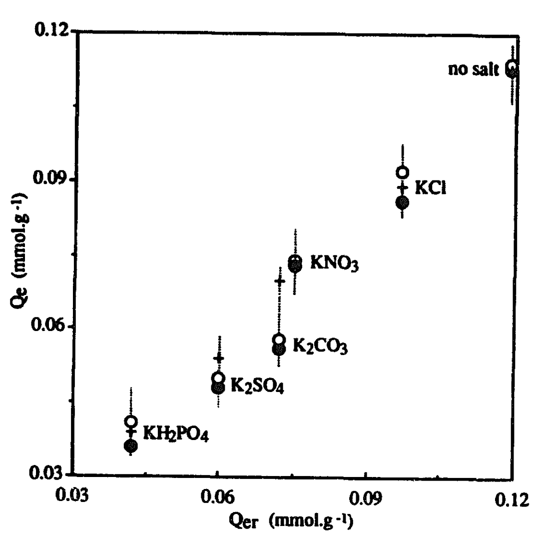

Fig. 2. Comparison of the specific adsorbed quantity of DCE (Q_e) at equilibrium following three procedures (Q_{er}, reference value): ×, simultaneous addition of DCE and salt; ●, pre-adsorption of salt; ○, pre-adsorption of DCE.

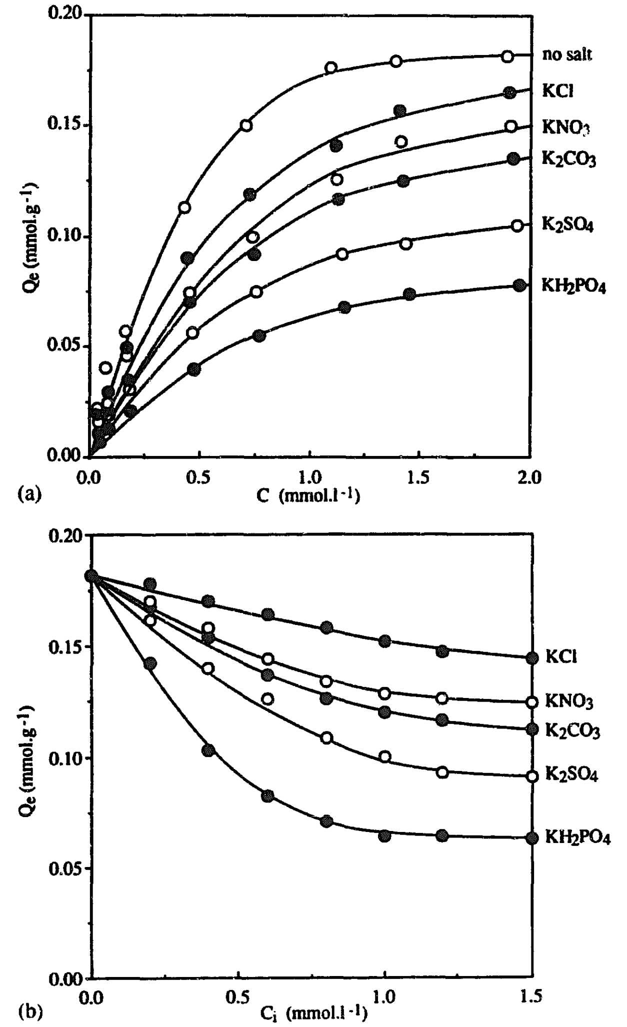

Fig. 3. (a) Isotherms of co-adsorption of DCE and salts (simultaneous addition of DCE and salt) (Q_e, specific adsorbed quantity of DCE at equilibrium; C, DCE concentration; initial salt concentration, 0.5 mmol l^{-1}). (b) Isotherms of co-adsorption of DCE and salts (pre-adsorption of DCE) (Q_e, specific adsorbed quantity of DCE at equilibrium; initial DCE concentration, 2.0 mmol l^{-1}; salt concentrations C_i on the abcissa are the initial concentrations).

4(b), where the relative concentration of DCE in the aqueous phase (C/C_0) is plotted against the time of irradiation in the presence of chloride or phosphate ions at various concentrations. Conditions of TiO_2 load, temperature and pH are the same as in the adsorption experiments.

Plots of $\ln(C/C_0)$ vs. time are approximately linear within the first hour of irradiation. An apparent first-order kinetic constant k_0 (min^{-1}) is obtained from the slope and the initial rate of degradation r_0 (mmol l^{-1} min^{-1}) is taken as k_0C_0.

4. Discussion

4.1. Active ions

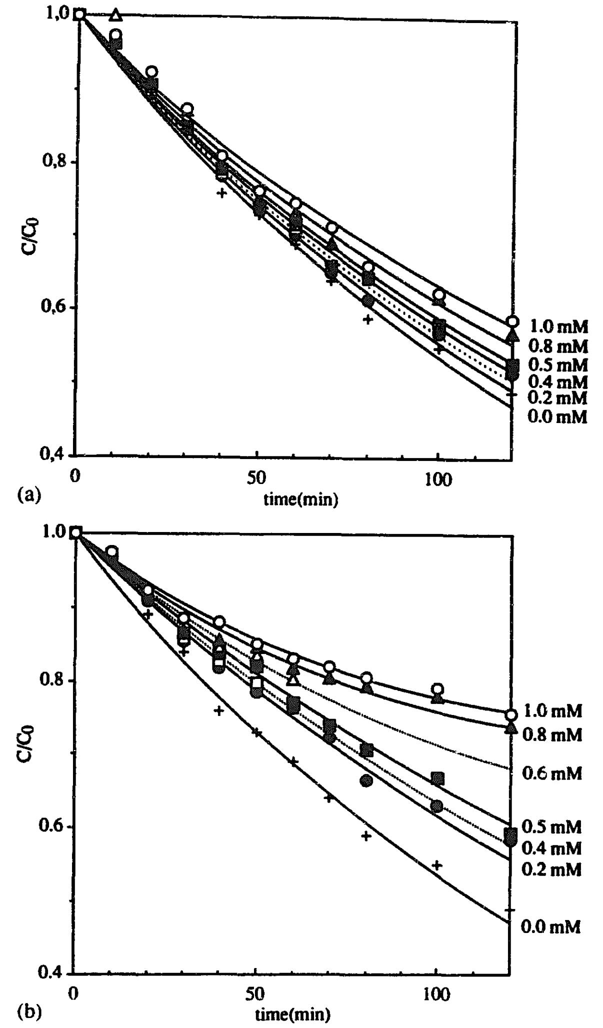

Fig. 4. (a) Kinetics of the photocatalytic degradation of DCE in the presence of chloride ions at various concentrations (C/C_0, relative concentration of DCE in the aqueous phase; DCE initial concentration, 0.5 mol l^{-1}; TiO_2 load, 0.6 g l^{-1}). The experiment at a chloride concentration of 0.4 mmol l^{-1} was stopped at 60 min. (b) Kinetics of the photocatalytic degradation of DCE in the presence of phosphate ions at various concentrations (C/C_0, relative concentration of DCE in the aqueous phase; DCE initial concentration, 0.5 mol l^{-1}; TiO_2 load, 0.6 g l^{-1}). The experiments at phosphate concentrations of 0.4 and 0.6 mmol l^{-1} were stopped at 60 min. Key to symbols: +, 0.0 mM; ●, 0.2 mM; □, 0.4 mM; ■, 0.5 mM; △, 0.6 mM; ▲, 0.8 mM; ○, 1.0 mM.

For convenience, the additives referred to in the figures are the actual salts added to the solution. However, the species actually involved in the adsorption process are the ions. The cation is always K^+. For KCl, KNO_3 and K_2SO_4, the anions are Cl^-, NO_3^- and SO_4^{2-}, but for K_2CO_3 and KH_2PO_4 the nature of the anion depends on the pH. The pH itself depends on the presence of the salt, as carbonic and phosphoric acids are not totally dissociated. A value of about pH 10 is obtained on addition of K_2CO_3 at a concentration of 0.5 mmol l^{-1}. At this pH value, the two anions CO_3^{2-} and HCO_3^- are present in approximately the same quantity and are referred to as "carbonate" ions. Phosphoric acid is stronger than carbonic acid and a value of about pH 8 is obtained in the same conditions, with the major ionic species being HPO_4^{2-} and $H_2PO_4^-$. These are referred to as "phosphate" ions.

4.2. Adsorption

4.2.1. Kinetics of adsorption

The kinetics of adsorption were analysed using the usual law

$$dQ/dt = k_a(Q_e - Q)$$

where Q is the specific adsorbed quantity, Q_e is the same quantity at equilibrium and k_a is a kinetic constant (min^{-1}). For an adsorbed quantity Q_0 at time zero, the quantity Q at time t verifies

$$\ln\left[\frac{Q-Q_e}{Q_0-Q_e}\right] = -k_a t \tag{1}$$

Variations of $\ln[\,|Q-Q_e|\,]$ vs. time are linear and the slopes give the kinetic constants. These are shown in Table 1.

It appears that k_a varies very little around a value of about 0.08 min^{-1} for DCE alone and in the presence of various salts. This suggests that the phenomenon is controlled by mass transfer. Diffractometry measurements of dilute suspensions indicate that the solid comprises particles with an average dimension of 5 μm. This is corroborated by the observation of the dry powder using electron microscopy. The suspension thus contains aggregates with dimensions of a few micrometres made up of elementary microcrystals with a dimension of about 20 nm. The kinetics of adsorption are dictated by mass transfer within these aggregates. As the process of co-adsorption involves both DCE and the salt ions, an approximately constant value of k_a suggests that the mass transfer of the ions is much faster than that of DCE and that DCE mass transfer controls the kinetics.

A low value of k_a was found in the particular case of adsorption of DCE after pre-adsorption of KH_2PO_4. Such slow kinetics are indeed visible in Fig. 1(b). As shown later, the adsorption of phosphate ions is very strong and the kinetics are likely to be controlled in this particular case by a complex desorption process. However, the strong adsorption of phosphate ions may cause an apparently higher value of k_a; DCE is very quickly displaced and, due to an excess local concentration, is extracted from the aggregates at a higher rate.

Table 1

Kinetic constants of adsorption k_a (min^{-1}) of DCE in the presence of various salts (from data shown in Figs. 1(a) and 1(b))

Salt	Simultaneous adsorption	Salt pre-adsorption	DCE pre-adsorption
None	0.085		
KCl	0.083	0.079	0.085
KNO_3	0.086	0.077	0.081
K_2CO_3	0.083	0.078	0.081
K_2SO_4	0.085	0.080	0.086
KH_2PO_4	0.086	0.051	0.096

4.2.2. Adsorption isotherms

As all the salts carry the cation K^+, the variations in the affinity for TiO_2 and the competition with DCE for adsorption are related to the different anions. These can be arranged in order of increasing affinity: $Cl^- < NO_3^- < [HCO_3^-, CO_3^{2-}] < SO_4^{2-} < [H_2PO_4^-, HPO_4^{2-}]$. It should be noted that this ranking applies to the present conditions of pH. For Cl^-, NO_3^- and SO_4^{2-}, pH ≈ 6. The pH is slightly basic for phosphate and carbonate ions. As the isoelectric point of titania lies at about pH 6 [9], this results in a negatively charged surface, repulsive to anions. A higher adsorption constant of these ions is therefore expected at pH 6.

Higher adsorption of phosphate ions compared with nitrate and chloride ions has been observed previously with a similar solid [10]. The adsorption of phosphate can take place as a ligand attached to a surface Ti^{4+} ion [11] by removal of an OH group, a bonding mechanism which is stronger than for Cl^-. Such a characteristic is also found in the adsorption of the sulphate ion [12]. Nitrate and carbonate ions appear to be intermediate cases.

The adsorption isotherms were analysed by a simple Langmuir adsorption model, with an adsorption constant K for DCE and K_i for the ion. For the classical co-adsorption on a single site, the isotherm is written as

$$\frac{Q_e}{Q_{max}} = \frac{KC}{1+KC+K_iC_i} \tag{2}$$

where Q_{max} is the maximum adsorbed quantity and C and C_i are the concentrations of DCE and the ion respectively.

The linear transform for adsorption at constant ion concentration is

$$\frac{C}{Q_e} = \frac{1}{Q_{max}}\left[\frac{1+K_iC_i}{K} + C\right] \tag{3}$$

and for constant DCE concentration is

$$\frac{1}{Q_e} = \frac{1}{Q_{max}}\left[\frac{1+KC}{KC} + \frac{K_i}{KC}C_i\right] \tag{4}$$

These are plotted in Figs. 5(a) and 5(b), giving in most cases a satisfactory linear relationship.

It should be noted that, for adsorptions at "constant" DCE concentration, the initial concentration of DCE (before adsorption) is the same in each experiment, so that the actual concentration C in Eq. (4) varies according to the importance of the ion adsorption dictated by K_iC_i. However, the variations in C are less than 20% in the extreme conditions, so that they do not significantly alter the data treatment.

Ion concentrations are only known at the initial concentration prior to adsorption. An estimation of the corrected values was carried out. Using the initial salt concentrations, an initial value of K_i was calculated and an adsorbed quantity of ion was then estimated by assuming an identical area of adsorbed ion or DCE molecule. The corrected actual ion concentrations were then deduced and the calculation of K_i was repeated. After several iterations, a final corrected ion concentration

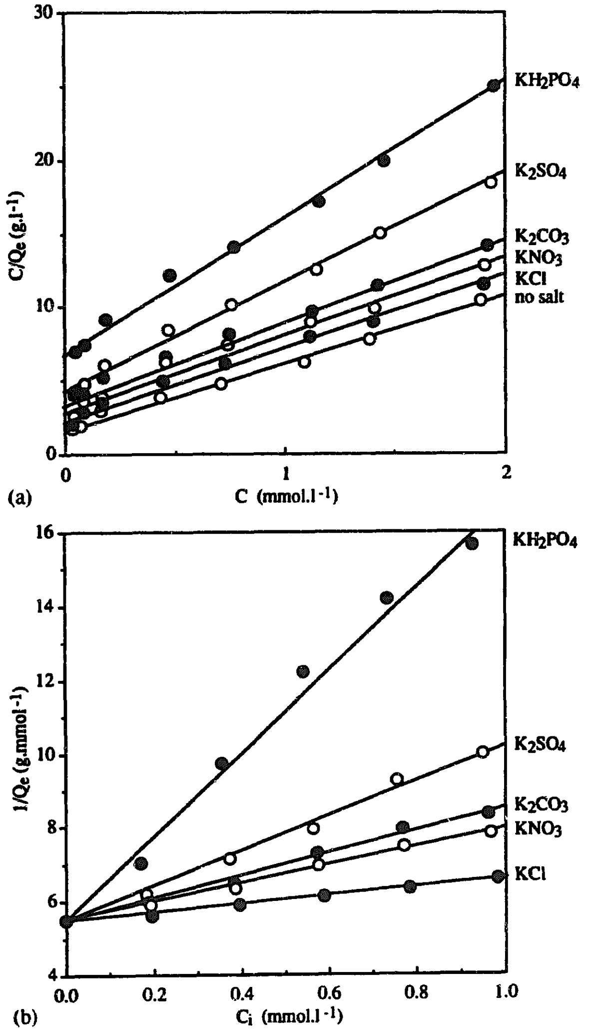

Fig. 5. (a) Linear isotherm of co-adsorption of DCE and salts (simultaneous addition of DCE and salt) (Q_e, specific adsorbed quantity of DCE at equilibrium; C, DCE concentration; initial salt concentration, 0.5 mmol l^{-1}). (b) Linear isotherm of co-adsorption of DCE and salts (pre-adsorption of DCE) (Q_e, specific adsorbed quantity of DCE at equilibrium; C_i, corrected ion concentration; initial DCE concentration, 2.0 mmol l^{-1}).

was obtained, which was coherent with the operative relationship of Eqs. (3) or (4). This correction was approximate and, on average, within a few per cent of the initial value (in the worst case, for a concentration of phosphate of 0.32 mmol l^{-1}, it reached 15%).

The values of Q_{max} and K, the adsorption constant of DCE, were obtained directly from the experiment without additive (see Fig. 5(a)). For each ion, the values of Q_{max} and K_i were obtained from the other plots shown in Figs. 5(a) and 5(b), making use of the value of K. These values are given in Table 2.

The results given in Table 2 show that, although satisfactory linear plots are obtained, a discrepancy takes place between the ion adsorption constants determined from the two sets of isotherms. In addition, the apparent maximum adsorbed quantity Q_{max} decreases as the adsorption affinity of the ions increases. However, this should be constant, as it is associated with the area accessible to DCE adsorption.

This shows that the simple Langmuir model, although convenient for each separate experiment, fails for the whole set of experiments. As an improvement of the model, a non-uniform surface is considered, with various sites exhibiting different adsorption competitiveness between DCE and the ion.

In the competition with the phosphate ion for adsorption, at a constant ion concentration, two sites of an equivalent quantity can be considered. At the first (about 0.11 mmol g^{-1}), the adsorption constants K and K_i are similar (2.6 and approximately 1.9 respectively), and at the second (about 0.11 mmol g^{-1}), K_i is much larger than K. Thus the adsorption of DCE only seems to occur on the first type of site, with the second being "locked" by the ions.

When the DCE concentration is maintained constant, an apparent variation in Q_{max} cannot be observed and so only the global effect is measured. This leads to a global adsorption constant K_i which is higher than that determined from the isotherms at a constant ion concentration.

Thus a discrepancy between the adsorption constants K_i is observed for the two sets of experiments due to the fact that the second experiment gives a global value, whereas the first is more sensitive to the multiplicity of site type.

When the ions are considered successively from the lowest (Cl^-) to the highest ($H_2PO_4^-$) affinity, the non-uniformity of the surface is revealed by the first experiment, whereas the second experiment shows an increase in the value of the apparent global adsorption constant.

Table 2
Adsorption parameters determined from the linear relationships of the Langmuir model

Ion	Isotherms at constant C_i		Isotherms at constant C	
	Q_{max} (mmol g^{-1})	K_i (l $mmol^{-1}$)	Q_{max} (mmol g^{-1})	K_i (l $mmol^{-1}$)
None	0.225	(K=2.6)	0.225	(K=2.6)
Cl^-	0.208	0.6	(0.225)	0.9
NO_3^-	0.196	1.8	(0.225)	1.9
[HCO_3^-, CO_3^{2-}]	0.190	1.9	(0.225)	2.4
SO_4^{2-}	0.137	1.1	(0.225)	3.8
[$H_2PO_4^-$, HPO_4^{2-}]	0.110	1.9	(0.225)	8.7

4.3. Inhibition of photodegradation

The degradation of the reactant R takes place through a photocatalytically initiated oxidation reaction according to the following mechanism

$h\nu + TiO_2 \rightarrow e^- + h^+ + TiO_2$

(photogeneration of an electron— —hole pair in the crystal)

OH^- (or H_2O) $+ h^+ \rightarrow OH^\cdot$

(formation of a surface hydroxyl radical)

$R \leftrightarrow R_{ads}$ (adsorption of the reactant)

$OH^\cdot + R_{ads} \rightarrow .....$

(initiation of oxidation via a free radical)

This is the so-called Langmuir–Hinshelwood (LH) mechanism, with the assumption that the rate-limiting process is the last process taking place on the surface. An alternative mechanism involves direct attack by the hole of the adsorbed reactant with reductive character, or reductive photoadsorption [13]. However, such a process is unlikely in the present case in which the reactant is an aliphatic chlorinated hydrocarbon. A previous study has shown that the photocatalytic degradation of DCE, using P25 catalyst, follows the LH mechanism in the range of concentration used in the present work [8].

According to the LH mechanism, added ions can inhibit the photodegradation in several ways:

1. light absorption reduction by an inner filter effect (Fe^{3+}) [14];
2. short-circuiting of the recombination of h^+ and e^- (Fe^{3+}) [15];
3. trapping of holes h^+ at the surface (I^-, Br^-) [16];
4. trapping of $OH^\cdot$ radicals or other oxidizing species [2,3,17];
5. competitive adsorption with the reactant on the catalyst surface (Pb^{2+} [4], Cl^- [1]).

In contrast, an enhancement of photodegradation can be found when photogenerated electrons are trapped at the surface (Ag^+, Fe^{3+} [14], Cu^{2+} [15]), and when the ions Fe^{2+} or Cu^+, produced by the reduction of Fe^{3+} or Cu^{2+}, act as catalysts in the Fenton reaction [15].

The common cation to all the added salts, K^+, is inert, and the wide range of inhibition observed with this cation indicates that only the anions are involved. The additives used in this study do not absorb the excitation light, and there is therefore no inner filter effect. Cl^- ions have been shown to be chemically inert in photocatalytic treatment [16], although inhibition occurs in the present case and in other reported studies [1–3,13]. This suggests that the observed inhibition can be interpreted as competitive adsorption.

In the LH mechanism, the rate of degradation is considered to be proportional to the surface coverage of the reactant. The initial degradation rate obeys the relationship

$$r_0 = k_{deg} \frac{KC_0}{1 + KC_0 + K_iC_i} \ (\mathrm{mol\ l^{-1}\ min^{-1}}) \qquad (5)$$

where k_{deg} is the rate constant, K is the adsorption constant of the reactant of concentration C_0 and K_i is the adsorption constant of an added ion of concentration C_i. This relationship can be written in a linear form

$$\frac{1}{r_0} = \frac{1}{k_{deg}KC_0}[(1 + KC_0) + K_iC_i] \qquad (6)$$

Variations of $1/r_0$ vs. C_i at constant C_0 are plotted in Fig. 6. The model is only roughly followed due to the difficulty in obtaining accurate measurements (although the rate value was obtained from concentration measurements at six successive times).

The values of the adsorption constant K_i for different ions were determined from these plots (taking into account an adsorption constant of DCE of 2.6 l mmol^{-1}) and are shown in Table 3. The ions are ranked according to their inhibition effect in a very similar order to that for competitive adsorption: $NO_3^- < Cl^- < [HCO_3^-, CO_3^{2-}] < SO_4^{2-} < [H_2PO_4^-, HPO_4^{2-}]$.

It should be noted that, as discussed above, the pH is slightly basic for carbonate and phosphate. However, the rate

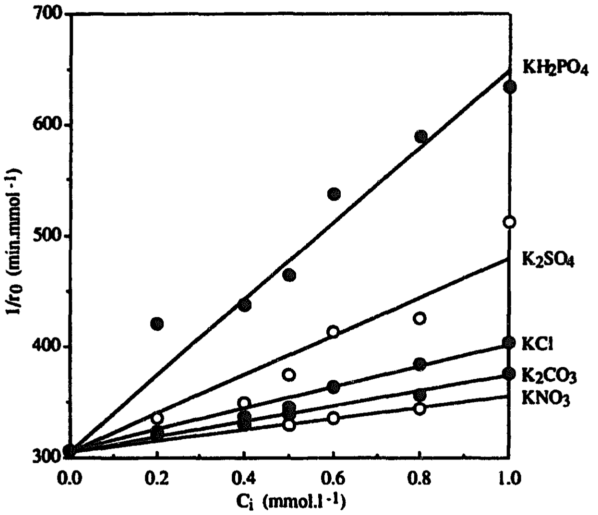

Fig. 6. Analysis of the inhibition by ions of the photocatalytic degradation of DCE (DCE concentration, 0.5 mmol l^{-1}; r_0, initial rate; C_i, salt concentration).

Table 3
Inhibition by ions of the catalytic degradation of DCE and comparison with competitive adsorption. DCE concentration, 0.5 mmol l^{-1}

Ion	From Fig. 6	$C_i = 0.5$ mmol l^{-1}	
	K_i (l mmol^{-1})	r_{0i}/r_0	Q_i/Q
Cl^-	0.51	0.90	0.81
NO_3^-	0.37	0.93	0.63
$[HCO_3^-, CO_3^{2-}]$	0.72	0.87	0.60
SO_4^{2-}	1.29	0.78	0.49
$[H_2PO_4^-, HPO_4^{2-}]$	2.57	0.64	0.34

of photodegradation is only slightly dependent on the pH value, as it increases by about 20% when the pH is increased from pH 5–6 to pH 10.5 by the addition of KOH. Such a pH would correspond to the addition of 1 mmol l^{-1} of carbonate. The inhibition observed when carbonate is added is slightly lower than the actual value: the addition of the salt enhances the rate of reaction by increasing the pH, but also inhibits it by adsorption competition. Taking into account the effect of pH, the values in Table 3 become 1.18 for the constant K_i and 0.80 for the ratio r_{0i}/r_0. This minor correction does not alter the ranking of carbonate ions with respect to the inhibition of photocatalytic degradation. In any case, it should be recalled that the comparison between adsorption and photodegradation, for each additive, was obtained using identical pH conditions.

It is difficult to compare the present results with other reported studies as the inhibition effect appears to vary according to the reactant and pH of the solution [2].

Inhibition by chloride ions usually takes place, but its extent varies. In the present study, a concentration of chloride ions of 1 mmol l^{-1} reduces the rate of photodegradation of DCE by about 10%, whereas the same inhibition can be estimated to require about 0.25 mmol l^{-1} in the degradation of chloroacetic acid [1] and 5–10 mmol l^{-1} in the degradation of salicylic acid, aniline or ethanol [2].

As in this study, the inhibition by nitrate ions was reported elsewhere to be very low, whereas the inhibition by phosphate ions was high [2], thus suggesting inhibition by competitive adsorption. However, a striking difference is found in the case of sulphate ions, which are much less effective than chloride ions in the degradation of phenols [13]. This suggests that a different mechanism of inhibition is involved, such as the trapping of oxidizing species.

It is interesting to compare the adsorption constants of the anions deduced from actual competitive adsorption and inhibition of photocatalytic degradation. A comparison of Tables 1 and 3 indicates lower values in the latter case. This is especially true for the values determined from adsorption isotherms at a constant DCE concentration.

It has been suggested above that the surface is not uniform and that there are a variety of sites with different relative affinities for DCE and ions. As a consequence, the apparent adsorption constant depends on the concentration range. Thus photocatalytic degradation and competitive adsorption were compared using the same concentration conditions. The concentration used was 0.5 mmol l^{-1} and the results are shown in Table 3. Table 3 gives the ratios of the rate of degradation and the adsorbed quantity of DCE in the presence of ions (subscript, i) to the same quantities in the absence of ions: r_{0i}/r_0 and Q_i/Q. On average, the inhibition effect on the photocatalytic degradation, $\alpha_{deg} = (1 - r_{0i}/r_0)$, is about half that on the adsorption of DCE, $\alpha_{ads} = (1 - Q_i/Q)$.

The Langmuir isotherm, associated with a uniform surface only, gives an apparent mean value for the adsorption constant. A smaller effect is apparent on the photocatalytic degradation than on competitive adsorption, which can be interpreted by considering various types of site. If sites of high affinity for the adsorption of ions have little photocatalytic activity, a reduction in DCE adsorption is not followed by a reduction in photocatalytic degradation to the same extent.

Another interpretation takes into account the mass transfer process. As shown above, the rate of adsorption of ions is slow and the rate of adsorption of DCE is about the same in the presence of ions. A careful comparison of the rate of adsorption of DCE (r_{ads}) with the rate of photocatalytic degradation (r_{deg}) [8] shows that r_{deg} is about half the value of r_{ads}, under the same experimental conditions as used in this work. It follows that the apparent rate of degradation r_{deg} is roughly due to two competitive processes: a physical process of DCE diffusion of intrinsic rate r_{mt} and an LH chemical process of intrinsic rate r_{LH}, where $r_{mt} \cong r_{LH}$, so that $r_{deg} \cong r_{mt}/2 \cong r_{LH}/2$. It should be noted that it has been shown in Ref. [8] that, by taking into account the mass transfer process, an apparent LH kinetic law is obtained. Thus treatment of the data according to a true LH mechanism is feasible. The addition of ions has a negligible effect on the physical process, and the effect of inhibition (α_{ads}) on r_{LH}, due to competitive adsorption. will therefore result in an effect of inhibition of about $\alpha_{deg} \cong \alpha_{ads}/2$ on the apparent rate, as is approximately shown in the experiments.

Carbonate ions react with hydroxyl radicals, producing the less reactive ion radical $^{\bullet}CO_3^-$ [17]. This additional inhibiting effect may take place in the present work, but appears to be of minor importance.

Inhibition of the photocatalytic reaction by NO_3^- appears to be lower than expected. Nitrate ions absorb UV light, leading to the formation of hydroxyl radicals [18]. Although they absorb very slightly in the present wavelength range, nitrate ions appear to affect the photodegradation of DCE. The rate of degradation in the presence of 0.5 mmol l^{-1} of KNO_3 and in the absence of catalyst is about 20% of that in the presence of catalyst, so that the inhibition effect of KNO_3 on the photocatalytic process may be partly hidden by an additional homogeneous "accelerating" effect.

5. Conclusions

The various inorganic ions studied here inhibit both the adsorption and photocatalytic degradation of DCE on titania. The inhibition effect on the adsorption is double that on the photocatalytic reaction. This does not disagree with the Langmuir–Hinshelwood mechanism considering that the reaction is partly controlled by a mass transfer process. On the whole, there is a definite coherence between the adsorption inhibition and the reaction inhibition, and the major effect of the various added anions can be attributed to competitive adsorption on the catalyst of the reactant and anions.

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