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Kinetics of Heterogeneous Photocatalytic Decomposition of 2,4-Dichlorophenoxyacetic Acid over Titanium Dioxide and Zinc Oxide in Aqueous Solution

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Abstract: The photocatalytic transformation of 2,4-D in aqueous solution containing a suspension of titanium dioxide or zinc oxide leads to the formation of intermediates which are totally mineralised to carbon dioxide and hydrogen chloride (2,4-dichlorophenol and chlorohydroquinone are the major intermediates). The products at the initial stage of the reaction were 2,4-dichlorophenol (2,4-DCP), chlorohydroquinone, 4-chloropyrocatechol, 2,4-dichloropyrocatechol and 1,4-chlorobenzoquinone. The initial rate of photodegradation was studied as a function of the initial concentration of reactants by the linearised form of the Langmuir–Hinshelwood equation, by which rate constants k and equilibrium adsorption constants K were evaluated. These constants were calculated at different temperatures between 25 and 60°C. The photodegradation rate increased with increase of pH. The photocatalytic transformation of 2,4-D over titanium dioxide or zinc oxide in solution containing hydrogen peroxide was studied. The latter accelerated the reaction rate of 2,4-D significantly.

It was found that chloride or bicarbonate ions slowed down the photodegradation rate of 2,4-D by scavenging hydroxyl radicals. Partial inhibition by ethanol is attributed to scavenging of the OH radicals involved in the first step of the reaction. © 1998 Society of Chemical Industry

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Key words: photocatalysis; 2,4-dichlorophenoxyacetic acid; zinc oxide; titanium dioxide; aqueous solution

1 INTRODUCTION

Increasing concern over surface water pollution by pesticides has been voiced in recent years. Major sources contributing to this pollution include surface run-off from agricultural land, direct application, domestic usage, industrial waste and large-scale total weed control operations on industrial sites, railways and road verges. Pollutants include chlorinated organic compounds which are resistant to chemical, photochemical and biological degradation in the environment, making disposal, particularly of contaminated water, difficult. The oxidative photocatalytic degradation of many chlorinated organic compounds by semiconductor particles, such as titanium dioxide or zinc

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oxide has been widely recognised as a promising method for the treatment of water and wastewater.[1–7]

The herbicide 2,4-D is widely used for spraying weeds. World Health Organisation (WHO) has given the recommended maximum concentration of 2,4-D in drinking water as 0·1 mg litre^{-1}. Extensive studies of the photocatalytic degradation of 2,4-D on semiconductor materials have been reported.[8] It has been demonstrated that the complete mineralisation of chlorinated hydrocarbons to form carbon dioxide and hydrogen chloride can be achieved by using titanium dioxide or zinc oxide in aqueous solution saturated with oxygen gas.[9–11]

It is generally accepted that the photocatalytic reaction is initiated by band gap photoexcitation of the titanium dioxide on zinc oxide with UV light having energy equal to or larger than the band gap of the semiconductor (3·2 eV). Electrons are photoexcited to the conduction band from the valence band, producing electron-hole pairs within the semiconductor solid. Some of the electrons and holes migrate to the semiconductor and initiate redox reactions with adsorbates through interfacial electron transfer.[2,3] Okamoto *et al.*[12] suggested that hydroxyl radicals were formed not only via holes and water but also via electrons and oxygen.

Draper & Fox[13] observed that direct electron-transfer oxidation instead of $^{\bullet}$OH radical-mediated oxidation is responsible for the oxidation of a variety of electron-transfer agents on semiconductors in aqueous suspension. Stafford *et al.*[14] showed that 4-chlorophenol can be photooxidised to hydroquinone on a titanium dioxide surface in the absence of water or oxygen.

In this study we have examined the kinetics of photodegradation of 2,4-D, which is used as a herbicide. Although titanium dioxide is recognised as the choice photocatalyst for water treatment because of its lack of toxicity, its stability and its low cost, we have also investigated zinc oxide, since the behaviour of this semiconductor towards hydrogen peroxide[15,16] is different from that of titanium dioxide.[17,18] The results obtained from these two different semiconductors are compared. Hydrogen peroxide corresponds to two electron transformations of oxygen and water. It is formed under photocatalytic conditions.[17,19] The irradiating wavelengths employed cannot directly photolyse this compound. Favourable effects were also reported when hydrogen peroxide was added to the water treated by heterogenous photocatalysis, again under conditions that precluded direct photolysis.[20–23]

An important parameter which affects the yield of 2,4-D photodegradation is the pH of the suspension. The inhibition of the photocatalysed degradation process of 2,4-D by Cl^- ions and HCO_3^- ions appears possible as the degradation rate decreases when enough sodium chloride or hydrogen carbonate is added. The main aim of the present work was to analyse the photoproducts of the photocatalysed degradation of 2,4-D and to propose a mechanism for the transformation.

2 EXPERIMENTAL DETAILS

2.1 Chemicals

2,4-dichlorophenoxyacetic acid (2,4-D) was provided by Aldrich (purity greater than 99%). Standards used for HPLC analyses were from Prolabo or Rhône-Poulenc Industries except for 3,5-dichlorocatechol, prepared by Dakin's method, i.e. oxidation of 3,5-dichlorosalicylic aldehyde by hydrogen peroxide in basic solution.[24]

Chlorobenzoquinone was obtained by the oxidation of chlorohydroquinone with lead acetate, using the same method as used by Bruce and Chaudry[25] for the oxidation of 4,4′-dihydroxybiphenyl into diphenoquinone.

Zinc oxide (ZnO) was provided by Vieille Montagne SA (France), and contained percentages of lead, iron and cadmium lower than 10^{-4}, 2×10^{-4} and $3{\cdot}5 \times 10^{-3}$ respectively. Its specific area was 9·4 m^2 g^{-1}.

Most of the experiments were carried out with titanium dioxide, (TiO_2; P25 Degussa AG Frankfurt, Germany). It was predominantly anatase (80% anatase, 20% rutile), with a surface area of 50(±5) m^2 g^{-1} and small amounts of SiO_2 and Al_2O_3.[26,27]

Substrates and standards for analyses were commercial compounds used as received.

2.2 Reactors and light sources

The device used for irradiation was a low pressure mercury lamp (Philips TLAD 15W/05) located along one of the focal axes of a cylindrical mirror with an elliptic base. The lamp had a maximum emission at 365 nm with a 50 nm half-width. The reactor, in Pyrex, was located along the other focal axis of the mirror. Its temperature was maintained between 15 and 20°C by cooling water-jacket. The air-saturated solution filled about 90% of the reactor. The volume over the solution was filled with pure oxygen and the reactor was closed with a stopcock to maintain an excess of oxygen in the solution and to limit the evaporation of 2,4-D. A magnetic stirrer maintained the zinc oxide or titanium dioxide in suspension and favoured the renewal of consumed oxygen in the solution. The reaction mixture, composed of 20 ml of 2,4-D and 2 g litre^{-1} of the oxide, was stirred for 30 min before being irradiated. The initial pH of the suspension was 7·6 with ZnO and 4·2 with TiO_2. The light intensity received by the reactor was evaluated with potassium ferrioxalate to be about 4×10^{15} photons cm^{-3} s^{-1}.

2.3 Analyses

Irradiated solutions were analysed by HPLC and GC-MS. HPLC used a Waters chromatograph equipped with an μBONDAPAK 250 mm × 4·6 mm C18-type column, after being filtered on a 0·45-μm Millipore filter. Acetonitrile + water (40 + 60 by volume) was used as the eluent. Products were detected at 280 nm with an L.C. Lambda-Max 481 spectrometer. UV spectra were recorded on a Secomam 1000 PC. For GC-MS analyses, the solutions were extracted with diethyl ether and injected into a FS SE 30 capillary column, length 25 m, internal diameter 0·25 mm. The spectrometer was a Nermag service 32 equipped with FID detection.

3 RESULTS AND DISCUSSION

3.1 Kinetics of 2,4-D disappearance and 2,4-D adsorption

The kinetics of disappearance of 2,4-D (initial concentration $C_0 = 5 \times 10^{-4}$ M) were studied under three different experimental conditions: (i) under UV illumination in the absence of semiconductors, (ii) in the dark with semiconductors, (iii) under UV illumination in the presence of semiconductors (Fig. 1). These experiments show that the photocatalytic degradation of 2,4-D in the presence of the semiconductors (TiO_2, ZnO) is more efficient than direct photolysis, the transformation is slower with ZnO than with TiO_2. The level of 2,4-D degradation depends on the mass of semiconductors in suspension.

The Langmuir–Hinshelwood kinetic model can be used to fit the experimental data. This model states that the initial rate of a unimolecular surface reaction (R_0) is proportional to the surface coverage (θ) and that the adsorption equilibrium of the solute is described by a Langmuir isotherm:[29]

$$R_0 = \frac{-\mathrm{d}C}{\mathrm{d}T} = K_\theta = \frac{KkC_0}{1 + KC_0} \qquad (1)$$

where k and K are the rate and adsorption constants respectively. A linearised form of eqn (1) has been employed:

$$\frac{1}{R_0} = \frac{1}{k} + \frac{1}{KkC_0} \qquad (2)$$

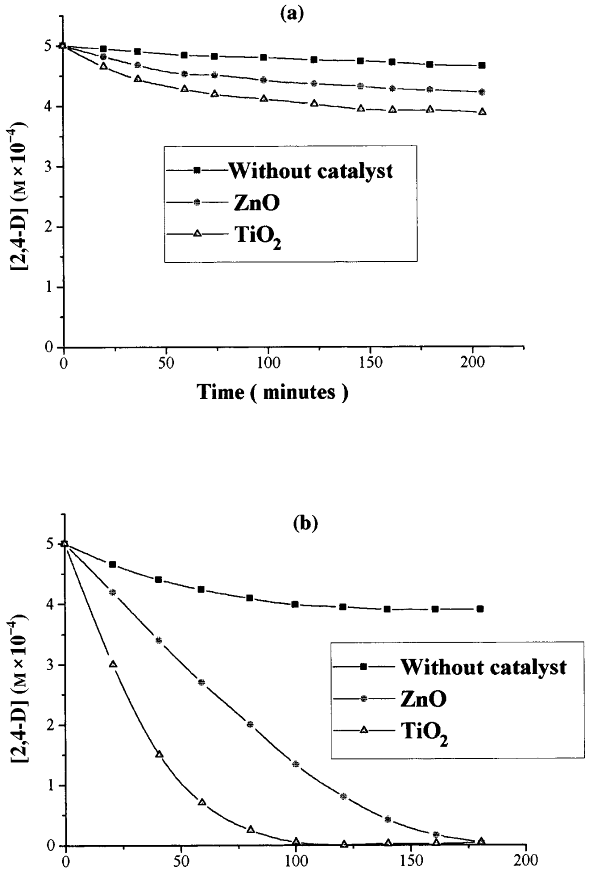


Fig. 1. Kinetics of the transformation of 2,4-D (5×10^{-4} M) with ZnO (2 g $litre^{-1}$) and TiO_2 (2 g $litre^{-1}$) (a) In the dark; (b) illuminated.

All experimental data reported in Fig. 2 as plots according to eqn (2). In the graphs, mean values of $1/R_0$ are shown together with the range of their standard deviation. Values of k and K were calculated by linear regression analysis of the experimental data.

The rate constants k were $0{\cdot}7 \times 10^{-4}$ mol $litre^{-1}$ min^{-1} for 2,4-D over ZnO and $2{\cdot}2 \times 10^{-4}$ mol $litre^{-1}$

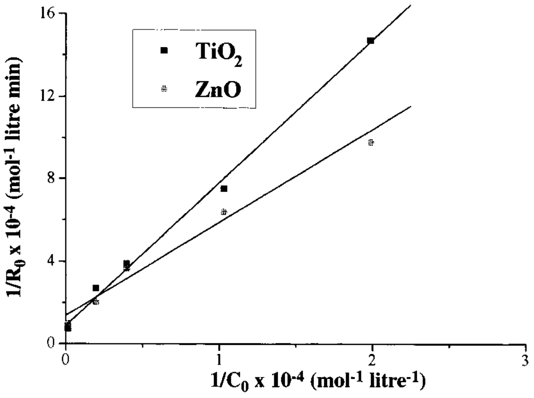


Fig. 2. Linearised plots of eqn (1) for the transformation of 2,4-D.

TABLE 1
Rate Constant (*k*) and Adsorption Equilibrium Constant (*K*) for 2,4-D Photooxidation at Different Temperatures (ZnO, 2 g litre^{-1}, pH = 7·6 and TiO_2, 2 g litre^{-1}), pH = 4·2)

	ZnO		*TiO_2*	
T (°*C*)	*k* (*mol litre*$^{-1}$ *min*$^{-1}$)	*K* (*litre*$^{-1}$ *mol*$^{-1}$)	*k* (*mol litre*$^{-1}$ *min*$^{-1}$)	*K* (*litre*$^{-1}$ *mol*$^{-1}$)
25	$0{\cdot}7 \times 10^{-4}$	$2{\cdot}0 \times 10^{3}$	$2{\cdot}2 \times 10^{-4}$	$0{\cdot}5 \times 10^{3}$
30	$6{\cdot}2 \times 10^{-4}$	$7{\cdot}8 \times 10^{2}$	$1{\cdot}8 \times 10^{-3}$	$1{\cdot}0 \times 10^{3}$
40	$8{\cdot}0 \times 10^{-4}$	$4{\cdot}5 \times 10^{2}$	$3{\cdot}4 \times 10^{-3}$	$8{\cdot}2 \times 10^{2}$
50	$2{\cdot}0 \times 10^{-3}$	$2{\cdot}0 \times 10^{2}$	$6{\cdot}4 \times 10^{-3}$	$6{\cdot}0 \times 10^{2}$
60	$4{\cdot}6 \times 10^{-3}$	$8{\cdot}0 \times 10^{1}$	$8{\cdot}2 \times 10^{-3}$	$3{\cdot}6 \times 10^{2}$

min^{-1} over TiO_2 at 25°C. The influence of the temperature on the process was studied by following the kinetics of 2,4-D disappearance at different temperatures between 25 and 60°C (Table 1).

3.2 Intermediate products of photocatalytic 2,4-D degradation

The products of the photodegradation of 2,4-D over TiO_2 and ZnO were identified by HPLC and by comparing the retention time of each peak with those of authentic standards. Analysis showed that 2,4-dichlorophenol (2,4-DCP), chlorohydroquinone, 4-chloropyrocatechol, 2,4-dichloropyrocatechol and chlorobenzoquinone were present in the medium at various irradiation times. Chlorobenzoquinone results from the redox tautomerism of chlorohydroquinone.[28] The major product was 2,4-DCP for both photocatalysts. The use of GC/MS corroborated the formation of these intermediates. The formation of 2,4-DCP can be explained by considering the attack of an ˙OH radical on the alkyl chain of the molecule, while chlorohydroquinone might be formed by the attack of an ˙OH radical on DCP.[29] The nature and results of intermediates are summarised in Table 2.

No formation of biphenyl derivatives was observed by GC-MS. These results are in good agreement with those obtained previously on 2,4-D[29,30] but are in contrast with the case of 2,4-dichlorophenol.[31]

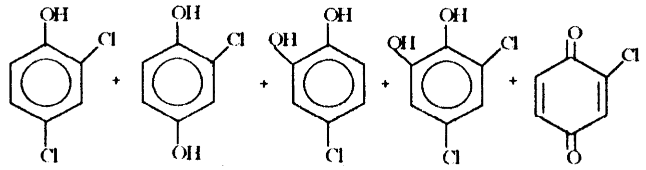
Titanium dioxide is the photocatalyst most extensively studied and its use has been suggested for the elimination of chlorinated solvents[32,33] and chloroaromatic derivatives.[34–35]

The concentration of identified photoproducts was measured at various irradiation times with ZnO and TiO_2 (P25) (Fig. 3).

3.3 Effect of pH

Figure 4 shows the effect of pH on the rate of photodegradation of 2,4-D (5×10^{-4} M) in the pH range 6·0–12·0. The semiconductor zinc oxide dissolves in the presence of highly acidic media and therefore the photocatalytic decomposition of 2,4-D could not be investigated in the lower pH range. It is observed that the rate of decomposition of 2,4-D increases with increasing pH of the medium. This observation is similar to that of Terzian *et al.*[36] who have reported that the degradation of cresol by TiO_2-UV is optimum at alkaline pH. Sabin *et al.*[37] have studied the oxidation of chlorophenols

TABLE 2
Photoproducts Observed in the Photocatalytic Transformation of 2,4-D, after a 15-min Irradiation



2,4-D	*Conversion extent (mole fraction)*	*Amount (% of 2,4-D converted)*				
ZnO	0·14	40	18	6	Traces	Traces
TiO_2	0·34	47	1·2	1·2	Traces	Traces

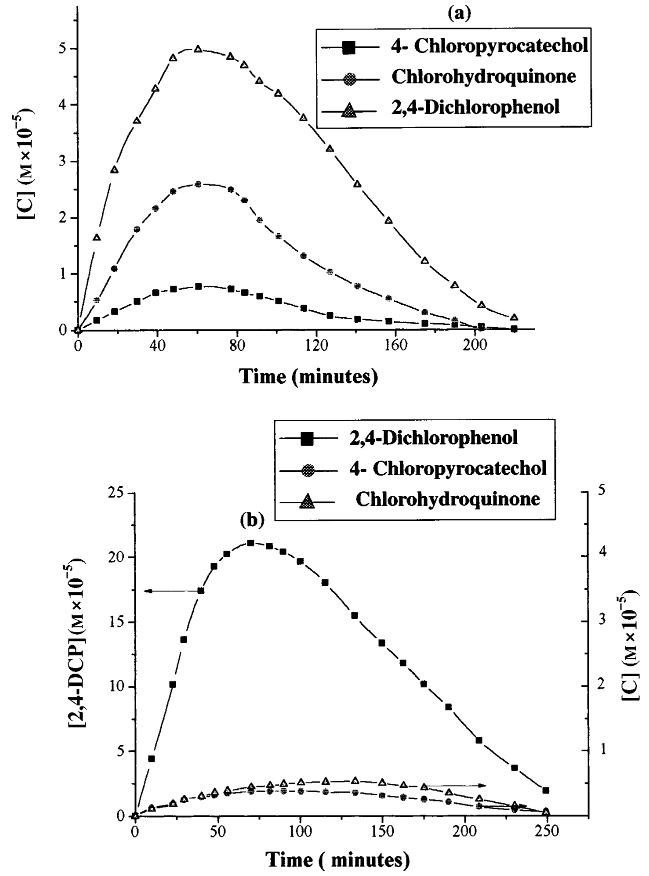


Fig. 3. Concentration of identified photoproducts from 2,4-D versus irradiation time (a) ZnO, (b) TiO_2.

under controlled pH, and reported that the oxidation rate is maximum under alkaline conditions.

The increase of photoreactivity with increasing pH is explained by process 3:

$$h^+ + OH^- \rightarrow {}^{\cdot}OH \quad (3)$$

3.4 Effects of additives

The effects of additives are very important in estimating the photodegradation rate of pollutants because many different kinds of organic and inorganic compounds may be present in water and wastewater.

In this study, the effects of some additives showing different reaction rates with aqueous electrons and hydroxyl radicals were studied.

3.4.1 Effect of added hydrogen peroxide on the photocatalytic degradation of 2,4-D

It is known that hydrogen peroxide can accelerate the photodegradation rate of organic compounds in photo-assisted reaction because of its strong oxidising power

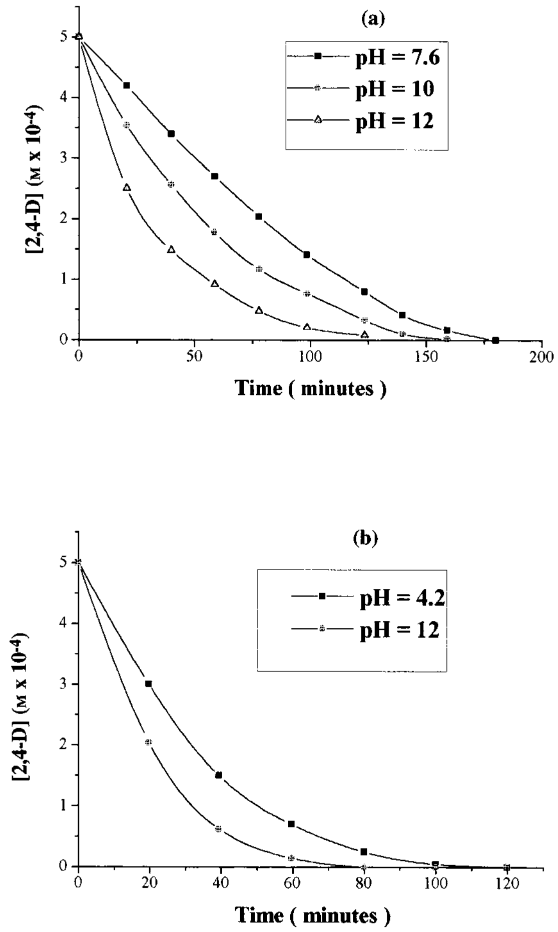


Fig. 4. Influence of pH on the photocatalytic transformation of 2,4-D (a) with ZnO and (b) with TiO_2.

and dissociation characteristics forming hydroxyl radicals.

In 1994 Amalric *et al.*[38] observed that the effect of H_2O_2 added to ZnO was negative and in the case of TiO_2 was either favourable or unfavourable depending on the initial ratio of $[H_2O_2]/[1,2\text{-DMB}]$(1,2-dimethoxybenzene). This can be explained on the basis of a competition between these two compounds for the adsorption sites and/or the photoproduced holes, the formation of additional ˙OH radicals and the detrimental modification of the TiO_2 surface.

As mentioned before, the beneficial effect of photocatalysis was demonstrated by comparing sensitised degradation with direct photolysis. Furthermore we observed that addition of H_2O_2 to the photocatalysts led to further increase in the photooxidation rate of 2,4-D. As shown in Fig. 5 the complete disappearance of 2,4-D was achieved within 140 to 155 min in the presence of ZnO and within 80 to 100 min in the presence of TiO_2.

Moreover, at the higher concentration of H_2O_2 the intermediate compounds disappeared at approximately the same time as the parent product, thus leading to a faster total mineralisation. We can conclude that these

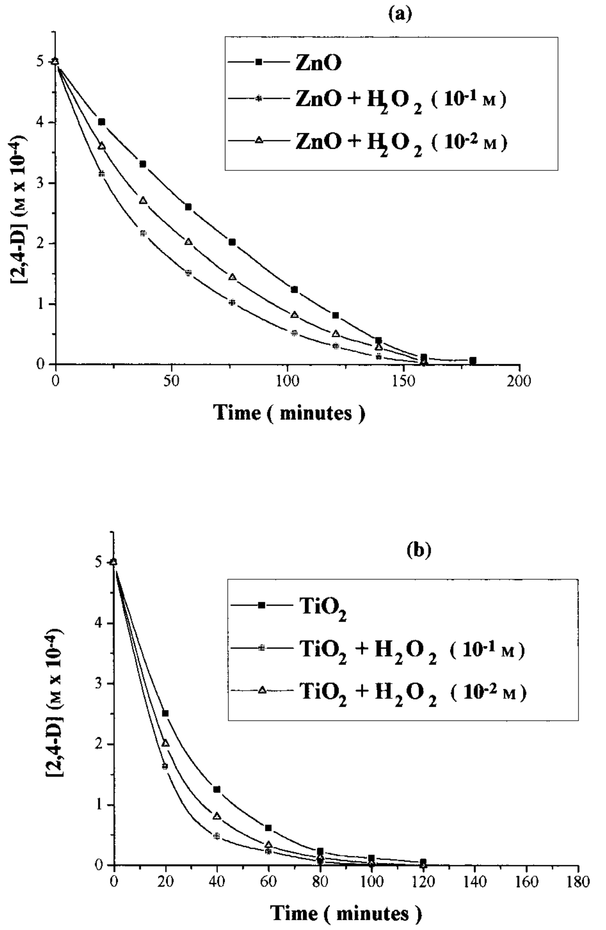


Fig. 5. Influence of [H_2O_2] on the photocatalytic transformation of 2,4-D (a) with ZnO and (b) with TiO_2.

intermediate compounds are less photostable under these conditions.

3.4.2 Effect of chloride ion concentration on the photocatalytic degradation of 2,4-D

The inhibiting effect of chloride ions on photocatalysed oxidation by ZnO and TiO_2 has been reported in the literature[39] and has been explained on the basis of the quenching of the degradation process by Cl^- ions via their reaction with $^{\bullet}OH$ radicals. The following rate constant is reported for this:[40]

$$Cl^- + OH^{\bullet} \rightarrow Cl^{\bullet} + OH^- \qquad (4)$$

$$K_{Cl^-} = 4{\cdot}3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

This can also be explained by protonation of the TiO_2 particle surface at high acidic concentrations (when the pH of the solution is less than the pKa of the TiO_2 surface), or by competition of Cl^- with hydrocarbons for the active adsorption sites of TiO_2 surfaces at low acidic concentrations.[41]

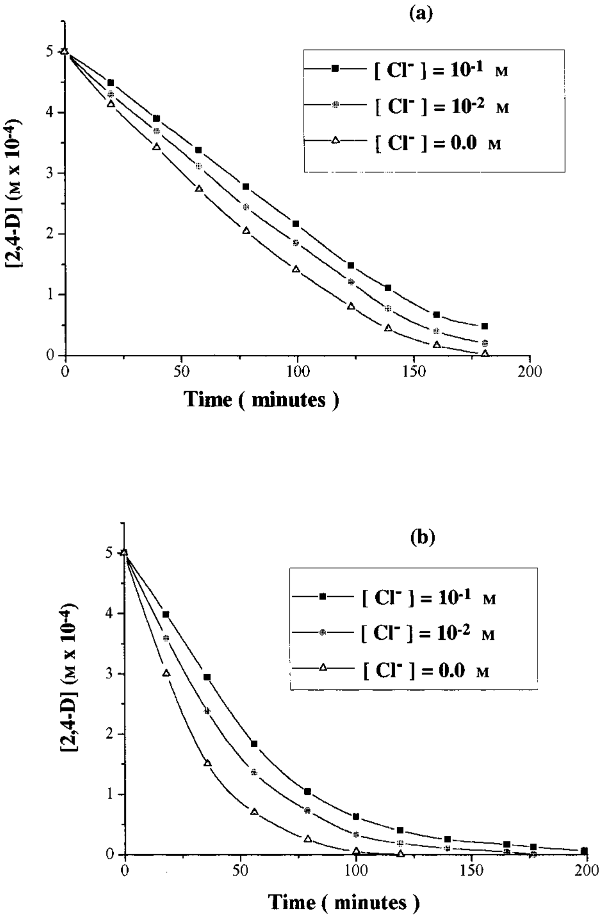


Fig. 6. Influence of [Cl^-] on the photocatalytic transformation of 2,4-D (a) with ZnO and (b) with TiO_2.

Experiments on the degradation of 2,4-D over ZnO and TiO_2 have been conducted in the presence of sodium chloride at 10^{-1} M and 10^{-2} M respectively. The results obtained and reported in Fig. 6 show that the inhibition effect is not significant.

3.4.3 Effect of hydrogencarbonate ion concentration on the photocatalytic degradation of 2,4-D

Since $^{\bullet}OH$ radicals are known to oxidise even carbonate ions and thus become scavenged, the protective effect of hydrogencarbonate ions was studied at two different concentrations of HCO_3^- (Fig. 7). As can be seen, by increasing the concentration of HCO_3^-, the rates significantly decreased. This inhibition is undoubtedly due to the scavenging of hydroxyl radicals. These results are interesting because bicarbonate ions are ubiquitous in natural waters.

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet -} + H_2O \qquad (5)$$

$$K_{HCO_3^-} = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$ [4,3]

3.4.4 Effect of ethanol on the photocatalytic degradation of 2,4-D

Ethanol was chosen since it does not absorb wavelengths longer than 260 nm and its reaction with $^{\bullet}OH$

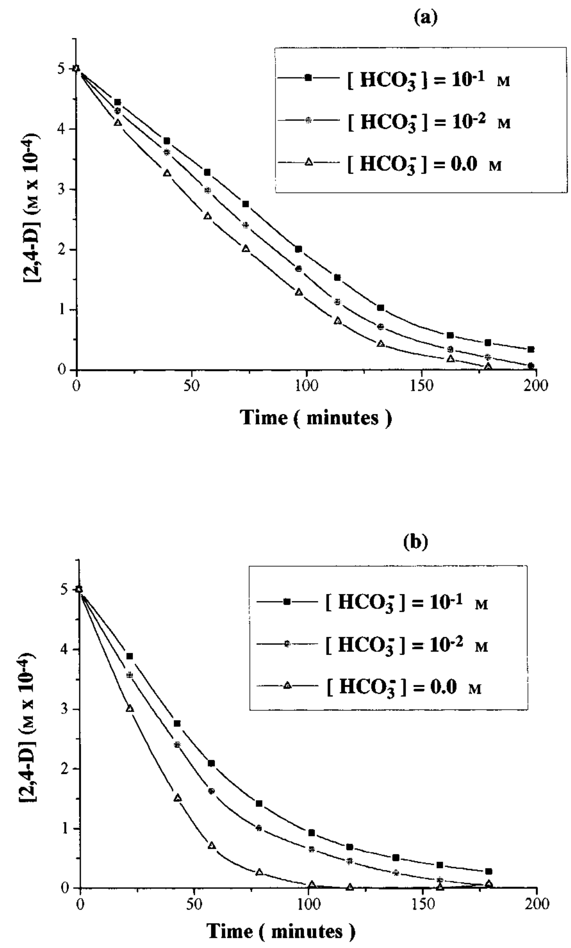


Fig. 7. Influence of [HCO_3^-] on the photocatalytic transformation of 2,4-D (a) with ZnO and (b) with TiO_2.

radicals is almost diffusion-controlled ($k = 1{\cdot}9 \times 10^9$).[40] The photocatalysed transformation of 2,4-D is about 70% inhibited by low concentrations of ethanol (0·08% v/v; (i.e. $1{\cdot}4 \times 10^{-2}$ mol litre^{-1}). The inhibition ratio is unchanged for ethanol concentrations as high as 2% v/v. It may be concluded, therefore, that two different pathways are involved in the photocatalysed transformation of 2,4-D. One of them involves hydroxyl radicals and is inhibited by ethanol. The other is attributed to a direct oxidation by positive holes formed on the irradiated photocatalyst as has previously been suggested.[42,43,44]

3.5 Mechanism of 2,4-D photocatalytic degradation

Many reports on the photocatalytic degradation of organic compounds in aqueous solutions have suggested the action of ˙OH radicals (Fig. 8).[45,46] These radicals can be produced by the surface reaction of the photoproduced holes with adsorbed OH^- ions or adsorbed water. The electrons reduce oxygen into superoxide ions which disproportionate after protonation into hydrogen peroxide and oxygen.[47] From the inhibiting effect of ethanol of the transformation of 2,4-D, it can be concluded that about 70% of the conversion involves hydroxyl radicals and about 30% can be attributed to the capture of a positive holes by adsorbed 2,4-D on semiconductors.[16,44] (Fig. 9).

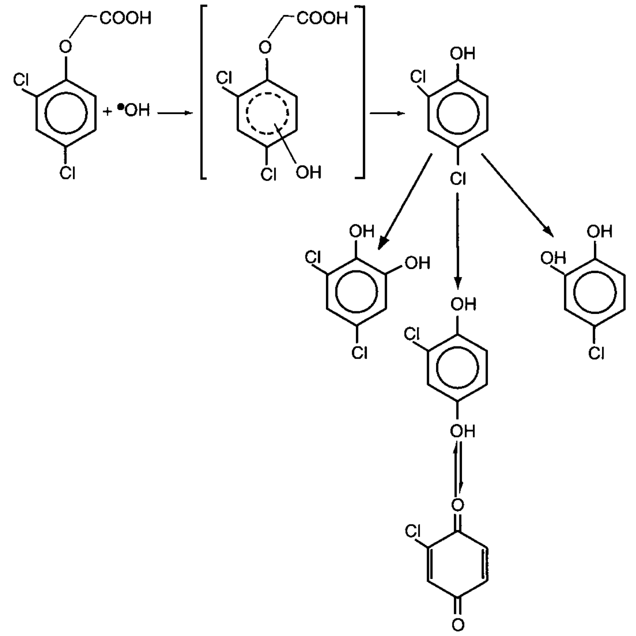


Fig. 8. Mechanism of 2,4-D degradation—major route.

4 CONCLUSION

The photocatalytic degradation of a pollutant; 2,4-D, in aqueous solutions was studied using two semiconductors, TiO_2 and ZnO, with different efficiencies; it appears that titanium dioxide (Degussa P25) is the better photocatalyst taking into account its good activity and lack of toxicity.

The same products are formed with the two photocatalysts. The majors intermediates are 2,4-dichlorophenol (2,4-DCP) and chlorohydroquinone.

For the chosen pollutant, 2,4-D, two methods of oxidation were observed: oxidation with ˙OH radicals originating on the surface of the photocatalyst; direct

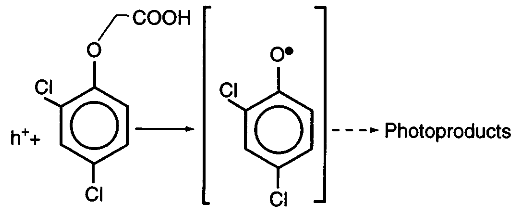


Fig. 9. Mechanism of 2,4-D degradation—minor route.

oxidation by holes created by the action of light on the semiconductor.

Nevertheless, after a long irradiation time ($t > 250$ min), all compounds are mineralised. This result is important in the field of water decontamination.

This photocatalytic method has good potential for application on a large scale. For this, it will be necessary to decrease the electron-hole recombination to increase the quantum yield of the photocatalytic reaction. Moreover, the problem of photocatalyst recovery remains. The solution to this problem will probably be achieved by the use of supported or immobilised semiconductors.[48,49]

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