Photocatalytic degradation of *para*-hydroxybenzoic acid: Relationship between substrate adsorption and photocatalytic degradation

V. Subramanian, V.G. Pangarkar, A.A.C.M. Beenackers

Abstract Dark adsorption and photocatalytic degradation of *para*-hydroxybenzoic acid (PHBA) was studied in the presence of Degussa P-25 titanium dioxide photocatalyst under concentrated solar radiation. This work includes the study of the effect of pH, and of the presence of different anions and cations on dark adsorption and photocatalytic degradation (PCD) of PHBA on titanium dioxide. The results obtained clearly indicate that there is a link between the extent of adsorption of PHBA and its PCD. Conditions that favor greater adsorption of PHBA also favor a greater PCD. This points to the possibility that the mechanism of PCD involves a surface reaction between adsorbed PHBA and $OH^\bullet$ radical. Anions were generally found to have a detrimental effect on the photocatalytic degradation of PHBA. Cl^- caused the greatest decrease in the PCD followed by NO_3^-, HCO_3^- and SO_4^{2-}. Cations Cu^{2+} and Fe^{2+} were not found to assist the degradation of PHBA, possibly due to the anions associated with them.

Introduction

Water pollution is a serious problem facing the chemical industry throughout the world. To reduce this problem many methods, viz., physical, chemical and biological, are available (Linsebigler et al. 1995) to achieve the reduction of pollutants in the treated effluents. Conventional methods of treatment such as stripping result only in transfer of pollutants from one phase to another and not its destruction. Other processes such as wet air oxidation, incineration etc. may be used for the degradation of highly refractory compounds. These methods provide good results but may not be cost effective. The above limitations have spurred research efforts for the development of advanced oxidation processes (AOPs) such as photocatalysis. Photocatalysis can be an economical process for converting complex organic molecules into simpler, non-toxic, environmentally acceptable constituents, ideally

carbon dioxide and water in the presence of catalysts such as titanium dioxide with UV radiation. If the UV radiation is from the Sun then this reduces the treatment cost drastically. A large body of literature is available which covers a broad spectrum of organic molecules that have been successfully degraded by this technique (Legrini et al. 1993; Zhao et al. 1998).

Factors which affect the process of photocatalysis are initial concentration of the pollutants, pH of the solution, catalyst type and loading, presence of ions (anions and cations), method of catalyst deposition (mobilized, immobilized), and energy source. Work has been conducted to various extents on different pollutants and extensive data are available in the literature. This article deals with the decontamination of an aqueous stream containing *para*-hydroxybenzoic acid (PHBA) using photocatalysis in conjunction with solar radiation. PHBA is a pollutant discharged from the pharmaceutical industry and since it is toxic to the environment its concentration has to be reduced before the stream is let out into the environment. An attempt has been made to delineate the effect of some of the above parameters on the rate of degradation of PHBA, using titanium dioxide as the photocatalyst.

Materials

Titanium dioxide (P-25) from Degussa was used in all experiments. PHBA (Aldrich) was used to prepare authentic reaction samples. H_2SO_4, $HClO_4$ and NaOH (Merck) were used for pH adjustment and were of analytical reagent (AR) grade. NaCl, $NaNO_3$, $NaHCO_3$ and Na_2SO_4, required for determining the effect of anions, were of AR grade and obtained from Loba Chemie, India. $FeSO_4$, $CuSO_4$ and $Cu(II)Cl_2$, required for studying the effect of cations, were obtained from s.d.fine chemicals, India. Solvents (methanol, acetonitrile) were of HPLC grade and obtained from s.d.fine chemicals, India. Distilled water was used throughout for reactions while deionized water was used for sample preparation and HPLC analysis.

Methods

Dark adsorption

50-ml aliquots were prepared containing 250 ppm and 500 ppm PHBA and titanium dioxide catalyst in steps of 0.05 g. The mixture was covered with a silver foil and kept on a shaker for 24 h to reach equilibrium adsorption stage (Cunningham et al. 1994). The solution was filtered and analyzed on a UV spectrophotometer (Chemito – 2100) at the λ_{max} of PHBA which is 246 nm.

V. Subramanian, V.G. Pangarkar (✉)
Department of Chemical Technology, University of Mumbai, Matunga, Mumbai-400 019, India
e-mail: vgp@udct.ernet.in
Fax: +91-22-4145614

A.A.C.M Beenackers
Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

$HClO_4$ and NaOH were used to adjust the pH to three different values for determination of dark adsorption and photocatalytic degradation.

Degradation experiments

A known concentration of PHBA with a fixed quantity of titanium dioxide was placed in a UV transparent quartz reactor with a volume of 500 ml (Fig. 1). A parabolic reflector with a projected area of 1400 cm^2 was used to concentrate the incident rays to form a bright band on the reactor wall as shown. The intensity of light was uniform and in the range 70–85 mW/cm^2 in all the experiments. Samples were analyzed at known intervals of time after the titanium dioxide was filtered out with a 0.22-μm membrane filter (micropore). The normal ground level intensity was measured with a luxmeter – "Suryamapi". The luxmeter was used to measure the intensity at the ground level and not the intensity inside the reflector. The samples were collected and then diluted with methanol (HPLC grade). Analysis was carried out with HPLC (TOSOH). The mobile phase used was an acetonitrile–water mixture (60:40) vol.%, and a flow rate of 1 ml/min was maintained throughout in all analyses. Total organic carbon (TOC) was determined using a Beckman Model 915 TOC Analyzer after stripping out dissolved CO_2 with pure nitrogen.

Results and discussion

Dark adsorption

Effect of pH

The pH of PHBA solution significantly affects the catalyst's degradation ability (Mills et al. 1993) as it affects the adsorption of the pollutant on the catalyst surface. Consequently, it was considered essential to study adsorption of PHBA over a broad pH range. The charge on the catalyst surface varies from positive to negative as the pH increases. Kondo and Jardim (1991) have reported that the zero point charge (zpc) of titanium dioxide is at ~6.5 pH. The net charge on the catalyst complex is zero at this pH. Tunesi and Anderson (1991) studied the ad-

sorption of salicylic acid (SA) on titanium dioxide. SA is an isomer of PHBA. Therefore considerable similarity is expected to exist between the behavior of these two compounds. Further SA and PHBA have been shown to exhibit similarity in the way they react by Matthews (1987). It was observed that there is a marginal increase in adsorption in the acidic range (Fig. 2). This could be attributed to the attraction between the anion $C_6H_5COO^-$ and the positively charged catalyst complex. Towards higher pH the catalyst is negatively charged. This reduces the degree of adsorption of organic anion on the catalyst as previously suggested (Fig. 2). Towards higher pH a decrease in charge transfer may be taking place due to electrostatic repulsion between similar species as observed by Tunesi and Anderson (1991). There is a marginal increase in the weight ratio of the adsorbed PHBA for the initial data points which can be explained by the above reasoning.

Effect of anions

The presence of ions may possibly affect adsorption. This may be because of the ions getting adsorbed on the catalyst surface, thereby lowering the extent of adsorption of the PHBA on the catalyst. Hence dark adsorption experiments were conducted with 0.1 M fixed concentration of various ions, i.e., nitrate, bicarbonate, sulfate and chloride. In case of chloride, nitrate, and sulfate the pH was neutral, i.e., at 7.4, whereas in the case of bicarbonate it was 8.5. This difference was not considered as significant enough to cause substantial change in the amount adsorbed. The results indicate that the above ions decrease the extent of adsorption of PHBA in the following manner: Chloride>nitrate>bicarbonate>sulfate (Fig. 3).

Thus adsorption of PHBA on titanium dioxide is inhibited most by chloride followed by nitrate, then bicarbonate and lastly by sulfate.

Effect of cations

The presence of metal ions can help in decreasing electron–hole recombination and thus increasing oxidation rate (Prairie et al. 1993a; Zhao et al.1998). The study with copper, for example, however, has not given improved result (Prairie et al. 1993b) while for Fe^{2+} other parameters such as oxygen pressure often play an important role.
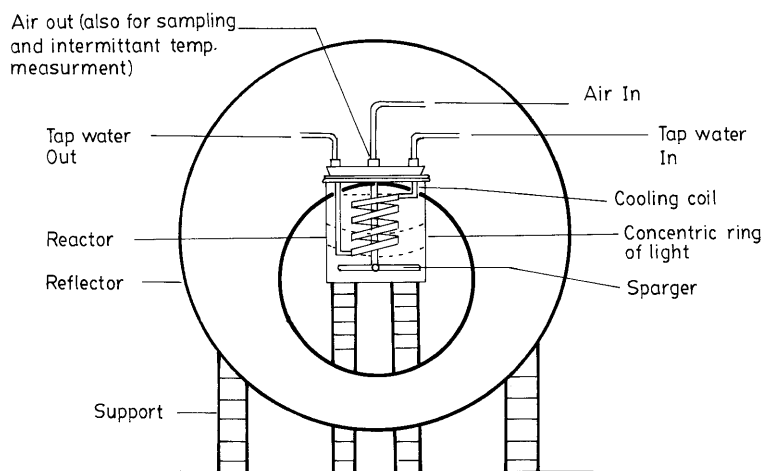

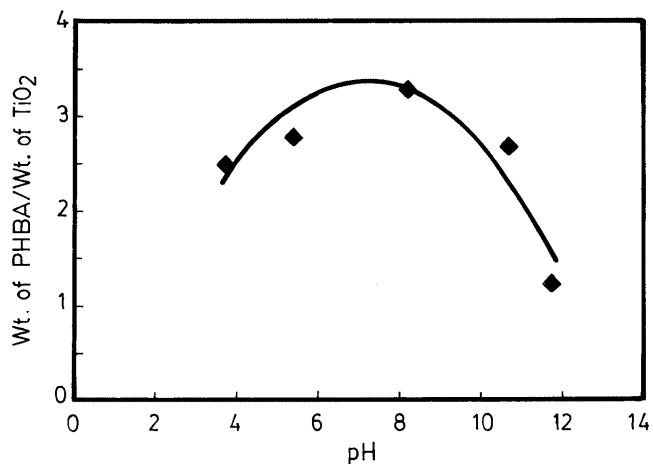**Fig. 1.** Experimental setup for the photocatalytic degradation of PHBA using concentrated UV light

Fig. 2. Effect of pH on dark adsorption of PHBA on Degussa P-25 TiO_2. Initial concentration of PHBA: 500 ppm

This prompted the study of effect of these ions on dark adsorption. Experiments were conducted with $FeSO_4$, $Cu(II)Cl_2$, and $CuSO_4$ and the results are summarized in Fig. 4. It can be observed that $Cu(II)Cl_2$, inhibits adsorption more than $CuSO_4$. This can be attributed to the presence of chloride ions as against sulfate ions as mentioned above. It was also observed that $CuSO_4$ inhibits adsorption less than $FeSO_4$.
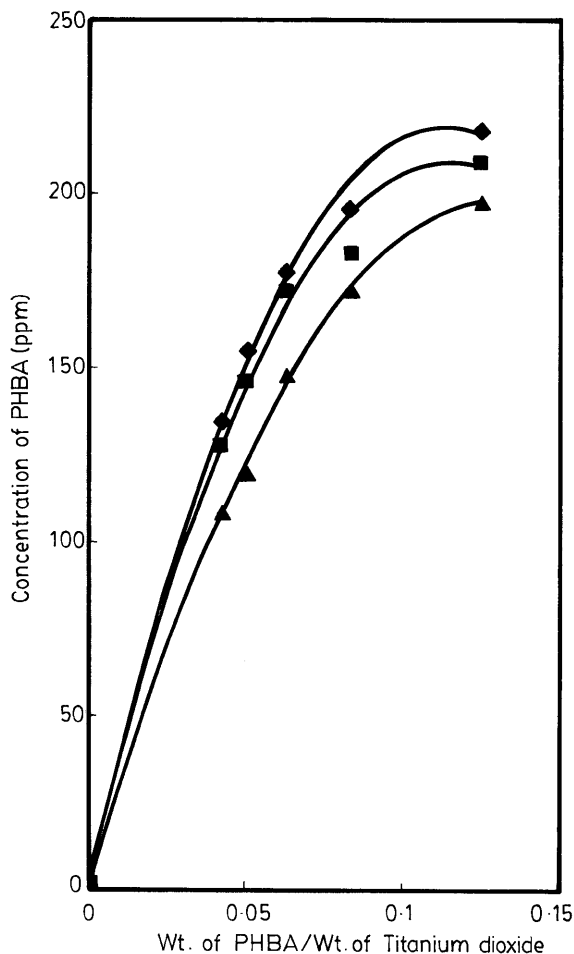

Fig. 4. Effect of cations on dark adsorption of PHBA on Degussa P-25 TiO_2. Initial PHBA concentration: 250 ppm. ♦ $FeSO_4$ (0.05 M), ■ $Cu(II)Cl_2$ (0.1 M), ▲ $CuSO_4$ (0.1 M)
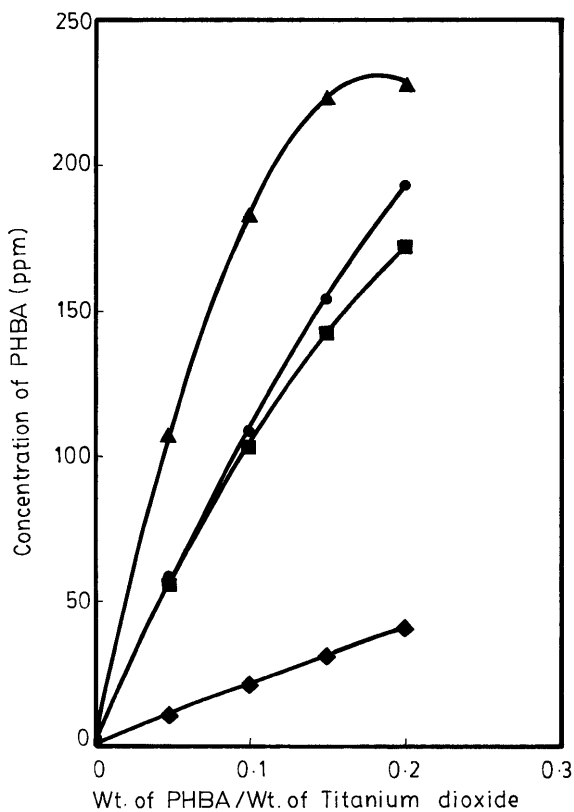

Fig. 3. Effect of anions on dark adsorption of PHBA on Degussa P-25 TiO_2. Initial PHBA concentration: 250 ppm. ♦ sodium sulfate (0.1 M), ■ sodium bicarbonate (0.1 M), ▲ sodium chloride (0.1 M), ● sodium nitrate (0.1 M)

Photocatalytic degradation of PHBA

Photocatalytic degradation (PCD) may involve generation of several intermediate compounds through which the original reactant passes on its way to complete mineralization to carbon dioxide and water. In this context, the reaction samples were carefully analyzed to determine if any such intermediates that formed could be detected. In all the experiments the results of these analyses indicated that no intermediate compound could be detected. For determination of any possible intermediates the HPLC runs were carried out for 45 min until a steady baseline was obtained. The resulting graph showed only one peak which also coincided with that of the authentic PHBA solution and also progressively decreased in area, indicating that there is a fall in the concentration of PHBA from the solution. Evidently, if any intermediates are formed, they are very short lived and therefore cannot be detected. This observation indicates that the present method using concentrated solar radiation is a clean technique, which results in complete degradation of the pollutant into harmless compounds – carbon dioxide and water. The HPLC analysis was further confirmed by TOC analysis which gave matching values with the organic carbon of PHBA detected by HPLC analysis.

Effect of pH

The adsorption of the pollutant depends upon the charge on the catalyst. The titanium dioxide catalyst has a net charge on it depending upon the pH – positive in acidic and negative in alkaline media. Variation of pH is instrumental in affecting the adsorption of ions on the catalyst surface. PCD rates were found to be affected by a change in pH. Increasing the pH towards the alkaline region was found to reduce PCD rates of many compounds, such as 2-chlorophenol, (Davis and Huang 1990) and 4-chlorophenol (Theurich et al. 1996). Therefore, the PCD of PHBA was carried out at three different pH values – 3.7, 6.4 and 9.4. Studies conducted on the PCD of Rhodamine B (Zhao et al. 1998) in the presence of dodecylbenzenesulphonate (DBS) at different pH, have shown that, as the pH is initially increased, there is an increase in the rate of PCD in the acidic range. The PCD rate attains a maximum value at pH 7 (approx.) and then decreases again as the pH is increased further in the alkaline range (Fig. 5). The above phenomena can be explained on the basis of the adsorption data, which also show a maximum in adsorption near the pH at which the PCD rate is maximum. Matthews and McEvoy (1992a) have made a similar observation for phenol.
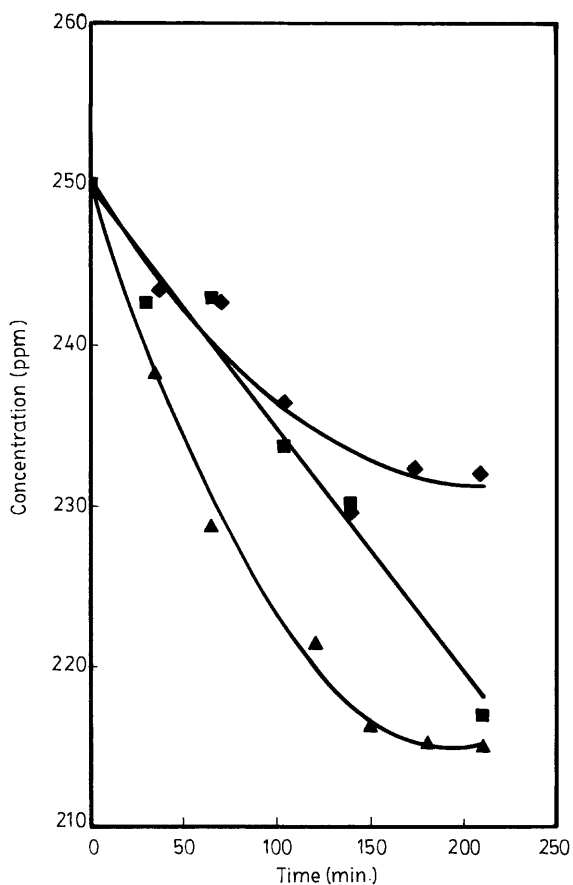
Apparent kinetics of PCD of PHBA

The order of reaction for PCD of pollutant with artificial UV light and natural light has been reported to be first order with respect to the pollutant concentration (Hoffmann et al. 1995) for phenol degradation (Matthews 1990). The data obtained in these batch experiments were analyzed by the standard methods for determining kinetics from batch experiments (Levenspiel 1991). Various schemes for kinetics, i.e., zero order, first order etc., were tried. Figure 6 shows the plot for order of reaction of PHBA degradation. In this work, however, the apparent reaction order was found to be zero with respect to PHBA. During the experiment the solar intensity variation was from 75 to 80 mW/cm^2 which can be ignored.

Effect of catalyst loading

Change in catalyst loading may or may not affect PCD rates (Yatmaz et al. 1993). Increase in catalyst loading may not necessarily increase degradation. This may be due to agglomeration of catalyst particles resulting in a net reduction in availability of active sites (Robert et al. 1997). Elsewhere, Matthews and McEvoy (1992b, c) observed that rates increase up to a catalyst loading of 0.04 wt.% and in fact the rate was lower at a catalyst loading of 0.1 wt.%. Hence it was thought necessary to study the effect of catalyst loading on PCD of PHBA. From Fig. 7, it can be observed that an increase in cata-
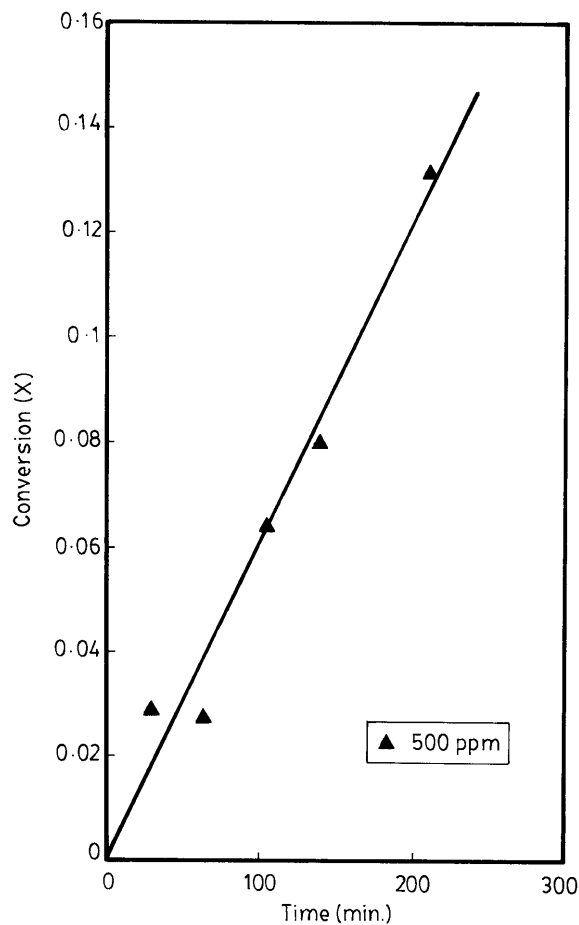
Fig. 5. Effect of pH on PCD of PHBA. Initial concentration of PHBA: 250 ppm. ◆ pH 3.7, ■ pH 9.4, ▲ pH 6.4

Fig. 6. Plot for apparent order of reaction for PCD of PHBA.

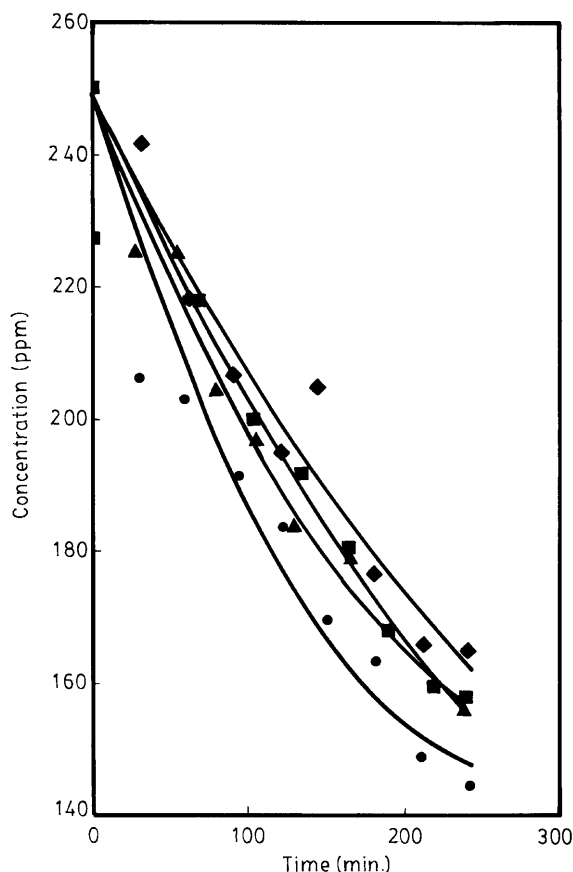**Fig. 7.** Effect of catalyst loading on PCD of PHBA. Initial concentration of PHBA: 250 ppm, solution pH: 3.7. ◆ 0.1% (w/w) TiO₂ catalyst, ■ 0.15% (w/w) TiO₂ catalyst, ▲ 0.2% (w/w) TiO₂ catalyst, ● 0.4% (w/w) TiO₂ catalyst

Fig. 8. Effect of anions on PCD of PHBA. Initial concentration of PHBA: 250 ppm, solution pH: 3.7. ◆ chloride (0.1 M), ■ nitrate (0.1 M), ▲ bicarbonate (0.1 M), ● sulfate (0.1 M)

lyst loading increases the PCD rates. This observation is consistent with the findings reported for phenol degradation (Okamoto et al. 1985), where there was an increase in the degradation of phenol even at a loading of 0.5 wt.% when high intensity radiation was used. However, the extent of degradation of PHBA is not proportional to the extent of increase in catalyst loading. A maximum of 40% degradation of PHBA could be carried out in 4 h with a catalyst loading of 0.4 wt.%. An increase in the catalyst loading increases the catalyst surface area available. This helps in the production of more OH• radicals that assist in increasing the degradation of PHBA. Increase in OH• radicals is due to enhancement in the photon scattering inside the reactor due to higher catalyst loading. In another case (Ku et al. 1996) an increase in loading was found to decrease PCD rates. The reason for this was attributed to the fall in the photon penetration. Such an effect was not found in the present work and this could be due to a higher limiting value for a fall of degradation rate with titanium dioxide with concentrated solar radiation.

Effect of anions

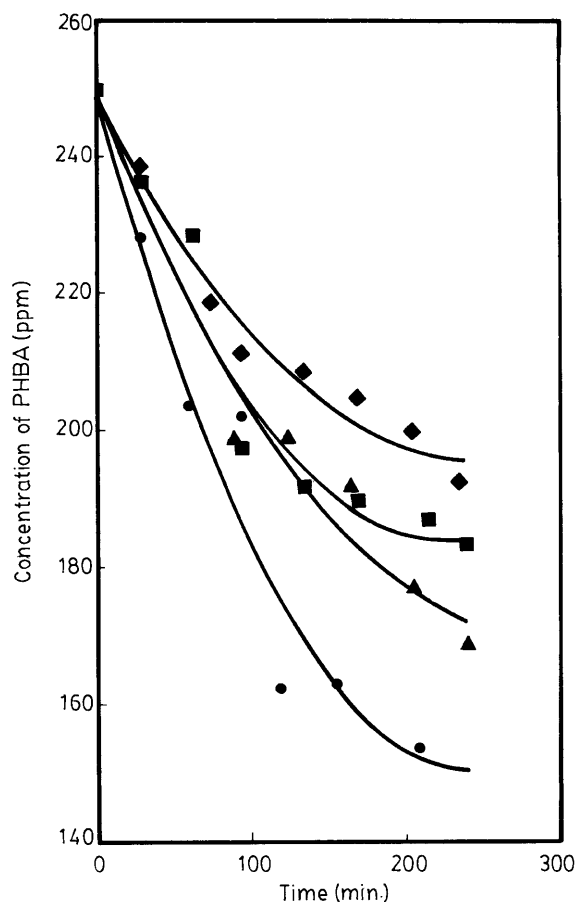In the presence of other ions the adsorbed quantity of PHBA decreases, presumably because the anions compete for the adsorbing catalyst surface. Exhaustive work by Matthews and co-workers on PCD rates of some pollutants (ethanol, aniline, SA) in the presence of anions such as perchlorate, nitrate, sulfate, chloride, and phosphates seems to indicate a varying extent of dependence of PCD on the ions (Matthews et al. 1990). The photocatalytic degradation was also found to be a function of ion concentration. In this work, PHBA degradation was carried out in the presence of chloride, nitrate, bicarbonate and sulfate. The cation associated with these ions was sodium in all these experiments. A 0.1-M concentration of these ions was used. Figure 8 shows the effect of these ions on the degradation of PHBA. The effect follows the order: chloride>nitrate>bicarbonate>sulfate.

Thus, the maximum inhibition of PCD of PHBA was observed with chloride and the minimum with sulfate. It can be observed from the adsorption data that the effect of the type of anion on adsorption also follows the above order. Thus there appears to be a link between adsorption and PCD. Adsorption on the catalyst surface seems to be a pre-requisite for efficient photocatalytic degradation. The possibility is well supported by the data on PCD of Rhodamine Blue (RhB) in visible light (Zhao et al. 1998).
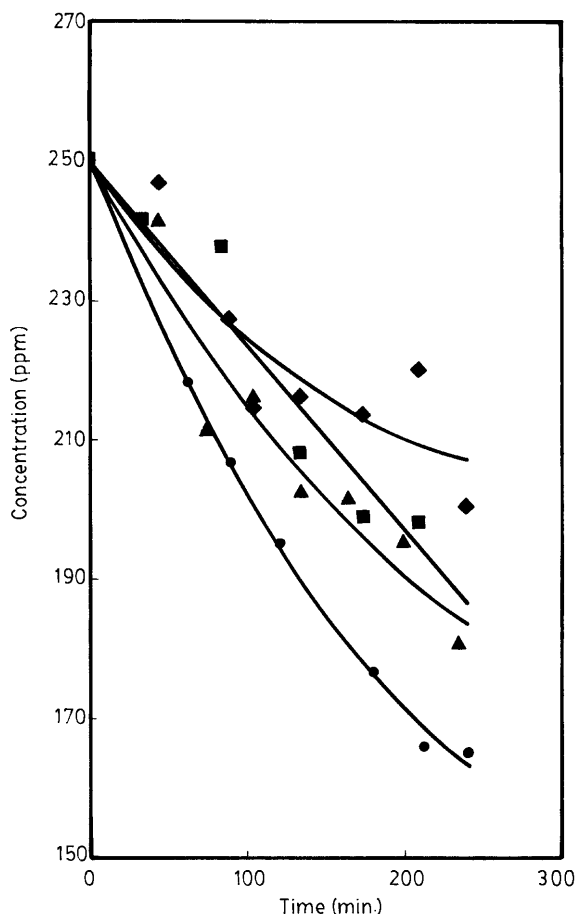
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Fig. 9. Effect of cations on PCD of PHBA. Initial concentration of PHBA: 250 ppm, solution pH: 3.7. ◆ ferrous sulfate (0.05 M), ■ copper chloride (0.1 M), ▲ copper sulfate (0.1 M), ● without cations (PHBA)

Fig. 10. Effect of change in anion concentration on PCD of PHBA. ◆ 0.1 M NaCl, ■ 0.5 M NaCl, ▲ 0.3 M NaCl, ● 0.1 M NaCl, * without NaCl (PHBA)

Effect of cations

Figure 9 shows plots of PHBA degradation in the presence of FeSO$_4$, CuSO$_4$, Cu(II)Cl$_2$ and in the absence of these compounds, i.e., PHBA alone. The aim here is to study if there is any effect of the above mentioned ions on the PCD of PHBA. It can be observed that degradation of PHBA is highest in the absence of salts. Fe^{2+} and Cu^{2+} help in preventing recombination of electrons and holes by taking away electrons from the catalyst and thereby assist in the degradation of pollutants (Prairie et al. 1993). However this phenomena is not substantiated by Fig. 9. This may be because, although the cation part of the salt (Fe^{2+} and Cu^{2+}) helps in promoting degradation, the anion part has a detrimental effect on PHBA degradation, as mentioned earlier (Fig. 3). Thus the combined effect of the presence of the two ions decides the extent of degradation of PHBA. Apparently, the negative effect of the anion dominates over the positive effect of the cation, resulting in lower overall degradation over the same period of time. If the data for experiments with Fe^{2+} and Cu^{2+} are compared, it is evident that Cu^{2+} plays a stronger positive role than Fe^{2+} in the overall degradation reaction. This trend is also substantiated with the work on phenol (Wei et al. 1990). The results from
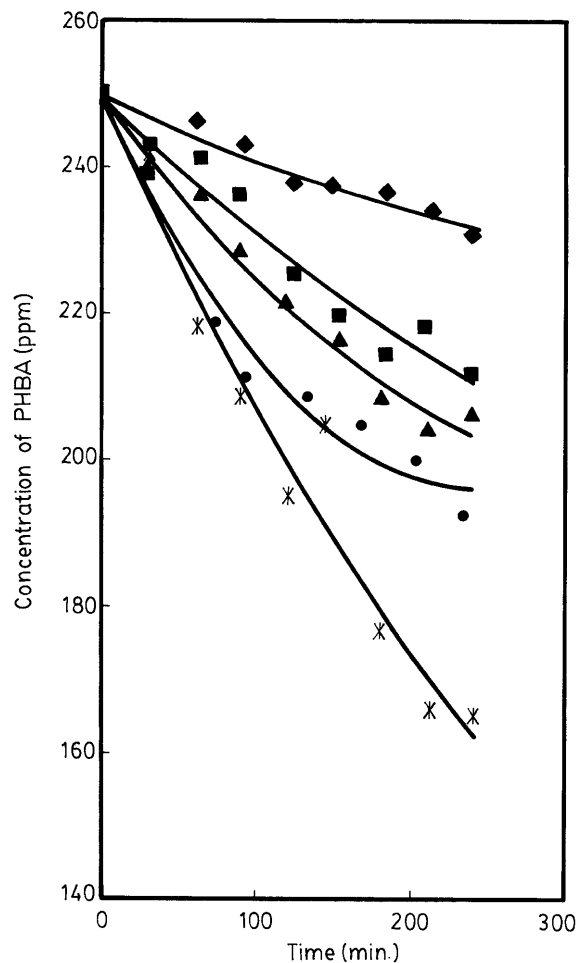
CuSO$_4$ and Cu(II)Cl$_2$ (Fig. 9) further support the conclusion of Fig. 3, indicating that the presence of chloride ion has a more detrimental effect on the degradation reaction of PHBA than sulfate ion. These observations can be considered fortunate since the effluent streams generated from industries contain more sulfate ions due to widespread use of sulfuric acid; as sulfuric acid is less corrosive than hydrochloric acid.

Effect of change in anion concentration

Chloride ion was found to be most detrimental in the photocatalytic degradation of PHBA. Therefore, it was thought necessary to study the effect of change in the concentration of chloride ions on the degradation of PHBA. This was studied at four concentrations of chloride, viz., 0.1, 0.3, 0.5 and 1 M. Figure 10 shows that an increase in the concentration of chloride ion results in a decrease in the degradation of PHBA. This is justified since the more chloride ions that are present in the solution the less will be the adsorption of PHBA and its consequent degradation.

Photocatalytic degradation of organic contaminants is largely brought about by the activity of the OH$^{\bullet}$ radicals (Legrini et al. 1993). Matthews (1988), and Turchi and

Ollis (1990) have proposed many mechanisms for the degradation of pollutants by this OH$^\bullet$ radical. The major pathways discussed are interaction between adsorbed OH$^\bullet$ radical and adsorbed pollutant; oxidation of pollutant in solution bulk by OH$^\bullet$ radical and diffusion of radical from surface formation site followed by later reaction with adsorbed or solution-phase molecule (Turchi and Ollis 1990). The results of this work indicate that there exists a definite relationship between adsorption of the pollutant on TiO$_2$ and its subsequent degradation. It was observed that conditions, which favor greater adsorption of PHBA on titanium dioxide also, favor greater PCD. These conditions include pH, presence/absence and type of cations and anions. Thus, the data obtained in this work point to the validity of the mechanism of PCD involving reaction between adsorbed PHBA and adsorbed OH$^\bullet$. This statement cannot be generalized at present in the absence of evidence with other organic compounds. However, there is reason to believe that a similar mechanism may be operative since in a majority of the cases the rate expression follows Langmuir–Hinshelwood kinetics (Chen et al. 1999).

Conclusion

Heterogeneous catalysis can be used to degrade PHBA in an aqueous solution over a wide range of concentration in the presence of concentrated solar radiation. From the data obtained in this work on degradation of PHBA it can be concluded that there exists a definite relationship between adsorption of the pollutant on titanium dioxide and its subsequent degradation. Conditions which favor adsorption also favor greater PCD indicating that the PCD mechanism may involve a surface reaction between adsorbed pollutant and OH$^\bullet$ radical.

Further, the following conclusions can also be drawn from the above study:

1. Adsorption of the pollutant on the catalyst surface depends on the pH of the solution, presence of the cations, anions, etc.
2. Increase in the pH initially increases the PCD rates; later on this rate falls at higher pH.
3. The apparent order of reaction for the PCD of PHBA was observed to be zero.
4. Increase in the catalyst loading increases the PCD of PHBA.
5. Anions inhibit adsorption and consequently, the PCD of PHBA in the following order:

   Chloride>nitrate>bicarbonate>sulfate.

   That is, chloride has maximum detrimental effect and sulfate has the least.
6. Fe^{2+} and Cu^{2+} do not substantially help in increasing degradation since their positive effect is eclipsed by the anion associated with them.
7. Increase in the concentration of anion (chloride) decreases degradation of PHBA.

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