Photocatalytic degradation of phosphamidon on semiconductor oxides

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Abstract

The photocatalytic degradation of a small concentration of an organo-phosphorous (OP) insecticide phosphamidon, in water, on ZnO and TiO_2 is investigated. Of the two semiconductor oxides, TiO_2 is found to be more effective as a photocatalyst for this reaction. Several factors such as concentration of phosphamidon, pH of the system, catalyst loading and presence of anions are found to influence the degradation rate. The reaction follows apparent first-order kinetics, though at higher concentrations, there is a reduction in the order of the reaction. There is a simultaneous formation and decomposition of H_2O_2 in the system, resulting in a periodic increase and decrease in its concentration. The catalyst TiO_2 is effective for the degradation of phosphamidon in direct sunlight and thus opens the possibility of solar decontamination of wastewater containing small amounts of OP pesticides.
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1. Introduction

Photocatalysis is emerging as an important technology for the treatment of organic contaminants in wastewater. Studies on the complete photocatalytic degradation of a variety of organics such as alcohols, aldehydes, ketones, carboxylic acids, ethers, esters, amines, nitro compounds, thioethers, mercaptans, etc. have been reported from many laboratories and the findings are summarised in excellent review articles on the subject [1–5]. However, the possible use of the technique for the removal of persistent organic pollutants, such as pesticides in water, started receiving the attention of researchers only

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recently [6–18]. Of these, organo-phosphorous (OP) pesticides [19–22] such as monocrotophos, fenitrothion and parathion, carbamate pesticides [23] and triazine herbicides [24] have received most of the attention. Another OP pesticide, phosphamidon (IUPAC name: 2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate), which has been used extensively as a rice insecticide around the world and is still popular in many developing countries does not seem to have received much attention in this respect. In the present study, the application of semiconductor photocatalysis for the degradation of small quantities of phosphamidon in water is examined.

When a semiconductor oxide is excited by radiation energy, at least equal to its bandwidth, in the presence of air or oxygen and water, oxidising species such as hydroxyl radicals and, to a lesser extent, superoxide anions are created. These species can very effectively degrade and even mineralise organic micro pollutants. As seen from the publications referred above and the numerous references cited therein, three catalysts that have been widely employed for the purpose are: TiO_2, ZnO and CdS. Of these, TiO_2 is considered particularly efficient due to its (i) high production capacity of hydroxyl radicals; (ii) spectral characteristics which allow excitation in a broad spectral range including sunlight spectrum; (iii) stability under harsh conditions; (iv) commercial availability at low price and (v) ease of preparation in the laboratory.

This paper presents the results of our ongoing studies on the possibility of using ZnO and TiO_2 as photocatalysts for the degradation of trace amounts of phosphamidon in water.

2. Experimental

2.1. Chemicals

Phosphamidon technical grade (97.5% purity) was provided by the Hindustan Insecticides Limited. The water used for all experiments was purified by double distillation. Other chemicals used were of reagent grade and used as such without further purification. The photocatalysts TiO_2 and ZnO were supplied by Merck India Limited. In both cases, the particles were approximately spherical and non-porous, with purity of over 99%. XRD analysis showed that the TiO_2 contains approximately 75% anatase and 25% rutile. The surface area of TiO_2 and ZnO, as determined by the BET technique, was approximately 25 and $22\,m^2/g$, respectively. The average particle size in both cases was approximately 35 nm. A phosphamidon solution in water was prepared by stirring a weighed amount of phosphamidon in water at room temperature. Appropriate dilute solutions were prepared from this stock solution by mixing with the required quantity of double distilled water.

2.2. Photocatalysis experiments and analytical methods

During the experiment, the catalyst was suspended in an aqueous solution of the insecticide in a Pyrex round bottomed flask. The reaction system was continuously stirred to achieve a homogeneous suspension and thermostated by circulating water to keep the temperature at $27\pm1\,^{\circ}C$. The water also served as a filter to remove IR light. The suspension was illuminated by a 500 W super high-pressure mercury lamp, mounted axially. The intensity

of the light was approximately $8 \, mW/cm^2$ in the wavelength range 330–390 nm (based on manufacturer's data). For solar experiments, 250 ml solution was exposed to sunlight for a fixed time daily between 9:30 and 16:00 h, for 12 consecutive days in April. After carrying out illumination for the specified period, the suspension was centrifuged and the super-natant solution was extracted [25] with methylene chloride, dried with anhydrous Na_2SO_4, concentrated by evaporation and analysed for phosphamidon by gas chromatography [26] using flame ionisation detector and $180 \times 0.6 \, cm$ glass column packed with 3% SE 30 (100–150 mesh size). The detector temperature was $240 \, °C$ and the column was maintained at $230 \, °C$. CO_2 formed after long illumination of a higher concentration of the insecticide was analysed by bubbling the gas through a saturated $Ba(OH)_2$ solution and estimating the amount of $BaCO_3$ formed. H_2O_2 was analysed by iodometry. Cl^- was analysed by colorimetry [27] after adding Ag_2CrO_4 and NH_3. The analysis of phosphate was performed colorimetrically [28] as follows.

An aliquot of the clear centrifuged reaction product was taken in a 25 ml volumetric flask and 2 ml 60% perchloric acid, 2 ml amidol reagent (prepared by dissolving 2 g of amidol and 40 g of pure sodium bisulphite in 200 ml distilled water) and 1 ml of ammonium molybdate solution (8.3%), were added one by one. The solution was made up to 25 ml and after an interval of 10 min, its extinction coefficient was determined. The amount of phosphate was calculated from a calibration curve obtained by applying same procedure to aliquots of standard phosphate (KH_2PO_4) solutions.

3. Results and discussion

Phosphamidon, in small concentrations in aqueous solution, is degraded and eventually mineralised upon illumination in the presence of suspended ZnO or TiO_2. Control experiments have shown that the presence of catalyst, light and oxygen are essential to affect the decomposition. The rate of disappearance of phosphamidon at the same initial concentration and under identical reaction conditions, in presence of ZnO or TiO_2 at same loading, is given in Fig. 1.
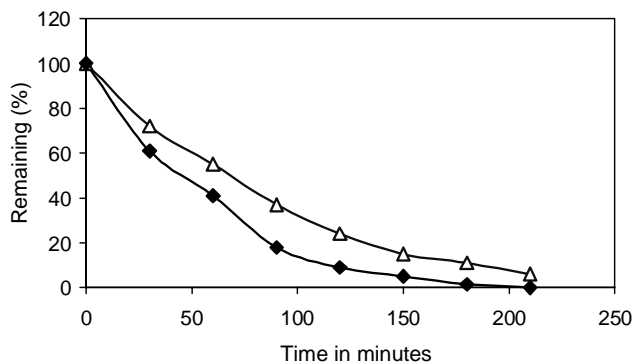

Fig. 1. Photocatalytic degradation of phosphamidon in presence of ZnO and TiO_2 catalysts. ($\blacklozenge$) TiO_2; ($\triangle$) ZnO; catalyst: 1 g/l; phosphamidon concentration: $1.0 \times 10^{-4} \, M$.
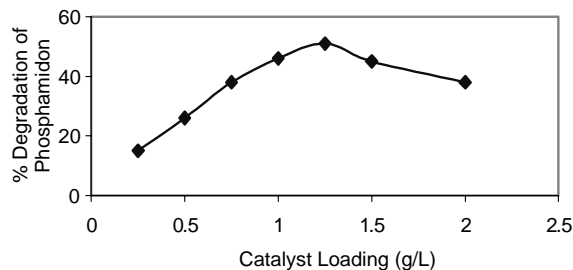
Fig. 2. Effect of catalyst loading on the photodegradation of phosphamidon. Concentration of phosphamidon: 1×10^{-4} M; irradiation time: 30 min.

As seen from the figure, TiO_2 is a superior catalyst, even though ZnO is also highly efficient for the photodegradation of phosphamidon. Hence, all further studies were carried out using TiO_2 catalysts.

The effect of catalyst loading on the degradation of phosphamidon was investigated using TiO_2 at different loadings, keeping all other parameters identical. The results of the study are shown in Fig. 2.

A steady increase in the degradation of phosphamidon is observed up to 1.25 g/l of catalyst loading followed by a slow decrease at higher loadings. The higher degradation with increase in catalyst loading can be attributed to the increase in catalyst surface area, increase of light absorption and consequently the creation of a higher number of active species. However, at higher loadings, beyond the optimum, part of the catalyst were in the dark and there was a decrease in the light penetration. Further, it was difficult to maintain the suspension homogeneous and the catalyst had a tendency to settle at the bottom of the reactor. Variation in the degree of settling, influences the consistency of the sampling process, total amount of light absorption and scattering of the incident light by the catalyst. These factors together contribute to a decrease in the efficiency of the catalyst at loadings above the optimum level. Similar observations were reported by other authors as well [29,30]. All further studies were made using TiO_2 loading of 1.25 g/l.

The effect of initial concentration of phosphamidon on the overall rate of degradation was studied by varying the concentration over a wide range. The results are shown in Fig. 3.
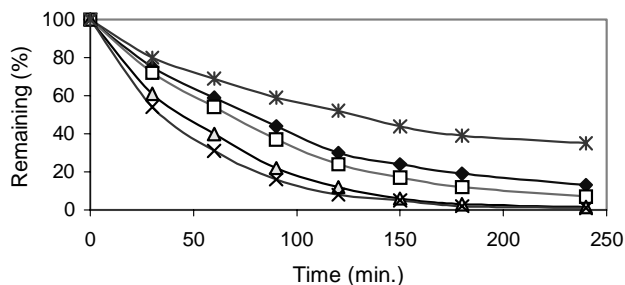

Fig. 3. Effect of initial concentration on the photocatalytic degradation of phosphamidon in water. (✴) 6.0×10^{-4} M; (◆) 4.5×10^{-4} M; (□) 3.0×10^{-4} M; (△) 1.5×10^{-4} M; (×) 1.0×10^{-4} M.

Table 1
Effect of initial concentration on the rate of degradation of phosphamidon

Initial concentration ($\times 10^{-4}$ M)	Rate ($\times 10^{-6}$ mol/min)
1.0	0.9
1.5	1.5
3.0	2.8
4.5	3.4
6.0	3.0

It is obvious that the rate of degradation increases with increase in the phosphamidon concentration. However, at very high concentrations the rate slows down, as reflected in the rate of degradation at 6.0×10^{-4} M (see Table 1).

Many authors [29,31] have reported that the TiO_2 photocatalysed degradation of OP compounds follow first-order kinetics. By applying the following simple first-order rate law [32],

$$\ln \left(\frac{[C]_i}{[C]_t} \right) = kt$$

to the results of the current study, it has been observed that there is a linear relationship between $\ln([C]_i/[C]_t)$ and time (t), which is consistent with first-order kinetics. The results of this application are presented in Fig. 4. The slope k of the best-fit line through the data points represents the first-order rate constants for the corresponding initial concentration values. The apparent kinetic parameters determined for the degradation of phosphamidon are summarised in Table 2.

The decrease in the rate of degradation (at higher concentrations) and thus the order of reaction with the increase in initial concentration of the reactant in TiO_2 photocatalysis has been reported by many other authors [29,33,34]. At high substrate concentration, the adsorbed reactant molecules may occupy all the catalytic sites on the TiO_2 surface and this leads to zero-order kinetics. At low concentration, the number of catalytic sites will not be a limiting factor and the rate of degradation is proportional to the substrate concentration, in accordance with apparent first-order kinetics. Reaction order smaller than unity are reported in the TiO_2 photocatalysis of phosphonic acids, as a result of slow diffusion of the product
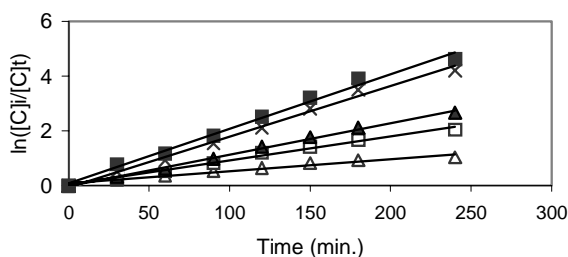

Fig. 4. Pseudo-first-order kinetics for the photocatalytic degradation of phosphamidon in water. (■) 1.0×10^{-4} M; (×) 1.5×10^{-4} M; (▲) 3.0×10^{-4} M; (□) 4.5×10^{-4} M; (△) 6.0×10^{-4} M.

Table 2
Apparent first-order rate constants and half-lives for the photodegradation of phosphamidon at different initial concentrations

Concentration ($\times 10^{-4}$ M)	Rate constant, k_{app} ($\times 10^{-3}$ min^{-1})	Half-life ($t_{1/2}$) (min)
1.0	20.1	31
1.5	16.5	49
3.0	9.09	65
4.5	6.61	85
6.0	5.60	147

from the surface of the catalyst [34]. Major products such as low molecular weight organic acids and phosphates, formed during the photocatalysed degradation of OP compounds, remain strongly adsorbed on to the surface of the catalyst through hydrogen bonding interactions with the hydroxylated surface of the catalyst [29]. This also leads to a reduction in the number of catalytic sites and a consequent reduction in the rate of degradation observed at high substrate concentration.

It has been reported by many workers [31,35–38] that pH of the solution is an important parameter in the photocatalysed degradation of organic wastes. This is due to the fact that pH influences the surface charge of the semiconductor, thereby affecting the interfacial electron transfer and the photoredox process [31]. In the present case, the experiments were carried out at an initial pH of 6–6.5. As the photodegradation progressed there was a slow decrease in the pH and the solution was becoming more acidic. This indicates the release of H$^+$ during the reaction. Preliminary studies showed that the rate of degradation decreased with decrease in pH and it proceeded much faster under alkaline pH. However, any meaningful conclusion on the effect of pH can be derived only from studies, using buffer solutions and maintaining a steady pH. Such studies are being undertaken in our laboratory at present.

The final products of degradation of phosphamidon (mixture of approximately 70% *Z*-isomer and 30% *E*-isomer) were examined by irradiating a higher concentration of the substrate in presence of TiO$_2$. As reported in the studies carried out on similar OP pesticides [31,35–37], the degradation leads to a complete mineralisation and the products are found to be Cl$^-$ and phosphate ions. With reference to the fate of nitrogen, the attack by hydroxyl radicals can induce cleavage of the C–N bond and the organic nitrogen can be transformed into NH$_4^+$, NO$_2^-$ and NO$_3^-$. In the current experiments, the presence of NH$_4^+$, NO$_2^-$ or NO$_3^-$ was not detected. This may be due to their extremely low concentrations and the possibility of them remaining adsorbed on to the surface during the experiment. The inability to account for all the nitrogen that is liberated during photocatalytic degradation of nitrogenous compounds has been reported earlier also [39–41]. However, based on the results of the studies reported earlier [14,39–41], under similar conditions, it is reasonable to assume that NH$_4^+$ (which gets eventually transformed [40] to NO$_3^-$ and H$^+$) and NO$_3^-$ are also formed as the mineralisation products, though the possibility of formation of small quantities of NO$_2^-$ by the direct photolysis of aqueous NO$_3^-$ cannot be ruled out [42].

The fate of nitrogen atoms in the photocatalytic degradation of nitrogenous organic compounds depends on the structure of the compound, especially the position and the number of N atoms. For example, the photocatalytic mineralisation of nitrogen containing compounds with one N atom such as alkyl and alkanolamines [40], amides [43] etc. was reported to
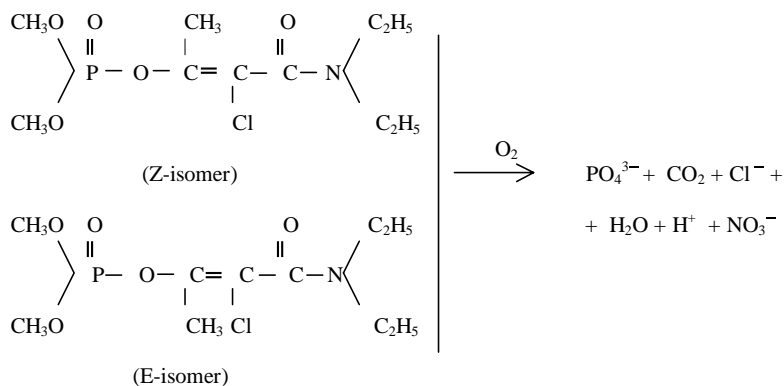
Fig. 5. Empirical reaction scheme for the photocatalytic mineralisation of phosphamidon.

yield only NH_4^+, NO_3^- and/or NO_2^- and no gaseous nitrogen. However, the photocatalytic oxidation of hydrazine derivatives [39] with N–N bonds, at TiO_2–H_2O interfaces, generates gaseous N_2 in addition to the formation of NH_4^+ and NO_3^-, respectively. Azo dyes such as congo red and alimentary (amaranth) with N=N azo group also yields gaseous dinitrogen under photocatalytic conditions [41]. In this case, the authors measured the evolution of nitrogen gas quantitatively and showed that it corresponds stoichiometrically to the mineralisation of the central N=N azo group. Based on such findings by other investigators under similar conditions, it is reasonable to assume that the possibility of formation of N_2 in the case of phosphamidon, with only one N atom at the tertiary amide moiety, is remote. The exact fate of nitrogen in the photocatalytic degradation of a number of nitrogen-containing organic compounds is being investigated in our laboratories at present. The overall mineralisation reaction may hence be empirically represented as in Fig. 5.

The effect of Cl^-, PO_4^{3-} and NO_3^- ions on the rate of degradation of phosphamidon was examined individually, by adding NaCl, Na_3PO_4 and $NaNO_3$ to the system such that the resultant solution contains 1.5×10^{-4} M of Cl^-, PO_4^{3-} and NO_3^- ions, before the irradiation begins. The results showed that under the reaction conditions, these ions have no significant effect on the rate of degradation of phosphamidon. However, at higher concentrations (10^{-1} M), all these ions inhibit the degradation considerably (see Fig. 6). This might be due to the competition of these ions for adsorption sites on the catalyst, thereby reducing the number of sites available for the organic substrate and O_2. The possibility of these anions penetrating into the inner co-ordination sphere of TiO_2 at concentrations exceeding 0.1 mol/l and pH close to the point-of-zero-charge (PZC, between 6 and 6.5), thereby reducing the rate of disappearance of various pollutants has been reported earlier also [44]. The inhibition efficiency of the three anions is in the order

$$PO_4^{3-} > Cl^- > NO_3^-.$$

Further investigations on the cause and effect are in progress now.

Wang et al. [38] have demonstrated that the effect of anions on the photocatalytic degradation of dichlorvos on TiO_2 depends on a variety of factors such as pH and origin of
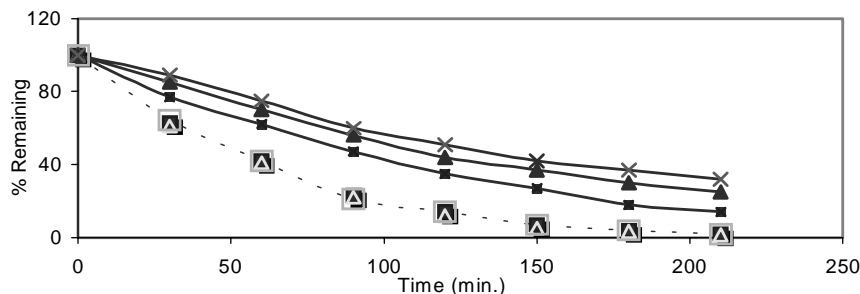
Fig. 6. Effect of anions on the photocatalytic degradation of phosphamidon in water. (i) 1×10^{-4} M phosphamidon; (ii) 1×10^{-4} M phosphamidon with 1×10^{-4} M NO_3^-; (iii) 1×10^{-4} M phosphamidon with 1×10^{-4} M Cl^-; (iv) 1×10^{-4} M phosphamidon with 1×10^{-4} M PO_4^{3-}. (■) 1×10^{-4} M phosphamidon with 1×10^{-1} M NO_3^-; (▲) 1×10^{-4} M phosphamidon with 1×10^{-1} M Cl^-; (×) 1×10^{-4} M phosphamidon with 1×10^{-1} M PO_4^{3-}.

the catalyst. Other authors [3,31,45] also reported similar observations. Studies, currently in progress in our laboratory, show that many common inorganic anions found in natural waters such as CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and NO_3^- as well as cations such as Ca^{2+}, Mg^{2+} and Fe^{3+} influence the rate of photocatalytic degradation of many organic pollutants. This effect depends on the nature of the pollutant, pH of the system, type of the catalyst, source of the catalyst (same catalyst, but prepared by different methods) etc [46].

Further, it has been observed that the reaction system also contained H_2O_2, formed during the photocatalytic reaction. However, the concentration of H_2O_2 does not show a steadily increasing trend, eventhough the degradation of phosphamidon continued unhindered. This possibly indicates the simultaneous formation and decomposition of H_2O_2 under the reaction conditions. This is further confirmed by the observation that in repeated experiments under identical conditions, the rate of disappearance of phosphamidon was quite reproducible, while the amount of H_2O_2 measured at identical intervals varied significantly. Since H_2O_2 is known to produce hydroxyl radicals [47] upon reduction by the electrons in the conduction band of TiO_2, addition of H_2O_2 to the current reaction system was expected to increase the amount of hydroxyl radicals. Preliminary studies have shown that addition of H_2O_2 enhances the rate of TiO_2 catalysed photodegradation of phosphamidon and the combined efficiency of the catalyst and H_2O_2 is more than the sum of the effect of H_2O_2 and the catalyst (see Table 3). This is consistent with the observations reported by many workers for the degradation of various OP compounds [7,29,35]. Detailed studies on the role of H_2O_2 under different reaction conditions are in progress.

The effect of H_2O_2 on the TiO_2 photocatalysed degradation of organic pollutants in water was examined by Almaric et al. [48] while studying the effect of antioxidant enzymes catalase and superoxide dimutase on the rate of TiO_2 and ZnO photocatalysed degradation of 1,2-dimethoxybenzene (DMB) in water. The authors demonstrated that the effect of H_2O_2 might be favourable or unfavourable, depending on the initial $[H_2O_2]/[DMB]$ ratio. This was attributed to the competition between H_2O_2 and DMB for the adsorption sites and/or photo-produced holes, the formation of additional $OH^\bullet$ radicals and the detrimental modification of TiO_2 surface.

Table 3
Effect of H_2O_2 on the photocatalysed degradation of phosphamidon

Reaction system	Degradation of phosphamidon (%)	
	Irradiation time (30 min)	Irradiation time (60 min)
No catalyst, no H_2O_2	0.5[a]	1.0[a]
Catalyst only	39.0	58.6
H_2O_2 only (20 mg/l)	5.5	8.3
Catalyst + H_2O_2	49.5	69.2

Phosphamidon concentration is 1.5×10^{-4} M.

[a] Approximate average of three experiments.

The reaction between the hydroxyl radicals and the substrate is expected to occur at or near the surface of the semiconductor, as no OH$^\bullet$ radicals are produced by direct photolysis, without the catalyst, under our experimental conditions. However, once the surface initiated reaction has begun, the OH$^\bullet$ radicals generated can propagate the decomposition of H_2O_2 in both the liquid phase as well as on the surface. Decomposition of H_2O_2 will result in the formation of more OH$^\bullet$ radicals, which can enhance the rate of degradation of phosphamidon. Thus, there is a simultaneous formation and decomposition of H_2O_2 and depending on the predominance of one or the other at any particular time, there is oscillation in its concentration. This aspect is being studied in detail at present.

The photocatalytic degradation of a series of alcohols on ZnO was reported [49] to be initially autocatalytic and this was attributed to the H_2O_2, formed in situ, that could act as a reserve of OH$^\bullet$ radicals. However, no such phenomenon was observed in the current study. Our initial results show that H_2O_2, added at a concentration comparable to the in situ formation, has no effect on the rate of ZnO catalysed degradation of phosphamidon. This is consistent with the findings of Almaric et al. [48] that H_2O_2, formed in situ, does not decompose on ZnO and consequently does not generate OH$^\bullet$ radicals capable of enhancing the degradation of the organic pollutant. On the other hand, the stability of H_2O_2 leads to unfavourable effects due to its competition for adsorption sites at higher concentrations. The effect of added H_2O_2 and the characteristics of ZnO prepared by different methods on the rate of degradation of various pollutants is under investigation in our laboratory.

When a semiconductor oxide is irradiated with light having energy higher than the band gap (in the case of TiO_2 it is ca. 3.2 eV), a pair of conduction band electron (e^-) and valence band hole (h^+) is generated. The charge carriers can subsequently recombine within the bulk of the material or migrate to the particle surface where they can also recombine or can be trapped at some defect site, eventually as surface bound $O^{\bullet-}$ radicals [20,50,51]. In the case of TiO_2, this will be followed by adsorption of molecular oxygen on the Ti(III) sites, which reduce O_2 to the superoxide radical anion $O_2^{\bullet-}$, while the positive charge carrier, Ti(IV)–O$^-$$^\bullet$–Ti(IV) can oxidise the surface hydroxyl groups or the surface bound water to surface bound OH$^\bullet$ radicals [14,52]. Radiolytic studies by Lawless et al. [53] showed that it is not possible to distinguish between the surface bound OH$^\bullet$ radicals and the Ti(IV)–O$^-$$^\bullet$–Ti(IV) species.

The overall catalytic process can hence be presented as follows:

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

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

$$h^+ + H_2O \rightarrow OH^\bullet + H^+ \tag{3}$$

$$h^+ + OH^- \rightarrow OH^\bullet \tag{4}$$

$$h^+ + RH \rightarrow R^\bullet + H^+ \tag{5}$$

$$O_2{}^{\bullet-} + H^+ \leftrightarrow HO_2{}^\bullet \tag{6}$$

$$HO_2{}^\bullet + HO_2{}^\bullet \rightarrow H_2O_2 + O_2 \tag{7}$$

$$O_2{}^{\bullet-} + HO_2{}^\bullet \rightarrow HO_2{}^- + O_2 \tag{8}$$

$$HO_2{}^- + H^+ \leftrightarrow H_2O_2 \tag{9}$$

Hydroxyl radicals are powerful oxidants of organics in aqueous solutions [54].

The mechanism of the formation of $OH^\bullet$ radicals from H_2O_2 on TiO_2 surface is found to be as follows [55–57]:

$$H_2O_2 + O_2{}^- \rightarrow OH^\bullet + O_2 + OH^- \tag{10}$$

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \tag{11}$$

$$H_2O_2 + e^- \, (TiO_2) \rightarrow OH^\bullet + OH^- \tag{12}$$

$$2OH^- + h^+ \rightarrow OH^\bullet + OH^- \tag{13}$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2{}^\bullet \tag{14}$$

$$HO_2{}^\bullet + H_2O_2 \rightarrow O_2 + H_2O + OH^\bullet \tag{15}$$

Almost all the studies reported so far indicate that, $OH^\bullet$ radicals, irrespective of whether they are free or surface bound, are the active oxidising species in photocatalytic degradations over TiO_2. EPR studies on irradiated TiO_2 have also identified the $OH^\bullet$ radicals by spin trap techniques [58]. No other radical species were detected under ambient conditions in aqueous dispersions. Studies on the photooxidation of aliphatic alcohols on ZnO [59,60] and TiO_2 [61] also suggested that the rate-determining step in these reactions is the formation of $OH^\bullet$ radicals.

4. Photocatalytic decomposition under solar radiation

The possibility of using TiO_2 as a photocatalyst for the degradation of phosphamidon in wastewater under natural sunlight was examined by conducting similar experiments, as described above, using solar radiation. Control experiments with solar irradiated phosphamidon solution in the absence of TiO_2 showed practically no degradation. In the presence of TiO_2, phosphamidon disappeared slowly but steadily. The rate did not vary significantly with the difference in the position of the sun. However, with the onset of darkness, the decomposition slowed down and stopped fully within 10–15 min. The degradation picked
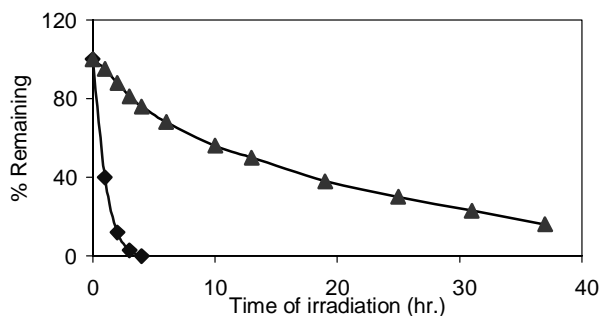
Fig. 7. Degradation of phosphamidon under UV and solar irradiation. Concentration 1.5×10^{-4} M; (■) UV irradiation; (▲) solar irradiation.

up again when exposed to sunlight next day morning. The rate of degradation over a 6-day period is shown in Fig. 7.

The complete disappearance of phosphamidon, at the experimental concentration of 1.5×10^{-4} M was achieved in over 75 h (in 12 days) of irradiation, even though the rate of degradation was becoming slower and slower with decrease in the concentration of the substrate. It is worthwhile to observe that the degradation continued under solar radiation without aerating the system or mixing. This will be an important consideration in the solar treatment of industrial wastewater.

5. Conclusion

The present study clearly shows that semiconductor oxides can be used as effective photocatalysts for the degradation of phosphamidon contaminated wastewater. Although a direct comparison of the efficiency of the two catalysts tested here, ZnO and TiO_2, may not be precise due to the difference in their surface characteristics, it appears that TiO_2 is by far superior in its efficiency to degrade phosphamidon. The difference in their activities may arise from a number of factors including the lifetime of the active species, surface area, concentration of hydroxyl groups, absorption and adsorption efficiency etc. The H_2O_2 formed in the system undergoes simultaneous decomposition, leading to a periodic increase and decrease in its concentration. This decomposition may be taking place on the surface as well as in the solution, depending on the concentration. The higher rate of degradation of phosphamidon in presence of TiO_2, compared to ZnO supports the view that the surface mediated process is more prominent in the degradation reaction.

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