

Research Article

Photocatalyzed Degradation of a Pesticide Derivative Glyphosate in Aqueous Suspensions of Titanium Dioxide

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The photocatalytic degradation of a herbicide derivative, glyphosate [(N-phosphonomethyl) glycine] has been investigated in aqueous suspensions of titanium dioxide at different pH values. This compound was found to degrade more efficiently under alkaline pH, where no adsorption takes place on the surface of the catalyst in the dark. The main degradation route involves the cleavage of the P–C bond giving rise to sarcosine and glycine as the intermediate products formed during the photooxidation process.

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1. INTRODUCTION

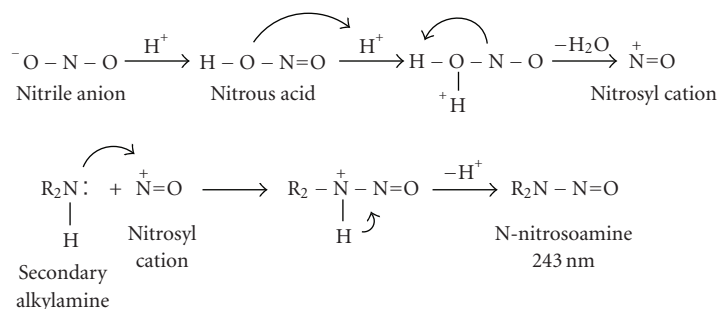
A wide variety of organic pollutants especially pesticides are introduced into the water system from various sources such as industrial effluents, agricultural runoff, and chemical spills [1, 2]. Their toxicity, stability to natural decomposition, and persistence in the environment have been the cause of much concern to the societies and regulatory authorities around the world [3, 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. However, many organic chemicals, especially those that are toxic or refractory, are not amendable to microbial degradation [5]. Recently, considerable attention has been focused on the use of semiconductor photocatalysis as a means to oxidise toxic organic chemicals [6–18]. The mechanism constituting heterogeneous photocatalytic oxidation processes has been discussed extensively in the literature (see, *inter alia*, [19, 20]). In many of these studies, although the initial disappearance of the pollutant is rapid, a number of by products are formed which can also be potentially harmful to the environment.

The organophosphates exhibit considerable persistence in groundwaters and are highly hydrophilic. These com-

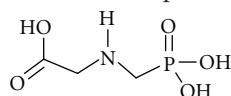
pounds are the most prevalent pesticides and remain the choice of most farmers because of their effectiveness against large numbers of insect species. They are potent acetylcholinesterase inhibitors and are utilised to control chewing and sucking insects and spider mites on ornamental plants, citrus fruits, stone fruits, and other agriculture crops. For example, the pesticide derivative, glyphosate is a nonselective systemic herbicide that can control most annual and perennial plants [21]. It controls weeds by inhibiting the synthesis of aromatic amino acids necessary for protein formation in susceptible plants. Glyphosate is strongly adsorbed to soil particles, which prevents it from excessive leaching or from being taken up from the soil by nontarget plants [22–26]. It is degraded primarily by microbial metabolism, but strong adsorption to soil can inhibit microbial metabolism and slow degradation. The half-life of glyphosate ranges from several weeks to years, but averages are two months. In water, glyphosate is rapidly dissipated through adsorption to suspended and bottom sediments and has a half-life of 10–12 days [22–24, 27–29].

Although originally thought to be unaffected by sunlight [24], later studies found glyphosate to be susceptible to photodegradation. A half-life of 4 days in deionised water under UV light has been reported [30]. Recently, the photocatalytic degradation of glyphosate in the presence of TiO₂ has been reported by Shifu and Yunzhang [31]. However, no effort has



SCHEME 1: Scheme showing the conversion of secondary amine to its N-nitroso derivative on treatment with nitrous acid in the presence of acid.

been made to look into the degradation products. Therefore, we have studied the degradation of glyphosate in aqueous suspension of TiO_2 with an aim to identify the products formed during the photooxidation process.



2. EXPERIMENTAL METHODS

2.1. Reagent and chemicals

Analytical grade glyphosate was obtained from Fluka and used without further purification. The water employed in this study was purified by a Millipore system. The photocatalyst titanium dioxide Degussa P25 was used in all the experiments reported here. Degussa P25 contains 75% anatase and 25% rutile with a specific BET surface area of $50 \text{ m}^2 \text{ g}^{-1}$ and a primary particle size of 20 nm [32].

2.2. Procedure

A solution of glyphosate at the desired concentration was prepared in water. For the irradiation experiments, 80 cm^3 of this desired solution was pipetted into a photochemical reactor. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or NaOH . The photoreactor was comprised of a quartz glass reaction vessel equipped with a magnetic stirring bar, a water circulating jacket, and opening for gas supplies, placed within a bespoke circular photoirradiation system (photochemical reactors LTD Buckingham, UK) comprised of 12×15 watt Blacklight UVA lamps ($\lambda_{\text{max}} = 312 \text{ nm}$), 42 cm long.

The required amount of the particulate photocatalyst was added to the glyphosate solution, and the solution was stirred in the dark for 10 minutes to allow equilibration of the system so that the loss of compound from the solution phase due to to-particle adsorption can 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. Photodegradation experiments were conducted by irradiating the sample solutions with 312 nm light, the irradiated solutions being continuously purged with air

throughout each experiment. Samples (5 cm^3) were collected before and at regular intervals during the irradiation. These were centrifuged before being subjected to analysis.

2.3. Sample analysis

Elucidation of the mechanism and kinetics of photocatalytically driven glyphosate degradation requires a means to follow the concentration of glyphosate as a function of time. Secondary amines such as glyphosate and sarcosine are most easily determined by spectroscopic analysis of their nitro derivative. All secondary alkyl or aryl amines yield N-nitrosoamines with an absorbance at or about $\lambda = 243 \text{ nm}$. Scheme 1 shows the route by which secondary amines are transformed to the N-nitroso compounds.

The procedure for both calibration measurements and the analysis of experimental samples, whether derived from dark adsorption experiments (*vide infra*) or photodegradation experiments, involves the shaking of centrifuged glyphosate adsorbed or irradiated solutions (1 cm^3 of expt. sample or 1 cm^3 of $1 \times 10^{-3} \text{ mol dm}^{-3}$ calibration solution) in the presence of water (5 cm^3), H_2SO_4 (1 : 1, 0.5 cm^3), KBr (25 %, 0.1 cm^3), and NaNO_2 (0.2 N, 0.5 cm^3) in a 25 cm^3 red volumetric flask for 30 minutes followed by dilution with water to 25 cm^3 . Absorbance was measured at 243 nm versus blank reagent containing all above reagents except glyphosate.

The product analysis was carried out using HPLC (Perkin Elmer 410 Bio) fitted with a nitrile column (cyanopropyl $5 \mu\text{m}$). The eluent consisted of pure water; the compounds were detected employing a UV-detector at 254 nm.

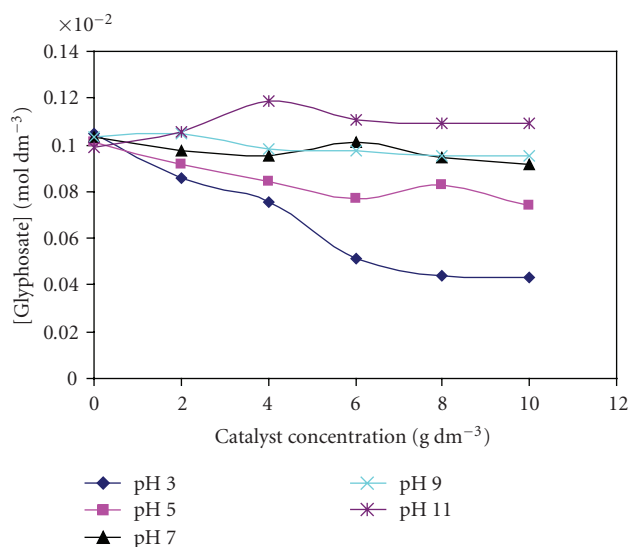
3. RESULTS AND DISCUSSION

3.1. Dark adsorption of Glyphosate onto TiO_2

The possible dark adsorption of glyphosate on the surface of the photocatalyst was investigated by stirring aqueous solutions of glyphosate ($1 \times 10^{-3} \text{ mol dm}^{-3}$, 35 cm^3) at a range of pH in the absence of illumination for 4 hours at different catalyst loadings ($2\text{--}10 \text{ g dm}^{-3}$). Analysis of samples after centrifugation using the N-nitroso method (*vide supra*) showed that greatest adsorption occurs at lower pH values and that the extent of adsorption decreases as pH increases, as can be seen in Figure 1.

TABLE 1: Table showing different forms of glyphosate and the net charge on glyphosate and the surface of TiO₂ as a function of pH.

TiO ₂ surface charge	Glyphosate species present	Net charge on glyphosate
+	$\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})_2$ \rightleftharpoons $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})\text{O}^-$	+1
	\rightleftharpoons $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})\text{O}^-$	0
	\rightleftharpoons $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})\text{O}^-$	-1
~	\rightleftharpoons $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})\text{O}^-$	-2
	\rightleftharpoons $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})\text{O}^-$	-3
	\rightleftharpoons $\text{HO}-\text{C}(=\text{O})-\text{CH}_2-\text{NH}_2^+-\text{CH}_2-\text{P}(=\text{O})(\text{OH})\text{O}^-$	-3

FIGURE 1: Glyphosate adsorption on the surface of Degussa P25 TiO₂ photocatalyst in the dark at different pH, assessed by measuring the concentration of free solution glyphosate as a function of solution loading of the catalyst.

This behaviour could be attributed to glyphosate containing three functional groups—phosphate, amino, and carboxylic—all of which can be protonated and deprotonated depending on individual functional group pK_a values.

The point of zero charge (pzc) of TiO₂ (Degussa P25) is widely reported as pH ~6.25 [33]. With this in mind, Table 1

shows the ionic structure of glyphosate indicating the net charge on the molecule and TiO₂ surface as different pH values.

At low pH values (~pH 3), the TiO₂ surface will be positively charged, while the phosphate group of glyphosate will be negatively charged leading to the expectation that the compound will adsorb the surface of TiO₂. In contrast, at higher pH values, the catalyst surface as well as the compound will be negatively charged, and hence adsorption in dark would not be expected, as evident from the experimental results shown in Figure 1. The Langmuir constants at pH 3 (glyphosate uncharged, where phosphate is -1 and the TiO₂ surface has a net positive charge) and pH 5 (when glyphosate is -1 (phosphate and carboxylate are both -1) and TiO₂ is slightly positive/near neutral) have been calculated as being 88610 and 1087 dm³ mol⁻¹, respectively. At pH 7 (when glyphosate is -2 (phosphate -2, carboxylate -1) and the TiO₂ surface has a net negative charge), there is little evidence of any adsorption. Results at pH 9 and pH 11 are similar to those at pH 7. Therefore, the Langmuir adsorption pattern is congruent with that expected from columbic arguments. The magnitude of the adsorption coefficient at pH 3 compared with that at pH 5 suggests that the primary locus of adsorption is through phosphate group.

3.2. Photocatalytic destruction of Glyphosate on TiO₂-loss of Glyphosate

Irradiation of an aqueous suspension of glyphosate (80 cm³, 1 × 10⁻³ mol dm³) in the presence of TiO₂ (Degussa P25,

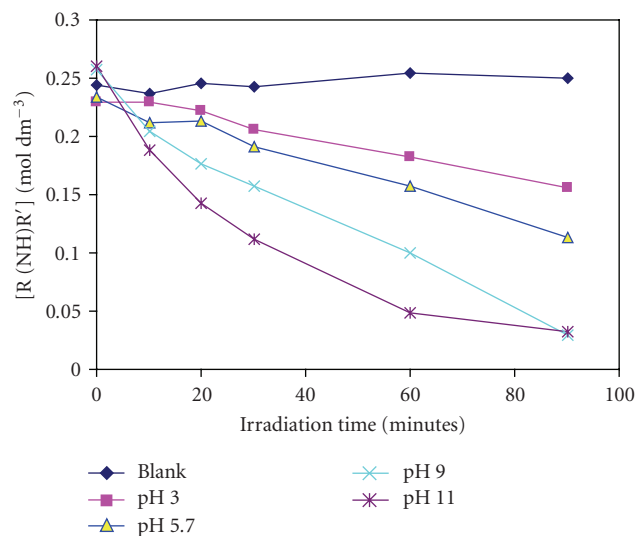


FIGURE 2: Photocatalytically induced loss of secondary amine functionality (measured using the N-nitroso method, see text) in glyphosate as a function of pH.

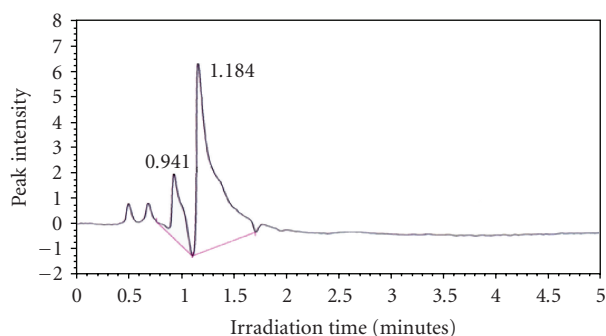


FIGURE 3: HPLC analysis of glyphosate in aqueous suspension of TiO_2 in the dark (zero irradiation time).

1 g dm^{-3}) using 312 nm light in a tubular photochemical reactor with constant stirring and bubbling of air led to a decrease in glyphosate concentration as a function of time. The photodegradation was investigated at pH values 3, 5.7, 7, 9, and 11. The decrease in secondary amine concentration (as determined by the N-nitroso method, vide supra) as a function of irradiation time at different pH values is shown in Figure 2. The net loss and rate of loss of secondary amine was found to increase with the increase in pH, the highest rate being observed at pH 11. Further, for data recorded at pH 3 and pH 5.7, there appears to be an induction period during which no loss of secondary amine is observed for a time immediately after the onset of illumination. We will return to this point below.

3.3. Photocatalytic destruction of Glyphosate on TiO_2 -product analysis

Figure 3 shows the HPLC trace of an aqueous suspension of glyphosate and TiO_2 at zero time irradiation indicating a strong peak at retention time $R_t = 1.184$ minutes and a medium peak at $R_t = 0.941$ minute. Irradiation of the

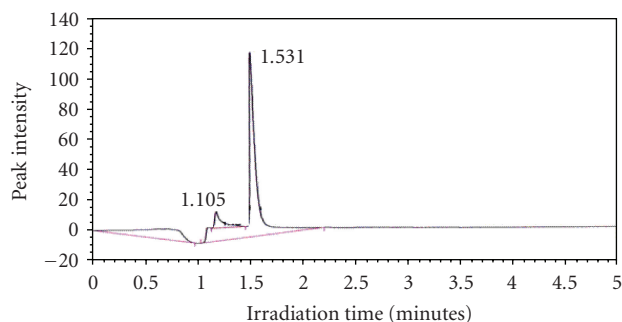


FIGURE 4: HPLC analysis of authentic sarcosine in aqueous solution.

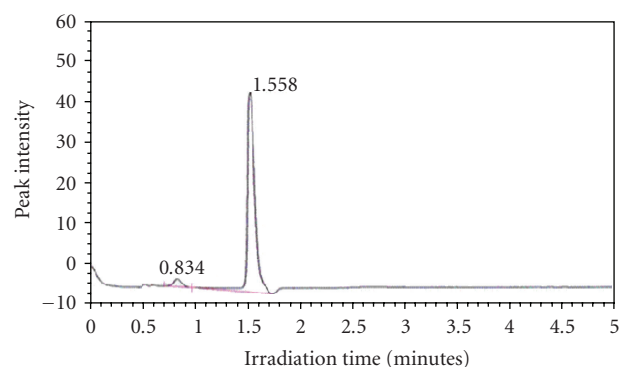


FIGURE 5: HPLC analysis of authentic glycine in aqueous solution.

solution for 90 minutes at pH 2 led to the formation of a product which is indicated by appearance of a strong peak at $R_t = 1.651$ minutes and a shoulder at $R_t = 1.599$ minutes in addition to the unchanged starting material (see Table 2). Said product exhibited an HPLC retention time and peak shape typical of a carboxylic acid (determined through comparison with HPLC analysis of methanoic and ethanoic acids on same instrument, not shown). However, during this period, no concomitant loss of secondary amine was observed leading us to conclude that the C–P bond had been broken in the formation of this product and that the product itself was most likely the amino acid sarcosine-N-methyl-2-aminoethanoic acid. The HPLC trace of authentic sarcosine is shown in Figure 4.

Primary product assignment was confirmed by adding authentic sarcosine to the photodegraded reaction mixture. Peaks in the HPLC trace recorded from this degraded sample/authentic sarcosine mix were found to be coincident with peaks in the HPLC trace recorded from the degraded reaction mixture alone (compare sample row 5 with sample row 4 in Table 2).

At longer times, both the concentration of secondary amine as determined by the N-nitroso method and the area of the peak at $R_t = 1.523$ minutes, associated with the secondary amine sarcosine, were seen to decrease with illumination time. The latter was accompanied by the concomitant formation of a second product peak at $R_t = 1.56$ minutes, in the vicinity of but not coincident with the sarcosine peak in the HPLC trace. Again, by addition of

TABLE 2: Table showing HPLC peaks retention times, R_t , for glyphosate, sarcosine, glycine (sample rows 1–3, resp.), irradiated mixtures of glyphosate at pH 3 and pH 11 (sample rows 4 and 6, resp.), and irradiated mixtures of glyphosate at pH 3 and pH 11 with authentic samples of sarcosine and glycine (sample rows 5 and 7, resp.). Peaks associated with glyphosate, sarcosine, and glycine are shown as **bold**, underlined, and double underlined text, respectively.

Sample	HPLC peak retention time (R_t)/minutes
1. Glyphosate (from Figure 3)	0.941 (min), 1.184 (s)
2. <u>Sarcosine</u> (from Figure 4)	<u>1.105</u> (w), <u>1.531</u> (s)
3. <u>Glycine</u> (from Figure 5)	<u>0.834</u> (w), <u>1.558</u> (s)
4. Glyphosate , 90 min Irradiation, pH3	0.948 (min), 1.061 (min), 1.13 (s), 1.599 (min), 1.651 (s)
5. Glyphosate (90 min irradiation, pH3) + authentic <u>Sarcosine</u>	0.948 (min), 1.039 (min), 1.117 (s), 1.523 (min), 1.651 (s),
6. Glyphosate (60 min irradiation, pH 11)	1.161 (s), 1.548 (min), 1.662 (min)
7. Glyphosate (60 min irradiation, pH 11) + authentic <u>Glycine</u>	1.108 (s), <u>1.543</u> (min), 1.665 (min)

s-strong, m-medium, w-weak.

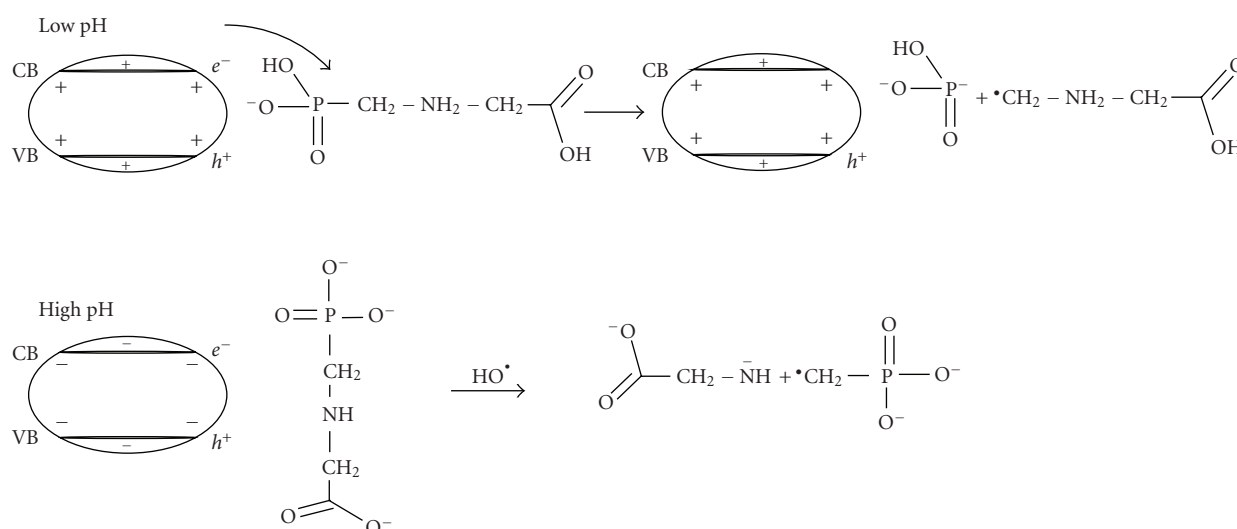


FIGURE 6: The interaction of glyphosate with the surface of TiO₂ in dark and the subsequent interaction of photogenerated electrons and hydroxyl radicals with glyphosate upon illumination of the TiO₂ with ultraband gap irradiation.

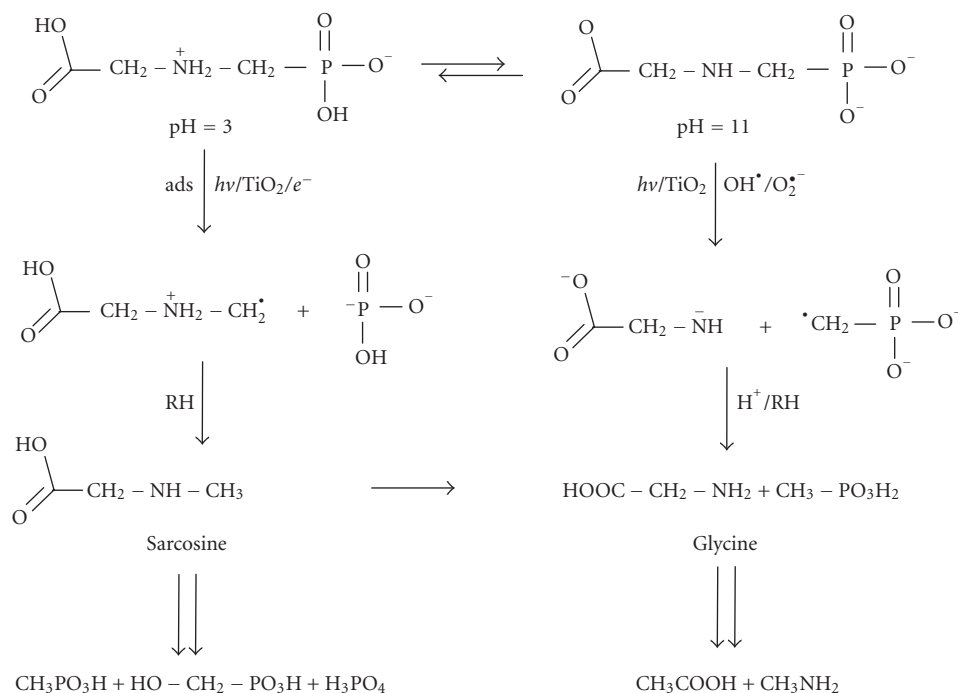
authentic material to photodegraded reaction mixtures, this second product was identified as glycine—2-aminoethanoic acid. The HPLC trace of authentic glycine is shown in Figure 5.

HPLC analysis of photodegraded reaction mixtures at pH 11 also indicates the formation of product (R_t = 1.548 and 1.662 minutes) in the vicinity of but not coincident with the sarcosine peak in the HPLC trace. No sarcosine peak was observed at any irradiation time at this pH. Following the methodology employed at pH 3, HPLC analyses of the photodegraded reaction mixture and samples of authentic materials shows that the primary reaction product is glycine (compare sample row 7 with sample row 6 in Table 2 and note coincidence of peaks at R_t = 1.548 minutes). This is most likely derived from C–N bond cleavage in nonadsorbed glyphosate (Figure 6).

The N-nitroso-based secondary amine analysis of Figure 2 indicates that at low pH, secondary amine is retained but glyphosate is lost due to loss of phosphate group and appearance of a peak in the carboxylic acid

region of the HPLC trace. In conjunction with the product identification and the fact that adsorption occurs at low pH, the results suggest that at low pH the photocatalytic reaction is most likely initiated by from-particle electron transfer. In contrast, under alkaline pH where little adsorption is seen to occur (Figure 1) solution-phase hydroxyl radical attack plays an important role, said hydroxide radicals having been generated in the reaction medium by photogenerated holes.

Figure 6 provides a schematic summary of these processes, wherein it is assumed that, at low pH, the photogenerated electron on irradiated TiO₂ attacks through -phosphate-adsorbed-glyphosate leading to the formation of carbon centered radical which then reacts to form nonadsorbed sarcosine. Readsorption of sarcosine onto the positively charged TiO₂ surface is then inhibited by the anticipated net positive charge on the molecule, arising from the protonation of the secondary amino nitrogen at this pH. At high pH, photoelectrochemically generated hydroxyl radicals attack nonadsorbed glyphosate, causing C–N bond fracture and ultimately forming glycine. It is pertinent to



SCHEME 2: Scheme showing the probable route for the degradation of glyphosate on irradiated TiO₂ at low and high pH.

mention here that photocatalysed degradation of glycine has a well-known mechanism and has been reported earlier [34]. Returning to pH 3, it can now be seen that sarcosine which is not adsorbed at the TiO₂ surface due to the loss of the phosphate group is then susceptible to similar solution-phase OH radical attack as nonadsorbed glyphosate at pH 11, so generating the same product, glycine. A mechanism consistent with these observations is shown in Scheme 2.

4. CONCLUSIONS

The pesticide derivative glyphosate has been found to degrade efficiently under alkaline conditions. Under acid conditions, it exhibits a strong, primarily coulombically driven dark adsorption onto the surface of the TiO₂ photocatalyst. Again, under acid conditions, the compound has been found to undergo efficiently photocatalytically promoted P–C bond cleavage leading to the formation of sarcosine and glycine like the main intermediate products. A probable degradation route involving a direct interfacial electron transfer reaction at low pH and hydroxyl radical /superoxide radical anion-mediated solution-phase oxidation at high pH on irradiated semiconductor particles has been proposed.

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