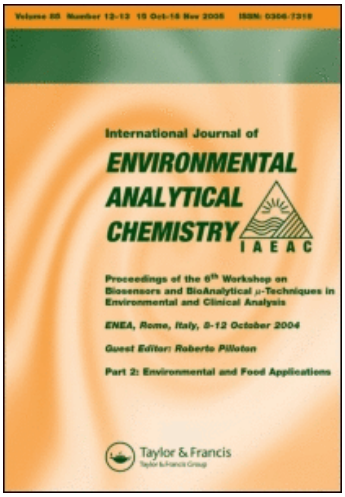

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Identification of hydrolytic metabolites of dyfonate in alkaline aqueous solutions by using high performance liquid chromatography – UV detection and gas chromatography-mass spectrometry

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Organophosphorus compounds, becoming the most commonly used pesticides in agriculture, are garnering more interest to be environment and health issues associated with their usage. These compounds run-off into surface water and leach into groundwater supplies where they have been detected. Dyfonate is commonly applied to the soil as an insecticide for the control of variety of insects. However, critical information on the transformation of dyfonate into its hydrolytic byproducts during water treatment is lacking, even though they have been used in the field for a long time. In this study, dyfonate hydrolysis at elevated pH levels, simulating a water treatment operation or similar process, was investigated. Dyfonate, an organophosphorus insecticide used to treat infestations primarily on corn, was investigated due to its greater rate of hydrolysis observed during our screening studies. The hydrolysis of dyfonate was investigated at pH 10, 11, and 12 in phosphate buffered water over the course of 7 days. Two hydrolysis products, thiophenol and phenyl disulfide, were detected. Dyfonate and thiophenol were analysed using high pressure liquid chromatography/UV detection (HPLC/UV), while phenyl disulfide was detected using gas chromatography/mass spectrometry (GC/MS). The relative concentration profiles of dyfonate and its hydrolysis products, as well as their transformation pathways, were also reported. The data from this study will help environmental researchers understanding the hydrolytic pathways of dyfonate and its metabolites at different pHs in a water treatment system.

Keywords: dyfonate; hydrolysis; hydrolysis products; transformation pathways

1. Introduction

Organophosphorus and carbamate compounds are among the most commonly used pesticides, and are on the verge of replacing organochloride compounds. The increased use of these compounds, particularly organophosphorus pesticides, raises concerns about their environmental and human health impact which to date are poorly addressed. Even though

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some studies have been performed on the pesticide transformation products in foods and estuarine water [1–8], the hydrolytic degradation process of pesticides in a water treatment facility has not been well studied. The primary concern on the environmental and health impacts of pesticides and their transformation products is due to the potential to affect the human nervous system. Additionally, some transformation products may have greater toxicity than the parent compounds [4,9,10]. It is thus imperative to study the transformation of specific pesticides and identify their transformation products.

O-ethyl S-phenyl ethylphosphonodithioate, also known as dyfonate or fonofos, is commonly applied to the soil as an insecticide for the control of aphids, corn borer, corn rootworm, corn wireworm, cutworms, white grubs, and some maggots on corn (95%), sugar cane, peanuts, tobacco, turf, and some vegetable crops. Dyfonate is typically applied with a water carrier using ground spray equipment at 1 to 4 lb/acre. It is considered a Class I toxicity pesticide (highly toxic) based on acute oral, dermal, eye, and inhalation effects [11]. Dyfonate is readily absorbed through skin, gastrointestinal, and respiratory tracts [12]. The molecular structures of dyfonate and its two potential hydrolysis products are shown in Figure 1.

Dyfonate is fairly water insoluble but has a moderate persistence (40 day field half-life) in soil [13]. Dyfonate readily hydrolyses but transformation products in water have not been identified [13,14]. The method of spray application for Dyfonate has the potential for run-off contamination of surface water and the moderate persistence can cause groundwater contamination at certain sites. Dyfonate has been found in groundwater at 0.01 to 0.1 $\mu g\,L^{-1}$ [15,16], and surface water at 0.01 $\mu g\,L^{-1}$ [17].

A few studies have isolated the transformation product of dyfonate [18,19], o-ethyl ethylphosphonothioic acid. However, both of these studies were in biological systems. The transformation products in biological systems may be very different from those in water treatment facilities because of the significant differences in matrices (such proteins, enzymes, and other macromolecules). In addition, the pHs in biological systems are very different from those of water treatment facilities. Therefore, the transformation process in biological systems may not apply to those of water treatment systems. However, the transformation products of hydrolysis in a water treatment facility have not been investigated, especially at different pHs. This information is very important, particularly to water treatment facilities that utilise raised pH processes, where hydrolysis can become an important transformation reaction.

In this study, dyfonate hydrolysis reactions were carried out at high pH in phosphate-buffered water systems to simulate treatment processes such as

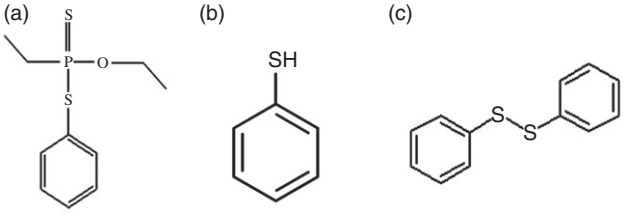

Figure 1. Molecular structures of dyfonate, thiophenol, and phenyl disulfide.

straight-lime or excess-lime softening. Dyfonate and two major hydrolysis products, thiophenol and phenyl disulfide, were separated, identified, and quantified using two methods of analysis. Thiophenol was separated with high performance liquid chromatography (HPLC), and identified and quantified by UV and photodiode array detection. Phenyl disulfide was separated using gas chromatography (GC), and identified and quantified using mass spectrometry (GC/MS). This study was intended to investigate the hydrolysis products of dyfonate, emphasising on identifying transformation products, mechanism, and relative reaction rate.

2. Experimental

2.1 *Reagents and chemicals*

Dyfonate (99.5%) was purchased from ChemService (West Chester, PA, USA). 2-Nitro-*m*-xylene (99%), thiophenol (≥99%) and phenyl disulfide (99%) were purchased from Aldrich (Milwaukee, WI, USA). Formic acid (96%, ACS grade) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Methanol (HPLC grade, 99.9%), acetonitrile (HPLC grade, 99.9%), water (HPLC grade, cas# 7732-18-5), sodium hydroxide (98.3%), and sodium phosphate (dibasic, 99%) were purchased from Fisher Scientific (Pittsburgh, PA, USA). D_{10}-Phenanthrene (98 atom % D) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The pH for the Na_2PO_4 buffer was adjusted with 1 M NaOH, which was prepared using HPLC/MS grade water.

Dyfonate, 2-nitro-*m*-xylene, thiophenol and phenyl disulfide were dissolved in methanol with the concentrations of 10 mg mL^{-1}, respectively as stock solutions and kept at −20°C for storage. Further dilutions of these stock solutions were applied depending on the individual experiments.

2.2 *Instruments*

The Hitachi M-8000 3DQ LC/MS^n systems with an L-7400 UV detector (San Jose, CA, USA), and the Waters 600 HPLC with autosampler and 996 Photodiode Array (PDA), were used for the analysis of dyfonate and one of its degradation products, thiophenol. Actually, MS was not used as a LC detector because both dyfonate and thiophenol were not ionisable by the MS ion sources. A Supelco C18 column (150 × 2.1 mm i.d., 5 μm, Bellefonte, PA, USA) was used for the separation at ambient temperature with a flow rate of 0.25 mL min^{-1}. The HPLC separation was performed at an isocratic elution with 50% deionised water containing 0.1% formic acid (pH 2.70) and 50% acetonitrile. The UV detector was set in a programmed mode with the wavelength 236 nm from 0 to 10 minute for thiophenol detection, and 240 nm from 10.1 min to 18 min for dyfonate detection. The injection volume was 20 μL.

An Agilent 6893 Series gas chromatograph (GC) with a 5973 Mass Selective Detector and a 7673 autosampler (Palo Alto, CA, USA) was used for separation and identification of dyfonate and phenyl disulfide. The carrier gas was high purity helium from Airgas (Ozark, MO) flowing at a rate of 1 mL min^{-1}. A 2-μL sample was injected in a splitless mode at an injection temperature of 280°C into a HP-5MS capillary column from Agilent (30 m × 0.25 mm i.d., 0.25 μm film thickness). The column had an inlet pressure of 13.5 psi, total flow of 54.1 mL min^{-1}, and injector purge flow of 50.0 mL min^{-1} at 0.3 minutes. A temperature gradient was programmed as follows: starting with an initial temperature

of 100°C, ramping at 40°C min^{-1} to 170°C, then 3°C min^{-1} to 185°C, 10°C min^{-1} to 220°C, and finally 60°C min^{-1} to 280°C, where it was held for 7 minutes. The total method time was approximately 18 minutes. The samples were scanned from 50 to 300 Da after a 3 minute solvent delay.

For all of the pH measurement, an Accumet XL 15 pH meter using an Accumet AccuCap combination pH electrode from Fisher Scientific (Pittsburgh, PA) was used through the entire study.

2.3 *Methods*

Hydrolysis experiments were conducted in duplicate at constant temperature (23.5 ± 1°C). The hydrolysis of dyfonate, thiophenol and phenyl disulfide were carried out individually under the same conditions, if not specified otherwise, with an initial concentration of 2.0 ppm (8.13 μM), 0.90 ppm (8.18 μM) and 0.45 ppm (2.06 μM), respectively. For HPLC/UV analysis, 2-nitro-*m*-xylene was chosen as an internal standard when quantification was performed. The reason to choose 2-nitro-*m*-xylene was that it has similar molecular structure as that of dyfonate and is stable under the conditions of this study, and it can be well separated from dyfonate and its transformation products in our study.

For GC/MS analysis, D_{10}-phenanthrene was chosen as an internal standard when quantification was performed. D_{10}-phenanthrene has been used as an internal standard for many pesticide studies in EPA methods and its function was to correct for the loss of analytes during sample preparation or sample injection. Liquid-liquid extraction (LLE) was preformed with 3.0 mL hexane added into 20 mL of reaction mixture after the hydrolysis reaction was completed. A 0.9 mL aliquot of the extract was mixed with 0.1 mL of internal standard (10 mg L^{-1} in methanol) to conduct a GC/MS analysis.

Hydrolysis of dyfonate at pH 10 was performed as following: a 30 μL aliquot of dyfonate stock solution (10 mg mL^{-1} in methanol) was spiked into 150 mL Na_2HPO_4 buffer (pH 10.02), forming an initial concentration of 2.0 mg L^{-1} (8.1 μM) for dyfonate. An initial sample of 0.95 mL reaction media was taken and mixed with 0.05 mL internal standard solution (0.2 mg mL^{-1}, in methanol) as an initial control for HPLC/UV analysis. A 20 mL volume of reaction media was taken, and mixed with 3.0 mL of hexane to perform a LLE as an initial control for GC/MS analysis. The remaining reaction media was distributed evenly to 5 amber bottles (reactors) with 20.95 mL reaction media in each bottle. Each bottle was wrapped with aluminum foil to prevent light penetration, and put on a shaker table at a speed of 200 rpm. At each desired time, 0.95 mL reaction media in each reactor was taken and mixed with 0.05 mL internal standard solution for HPLC/UV analysis, and the remaining solutions were used to conduct LLE for GC/MS analysis. Hydrolysis at pH 11.00 and 12.01 was carried out using the same procedure. Since we were simulating the conditions at water treatment facilities where straight-lime or excess-lime softening was applied, only high pH hydrolysis reactions in phosphate-buffered water systems were carried out in this study.

The hydrolysis of thiophenol and phenyl disulfide, at pH 10, 11, and 12, were carried out as the same way as that for dyfonate, except that the stock solution concentrations of the thiophenol and phenyl disulfide were 4.5 mg mL^{-1} and 2.25 mg mL^{-1}, respectively. The initial hydrolysis concentrations of thiophenol and phenyl disulfide were 0.90 mg L^{-1} (8.2 μM) and 0.45 mg L^{-1} (2.1 μM), respectively.

Blank experiments were performed in a similar way to the hydrolysis of samples except that the same volume of methanol was added to replace the stock sample solutions of dyfonate, thiophenol, and phenyl disulfide.

3. Results and discussion

3.1 *Identification of hydrolysis products of dyfonate*

Products of the hydrolysis reaction of dyfonate at pH 12 were analysed by HPLC/UV after 7 days of reaction. Figure 2 shows the chromatograms of blank, reaction mixture, standard, and internal standard. One of the hydrolysis products of dyfonate had the same retention time as that of thiophenol. To confirm the identity of the product, HPLC with PDA detector was employed to provide the spectra for thiophenol peak and the product peak. Both spectra, as shown in Figure 3, are identical, implying that one of the hydrolysis products of dyfonate is thiophenol. The same degradation product has been identified in the studies of dyfonate in biological microsomes [19–21]. In addition, standard addition of dyfonate was also used to further confirm the thiophenol identification. It is worth mentioning that the identification of hydrolysis products of dyfonate by LC/MS was not applied because none of the hydrolysis products can be ionised with the ionisation sources we have in our laboratory including electro spray ionisation (ESI), sonic spray ionisation (SSI), and atmospheric pressure chemical ionisation (APCI). This phenomenon needs to be further investigated.

To identify and quantify other hydrolysis products of dyfonate at different pH levels, hexane LLE followed by GC/MS analysis was applied. The aqueous layer was analysed by HPLC/UV after LLE of the hydrolysis of dyfonate with hexane to determine the extraction efficiency. Both the dyfonate and the thiophenol were no longer detectable after hexane extraction (chromatograms are not shown). This indicates that the efficiency of the LLE system for both compounds was high enough for further identification. Since this study was to simulate water treatment processes such as straight-lime or excess-lime softening, the hydrolysis of dyfonate from pH's 10–12 was systematically studied.

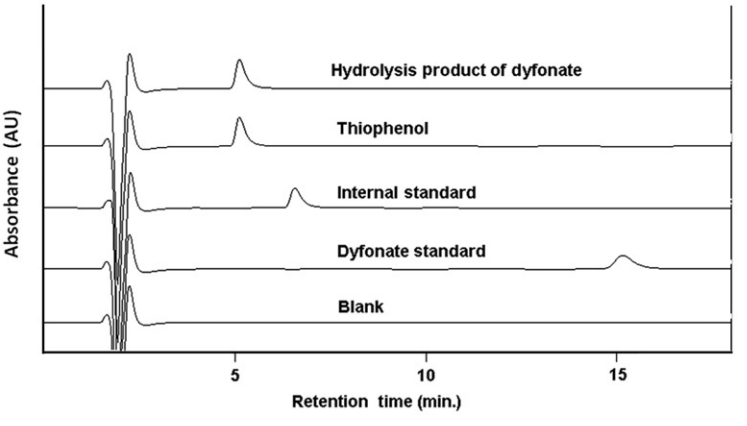

Figure 2. UV chromatograms of blank, hydrolysis product of dyfonate and other standards. The hydrolysis time was 7 days at pH 12.0.

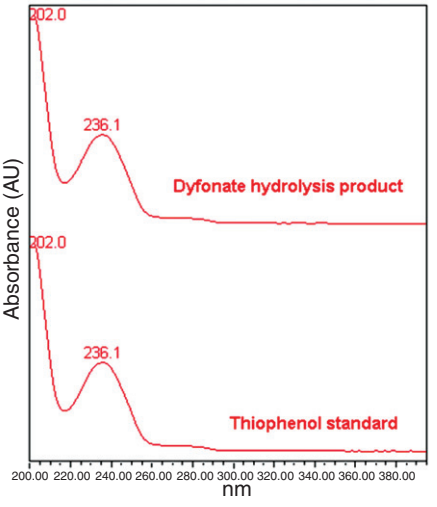

Figure 3. UV spectra of dyfonate hydrolysis product and thiophenol standard extracted at the retention time of the corresponding peak. The hydrolysis time was 7 days at pH 12.0.

The hexane extract of the hydrolysis of dyfonate was analysed by GC/MS, and the total ion chromatogram (TIC) of a dyfonate hydrolysis sample at pH 11.00 was shown in Figure 4a. There were two main peaks in the TIC of dyfonate hydrolysis sample with the retention times labelled in the figure. The peak with retention time of 6.442 min is dyfonate and the peak with retention time of 7.168 min is phenyl disulfide. The identifications of these two compounds were performed using standard addition and UV spectra from the PDA detector (not shown). The GC/MS spectrum of each peak was collected, and the identity of each compound was obtained by spectral matching software (as shown in Figure 4b and 4c). Based on the results from Figure 4b and 4c, these compounds were identified as dyfonate and phenyl disulfide. Since three independent identification techniques were used, the identifications of these peaks should be accurate.

To further confirm the identity of the peak with a retention time of 7.168 minutes, standard phenyl disulfide was spiked to a pH of 7 with a NaH_2PO_4 buffer, and extracted with hexane, followed by GC/MS analysis. The chromatogram and mass spectra were shown in Figure 5a and 5b, indicating that phenyl disulfide was the hydrolysis product of dyfonate at pH 11. Combining the results in Figures 2–5, the hydrolysis products of dyfonate change significantly with pH in the range 11–12. At $pH \leq 11$, phenyl disulfide was formed and at $pH \geq 12$, thiophenol was formed. Therefore, were studied to investigate the transformation mechanism.

3.2 *Time response of the hydrolysis of dyfonate, thiophenol and phenyl disulfide*

A 200-hour time response study was performed. Based on the results of quantitative determinations, the concentration profiles of the components in dyfonate hydrolysis reaction system were shown in Figure 6a, 6b, and 6c. We can conclude from the concentration profile in Figure 6a that dyfonate is completely degraded at pH 12 to form thiophenol after 48 hours. No other degradates were detected.

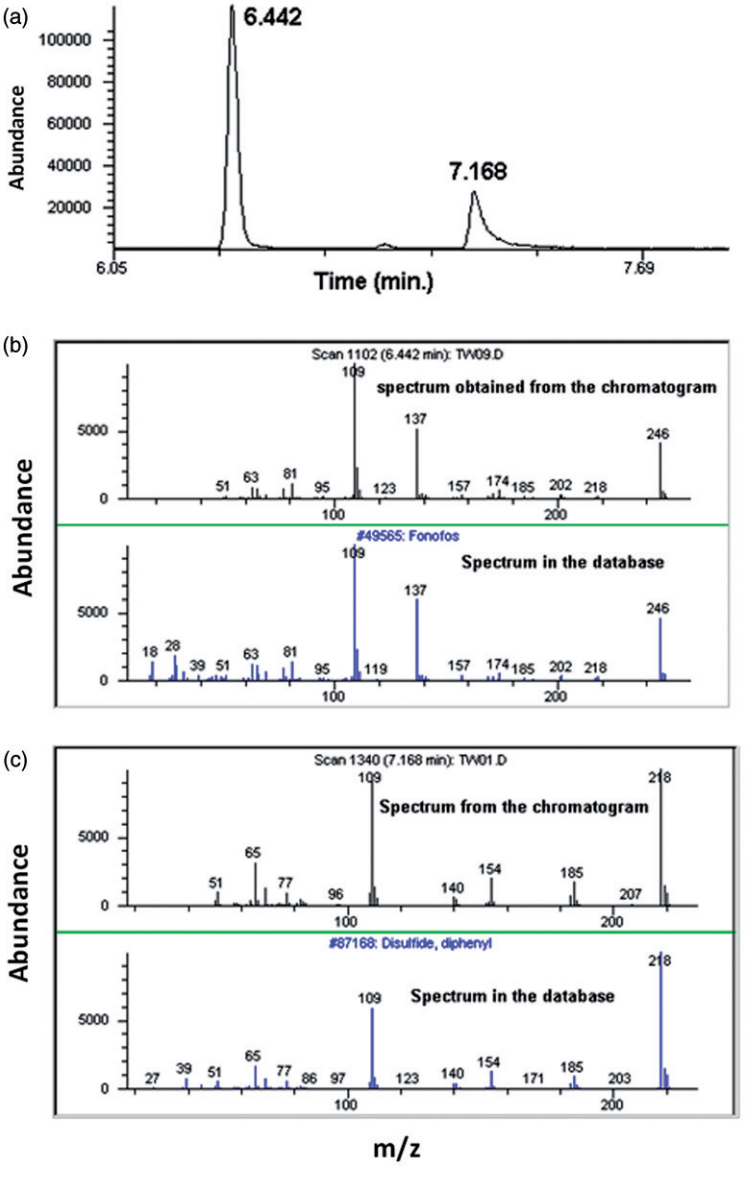

Figure 4. (a) GC/MS TIC of dyfonate hydrolysis sample at pH 11.00; (b) Mass spectrum of the peak with retention time 6.442 minutes and mass spectrum in the database. (Fonofos = dyfonate); (c) Mass spectrum of the peak with retention time 7.168 minutes and mass spectrum in the database. (Disulfide, diphenyl = phenyl disulfide).

Figure 6b shows the hydrolysis rate of dyfonate at pH 11. It demonstrates that the levels of both dyfonate and thiophenol are constant after 96 hours, and no other degradates are detected. Dyfonate and thiophenol reach an equilibrium state after about 90 hours. It is also clear that the hydrolysis rate of dyfonate at pH 11 is much slower than that at pH 12. Figure 6c shows that the concentration of dyfonate keeps constant

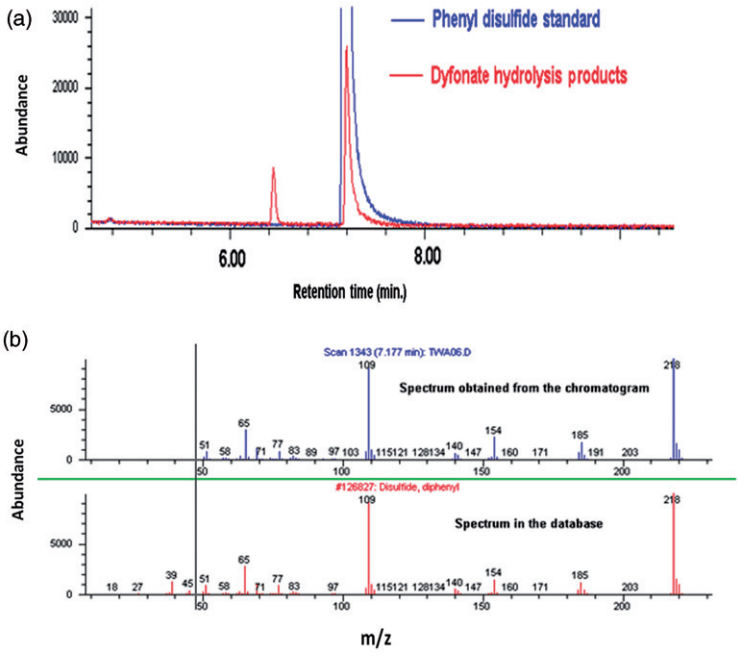

Figure 5. (a) GC/MS TIC of phenyl disulfide standard and hydrolysis product of dyfonate at pH 11; (b) Mass spectrum of phenyl disulfide standard and mass spectrum in the database.

throughout the whole experiment at pH 10, and no degradates were detected. It indicates that dyfonate is stable at pH 10.

The concentration profile of thiophenol hydrolysis at a pH range from 10–12 was shown in Figure 7. Figure 7a showed that thiophenol was very stable at pH 12. When solution pH was decreased to 11, as shown in Figure 7b, it was found that the level of thiophenol gradually decreased in time, while the concentration of phenyl disulfide, which was the degradate of thiophenol, increased slowly, and then kept almost constant throughout the whole experiment. No dyfonate was detected. It was interesting that the concentration of thiophenol decreased even faster at pH 10 than that of pH 11, which was shown in Figure 7c, while the concentration of phenyl disulfide, the degradate of thiophenol, increased faster accordingly than that at pH 11, then decreased very slowly throughout the whole experiment. It was suspected that unidentified compound(s) was associated with the process. But we were not able to identify the compounds at this time. Further study was planned to investigate this phenomenon. These results indicate that thiophenol is less stable at pH 10 than that at pH 11, but quite stable at pH 12. No dyfonate was detected in this experiment, which means that the degradation of dyfonate to thiophenol was an irreversible reaction.

When phenyl disulfide was hydrolysed at pH 11 and 12, it was found that phenyl disulfide degraded quickly and thiophenol was produced, as shown in Figure 8a and 8b. No dyfonate was detected. However, when phenyl disulfide was hydrolysed at pH 10, no thiophenol and dyfonate were detected, and the concentration of phenyl disulfide was maintained almost at the same level, as shown in Figure 8c, indicating that phenyl disulfide is rather stable at pH 10.

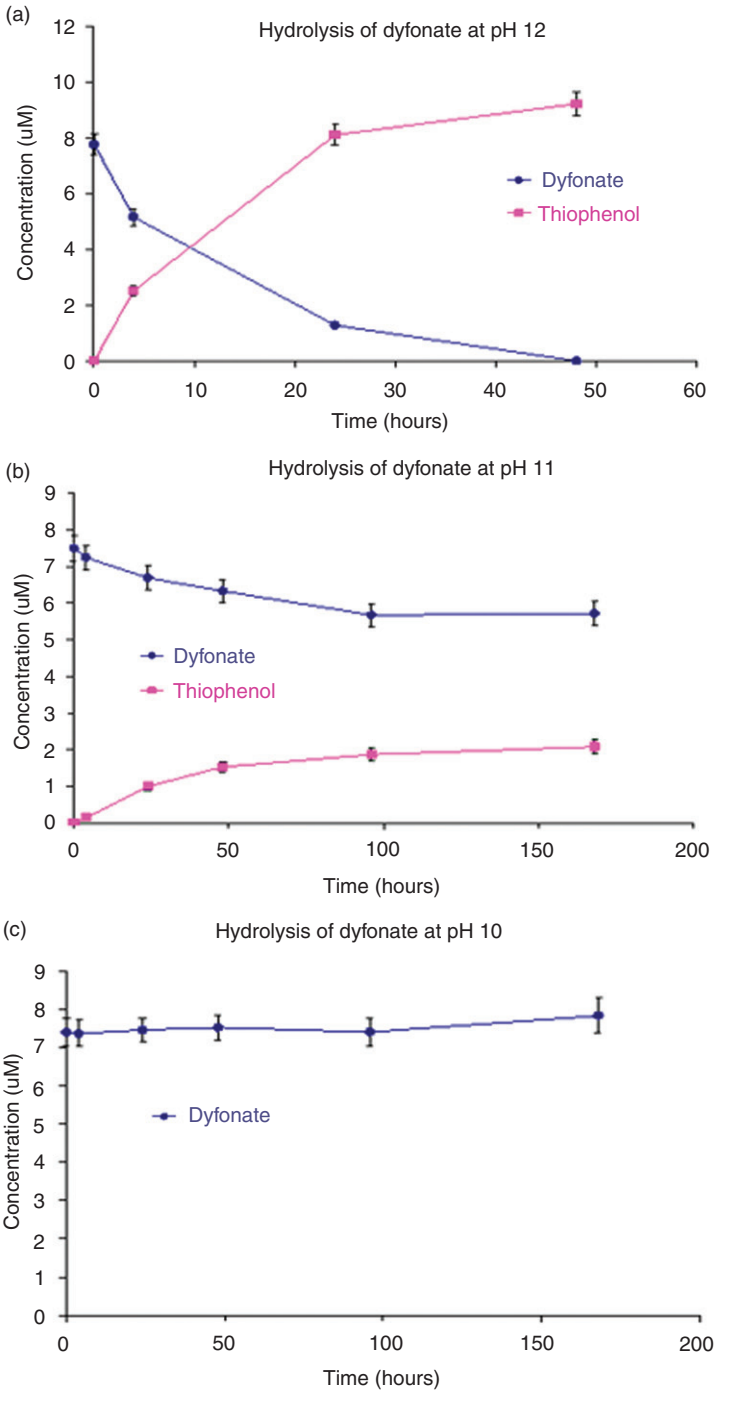

Figure 6. Concentration profile of the components in hydrolysis of dyfonate system at (a) pH 12, (b) 11, and (c) 10. Every data point is the average of duplicated measurements. The error bars represent the average difference of the duplicate. The range of relative percentage differences of the duplicate for dyfonate system is 8.60–11.67%.

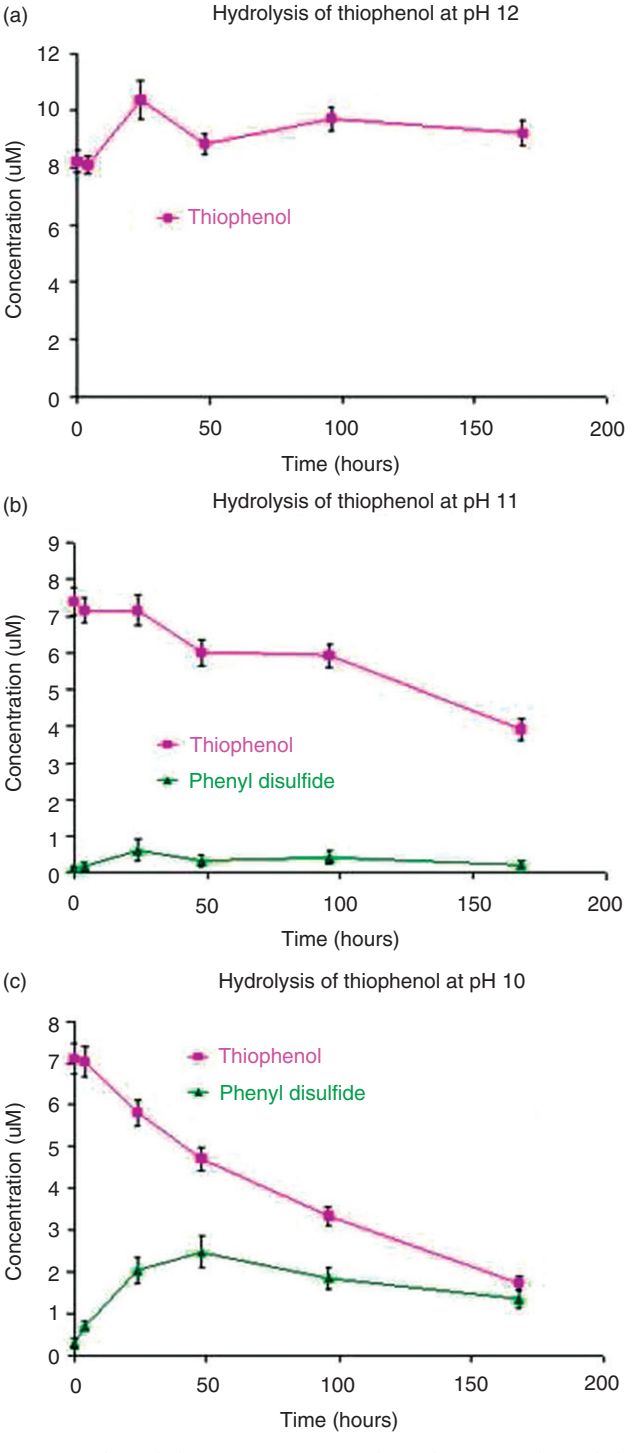

Figure 7. Concentration profile of the components in degradation studies of thiophenol system at (a) pH 12, (b) 11, and (c) 10. The other conditions are the same as those of Figure 5. The range of relative percentage differences of the duplicate for thiophenol system is 8.17–13.08%.

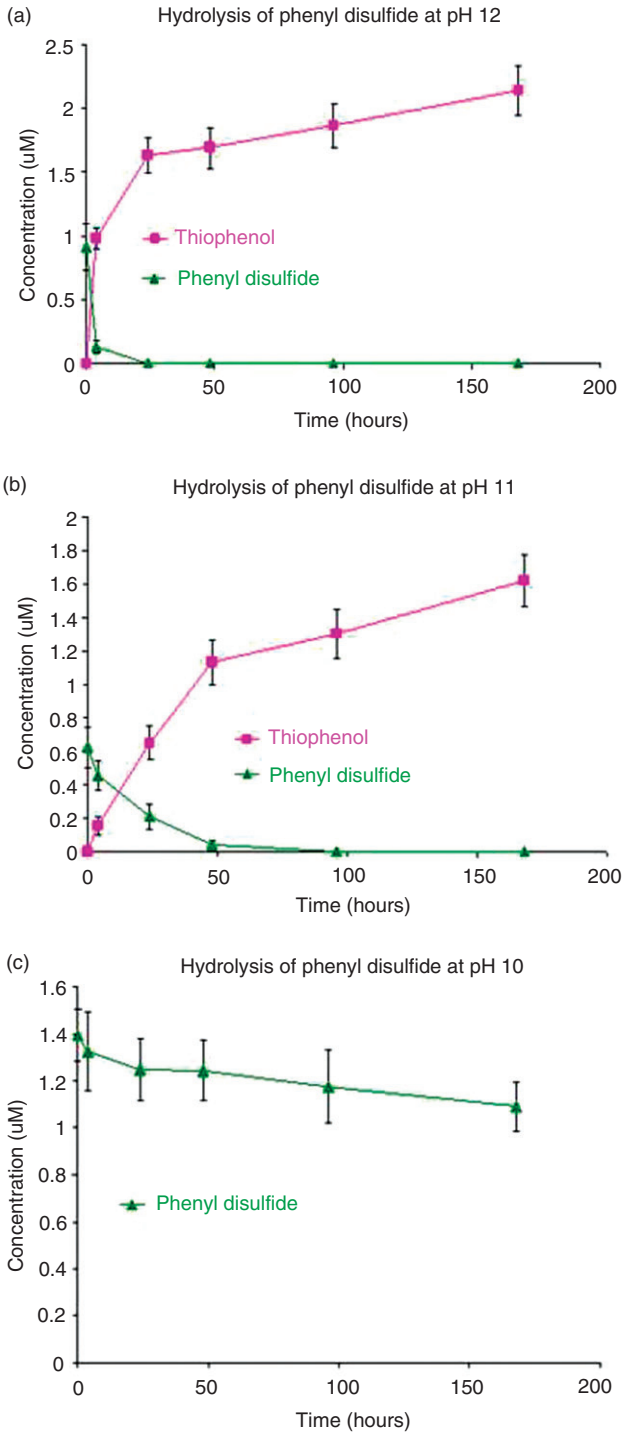

Figure 8. Concentration profile of the components in hydrolysis of phenyl disulfide system at (a) pH 12, (b) 11, and (c) 10. The other conditions are the same as those in Figure 5. The range of relative percentage differences of the duplicate for phenyl disulfide system is 17.07–18.08%.

Based on the results above, we can see clearly that phenyl disulfide was not detected in the hydrolysis of dyfonate at pH 11 (Figure 6b) but a significant amount of phenyl disulfide was detected in the hydrolysis of thiophenol at pH 11 and 10 (Figure 7b and 7c, respectively). The reason was that the thiophenol concentration generated through the dyfonate hydrolysis was much lower than the initial thiophenol concentration in the thiophenol hydrolysis system, hence, produced an even lower level of phenyl disulfide, which was below the detection limit of this MS instrument for phenyl disulfide.

It is worth indicating that every experiment was conducted in duplicate, and all of the data points are the averages of duplicated measurements. Due to the complexity in scaling relative percentage difference of the duplicate (%RPD) in Figures 6–8, the average difference of the duplicate, which was calculated by the following formula:

$$E = \left| \frac{X_1 - X_2}{2} \right|,$$

was used as error bars in Figures 6–8 to indicate the reproducibility of the duplicate. However, the relative percentage difference of the duplicate (%RPD) of each data point was also calculated using the equation:

$$\%\mathrm{RPD} = \left| \frac{X_1 - X_2}{2} \right| \times 100\%$$

and the %RPD ranges for each figure were indicated in the figure legend.

3.3 *Pathway of the degradation of dyfonate in alkaline aqueous solution*

Based on the time response studies, and mass balances of dyfonate hydrolysis, a pathway of the degradation of dyfonate in alkaline aqueous solution is proposed, which is shown in Figure 9. In an alkaline aqueous solution, dyfonate will be hydrolysed to produce thiophenol, as shown in our study. When the pH drops below 11, thiophenol will

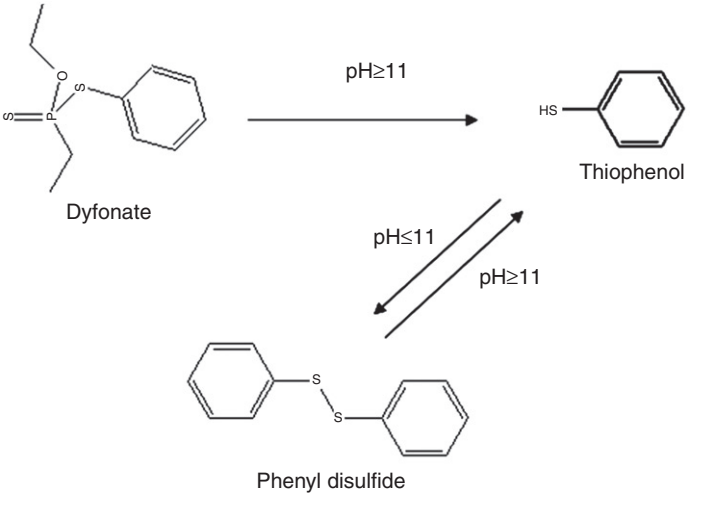

Figure 9. Proposed pathways of the degradation of dyfonate in alkaline aqueous solution.

degradate and produce phenyl disulfide. Based on our best knowledge, the formation of phenyl disulfide during the hydrolysis of dyfonate in water treatment processes has not been reported. The data from this study can serve as a valuable guidance by water treatment facilities for their water treatment process due to the fact that the hydrolytic degradation of dyfonate is very pH sensitive. A report indicated that phenyl disulfide can be reduced back to thiophenol using sodium borohydride followed by acidification [22]. However, formation of thiophenol from phenyl disulfide at a high pH aqueous solution (pH 11) was observed in our studies without any reducing agent in the solution (as we know). According to this reaction type (as it is occurred very often in biochemistry), it should be categorised as an oxidation-reduction reaction (from –S-S-bond to –SH). However, there is no reducing agent being identified. Therefore, there must be a different mechanism involved for this conversion, which deserves further investigation.

4. Conclusion

A comprehensive study on the hydrolysis of dyfonate and its degradation products in alkaline aqueous solution was conducted. The results show that dyfonate can be hydrolysed to produce thiophenol at pH 11 or higher. The thiophenol will react with each other to produce phenyl disulfide at pH 11 or lower. Phenyl disulfide can be transformed into thiophenol at pH 11 or higher. Therefore, both thiophenol and phenyl disulfide can be detected simultaneously only at pH 11. This reaction was discovered at the first time based on our knowledge. The data from this comprehensive study can serve as a valuable reference for water treatment facilities and environmental researchers. It will help environmental researchers to understand the hydrolytic pathways of dyfonate and its metabolites at different pHs in a water treatment system.

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