Comparative photocatalytic study of two selected pesticide derivatives, indole-3-acetic acid and indole-3-butyric acid in aqueous suspensions of titanium dioxide

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Abstract

Heterogeneous photocatalysed degradation of two selected pesticide derivatives such as indole-3-acetic acid (IAA) and indole-3-butyric acid (IBA) has been investigated in aqueous suspensions of titanium dioxide 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 degradation kinetics was studied under different conditions such as pH, types of TiO_2, substrate and catalyst concentration, and in the presence of electron acceptor such as hydrogen peroxide (H_2O_2) besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 showed comparatively highest photocatalytics. The pesticide derivative, indole-3-acetic acid was found to degrade slightly faster than indole-3-butyric acid.
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Keywords: Photocatalysis; Indole-3-acetic acid; Indole-3-butyric acid; Titanium dioxide

1. Introduction

A wide variety of organic pollutants especially pesticides are introduced into the water system from various sources such as industrial effluents, agricultural runoff and chemical spills [1,2]. 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 [3].

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. However, many organic chemicals, especially those that are toxic or refractory, are not amendable to

microbial degradation. Recently considerable attention has been focussed on the use of semiconductor as a means to oxidize toxic organic chemicals [4–12]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature [13,14]. Briefly, when a semiconductor such as TiO_2 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}^+). 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 ($O_2^{\bullet-}$) as indicated in the following Eqs. (1)–(4).

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \tag{1}$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \tag{2}$$

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$$O_2^{\bullet-} + H_2O \rightarrow OH^{\bullet} + OH^- + O_2 + HO_2^- \qquad (3)$$

$$H_2O + h_{vb}^+ \rightarrow OH^{\bullet} + H^+ \qquad (4)$$
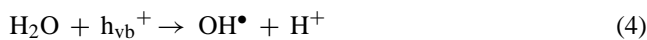
It has been suggested that the hydroxyl radicals ($OH^{\bullet}$) and superoxide radical anions ($O_2^{\bullet-}$) are the primary oxidizing species in the photocatalytic oxidation processes. In many of these studies, although the initial disappearance of the pollutant is rapid, a number of by-products are formed, which can potentially be harmful to the environment.

The pesticide derivative, indole-3-acetic acid (IAA) is a plant growth regulator that affects cell division and cell elongation and it is used to stimulate rooting and cuttings of herbaceous and woody ornamental plants. The pesticide derivative, indole-3-butyric acid (IBA) enhances the growth and development of food crops and ornamentals plants when applied to soil, cuttings or leaves. As pesticides, these chemical substances attract, kill and repel insects. They also help to keep cats and dogs away from places where they are not wanted.

To the best of our knowledge, no efforts have been made to study the photocatalysed degradation of these two systems. We have, therefore, made an attempt to study the degradation of IAA and IBA in aqueous suspension of titanium dioxide under a variety of condition.
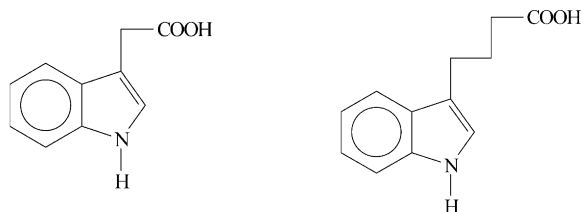
Indole-3-acetic acid   **Indole-3-butyric acid**

2. Experimental methods

2.1. Reagent and chemicals

Indole-3-acetic acid and indole-3-butyric acid were obtained from Otto Chemika Biochemika Reagents, Mumbai, India and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide Degussa P25 was used in most of the experiments, whereas other catalyst powders, namely, Hombikat UV100 (Sachtleben Chemie GmbH), PC500 (Millennium Inorganics) and TTP (Travancore Titanium Products, India) were used for comparative studies. Degussa P25 contains 80% anatase and 20% rutile with a specific BET surface area of $50\,m^2\,g^{-1}$ and a primary particle size of 20 nm [15]. Hombikat UV100 consists of 100% pure anatase with a specific BET surface area of $250\,m^2\,g^{-1}$ and a primary particle size of 5 nm [16]. The photocatalyst PC500 has a BET-surface area of $287\,m^2\,g^{-1}$ with 100% anatase and primary particle size of 5–10 nm [17] whereas, TTP has a BET-surface area of $9.82\,m^2\,g^{-1}$. The other chemicals used
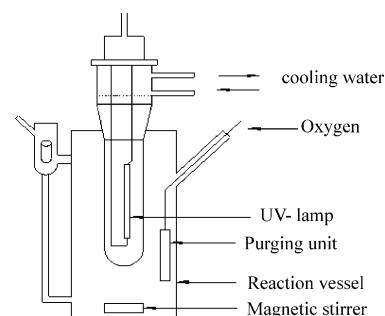

Fig. 1. Schematic diagram of the photochemical reaction vessel used for the irradiation experiments.

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

2.2. Procedure

Solutions of pesticide derivative IAA and IBA of the desired concentration were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, a water circulating jacket and an opening for supply of molecular oxygen was used. A simplified diagram of the reactor system is shown in Fig. 1.

For irradiation experiment, $250\,cm^3$ solution was taken into the photoreactor and required amount of photocatalyst was added and the solution was stirred and bubbled with molecular oxygen for at least 15 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or NaOH. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. 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 ($8\,cm^3$) were collected before and at regular intervals during the irradiation. They were centrifuged before analysis.

2.3. Analysis

The mineralization of the pesticide derivatives was monitored by measuring the Total Organic Carbon (TOC) content with a Shimadzu TOC 5000A 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 IAA was followed at 222.6 nm whereas the absorbance of IBA was followed at 221.9 nm wavelength after 43.33% dilution.

For the characterization of the intermediate products, an aqueous solution (0.25 mM, $250\,cm^3$) of the pesticide derivatives containing photocatalyst (Degussa P25, $1\,g\,L^{-1}$) was taken in the immersion well photochemical reactor and was

irradiated with a 125 W medium pressure mercury lamp for 2 h. The photocatalyst was removed through filtration. The filtrate was extracted with chloroform, which was subsequently dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC/MS. For GC/MS analysis a Shimadzu gas chromatograph and mass spectrometer (GCMS-QP 5050) equipped with a 25 m CP SIL 19 CB ($d = 0.25$ mm) capillary column, operating temperature programmed (injection temperature, Column temperature, 260 °C for 53 min at the rate of 10 °C min^{-1}) in split mode, injection volume (1.0 μL).

3. Results and discussion

3.1.1. Photolysis of TiO₂ suspensions containing pesticide derivatives

Irradiation of an aqueous solution of pesticide derivative IAA and IBA in the presence of TiO₂ samples, led to 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 pesticide derivatives is shown in Figs. 2–5. It was observed that 95% decomposition and 76% mineralization of IAA takes place. Whereas, in case of IBA, 93% decomposition and 74.5% mineralization, was observed after 40 min of irradiation. The degradation and mineralization curves of both the pesticide derivatives can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. For each experiment, the degradation rate for the mineralization and decomposition of the pesticide derivatives was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of the TOC and absorbance of the pes-
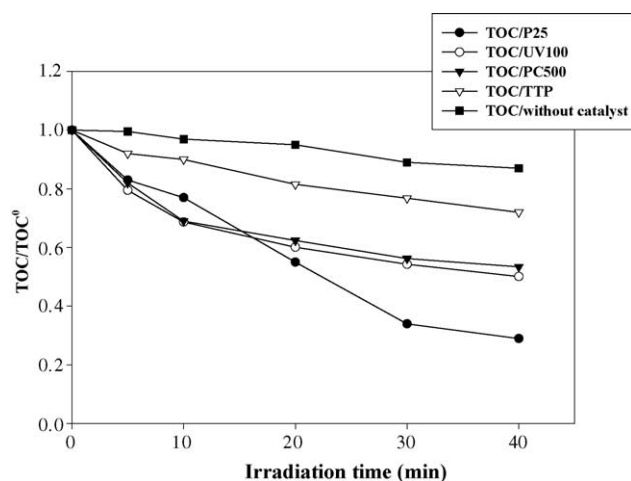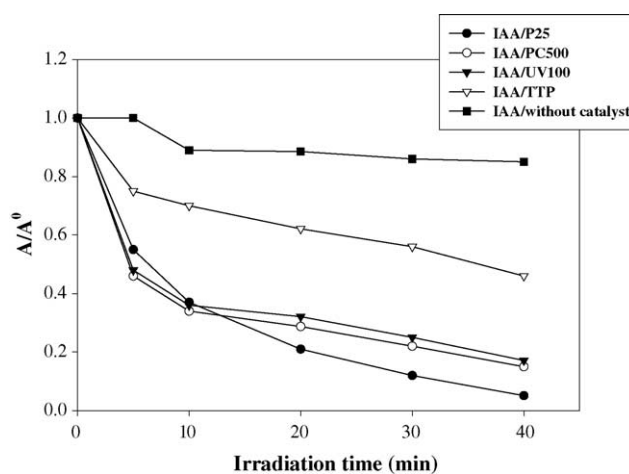

Fig. 3. Change in absorption intensity at 222.6 nm as a function of irradiation time for an aqueous solution of IAA in the presence and absence of different photocatalysts. Experimental conditions: substrate concentration (0.2 mM), $V = 250$ cm^3, immersion well photo-reactor, 125 W medium pressure Hg lamp, Degussa P25 (1 g L^{-1}), Sachtleben Hombikat UV100 (1 g L^{-1}), PC500 (1 g L^{-1}), TTP (1 g L^{-1}), cont. O₂ purging and stirring, irradiation time = 40 min.

ticide derivatives as a function of irradiation time, i.e. first order 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 compounds using formula given below,

$$\frac{-d[TOC]}{dt} = kc^n$$

$$\frac{-d[A]}{dt} = kc^n$$

Fig. 2. Depletion in TOC as a function of irradiation time for an aqueous solution of IAA in the presence and absence of different photocatalysts. *Experimental conditions*: substrate concentration (0.2 mM), $V = 250$ cm^3, immersion well photo-reactor, 125 W medium pressure Hg lamp, Degussa P25 (1 g L^{-1}), Sachtleben Hombikat UV100 (1 g L^{-1}), PC500 (1 g L^{-1}), TTP (1 g L^{-1}), cont. O₂ purging and stirring, irradiation time = 40 min.
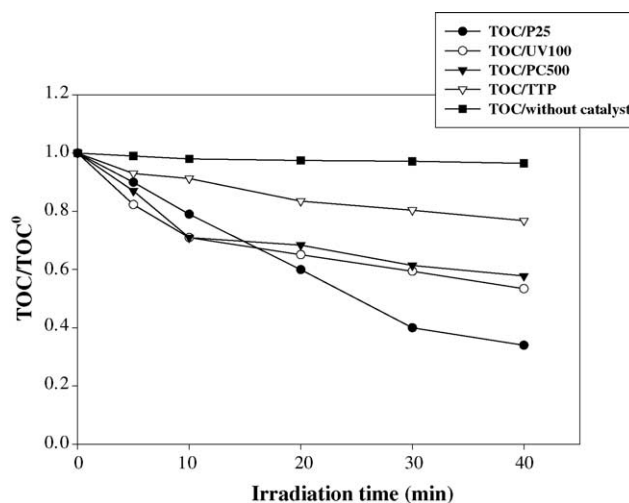

Fig. 4. Depletion in TOC as a function of irradiation time for an aqueous solution of IBA in the presence and absence of different photocatalysts. Experimental conditions: substrate concentration (0.18 mM), $V = 250$ cm^3, immersion well photo-reactor, 125 W medium pressure Hg lamp, Degussa P25 (1 g L^{-1}), Sachtleben Hombikat UV100 (1 g L^{-1}), PC500 (1 g L^{-1}), TTP (1 g L^{-1}), cont. O₂ purging and stirring, irradiation time = 40 min.
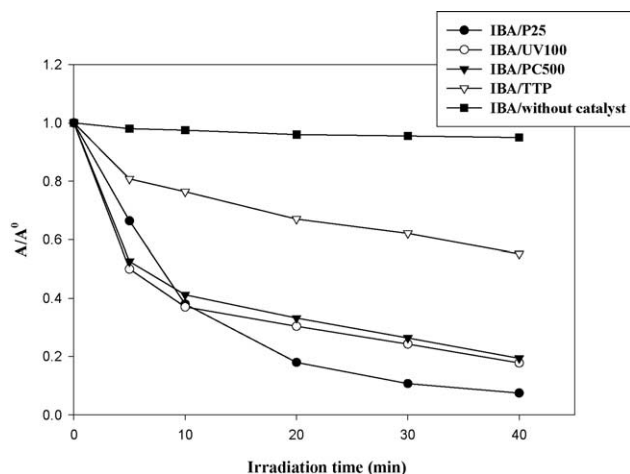
Fig. 5. Change in absorption intensity at 221.9 nm as a function of irradiation time for an aqueous solution of IBA in the presence and absence of different photocatalysts. Experimental conditions: substrate concentration (0.18 mM), $V = 250 \, cm^3$, immersion well photo-reactor, 125 W medium pressure Hg lamp, Degussa P25 ($1 \, g \, L^{-1}$), Sachtleben Hombikat UV100 ($1 \, g \, L^{-1}$), PC500 ($1 \, g \, L^{-1}$), TTP ($1 \, g \, L^{-1}$), cont. O_2 purging and stirring, irradiation time = 40 min.

where TOC is the total organic carbon, A the absorbance, k the rate constant, c the concentration of the pollutant and n is the order of reaction.

The degradation rate was calculated in terms of [mole $L^{-1} \, min^{-1}$]. Using the ferrioxalate actinometry, an average light intensity entering the irradiated solution was determined to be 15.5×10^{-6} Einstein min^{-1}.

Blank experiments of both the pesticide derivatives were carried out in the absence of photocatalyst, where no observable loss of compounds was found that can be seen from Figs. 2–5.
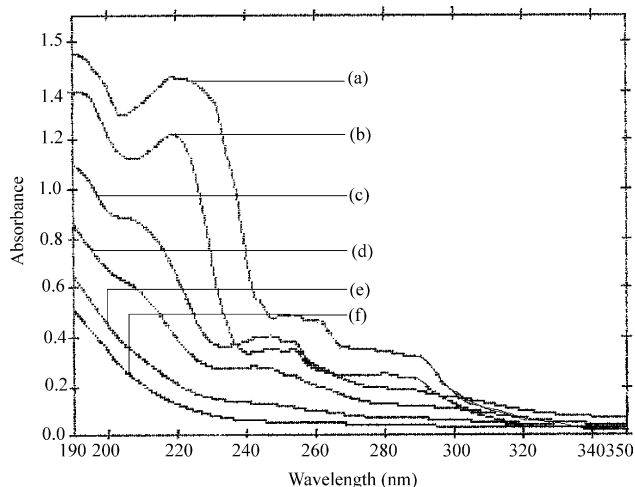

Fig. 6. Change in absorption spectrum on irradiation of aqueous suspension of TiO$_2$ containing IAA (0.2 mM, 250 cm^3). Light source: 'Pyrex' filtered output of a 125 W medium pressure mercury lamp. Irradiation time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min and (f) 40 min.

Fig. 7. Change in absorption spectrum on irradiation of aqueous suspension of TiO$_2$ containing IBA (0.18 mM, 250 cm^3). Light source: 'Pyrex' filtered output of a 125 W medium pressure mercury lamp. Irradiation time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min and (f) 40 min.
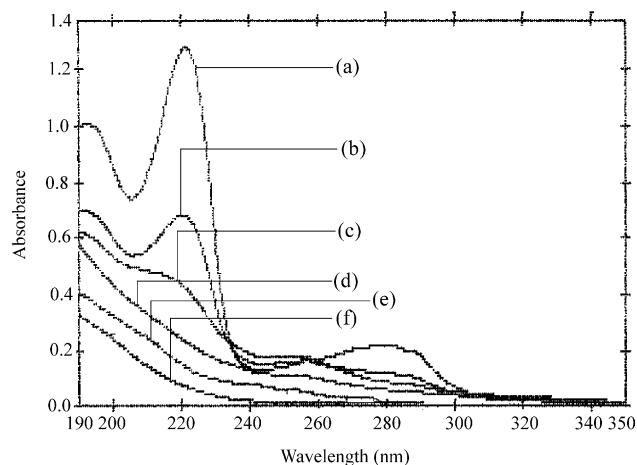
The course of reaction of the substrate decay of IAA and IBA in aqueous suspensions of TiO$_2$ has also been followed UV spectroscopically as a function of irradiation time as shown in Figs. 6 and 7, respectively. It could be seen from both the figures that the absorption intensity decreases with the increasing irradiation time.

The adsorption of pesticide derivatives IAA and IBA on the surface of the photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h in a round-bottomed flask containing varying amount of photocatalyst such as 0.5, 1, 2 and 5 $g \, L^{-1}$. Analysis of the solution after centrifugation indicates some observable loss of compound in case of both the pesticide derivatives as illustrated in Figs. 8 and 9, respectively. It can be seen from the figures that the adsorption of pesticide derivative, IAA on the surface of photocatalyst, is better and hence, degrades more efficiently as compared to IBA.
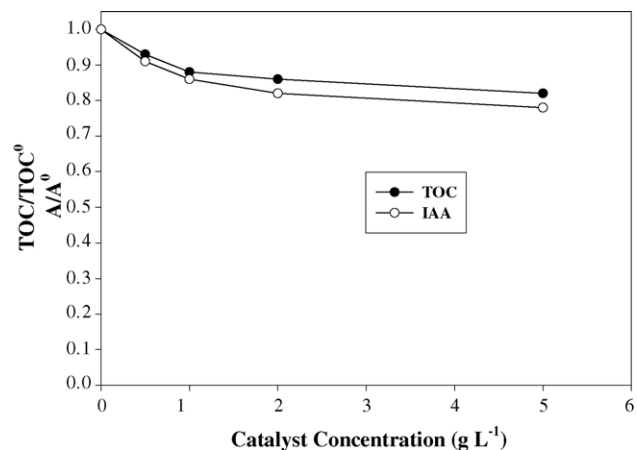

Fig. 8. Effect of titanium dioxide concentration on the TOC content and absorbance of a solution of IAA (0.2 mM) after its adsorption onto titanium dioxide in the dark.
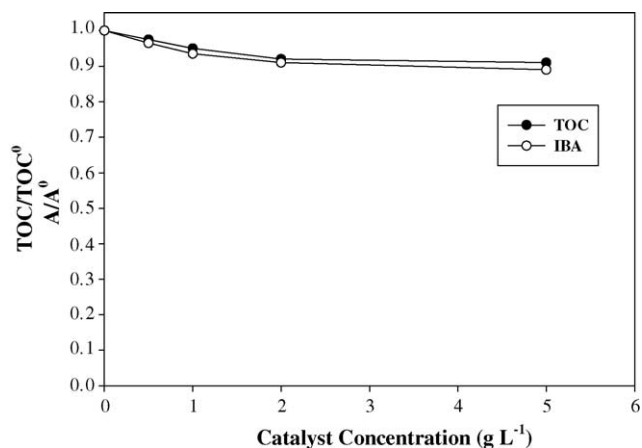
Fig. 9. Effect of titanium dioxide concentration on the TOC content and absorbance of a solution of IBA (0.18 mM) after its adsorption onto titanium dioxide in the dark.

3.2. Comparison of different photocatalysts

We have tested the photocatalytic activity of four different commercially available TiO_2 powders (namely, P25, UV100, PC500 and TTP) on the degradation kinetics of pesticide derivatives under investigation. It has been observed that, from Figs. 10 and 11, respectively, the degradation of both the pesticide derivative proceeds much more rapidly in the presence of Degussa P25 as compared with other TiO_2 samples. The reason for the better photocatalytic activity of Degussa P25 could be attributed to the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron–hole pairs. The electron transfer, from the rutile C_B to electron traps in anatase phase, takes

Fig. 10. Comparison of degradation rate for the mineralization and decomposition of IAA in the presence of different photocatalysts. Experimental conditions: substrate concentration (0.2 mM), $V = 250 \, cm^3$, Degussa P25 ($1 \, g \, L^{-1}$), Sachtleben Hombikat UV100 ($1 \, g \, L^{-1}$), PC500 ($1 \, g \, L^{-1}$), TTP ($1 \, g \, L^{-1}$), immersion well photo-reactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 40 min.
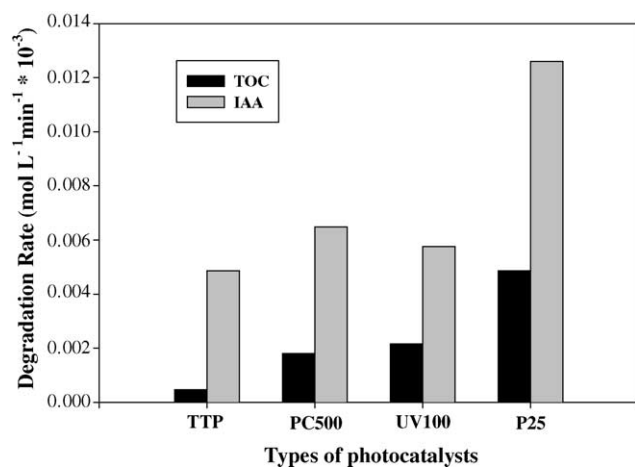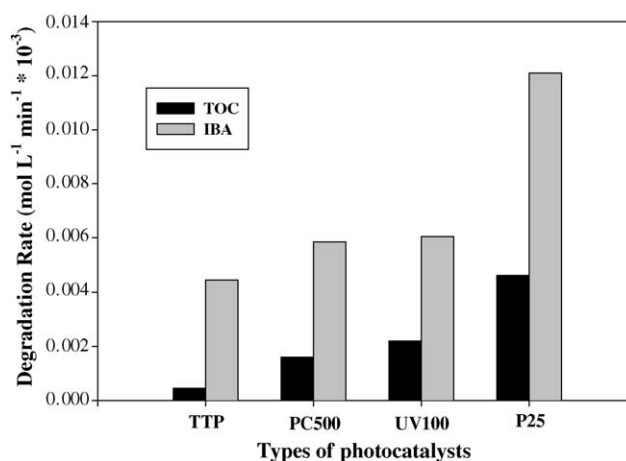

Fig. 11. Comparison of degradation rate for the mineralization and decomposition of IBA in the presence of different photocatalysts. Experimental conditions: substrate concentration (0.18 mM), $V = 250 \, cm^3$, Degussa P25 ($1 \, g \, L^{-1}$), Sachtleben Hombikat UV100 ($1 \, g \, L^{-1}$), PC500 ($1 \, g \, L^{-1}$), TTP ($1 \, g \, L^{-1}$), immersion well photo-reactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 40 min.

place. Recombination is thus inhibited, allowing the hole to move to the surface of the particle and react [18].

In all the following experiments, Degussa P25 was used as the photocatalyst since this material exhibited the highest overall activity for the degradation of model compounds.

3.3. pH effect

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms, therefore, we have investigated its influence on photocatalytic activity in detail in the pH range between 4 and 11. The degradation rate for the TOC depletion and decomposition of pesticide derivatives under investigation as a function of reaction pH is shown in Tables 1 and 2. The efficiency of the degradation rate for the mineralization and decomposition of both the compounds increases with the increase in reaction pH from 4 to 9 and a further increase in pH led to decrease in the degradation. The higher efficiency of degradation in alkaline medium may be attributed to more efficient generation of hydroxyl radicals by TiO_2 with increasing concentration of OH^-. In the case of Degussa P25, the zero point of charge (pH_{zpc}) is at pH 6.25. Hence, at more acidic pH values, the particle surface is positively charged, while at pH values above 6.25, it is negatively charged. After an optimal concentration of OH^-, unfavorable electrical forces generate viz., repulsion occurs between the negatively charged surface of the catalyst and OH^-. Consequently, the degradation efficiency decreases at higher pH. Another reason for this behavior could be attributed to UV screening the TiO_2 particles due to higher concentration of OH^- present in the solution [19].

Table 1

Photocatalytic degradation of indole-3-acetic acid (IAA) in aqueous suspension under different conditions

Parameter	Degradation rate ($\times 10^{-3}$ moles L^{-1} min^{-1})	
	Mineralization	Decomposition
pH		
5.2	0.00486	0.01260
7.0	0.00612	0.01422
9.1	0.00630	0.01451
10.8	0.00461	0.01320
Substrate concentration (mM)		
0.20	0.00486	0.01260
0.30	0.00632	0.01773
0.40	0.00302	0.01361
0.60	0.00183	0.00562
Catalyst concentration (P25, g L^{-1})		
0.5	0.00414	0.01170
1.0	0.00486	0.01260
2.0	0.00673	0.01371
5.0	0.00604	0.01302

3.4. Effect of substrate concentration

It is important both from mechanistic and application points of view to study the dependence of photocatalytic reaction rate on the substrate concentrations. Hence the influence of substrate concentration varying from 0.18 to 0.6 mM on the degradation rate has been studied in the presence of different TiO_2 powders namely Degussa P25, UV100 and PC500. It could be seen from Tables 1 and 2 that in presence of P25, for both the pesticide derivatives, the optimal substrate concentration is 0.3 mM, however, in presence of UV100 and PC500, the optimal substrate concentration is 0.4 mM as illustrated in Figs. 12 and 13, respectively. A further increase in the concentration of both the substrate led to decrease in the degradation rate. This may be due to the fact that as the concentration of model pollutant increases, more

Table 2

Photocatalytic degradation of indole-3-butyric acid (IBA) in aqueous suspension under different conditions

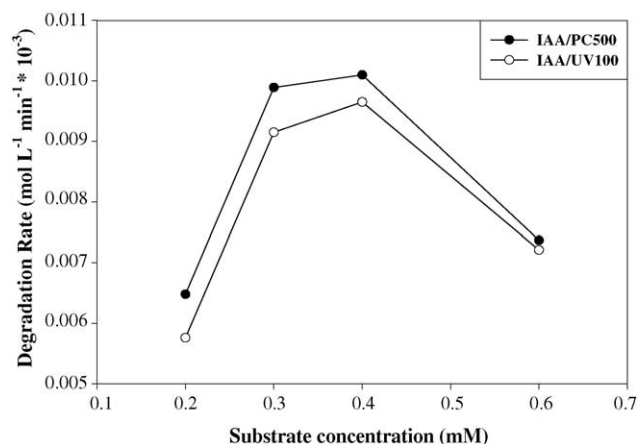| Parameter	Degradation rate ($\times 10^{-3}$ moles L^{-1} min^{-1})	
	Mineralization	Decomposition
pH		
4.1	0.00463	0.01210
6.2	0.00600	0.01401
8.8	0.00620	0.01424
11.0	0.00451	0.01280
Substrate concentration (mM)		
0.18	0.00463	0.01210
0.30	0.00592	0.01612
0.40	0.00510	0.01481
0.60	0.00312	0.00821
Catalyst concentration (P25, g L^{-1})		
0.5	0.00400	0.01152
1.0	0.00463	0.01210
2.0	0.00638	0.01282
5.0	0.00644	0.01293

Fig. 12. Influence of substrate concentration on the degradation rate for the decomposition of IAA in presence of UV100 and PC500. Experimental conditions: substrate concentrations (0.2, 0.3, 0.4 and 0.6 mM), $V = 250$ cm^3, immersion well photo-reactor, 125 W medium pressure Hg lamp, catalyst concentration (1 g L^{-1}), cont. O_2 purging and stirring, irradiation time = 40 min.

and more molecules of the compound get adsorbed on the surface of the photocatalyst. Therefore, the requirement of reactive species ($OH^{\bullet}$ and $O_2^{\bullet-}$) needed for the degradation also increases. However, the generations of relative amounts of $OH^{\bullet}$ and $O_2^{\bullet-}$ on the surface of the catalyst do not increase as the intensity of light, irradiation time and amount of catalyst are constant. Consequently, the degradation efficiency of the model pollutant decreases as the substrate concentration increases.

3.5. Effect of catalyst concentration

Whether in static, slurry or dynamic flow reactors, the initial reaction rates were found to be directly proportional
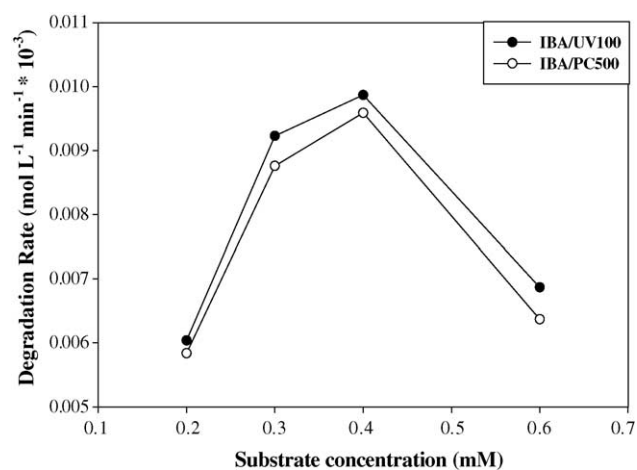

Fig. 13. Influence of substrate concentration on the degradation rate for the decomposition of IBA in presence of UV100 and PC500. Experimental conditions: substrate concentrations (0.18, 0.3, 0.4 and 0.6 mM), $V = 250$ cm^3, immersion well photo-reactor, 125 W medium pressure Hg lamp, catalyst concentration (1 g L^{-1}), cont. O_2 purging and stirring, irradiation time = 40 min.
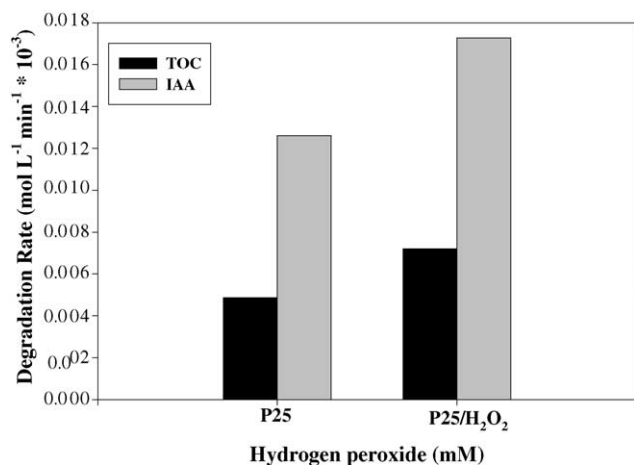
Fig. 14. Comparison of degradation rate for the mineralization and decomposition of IAA in the presence of hydrogen peroxide. Experimental conditions: substrate concentration (0.2 mM), $V = 250\,cm^3$, TiO_2 (Degussa P25, $1\,g\,L^{-1}$), H_2O_2 (10 mM), immersion well photo-reactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 40 min.

to catalyst concentration indicating a heterogeneous regime. However, it has been observed that above a certain concentration, the reaction rate levels off and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a defined amount of TiO_2 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 $[(TiO_2)_{OPT}]$ has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons. Therefore, the effect of catalyst concentration on the degradation kinetics of pesticide derivatives
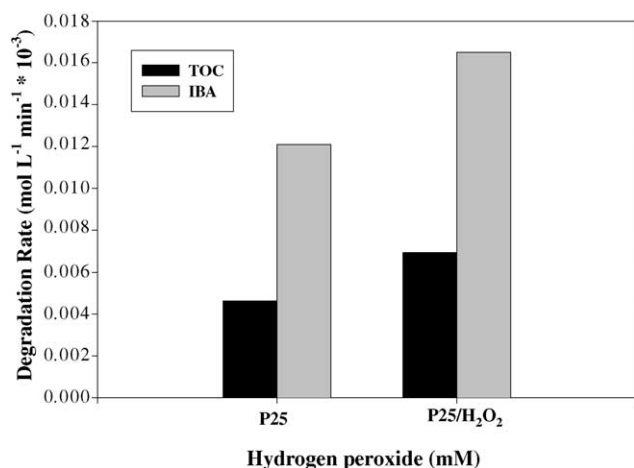

Fig. 15. Comparison of degradation rate for the mineralization and decomposition of IBA in the presence of hydrogen peroxide. Experimental conditions: substrate concentration (0.18 mM), $V = 250\,cm^3$, TiO_2 (Degussa P25, $1\,g\,L^{-1}$), H_2O_2 (10 mM), immersion well photo-reactor, 125 W medium pressure Hg lamp, cont. O_2 purging and stirring, irradiation time = 40 min.
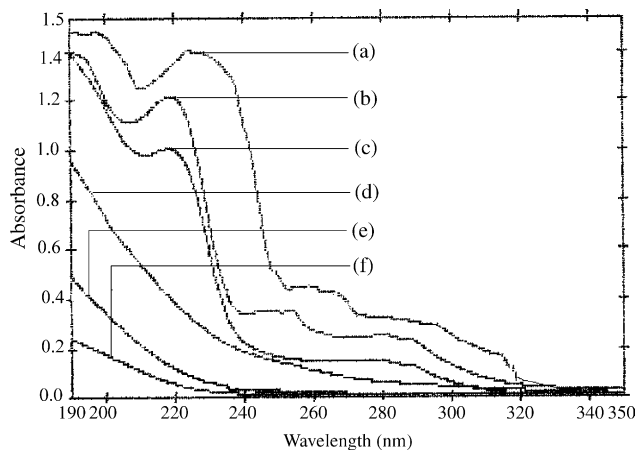

Fig. 16. Change in absorption spectrum on irradiation of aqueous suspension of H_2O_2/TiO_2 containing IAA (0.2 mM, $250\,cm^3$). Light source: 'Pyrex' filtered output of a 125 W medium pressure mercury lamp. Irradiation time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min and (f) 40 min.

was investigated employing different concentrations of Degussa P25, varying from 0.5 to $5\,g\,L^{-1}$ and results have been shown in Tables 1 and 2, respectively and are in agreement with numerous studies reported in the literature [20].

3.6. Effect of electron acceptors

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, electron acceptors such as hydrogen peroxide, was added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the electron/hole (e^-/h^+) pair 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. With this view, we have studied the effect of electron acceptors such as hydrogen peroxide on the photocatalytic degradation of the model
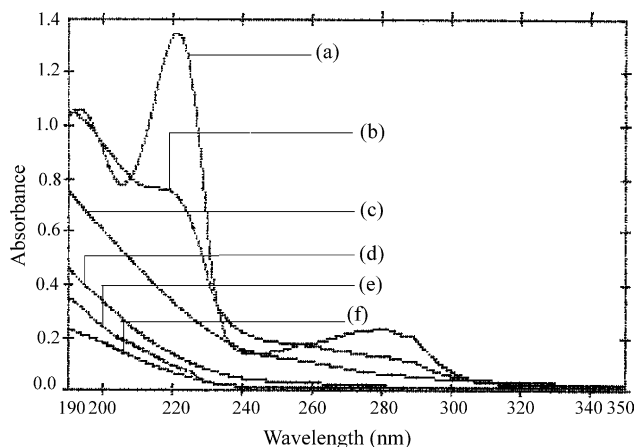

Fig. 17. Change in absorption spectrum on irradiation of aqueous suspension of H_2O_2/TiO_2 containing IBA (0.18 mM, $250\,cm^3$). Light source: 'Pyrex' filtered output of a 125 W medium pressure mercury lamp. Irradiation time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min and (f) 40 min.

compounds under investigation and the results have been illustrated in Figs. 14 and 15, respectively. Hydrogen peroxide is known to generate hydroxyl radicals according to the following Eqs. (5) and (6). As expected, the addition of hydrogen peroxide found to enhance the degradation rate as shown in figures.

$$H_2O_2 + e_{cb}^- \rightarrow OH^\bullet + OH^- \tag{5}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\bullet + OH^- + O_2 \tag{6}$$

There was no observable loss of the compound when irradiations were carried out using this additive in the absence of TiO$_2$ particle.

The course of reaction of the substrate decay of IAA and IBA in aqueous suspensions of H$_2$O$_2$/TiO$_2$ has also been followed UV spectroscopically as a function of irradiation time as shown in Figs. 16 and 17, respectively. It could be seen from both the figures that the absorption intensity decreases with the increasing irradiation time.

3.7. Intermediate products

An aqueous suspension of pesticide derivatives in presence of TiO$_2$ was irradiated with a 125 W medium pressure mercury lamp for 2 h. The GC/MS analysis of the irradiated mixture showed the formation of several intermediate prod-
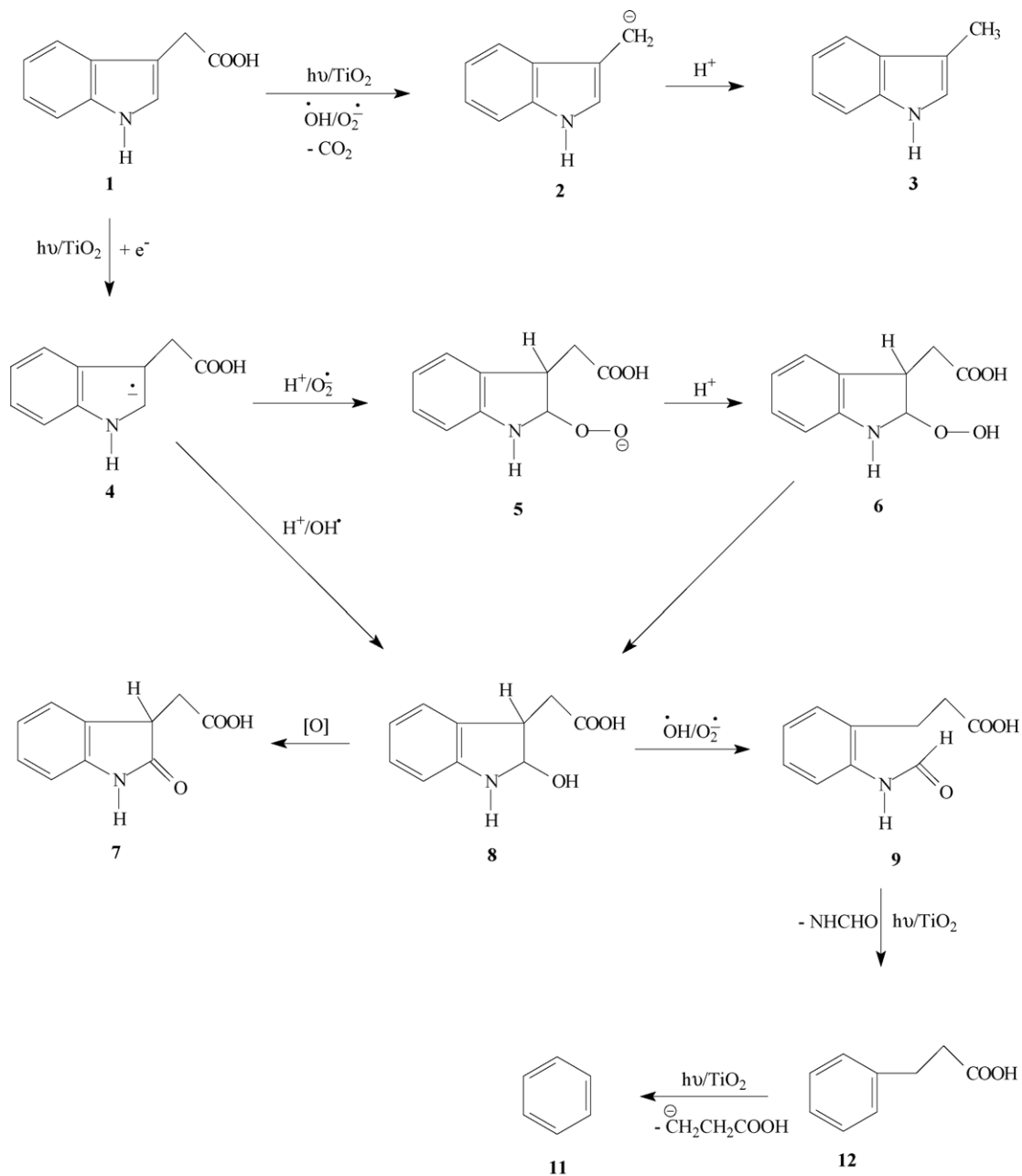
Scheme 1.

ucts. A probable degradation pathway for the photocatalytic reaction of the pesticide derivative IAA, involving electron transfer reaction and reaction with hydroxyl radical and superoxide radical anions is proposed in Scheme 1.

4. Conclusion

TiO$_2$ can efficiently photocatalyse the pesticide derivative indole-3-acetic acid (IAA) and indole-3-butyric acid (IBA) in presence of light and oxygen. The indole-3-acetic acid was found to degrade slightly faster as compared to the indole-3-butyric acid. The photocatalyst Degussa P25 was found to be more efficient as compared with other photocatalyst TiO$_2$ powders. The addition of electron acceptor enhanced the degradation rate of the pollutants. The observations of 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 best degradation condition depends strongly on the kind of pollutant.

Acknowledgements

References

[1] Z.Z. Cohen, C. Eiden, M.N. Lober, in: W.Y. Gerner (Ed.), Evaluation of Pesticide in Ground Water, ACS Symposium Series 315, American Chemical Society, Washington, DC, 1986, pp. 170–196.

[2] L. Muszkat, D. Raucher, M. Magaritz, D. Ronen, in: U. Zoller (Ed.), Groundwater Contamination and Control, Marcel Dekker, 1994, pp. 257–271.

[3] R.M. Dowd, M.P. Anderson, M.L. Johnson, Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Ground Monitoring Geophysical Methods, National Water Well Association Dublin OH, 1998, pp. 1365–1379.

[4] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air, National Renewal Energy Laboratory, USA, 1999.

[5] J.M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants, Catal. Today 53 (1999) 115.

[6] M.I. Litter, Heterogeneous photocatalysis transition metal ions in photocatalytic systems, Appl. Catal. B: Environ. 23 (1999) 89.

[7] A. Vidal, Z. Dinya, F. Mogyorodi Jr, F. Mogyorodi, Photocatalytic degradation of thiocarbamate herbicide active ingredients in water, Appl. Catal. B: Environ. 21 (1999) 259.

[8] O.M. Alfano, D. Bahnemann, A.E. Cassano, R. Dillert, R. Goslich, Photocatalysis in water environments using artificial and solar light, Catal. Today 58 (2000) 199.

[9] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C: Rev. 1 (2000) 1.

[10] K. Macounová, J. Urban, H. Krýsová, J. Krýsa, J. Jirkovský, J. Ludvík, Photodegradation of metamitron (4-amino-6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one) on TiO$_2$, J. Photochem. Photobiol. A: Chem. 140 (2001) 93.

[11] A. Topalov, B. Abramović, D.G. Molnár, J. Csanadi, O. Arcson, Photocatalytic degradation of the herbicide, 4-chloro-2-methyl phenoxy acetic acid (MCPA) over TiO$_2$, J. Photochem. Photobiol. A: Chem. 140 (2001) 249.

[12] X. Li, J.W. Cubbage, W.S. Jenks, Variation in the chemistry of TiO$_2$-mediated degradation of hydroxy and methoxy benzenes. Electron transfer and HO$_{ads}$ initiated chemistry, J. Photochem. Photobiol. A: Chem. 140 (2001) 69.

[13] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic contaminants: mechanisms involving hydroxyl radical attack, J. Catal. 122 (1990) 178.

[14] R.W. Matthews, S.R. McEvoy, Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide, J. Photochem. Photobiol. A: Chem. 64 (1992) 231.

[15] 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.

[16] 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.

[17] S. Rauer, Untersunchung von kommerziell erhaltlichen Titandioxiden hinsichtlich ihrer photokatalytischen Aktivtat, Diplomarbeit, fachhochschule Hannover, Fachbereich Maschinenbau Vertiefung Umwelt-und Verfahrenstechnil, Hannover, Germany, 1998.

[18] 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.

[19] A. Mills, R.H. Davies, D. Worsley, Water purification by semiconductor photocatalysis, Chem. Soc. Rev. 22 (1993) 417.

[20] M. Muneer, H.K. Singh, D. Bahnemann, Semiconductor-mediated photocatalysed degradation of two selected priority organic pollutants, benzidine and 1,2-diphenylhydrazine, in aqueous suspension, Chemosphere 49 (2002) 193–203.