

Heterogeneous photocatalysed degradation of 4-chlorophenoxyacetic acid in aqueous suspensions

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Abstract

The photocatalysed degradation of 4-chlorophenoxyacetic acid (4-CPA, **1**) has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in total organic carbon (TOC) content as a function of irradiation time. The influence of various parameters such as, different types of titanium dioxide (TiO_2) powders, pH, catalyst and substrate concentrations, and in the presence of electron acceptor such as hydrogen peroxide (H_2O_2) besides molecular oxygen has been investigated. The effects of these parameters on the degradation rates were found to be significant. The volatile degradation product 4-chlorophenol was analyzed by GC–MS technique and probable pathways for the formation of product has been proposed.

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1. Introduction

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]. These compounds due to their chemical stability, resistance to biodegradation and sufficient water solubility can either penetrate deep into the ground water or can be washed away to the surface water bodies [3]. Their toxicity, stability to natural decomposition and persistence in the environment, has 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. Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention, as it is relatively cheap. But very often it is unable to reduce the power of the contaminant and is susceptible to toxic compounds that inactivate the waste degrading microorganisms. For the removal of such recalcitrant pollutants, traditional physical tech-

niques (adsorption on activated carbon, ultrafiltration, reverse osmosis) can be used. Nevertheless, they are non-destructive, since they just transfer organic matter from water to sludge. Chemical treatment of polluted surface and groundwater is a part of long-term strategy to improve the quality of water by eliminating toxic compounds of human origin before returning the water to its natural cycles. This type of treatment is suitable when a biological processing plant cannot be adapted to certain types of pollutants and it is costly also.

Heterogeneous photocatalysis has emerged as an alternative for the detoxification of water [5]. The detailed mechanism could be understood considering a semiconductor particle which is commonly characterized by energy gap between its electronically populated valence band and its largely vacant conduction band [6]. When a semiconductor such as TiO_2 absorbs a photon of energy equal to or greater than its band gap energy, 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 H_2O or OH^- to produce the hydroxyl radical and e_{cb}^- is picked up by oxygen to generate superoxide radical anion ($\text{O}_2^{\bullet-}$), as

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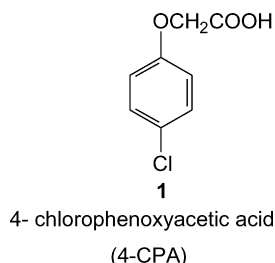
indicated in the following Eqs. (1)–(3):



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

4-Chlorophenoxyacetic acid (4-CPA, **1**) is used as a herbicide, in the food industry as a plant growth regulator to restrict root growth during seed germination of mung beans and it has a water solubility of 0.957 g L^{-1} [7].

Photocatalysed degradation of 4-chlorophenoxyacetic acid (**1**) by iron(III) phthalocyanine modified TiO_2 was investigated before [8]. Despite of this study no major efforts have been made to investigate the detailed degradation kinetics of these compounds. With this view we have under taken a detailed study on the photodegradation of 4-chlorophenoxyacetic acid (4-CPA, **1**) sensitized by TiO_2 in aqueous solution under UV light source. The studies were carried out using various reaction parameters, e.g. reaction pH, substrate concentration, catalyst concentrations, type of photocatalysts and an electron acceptor such as H_2O_2 . An attempt has also been made to identify the volatile intermediate products formed during the photooxidative process through GC–MS analysis technique.



2. Experimental

2.1. Reagents and chemicals

4-Chlorophenoxyacetic acid (**1**) was obtained from Aldrich and used as such without any further purification. The photocatalyst, titanium dioxide Degussa P25 (Degussa AG), was used in most of the experiment. 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 75% anatase and 25% rutile with a specific BET-surface area of $50 \text{ m}^2 \text{ g}^{-1}$ and primary particle size of 20 nm [9]. 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 [10]. 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 [11], 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.

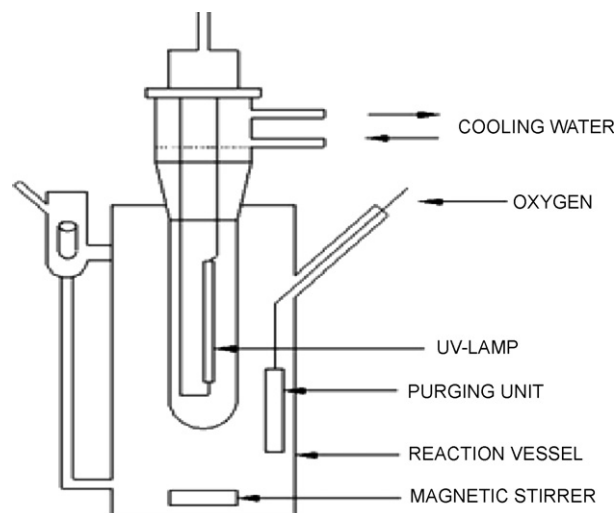


Fig. 1. Schematic diagram of photochemical reactor.

2.2. Procedure

Solutions of 4-CPA (**1**) of desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made (35 cm \times 6 cm) of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen was used. A schematic diagram of the reactor is shown in Fig. 1.

For the irradiation experiment, aqueous solution (250 mL) of the compound was taken into the photoreactor, required amount of photocatalyst was added, 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. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. 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 (lamp sleeve = 6 cm, Philips, radiant flux $\approx 0.4890 \text{ W/m}^2$ measured at the inner wall of the annular reactor) placed at the centre of the inner jacket. The wavelength interval for measuring the radiant flux was in between 290 and 390 nm. IR-radiations were eliminated by a water jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation and analyzed after centrifugation.

2.3. Analysis

The mineralization of 4-chlorophenoxyacetic acid (**1**) was monitored by measured total organic carbon (TOC) with a Shimadzu TOC analyzer by directly injecting the aqueous solution whereas the degradation was monitored by measuring the absorbance on a Shimadzu UV–vis spectrophotometer (model 1601). The absorbance of 4-CPA followed at 227.5 nm.

For the characterization of intermediate products, aqueous solution (250 mL) of compound containing TiO_2 (P25, 1 g L^{-1})

was taken in the immersion well photochemical reactor. The mixture was irradiated with a 125 W medium pressure mercury lamp at different time intervals and the formation of products were 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 25m CP SIL 19 CB ($d = 0.25$ mm) capillary column, operating temperature programmed (injection temperature 100°C which was raised to 220°C at the rate of $10^\circ\text{C min}^{-1}$, analysis run for 40 min) in splitless mode injection volume ($1.0\ \mu\text{L}$) with helium as a carrier gas was used.

3. Results and discussion

3.1. Photolysis of TiO_2 suspensions containing 4-CPA (I)

Irradiation of an aqueous solution of 4-CPA (**1**, $0.5\ \text{mM}$, $250\ \text{mL}$) in the presence of TiO_2 Degussa (P25, $1\ \text{g L}^{-1}$) with a 125 W medium pressure mercury lamp (Philips, radiant flux $\approx 0.4890\ \text{W/m}^2$ measured at the inner wall of the annular reactor) lead to a decrease in the absorption intensity and depletion in TOC as a function of time. The change in absorption intensity and depletion in TOC as a function of irradiation time for the photocatalytic degradation of 4-CPA in the presence and absence of TiO_2 is shown in Fig. 2. The compound under investigation undergoes decomposition when irradiated in the presence of TiO_2 , whereas no observable loss of compound was seen in the absence of TiO_2 . The degradation curve of the compound can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the degradation for the mineralization and decomposition of the model pollutant was calculated from initial slope obtained by linear regression from a plot of the natural logarithm of the TOC and absorbance of the model pollutant as a function of irradiation time, i.e., first order

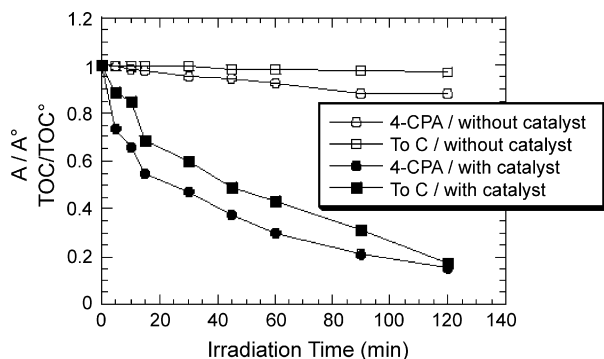


Fig. 2. Depletion in TOC and change in absorption intensity at $227.5\ \text{nm}$ as a function of time for irradiation of an aqueous solution of 4-chlorophenoxyacetic acid (**1**) in the presence and absence of TiO_2 . Experimental conditions—4-chlorophenoxyacetic acid ($0.5\ \text{mM}$); photocatalyst: TiO_2 (Degussa P25) $1\ \text{g L}^{-1}$; pH 3; immersion well photochemical reactor; 125 W medium pressure Hg lamp (radiant flux $\approx 0.4890\ \text{mW/cm}^2$); irradiation time = 120 min.

degradation kinetics. The resulting first order rate constant has been used in all the subsequent plots to calculate the degradation rate for the mineralization and decomposition of the compound using formula given below:

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

$$-\frac{d[A]}{dt} = kc \quad (5)$$

where k = rate constant and c = concentration of the pollutant. The degradation rate was calculated in terms of M min^{-1} .

Control experiments were carried out in all cases, employing unirradiated blank solutions where no observable loss of the compound due to adsorption on the catalyst was found. 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 and catalyst concentration

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity, non-toxic, relatively inexpensive and stable in aqueous solution. Several reviews have been written regarding the mechanistic and kinetic details as well as the influence of experimental parameters. The aim of present study was to determine the best photocatalyst among commercially available different TiO_2 material and find further means to accelerate the efficiency of the photocatalytic process.

We have tested the photocatalytic activity of four different commercially available TiO_2 powders (namely Degussa P25, Hombikat UV100, Millennium Inorganic PC500 and Travancore Titanium Products, India) employing various catalyst concentrations on the degradation kinetic of the pollutant under investigation. The degradation rate obtained for the decomposition (decrease in absorption intensity) of 4-CPA, in the presence of different types of TiO_2 powders is shown in Fig. 3a. It could be seen from the figure that in the presence of Degussa P25 the degradation rate for the decomposition of the compound increases with the increase in catalyst concentration from 0.5 to $2\ \text{g L}^{-1}$. Further increase in catalyst concentration from 2 to $5\ \text{g L}^{-1}$ led to decrease in the degradation rate and highest efficiency was observed when catalyst loading was $2\ \text{g L}^{-1}$. In contrast, in the presence of UV100 the degradation rate was found to increase contentiously with the increase in catalyst concentration from 0.5 to $5\ \text{g L}^{-1}$. On the other hand the photocatalysts such as PC500 and TTP were used, the degradation rate was found to be more or less same at all catalyst concentration within experimental error limit.

The percent photonic efficiency calculated using Eqs. (6) and (7) for the degradation and mineralization of 4-CPA in the presence of different type of photocatalysts is shown in Fig. 3b. Light intensity was measured at inner wall of the annular photoreactor and was found to be $0.4890\ \text{W/m}^2$:

$$\zeta (\%) = \frac{\text{degradation rate}}{\text{light intensity}} \times 100 \quad (6)$$

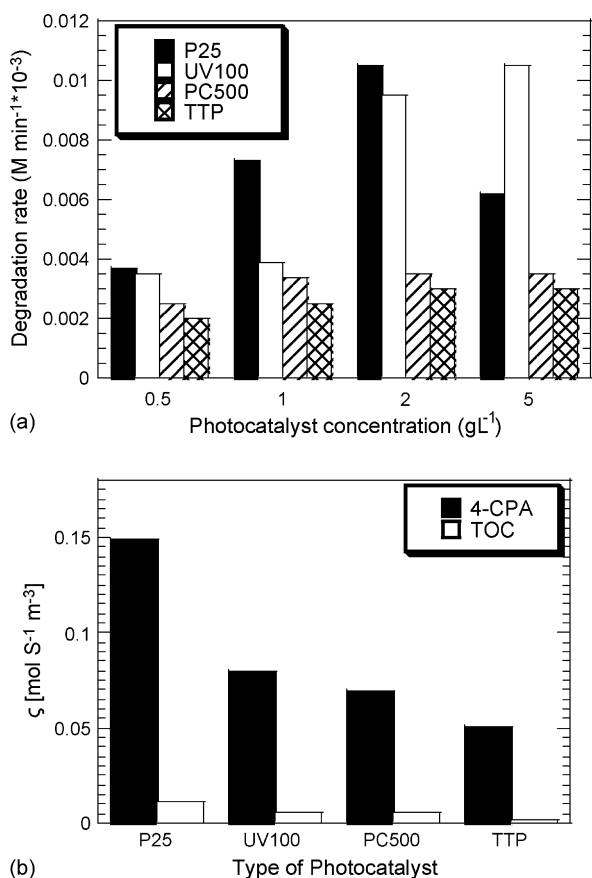


Fig. 3. (a) Degradation rate for the decomposition of 4-chlorophenoxyacetic acid (1) in the presence of different photocatalyst at different catalyst concentrations. Experimental conditions—4-chlorophenoxyacetic acid (0.5 mM); photocatalysts: TiO_2 [Degussa P25, Hombikat UV100, PC500 and TTP (0.5, 1, 2 and 5 g L^{-1}); irradiation time = 120 min. (b) Percent photonic efficiency for the decomposition and mineralization of 4-chlorophenoxyacetic acid (1) in the presence of different photocatalysts. Experimental conditions—4-chlorophenoxyacetic acid (0.5 mM); photocatalysts: TiO_2 ; pH 3 (Degussa P25, Hombikat UV100, PC500 and TTP, 1 g L^{-1}); irradiation time = 120 min.

$$\zeta_{\text{TOC}} (\%) = \frac{\text{degradation rate}}{\text{light intensity}} \times \frac{100}{M_C} \quad (7)$$

where ζ = photonic efficiency and $M_C = 12 \text{ g mol}^{-1}$.

The photonic efficiency for the degradation and mineralization of the compound was found to be better in the presence of Degussa P25 photocatalyst.

The differences in the photocatalytic activity are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface, since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs. Earlier studies have shown that Degussa P25 showed better activity for the photocatalytic degradation of a large number of organic compounds [12–15]. Also Linder et al. [16] showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. On the other hand Hombikat UV100 was also found to be better for the degradation of benzidine, 1,2-diphenyl hydrazine and ramazol brilliant blue R reported earlier [17,18].

The better efficiency of Degussa P25 photocatalyst could be explained by a quantum size effect [19,20 and references cited therein]. When the particles become too small, there is a 'blue shift' with an increase of the band gap energy, detrimental to the near UV-photon absorption, and an increase of the electron-hole recombination. Too high specific area is not beneficial for an optimum efficiency. Another explanation for the greater photo effectiveness of mixed phase titania photocatalyst (here Degussa 25) could be due to three factors: (1) the smaller band gap of rutile extends the useful range of photoactivity into the visible region; (2) the stabilization of charge separation by electron transfer from rutile to anatase slows the recombination; (3) the small size of the rutile crystallites facilitates the electron transfer [21].

These results indicate that the activity of the photocatalyst also depends on the type of the model pollutant. In all following experiments, Degussa P25 was used as the photocatalyst, since this material exhibited highest overall activity for the degradation of the pollutants.

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 also the size of aggregates it forms. Employing Degussa P25 as a photocatalyst the decomposition and mineralization of 4-CPA in the aqueous suspension of TiO_2 was studied in the pH range between 3 and 11. The degradation rate for the decomposition and for the TOC depletion of 4-CPA as a function of reaction pH are shown in Fig. 4. It could be seen from the figure that the compound can be photocatalytically degraded considerably faster at lower pH values.

The zero point of charge (pH_{zpc}) of Degussa P25 has been reported as 6.25. Hence, at more acidic pH values, the particle surface is positively charged, while at pH values above pH_{zpc} , it is negatively charged [22]. The model compound contains COOH group and hence they can be protonated and deprotonated under acidic and basic conditions, respectively, depending upon

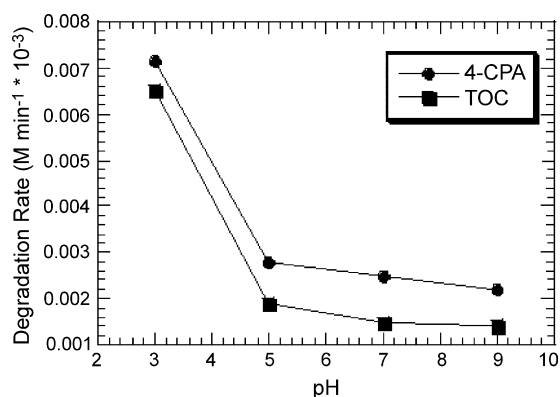


Fig. 4. Degradation rate for the decomposition and mineralization of 4-chlorophenoxyacetic acid (1) at different pH. Experimental conditions—4-CPA (0.5 mM); photocatalysts: TiO_2 Degussa P25 (1 g L^{-1}); reaction pH (3, 5, 7 and 9); irradiation time = 120 min.

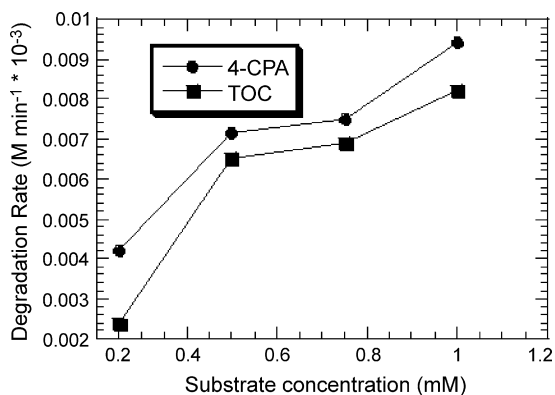


Fig. 5. Degradation rate for the decomposition and mineralization of 4-chlorophenoxyacetic acid (**1**) at different substrate concentration. Experimental conditions—4-chlorophenoxyacetic acid (0.5 mM); photocatalysts: TiO₂ Degussa P25 (1 g L⁻¹); pH 3; substrate concentration (0.25, 0.5, 0.75 and 1.0 mM); irradiation time = 120 min.

the pK_a value. The pK_a value of compound is reported as 3.56 [23]. Since the compound under investigation is found to degrade efficiently under acidic pH, the results indicate that this structural orientation is favorable for the attack of the reactive species. A similar result on the effect of reaction pH on the degradation rate is reported earlier [24].

3.4. Effect of substrate concentration

It is important both from a mechanistic and an application point of view to study the dependence of substrate concentration on the photocatalytic reaction rate. Therefore, effect of substrate concentrations on the degradation of compound was studied at varying concentrations of the substrate from 0.25 to 1.5 mM. The degradation rate for the decomposition and TOC depletion of 4-CPA as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Fig. 5. The rate was found to increase with the increase in substrate concentration. The results are in agreement in number of studies reported before [25–27].

3.5. Effect of electron acceptor

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 wastewater where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified.

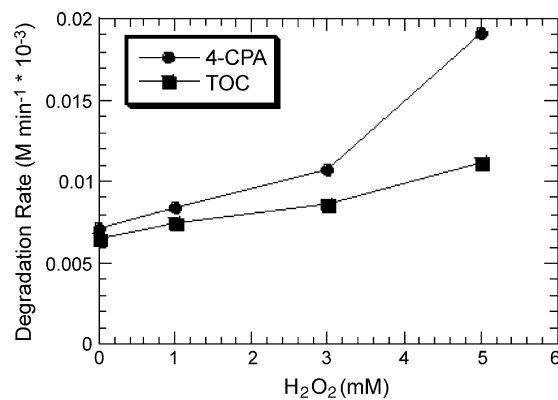
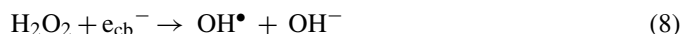


Fig. 6. Degradation rate for the degradation and mineralization of 4-chlorophenoxyacetic acid (**1**) at different H₂O₂ concentrations. Experimental conditions—4-chlorophenoxyacetic acid (0.5 mM); photocatalysts: TiO₂ Degussa P25 (1 g L⁻¹); pH 3; H₂O₂ concentrations (0, 1, 3 and 5 mM); irradiation time = 120 min.

The effect of electron acceptor such as hydrogen peroxide on the photocatalytic degradation of 4-CPA, in addition to the molecular oxygen was investigated at varying concentrations. The degradation rate for the mineralization and decomposition of the compound 4-CPA in the presence of H₂O₂ is shown in Fig. 6. The rate was found to increase with increase in H₂O₂ concentration.

Hydrogen peroxide is known to generate hydroxyl radicals by the mechanisms shown in Eq. (8):

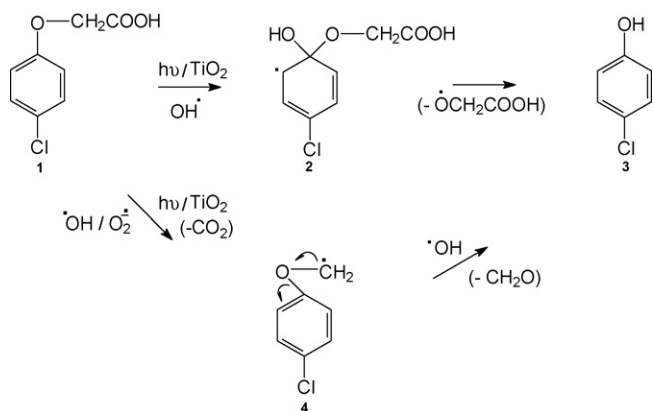


As expected H₂O₂ showed beneficial effect on the photocatalytic degradation of the compound under investigation as evident from Fig. 6.

3.6. Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the compound 4-CPA, in aqueous suspensions of titanium dioxide through GC–MS analysis.

Irradiation of an aqueous suspension of 4-chlorophenoxyacetic acid (**1**, 0.5 mM, 250 mL) in the presence of Degussa P25 (1 g L⁻¹) for 1 h followed by workup by the reaction mixture through removal of catalyst, extraction of aqueous suspension in chloroform. Removal of the solvent under reduced pressure, gave a residual mass, which was analyzed by GC–MS. The analysis showed the formation of one intermediate product, 4-chlorophenol (**3**) appearing at retention time (t_R) 6.6 min. The product was identified by comparing its molecular ion and fragment ion peak with those reported in the NIST library. A plausible mechanism for the formation of product, **3** involving reactions with hydroxyl radicals formed in the photocatalytic process is shown in Scheme 1. The model compound, 4-CPA undergoes addition of a hydroxyl radical formed in the photocatalytic process leading to the formation of a radical species **2** as an intermediate, which may undergo loss of ($\bullet\text{OCH}_2\text{COOH}$) group to give the observed product 4-chlorophenol (**3**). Alternatively, the model compound 4-CPA



Scheme 1.

(1) on addition of hydroxyl radical followed by loss of CO_2 may lead to the formation of the intermediate radical species 4, which upon loss of formaldehyde molecule followed by addition of hydroxyl radical led to the formation of the observed product 4-chlorophenol (3).

4. Conclusion

TiO_2 can efficiently catalyse the photomineralization of 4-CPA in the presence of light. The photocatalyst Degussa P25 showed better photocatalytic activity for the degradation of the model pollutant under investigation when catalyst concentration such as 0.5 to 2 g L^{-1} was used. Whereas Hombikat UV100 shows better activity at 5 g L^{-1} . The addition of electron acceptor such as hydrogen peroxide can enhance the decomposition of model system. These investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes. The analysis of the intermediate product 4-chlorophenol, formed during the photodegradation process could be a useful source of information on the degradation pathways.

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References

- [1] Z.Z. Cohen, C. Eiden, M.N. Lober, in: W.Y. Gerner (Ed.), Evaluation of Pesticide in Ground Water, ACS Symp. Ser. 315, American Chemical Society, Washington, DC, 1986, pp. 170–196.
- [2] L. Muszkat, D. Raucher, M. Mogaritz, D. Ronen, in: U. Zoller (Ed.), Groundwater Contamination and Control, Marcel Dekker, 1994, pp. 257–271.
- [3] I.T. Yasur, M. Rosner, A. Hadas, D. Russo, B. Yaron, Leaching of *tert*-butylazine and bromacil through field soil, *Water Air Soil Pollut.* 113 (1999) 319–335.
- [4] R.M. Dowd, M.P. Anderson, M.L. Johnson, Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring Geophysical Methods, National Water Well Association, Dublin, OH, 1998, pp. 1365–1379.
- [5] N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis. Fundamentals and Applications*, Wiley/Interscience, New York, 1989.
- [6] N.A. Lewis, M.L. Rosenbuth, in: N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis-Fundamentals and Applications*, John Wiley & Sons, New York, 1989, p. 45.
- [7] R.M. Dannenfelser, S.H. Yalkowsky, Data base of aqueous solubility for organic non-electrolytes, *Sci. Total Environ.* 109 (1991) 625–628.
- [8] K.T. Ranjit, I. Willner, S. Bossmann, B. Stefan, A. Braun, Photocatalytic mineralization of toxin chemicals with illuminated TiO_2 , *J. Phys. Chem. B* 102 (1998) 9397–9403.
- [9] R.I. Bickley, T.G. Carreno, J.S. Lees, L. Palmisano, R.J.D. Tilley, A spectral investigation of titanium dioxide photocatalysts, *J. Solid State Chem.* 92 (1992) 178–190.
- [10] M. Lindner, D. Bahnemann, B. Hirthe, W.D. Griebler, Solar water detoxification: novel TiO_2 powders as highly active photocatalysts, *J. Sol. Energy Eng.* 119 (1997) 120–125.
- [11] S. Rauer, Untersuchung von kommerziell erhältlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivität, Diplomarbeit, fachhochschule Hannover, Fachbereich Maschinenbau Vertiefung Umwelt-und Verfahrenstechnik, Hannover, Germany, 1998.
- [12] D. Vionea, C. Minero, V. Maurino, M.E. Carloti, T. Picatonotto, E. Pelizzetti, Degradation of phenol and benzoic acid in the presence of a TiO_2 -based heterogeneous photocatalyst, *Appl. Catal. B: Environ.* 58 (2005) 79–88.
- [13] M.H. Florencio, E. Pires, A.L. Castro, M.R. Nunes, C. Borges, F.M. Costa, Photodegradation of Diquat and Paraquat in aqueous solutions by titanium dioxide: evolution of degradation reactions and characterization of intermediates, *Chemosphere* 55 (2004) 345–355.
- [14] C. Guillard, J. Disdier, J.M. Herrmann, C. Lehaut, T. Chopin, S. Malato, J. Blanco, Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol, *Catal. Today* 54 (1999) 217–228.
- [15] Y. Bessekhouad, D. Robert, J.-V. Weber, N. Chaoui, Effect of alkaline-doped TiO_2 on photocatalytic efficiency, *J. Photochem. Photobiol. A: Chem.* 167 (2004) 49–57.
- [16] M. Linder, D.W. Bahnemann, B. Hirthe, W.D. Griebler, Novel TiO_2 powders as highly active photocatalysts, in: W.R. Stine, T. Tanaka, D.E. Claridge (Eds.), *Solar Water Detoxification; Solar Engineering*, ASME, New York, 1995, p. 339.
- [17] M. Muneer, H.K. Singh, D. Bahnemann, Semiconductor mediated photocatalysed degradation of two selected priority organic pollutants, benzidine and 1,2-diphenylhydrazine in aqueous suspensions, *Chemosphere* 49 (2002) 193–203.
- [18] M. Saquib, M. Muneer, Semiconductor mediated photocatalysed degradation of an anthraquinone dye, remazol brilliant blue R under sunlight and artificial light source, *Dyes Pigments* 53 (2002) 237–249.
- [19] A.J. Nozik, in: D.F. Ollis, H. El-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 391.
- [20] H. Weller, Colloidal semiconductor Q-particles: chemistry in the transition region between solid state and molecules, *Angew. Chem. Int. Ed. Eng.* 32 (1993) 41–53.
- [21] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, Explaining the enhanced photocatalytic activity of Degussa P25 mixed phase TiO_2 using EPR, *J. Phys. Chem. B* 107 (2003) 4545–4549.
- [22] H. Hiegendorff, Untersuchungen zur Bedeutung der Adsorption in der Photokatalyse, Ph.D. Thesis, Department of Chemistry, University of Hannover, Hannover, Germany, 1996.
- [23] B.W. George, J.L. White, in: F.A. Gunther (Ed.), *Residue Rev.*, vol. 10, Springer, New York, 1965, p. 97.

- [24] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, Iron(III) phthalocyanin-modified titanium dioxide: a novel photocatalyst for the enhanced photodegradation of organic pollutants, *Chem. Eng. Commun.* 139 (1995) 1–13.
- [25] F. Sabin, T. Turk, A. Vogler, Photooxidation of organic compounds in the presence of titanium dioxide: determination of efficiency, *J. Photochem. Photobiol. A: Chem.* 63 (1992) 99–106.
- [26] K.W. Krosley, D.M. Collard, J. Adamson, M.A. Fox, Degradation of organophosphoric acid-catalyzed by irradiated titanium dioxide, *J. Photochem. Photobiol. A: Chem.* 69 (1993) 357–360.
- [27] K.E. O'Shea, I. Garcia, M. Aguilar, TiO₂ photocatalytic degradation of dimethyl and diethyl-methyl phosphonate, effects of catalyst and environmental factor, *Res. Chem. Intermed.* 23 (1997) 325–340.