

Titanium dioxide mediated photocatalysed degradation of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid, in aqueous suspensions

Hemant K. Singh^a, Mohd Saquib^a, Malik M. Haque^a,
Mohammad Muneer^{a,*},¹, Detlef W. Bahnemann^b

^a Department of Chemistry, Aligarh Muslim University, Aligarh (U.P.), India

^b Institut für Technische Chemie, Universität Hannover, Hannover, Germany

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Abstract

The photocatalysed degradation of phenoxyacetic acid (PAA, **1**) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, **2**), has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by depletion in total organic carbon (TOC) content as a function of irradiation time. The influence of various parameters such as, different types of TiO₂ powders, pH, catalyst and substrate concentrations, and in the presence of electron acceptors such as hydrogen peroxide (H₂O₂) and potassium bromate (KBrO₃) besides molecular oxygen have been investigated. The effects of these parameters on the degradation rates were found to be significant. TiO₂, Degussa P25 was found to be more efficient for the degradation of both the compounds under investigation as compared with other TiO₂ powders. The degradation products were analyzed by GC–MS analysis technique and probable pathways for the formation of different products have been proposed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Photocatalysed degradation; Phenoxyacetic acid; 2,4,5-Trichlorophenoxyacetic acid; Titanium dioxide

1. Introduction

Recent decades have witnessed increased contamination of the Earth's drinking water. A wide variety of organics are introduced into the water system from various sources such as industrial effluents, agricultural runoffs and chemical spills [1,2]. A large number of herbicides are applied on the agricultural fields, which apart from killing their respective weed, due to their chemical stability, resistance to biodegradation and sufficient water solubility can either penetrates deep into the ground water aquifers or can be washed away to the surface water bodies [3]. These compounds due to their toxicity, stability to natural decomposition and persistence in the environment, have been the cause of much concern to the societies and regulation authorities around the world [4]. The control of organic pollutants in water is an important measure in environmental protection. Het-

erogeneous photocatalysis has emerged as an alternative for the detoxification of recalcitrant organic pollutants in water.

Recently considerable attention has been focused on the use of semiconductor as a means to oxidize toxic organic chemicals. The photocatalysed degradation of various organics systems employing irradiated TiO₂ is well documented in the literature [5]. When a semiconductor such as TiO₂ absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e_{cb}^-) leaving behind an electron vacancy or "hole" in the valence band (h_{vb}^+), as shown in Eq. (1). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}^+ may react with surface-bound H₂O or OH⁻ to produce the hydroxyl radical and e_{cb}^- is picked up by oxygen to generate superoxide radical anion (O₂^{•-}), as indicated in the following Eqs. (1)–(3):



* Corresponding author. Present address: Marie Curie Fellow Centre for Material Science, Faculty of Science, University of Central Lancashire, Preston PR1 2HE, UK. Tel.: +44 1772 893578.

E-mail address: mmuneer@uclan.ac.uk (M. Muneer).

¹ On leave from AMU Aligarh, India.

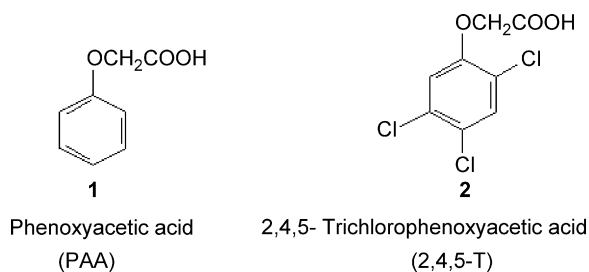


Fig. 1. Chemical structure of phenoxyacetic acid (PAA, **1**) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, **2**).

It has been suggested that the hydroxyl radicals ($\bullet\text{OH}$) and superoxide radical anions ($\text{O}_2^{\bullet-}$) are the primary oxidizing species in the photocatalytic oxidation processes.

Phenoxyacetic acid (PAA) is used as a fungicide. It is also used as intermediate for dyes, pharmaceuticals and pesticides. It has a water solubility of 12 g L^{-1} [6]. PAA and 2,4,5-T has been detected in water [7,8].

Photoredox reaction of phenoxyacetic acid and photocatalysed degradation over supported TiO_2 in a flow system have also been reported [9,10]. The amine salts of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) are extensively used for the control of dicotyledonous weeds in cereal crops. It has been used to kill weeds in the fields of wheat, barley, oats, rye, rice, maize and sorghum. 2,4,5-T has water solubility of 4.5 g L^{-1} [11]. Sunlight photodegradation of 2,4,5-T on titanium dioxide has already been reported earlier [12]. In spite of all these studies no major efforts have been made to investigate the detailed degradation kinetics along with the intermediate products of these compounds under UV light. With this view we have undertaken a detailed study on the photodegradation of PAA (**1**) and 2,4,5-T (**2**) shown in Fig. 1 sensitized by TiO_2 in aqueous solution under UV light source examining various reaction parameters, e.g. reaction pH, substrate and catalyst concentrations, type of photocatalysts and attempt has also been made to identify the intermediate products formed during the photooxidative process through GC–MS analysis technique.

2. Experimental methods

2.1. Reagents and chemicals

Reagent grade phenoxyacetic acid (**1**), and 2,4,5-trichlorophenoxyacetic acid (**2**) were obtained from Aldrich and were used as such without any further purification. The photocatalyst titanium dioxide P25 (Degussa AG), was used in most of the experiments. Other catalyst powders namely Hombikat UV100 (Sachtleben Chemie GmbH), PC500 (Millennium Inorganic Chemicals) and TTP (Travancore Titanium Products, India) were used for comparative studies. Degussa P25 consists of 80% anatase and 20% rutile with a specific BET-surface area of $50\text{ m}^2\text{ g}^{-1}$ and primary particle size of 20 nm [13]. Hombikat UV100 consist of 100% anatase with a specific BET-surface area $>250\text{ m}^2\text{ g}^{-1}$ and primary particle size of 5 nm [14]. The photocatalyst PC500 has a BET-surface area of $287\text{ m}^2\text{ g}^{-1}$ with 100% anatase and primary particle size of 5–10 nm [15] whereas; TTP has a BET-surface area of $9.82\text{ m}^2\text{ g}^{-1}$. The other chemicals

used in this study such as NaOH, HNO_3 , H_2O_2 and KBrO_3 were obtained from Merck.

2.2. Procedure

Solutions of the PAA (**1**) and 2,4,5-T (**2**) of desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen was used. For irradiation experiment, aqueous solution (250 mL) of the compound was taken into the photoreactor, the required amount of photocatalyst was added and the solution was stirred and bubbled with molecular oxygen for at least 30 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption could be taken into account. pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or NaOH. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). Samples (10 mL) were collected before and at regular intervals during the irradiation and analyzed after centrifugation.

2.3. Analysis

The degradation was monitored by measuring the total organic carbon (TOC) content with a Shimadzu TOC 5000A Analyzer (Shimadzu Corporation, Japan) by directly injecting a centrifuged sample. Samples were acidified and purged to remove inorganic carbon.

2.4. Characterization of intermediate photoproducts

For the characterization of intermediate products, aqueous solutions (250 mL) of compounds containing TiO_2 (P25, 1 g L^{-1}) were taken in the immersion well photochemical reactor. The mixture was irradiated with a 125 W medium pressure mercury lamp (Philips, India) at different time intervals and the formation of product was followed using thin layer chromatography technique. The photocatalyst was removed through filtration and the filtrate was extracted with chloroform, which was subsequently dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC–MS analysis technique. For GC–MS analysis a Shimadzu Gas chromatograph and mass spectrometer (GCMS-QP 5050) equipped with a 25 m CP SIL 19 CB ($d=0.25\text{ mm}$) capillary column, operating temperature programmed ($220\text{ }^\circ\text{C}$ for 40 min at the rate of $10\text{ }^\circ\text{C min}^{-1}$) in splitless mode injection volume ($1.0\text{ }\mu\text{L}$) with helium as a carrier gas was used.

3. Results and discussion

3.1. Photolysis of phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid in the presence of TiO_2

An aqueous suspension of PAA (**1**) and 2,4,5-T (**2**) was irradiated in the presence of TiO_2 by the pyrex filtered output of a

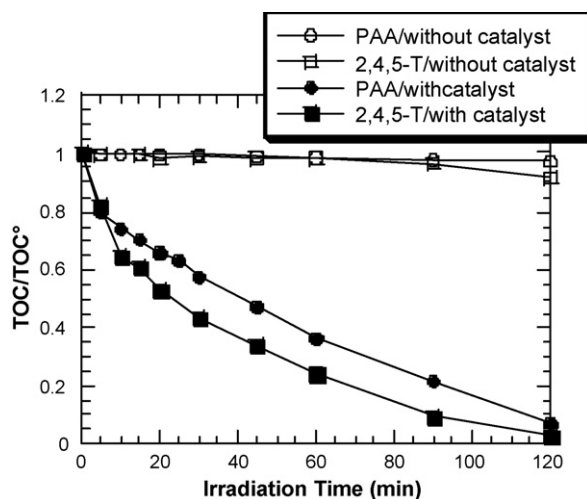


Fig. 2. Depletion in TOC as a function of irradiation time for an aqueous solution of PAA (**1**) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in the presence and absence of TiO₂. Experimental conditions: PAA (1 mM), 2,4,5-T (0.5 mM) V = 250 mL, immersion well photoreactor, 125 W medium pressure Hg lamp, photocatalyst: TiO₂ (Degussa P25) 1 g L⁻¹, continuous O₂ purging and stirring, irradiation time = 120 min.

125 W medium pressure mercury lamp. The depletion in TOC content as a function of irradiation time for the compounds **1** and **2** is shown in Fig. 2. Both compounds under investigation underwent decomposition when irradiated in the presence of TiO₂, whereas no observable loss of compound was seen in the absence of TiO₂. The degradation curves of **1** and **2**, follow exponential decay kinetics. For each experiment the degradation rate for the mineralization (depletion in TOC content) of the model pollutants was calculated from the initial slope obtained by linear regression from a plot of natural logarithm of the TOC content of the compounds as a function of irradiation time. The resulting first order rate constant was used in all subsequent plots to calculate the degradation rate using the formula given below:

$$\frac{-d[\text{TOC}]}{dt} = kc^n \quad (4)$$

where k is the rate constant, c the concentration of the pollutant, and n is the order of reaction.

Control experiments were carried out in all cases, employing unirradiated blank solutions. There was no observable loss of the compound due to adsorption on the catalyst in unirradiated blank solutions. The zero irradiation time readings were obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.2. Comparison of different photocatalysts

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity, non-toxic, relatively inexpensive and stable in aqueous solution. The aim of this task was to identify the most effective photocatalyst among the different TiO₂ brands and to optimize the efficiency of reaction. Photocatalytic activity of four different commercially available TiO₂ powders (namely Degussa P25, Hombikat UV100, Millennium Inorganic

Table 1

Degradation rate for the mineralization of PAA (**1**) and 2,4,5-T (**3**) in the presence of different photocatalysts

Type of photocatalyst (1 g L ⁻¹)	Degradation rate for the mineralization (10 ⁻³ × M min ⁻¹)	
	PAA	2,4,5-T
P25	0.0152	0.0255
UV100	0.0136	0.0057
PC500	0.0088	0.0081
TTP	0.002	0.0013

Experimental conditions: PAA (1.0 mM), 2,4,5-T (0.5 mM) photocatalysts: TiO₂ Degussa P25 (1 g L⁻¹), Hombikat UV100 (1 g L⁻¹), PC500 (1 g L⁻¹), irradiation time = 120 min.

PC500 and Travancore Titanium Products, India) were tested on the degradation kinetics of the pollutants under investigation. The degradation rates obtained for the TOC depletion of **1** and **2**, in the presence of different types of TiO₂ powders at 1 g L⁻¹ is shown in Table 1. It has been observed that the degradation of the pollutants proceeds much more rapidly in the presence of Degussa P25 as compared with other TiO₂ samples under UV light source.

Other researchers have also shown better efficiency in Degussa P25 on a large number of organic compounds [16–18]. On the other hand Lindner et al. [19] showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. Also Hombikat UV100 was found to be better for the degradation of benzidine and 1,2-diphenyl hydrazine as reported earlier [20]. The better photocatalytic activity of Degussa P25 could be attributed to the existence of small nanocrystallites of rutile TiO₂ dispersed within an anatase matrix. The smaller band gap of rutile catches the photons generating electron–hole pairs. Electrons are transferred from the rutile conduction band to electron traps in anatase phase. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react. In the rest of the experiments, Degussa P25 was used as the photocatalyst, since this material exhibited highest overall activity for the degradation of the pollutants [21].

3.3. Effect of pH

An important parameter in the heterogeneous photocatalysis is the reaction pH, since it influences the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutant and the size of aggregates formed. The mineralization of PAA (**1**) and 2,4,5-T (**2**) in the aqueous suspension of TiO₂ (Degussa P25) was studied in the pH range between 3 and 9. The degradation rate for the TOC depletion of **1** and **2** as a function of reaction pH are shown in Table 2. It has been found that on increasing the reaction pH of both the compounds the degradation rate decreases. These results indicate that the model compounds can be photocatalytically degraded considerably faster at lower pH values. Similar kind of results of the effect of reaction pH on the degradation rate of the 2,4-D (phenoxyacetic acid herbicide) was reported earlier [22].

Table 2

Degradation rate for the mineralization of PAA (**1**) and 2,4,5-T (**3**) at different pH

pH	Degradation rate for the mineralization ($10^{-3} \times \text{M min}^{-1}$)	
	PAA	2,4,5-T
3	0.0152	0.0255
5	0.0136	0.0182
7	0.0079	0.0145
9	0.0047	0.0126

Experimental conditions: phenoxyacetic acid (1.0 mM), 2,4,5-T (0.5 mM) photocatalysts: TiO₂ Degussa P25 (1 g L⁻¹), reaction pH (3, 5, 7 and 9), irradiation time = 120 min.

3.4. Effect of substrate concentration

It is important both from mechanistic and application point of view to study the dependence of substrate concentration on the photocatalytic reaction rate. As oxidation proceeds, less and less of the surface of the TiO₂ particle is covered as the pollutant is decomposed. Effect of substrate concentrations on the degradation of compounds **1** and **2** was studied at different concentrations.

TOC depletion rate is shown in Table 3 as a function of substrate concentration employing TiO₂ Degussa P25 (1 g L⁻¹) as a photocatalyst. As expected, the degradation rate for the mineralization increases with the increase in substrate concentrations and the results are in agreement with a number of studies reported earlier.

3.5. Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of the compounds **1** and **2** was studied employing different concentrations of Degussa P25, Hombikat UV100 and PC500. The influence of photocatalyst concentration on the degradation rate for the TOC depletion of **1** and **2** employing three different TiO₂ powders is shown in Table 4. In the case of compound **1**, it was found that the Degussa P25 was more efficient as compared to the other TiO₂ powders at all

Table 3

Degradation rate for the mineralization of PAA (**1**) and 2,4,5-T (**3**) at different substrate concentration

Initial substrate concentration (mM)	Degradation rate for the mineralization ($10^{-3} \times \text{M min}^{-1}$)
PAA	
0.50	0.0060
0.75	0.0090
1.00	0.0152
1.50	0.0315
2,4,5-T	
0.25	0.0192
0.50	0.0250
0.75	0.0265
1.00	0.0300

Experimental conditions: PAA (1.0 mM), 2,4,5-T (0.5 mM) photocatalysts: TiO₂ Degussa P25 (1 g L⁻¹), substrate concentration (0.25–1.5 mM).

Table 4

Degradation rate for the mineralization of PAA (**1**) and 2,4,5-T (**3**) at different catalyst concentrations of three different TiO₂ powders

Photocatalyst concentration (g L ⁻¹)	Degradation rate for the mineralization ($10^{-3} \times \text{M min}^{-1}$)	
	PAA	2,4,5-T
P25		
0.25	0.0114	
0.5	0.0120	0.0134
1.0	0.0152	0.0255
2.0	0.0140	
3.0		0.0291
5.0		0.024
UV100		
0.25	0.0045	
0.5	0.005	0.0052
1.0	0.0136	0.0057
2.0	0.0064	
3.0		0.0071
5.0		0.0063
PC500		
0.25	0.0032	
0.5	0.0038	0.004
1.0	0.0088	0.008
2.0	0.0036	
3.0		0.011
5.0		0.010

Experimental conditions: PAA (1.0 mM), 2,4,5-T (0.5 mM), photocatalysts: TiO₂ (Degussa P25, UV100 and PC500), catalyst concentrations (0.25–5.0 g L⁻¹), irradiation time = 120 min.

the employed concentrations and the order of efficiency was P25 > UV100 > PC500. It was observed that the degradation rate increased with the increase in catalyst loading up to 1 g L⁻¹ and, on further increase in catalyst loading, the degradation rate lead to decreased for all the employed catalyst powders.

The influence of photocatalyst concentration on the degradation rate for the TOC depletion of **2** was investigated employing three different TiO₂ powders varying from 0.5 to 5.0 g L⁻¹. Degussa P25 was found to be more efficient than UV100 and PC500 with the following order: P25 > PC500 > UV100. It was observed that the degradation rate increased with the increase in catalyst concentration up to 3 g L⁻¹ and on subsequent addition of catalyst leads to the leveling off of the degradation rate.

Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, in some cases it was observed that above a certain concentration, the reaction rate even decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO₂ in which all the particles, i.e., the entire surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration [(TiO₂)_{OPT}] has to be found, in order to avoid excess catalyst and ensure total absorption of efficient photons. Our results have

Table 5
Degradation rate for the mineralization of PAA (**1**) and 2,4,5-T (**3**) at different electron acceptor concentrations

Additives	Degradation rate for the mineralization ($10^{-3} \times \text{M min}^{-1}$)	
	PAA	2,4,5-T
P25	0.0152	0.0255
P25/KBrO ₃ (mM)		
1.0	0.0242	0.0342
3.0	0.0260	0.0424
5.0	0.0380	0.0490
P25/H ₂ O ₂ (mM)		
1.0	0.0163	0.0417
3.0	0.0200	0.0432
5.0	0.0220	0.0437

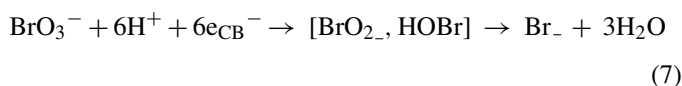
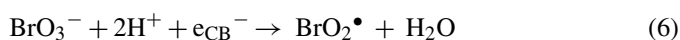
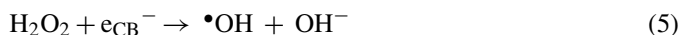
Experimental conditions: PAA (1.0 mM), 2,4,5-T (0.5 mM), photocatalysts: TiO₂ (Degussa P25, 1 g L⁻¹), KBrO₃ H₂O₂, concentrations (1,3,5 mM), irradiation time = 120 min.

also shown that 1 g L⁻¹ catalyst concentration was better as compared to very high catalyst concentrations.

3.6. Effect of electron acceptors

One practical problem in using TiO₂ as a photocatalyst is the undesired electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and thus represent the major energy—wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron–hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as, i.e., (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds and (4) to avoid problems caused by low oxygen concentration. In highly toxic waste water where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified. The effect of electron acceptors such as potassium bromate and hydrogen peroxide on the photocatalytic degradation of **1** and **2** in addition to the molecular oxygen was investigated at varying concentrations. The degradation rate for the mineralization (TOC depletion) of the compounds **1–2** in the presence of different electron acceptors is shown in Table 5.

Hydrogen peroxide, bromate ions are known to generate hydroxyl radicals by the mechanisms shown in Eqs. (8)–(10);



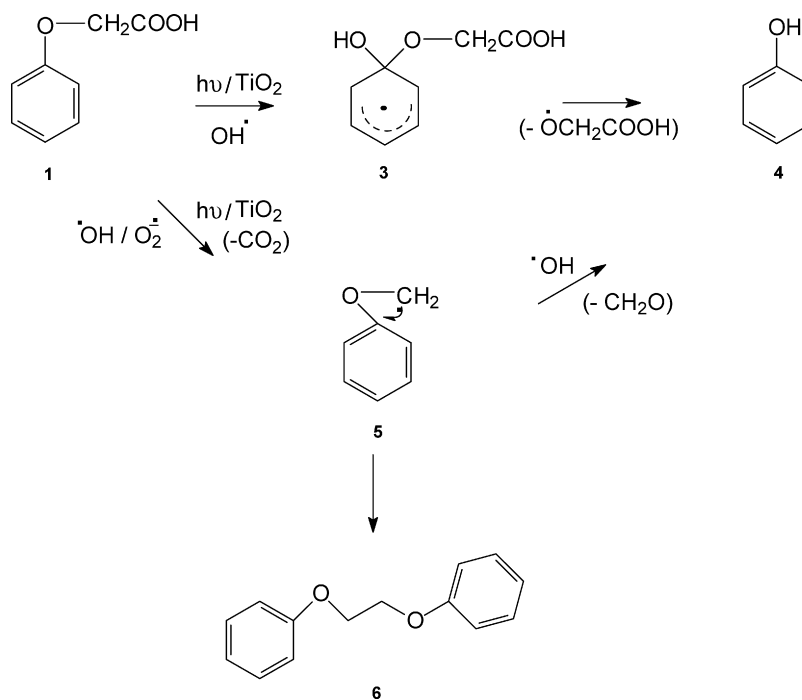
As expected, both the additives showed beneficial effect on the photocatalytic degradation of compounds under investigation as

evident from the Table. However the addition of bromate ions markedly enhanced the degradation, indicating that this compound is more effective electron acceptor as compared with other oxidants employed in this study. The respective one electron reduction potentials (measured against NHE) of different species are $E(\text{O}_2/\text{O}_2\bullet^-) = -155$ mV, $E(\text{H}_2\text{O}_2/\bullet\text{OH}) = 800$ mV and $E(\text{BrO}_3^-/\text{BrO}_2\bullet) = 1150$ mV [23]. From thermodynamic point of view both the additives should therefore be more efficient electron acceptors than molecular oxygen. Since the addition of bromate ions markedly enhanced the degradation, which can be attributed to the large number of electron involvement as shown in Eq. (10). Another possible explanation might be a change in the reaction mechanism of the photocatalytic degradation, since the reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing reagents eq. BrO₂⁻ and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Lindner has also proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions considering direct oxidation of the substrate by bromate ions [24]. A similar mechanism might also be operative in the cases of the model compounds studied in this work.

3.7. Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the compounds **1** and **2** in aqueous suspensions of titanium dioxide through GC/MS analysis.

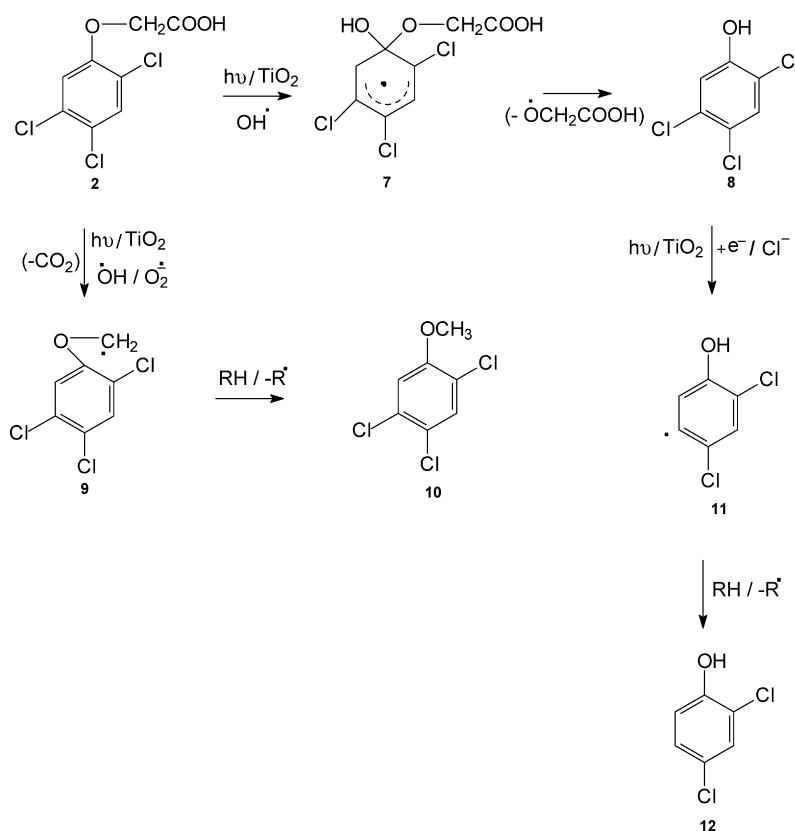
An aqueous suspension of phenoxyacetic acid (1 mM, 250 mL) in the presence of Degussa P25 (1 g L⁻¹) was irradiated for 15, 30 and 60 min in separate runs. The catalyst was removed by filtration and the solution was extracted with chloroform, which was dried over anhydrous sodium sulfate. The removal of the solvent under reduced pressure gave a residual mass, which was analyzed by GC–MS analysis. The GC/MS analysis of the irradiated samples of phenoxyacetic acid (**1**) showed the formation of two intermediate product phenol and 1,2-diphenoxyethane appearing at retention time (t_R) 2.92 and 9.84 min, respectively. These two products were identified by comparing their molecular ion and mass fragmentation peaks with those reported in the library. A plausible mechanism for the formation of these two products, involving reactions with hydroxyl radicals formed in the photocatalytic process could be understood in terms of the pathways shown in Scheme 1. The model compound undergoes addition of a hydroxyl radical formed in the photocatalytic process leading to the formation of a radical species **3**, which may undergo loss of ($\bullet\text{OCH}_2\text{COOH}$) group to give the observed product phenol (**4**). Alternatively, the model compound **1** on addition of hydroxyl radical followed by loss of CO₂ may lead to the formation of the radical species **5**. This species can either lose formaldehyde molecule followed by addition of hydroxyl radical led to the formation of phenol or can combine with another radical species leading to the formation of the 1,2-diphenoxyethane (**6**).



Scheme 1.

An aqueous suspension of 2,4,5-T (0.5 mM, 250 mL) in the presence of Degussa P25 (1 g L^{-1}) was irradiated for 15, 30 and 60 min in separate runs. The GC/MS analysis of the irradiated samples of 2,4,5-T (2) showed the formation of

three intermediate products namely, 2,4,5-trichlorophenol (8), 2,4-dichlorophenol (12) and 1,2,4-trichloro-5-methoxy benzene (10) appearing at retention times 4.11, 6.30 and 12.86 min, respectively, and were identified by comparing their molecu-



Scheme 2.

lar ion and mass fragmentation peaks with those reported in the library.

A plausible mechanism for the formation of products **8**, **10** and **12**, involving electron transfer reaction and reaction with hydroxyl radicals formed in the photocatalytic process could be understood in terms of the pathways shown in **Scheme 2**. The model compound **2** on addition of a hydroxyl radical can lead to the formation of a radical species **7**, which may undergo loss of ($\bullet\text{OCH}_2\text{COOH}$) group to give the observed product 2,4,5-trichlorophenol (**8**). Alternatively, the model compound **2** upon the transfer of an electron followed by loss of CO_2 may lead to the formation of the radical species **9**. This species abstracts a hydrogen atom to form the observed product 1,2,4-trichloro-5-methoxy benzene (**10**). The product, **8** on further transfer of an electron may undergo loss of chlorine atom followed hydrogen atom abstraction giving 2,4-dichlorophenol (**12**) as shown in **Scheme 2**.

4. Conclusion

The results of this study clearly indicate that TiO_2 can efficiently catalyse the photomineralisation of the phenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid in the presence of light and oxygen. The results also indicate that degradation rates could be influenced not only by the different parameters such as type of photocatalyst, catalyst concentration, substrate concentration, pH and additives and their concentration but also by the model pollutants. The intermediate products formed during the process are also a useful source of information for the degradation pathways.

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