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Prasertwongchai, A., **Ratpukdi, T.**, Anotai, J., Khan, E. (2012) Degradation of Profenofos in Aqueous Solution by Vacuum Ultraviolet Process, *Proceeding of International Conference on Sustainable Environmental Technologies* 2[nd], Century Park Hotel, Bangkok, Thailand, April 26-27, 2012

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Nongsung, P., Anotai, J., Khan,E., **Ratpukdi, T.** Effect of Nitrate on the Removal of Profenofos Pesticides by Vacuum Ultraviolet. **In Preparation to submit to Journal of Hazardous Materials**

2012 International Conference
On Sustainavle Environmental
Technologies (ICSET)

Degradation of Profenofos in Aqueous Solution by Vacuum Ultraviolet Process

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Abstract
The degradation of profenofos (organophosphate pesticide) in water using VUV (185+254 nm) and UV (254 nm) processes was investigated. The effects of profenofos concentration, pH, bicarbonate, types of gas in aeration were studied. VUV process showed superior degradation performance than UV process. It was found that high concentrations resulted in decreasing of profenofos degradation. pH and bicarbonate were found to have little effect on profenofos removal. Aeration with N_2 and air increased the rate of profenofos mineralization significantly by 15% and 77%, respectively.

Keywords: profenofos, organophophate pesticide, vacuum ultraviolet (VUV), AOPs, drinking water

1. Introduction

Nowadays, the increasing demand of agricultural products has forced the producers to use more pesticides in order to protect their crops. The extensive use of pesticides has become a great concern since many of them will remain in the food chain and environments. The applied pesticides do not always stay at the sites but they can be also transported to other locations, especially the sources of drinking water. Profenofos (*O*-(4-bromo-2-chlorophenyl) *O*-ethyl *S*-propyl phosphorothioate) is one of the organophophorous pesticides that have been widely used for several crops (cotton, fruits, and vegetables) in many different parts of the world [1]. Profenofos is not only extremely toxic to fish and macro-invertebrates but also has both acute and chronic effects to human by inhibiting acetylcholinesterase enzyme activity which controls the nerve system [2]. Profenofos has been classified as a moderately hazardous (toxicity class II) pesticide by the World Health Organiztion and it has standard concentration of profenofos in water equal 0.3 µg/L as recommended by the Australia Drinking Water Guidelines for Pesticides[3]. Due to its extensive use, petsticides can remain in environment. From Jaipieam et al., (2009) studied organophosphate pesticide residues in drinking water from artesian well and found that water samples in agricultural areas contained profenofos exceeding the Australia Drinking Water Guidelines for Pesticides up to 1.5 and 4.4 times in dry and wet seasons, respectively.

To remove profenofos from water, it requires special treatment such as advanced oxidation processes (AOPs) which generates hydroxyl radicals for oxidizing the profenofos pesticide. Although AOPs were able to remove profenofos effectively, they may not be applicable to some areas, for example in remote agricultural areas where people have a limited resource of water supplies and might have to only rely on the contaminated source of drinking water. This is because AOPs are typically sophisticated setup, expensive, and require the addition of chemicals as well as well trained personnel for operation.

Vacuum Ultraviolet (VUV) is the process that has advantages over the others AOPs because it can directly create hydroxyl radicals by photolysis of water molecules (Eq.1 and 2). Its setup is fairly simple and easy to use. Based on these advantages and successful applications of VUV for other contaminants [4, 5], VUV process is suitable

3.1 Profenofos degradation with VUV and UV processes

Fig.2 shows the degradation of profenofos under VUV and UV irradiation. Apparently, VUV process had higher performance in profenofos removal than UV process for all three initial concentrations. For profenofos concentration 8.5 mg/L, 97% removal was observed for VUV process at 25 min while only 64% removal was achieved by UV process. Higher profenofos removal was by VUV process was due to the direct photolysis of 185 nm and 254 nm and reaction of hydroxyl radicals. As well known, in VUV photolysis of water, hydroxyl radicals and other oxidants are formed according to (Eq.1 and Eq.2). Hence, hydroxyl radicals, which have high power oxidant, can directly react with profenofos. But in UV process, profenofos was degraded only one process was direct photolysis at UV wavelength of 254 nm.

For the effect of initial concentrations, experiment at initial concentrations of 2, 4.5, and 8.5 mg/L were conducted. Profenofos removal trends seem to fit the first order kinetic model (Table 1). It is noticed that at higher concentration of profenofos the removal rate decreased. This result had similar result of Han et al. [7] who investigated photocatalysis of *p*-chloro benzoic acid in aqueous solution. From the Table 1, it could be explained that once profenofos was degraded there was intermediate products. The byproducts also react with hydroxyl radicals and absorb UV and VUV. As a result, these intermediate products competed with the parent compound (profenofos) for degradation. The higher the initial profenofos concentration resulted in more intermediate products formation which in turn lowered the profenofos degradation rate (Table 1)

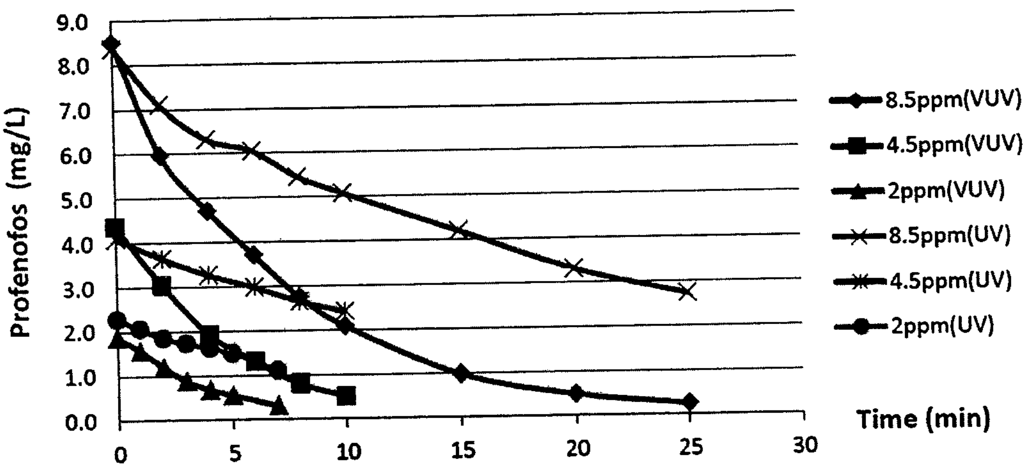

Figure2. Profenfos removal by VUV and UV processes. Effect of initial concentrations.

Table1. Degradation rate of profenofos by UV and VUV processes

Initial concentration (mg/L)	Degradation rate (k, min^{-1}) (r^2)	
	UV	VUV
2	0.0977 (0.9747)	0.2609 (0.9971)
4.5	0.0529 (0.9987)	0.2170 (0.9982)
8	0.0428 (0.9929)	0.1409 (0.9993)

3.2 Effect of initial pH

The effect of initial pHs were conducted at pH of 5, 7, and 9. From Fig.3, the profenofos degradation efficiencies all three initial pHs were similar (about 97%). And the rate constants for the degradation of profenofos all three initial pH ranged from 0.1409 to 0.1507 min^{-1}. Therefore, it can be concluded that initial pH have little impact on profenofos efficiency removal. Imoberdorf and Mohseni [8] reported the similar finding when studied the degradation of natural organic matter in surface water by VUV process.

to solve the profenofos contamination problem as a point of use treatment for people in remote area. This research investigated the degradation of profenofos using VUV process. The parameters affecting the process performance including pH, profenofos concentrations, bicarbonate concentrations and aeration were studied. The experiment of UV process was also conducted for comparison purpose.

$$H_2O + h\nu\,(<190nm) \longrightarrow H^{\bullet} + OH^{\bullet} \quad \text{(Eq.1)}$$

$$H_2O + h\nu\,(<190nm) \longrightarrow OH^{\bullet} + H^{+} + e^{-} \quad \text{(Eq.2)}$$

2. Materials and Methods

2.1 Water sample

Water samples used in the experiments were synthesized from profenofos (Syngenta Crop Protection, Ltd.) and deionized water.

2.2 Experimental setup

The reactor of VUV of process was a 2-L glass cylinder reactor which has a diameter of 8 cm and a height of 54 cm (Fig. 1). The volume of water used for experiment was 1.8 L. The reactor was equipped with a VUV lamp (model GPS383T5/VH/HO, Universal Light Source, Inc.) at the center of the reactor. Mixing was provided using magnetic stirring system and had glass tube in the reactor for drawing water sample. The lamp had a power input of 30 W per lamp. The quartz sleeves of VUV lamps are a synthetic grade and have a transmissivity of 85% at 185 nm. The VUV lamp has major emission spectra at 254 nm with relative emission of 10% at 185 nm. The photon flux at 254 nm was 9.39×10^{-6} Einstein/s corresponding to the power output of 4.43 W. The power output at 185 nm was 8.45×10^{-7} Einstein/s (0.55W) according to the information given by the lamp manufacturer. UV process was setup in the same reactor used for VUV process except that a UV lamp (model GPH383T5/L/HO universal Light Soure, Inc.) was replaced. The UV lamp has emission spectra only 254 nm.

2.3 Experimental Design and Procedure

For each experimental run, 1.8 L of water sample was treated in the reactor. In the profenofos concentration experiment varied initial concentration was 2, 4.5, and 8.5 mg/L for both VUV and UV process. For experiments requiring pH adjustment, H_2SO_4 or NaOH was added to adjust the pH of the water to the initial pH of 5, 7, and 9. $NaHCO_3$ was used to increase alkalinity to study the effect of alkalinity in VUV process. The concentration of bicarbonate were 100, 200, and 300 mg HCO_3^-/L. In aeration experiment, air and nitrogen (99.99%) were bubbled into the reactor through diffuser at flow rate 5 L/min to investigate the effect of aeration in the degradation and mineralization of profenofos.

2.4 Analyses

Profenofos levels were determined using gas chromatograph (GC 6890 series, Agilent Technologogies, Inc) equipped with a Ni^{63} electron capture detector with DB5-MS column (length 30 m, diameter 0.25 mm). Profenofos residues were extracted in hexane from water samples by using liquid-liquid extraction prior to analysis. The water sample to hexane ratio was 1:1. The operating condition: initial temperature 120°C, then heated at 7°C/min to a final temperature of 250°C. The total run time was 22.5 min. The splitless mode was used for injection. The injector temperature was set at 240°C and the detector temperature was at 300°C. Nitrogen gas (99.999%) was used as the carrier gas with a gas flow at 23.3 cm/s linear velocity. The mineralization rates of profenofos were determined by total organic carbon (TOC) analyzer (TOC-Vcph, SHIMADZU)

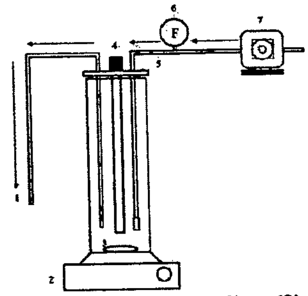

Figure1. Reactor of VUV and UV process: (1) glass tube sampling, (2) magnetic stirrer, (3) magnetic bar, (4) VUV and UV lamp, (5) gas diffuser (6) flow meter, (7) air pump and nitrogen tank

3. Results and Discussion

3.1 Profenofos degradation with VUV and UV processes

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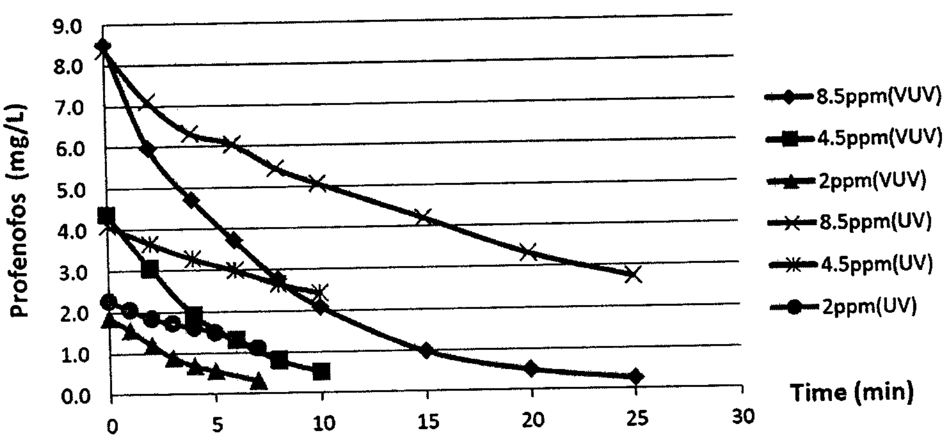

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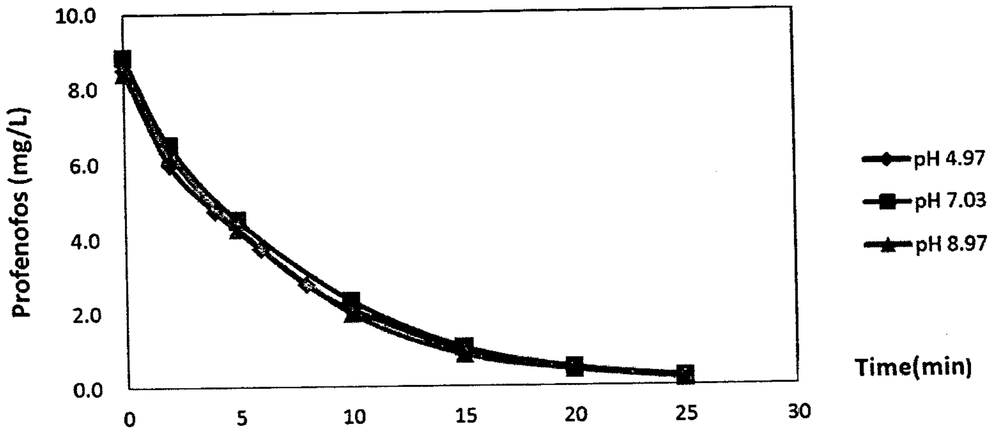

Figure 3. Profenofos removal by VUV process. Effect of initial pH.

3.3 Effect of bicarbonate

In order to study the effect of bicarbonate on degradation of profenofos in VUV processes were investigated by adding $NaHCO_3$ at different concentration to the water. From Fig.4, the higher concentration of bicarbonate decreased the profenofos degradation rates. The first order degradation rates were 0.1274, 0.1197, and 0.1048 min^{-1} for 100, 200, and 300 mg HCO^-_3/L, respectively. The addition of bicarbonate decreased the first order degradations decreased by 30-50% when comparing with that of no $NaHCO_3$. The decrease of the first order degradation rate should be from bicarbonate in water react with $OH^\bullet$. According to Eq.3 [8], bicarbonate was scavengers of $OH^\bullet$ and reduce the concentration of $OH^\bullet$ available to degrade profenofos. Another reason was the bicarbonate can absorb light in wavelength 185 nm [9] so reducing the photons available for the photolysis according to Eq.1 and 2. Similar results of the experiment was reported by Wu et al. [10] who experimented photo transformation of parathion and chloropyrifos and He et al. [11] who experimented removal microcystin-LR by UV-C/H_2O_2 process. Both of studies [10, 11] summarized that bicarbonate had adverse effect on AOPs which produced $OH^\bullet$ oxidized organic compounds in water.

$$OH^\bullet + HCO_3^- \longrightarrow CO_3^{\bullet -} + H_2O \qquad \text{(Eq.3)}$$

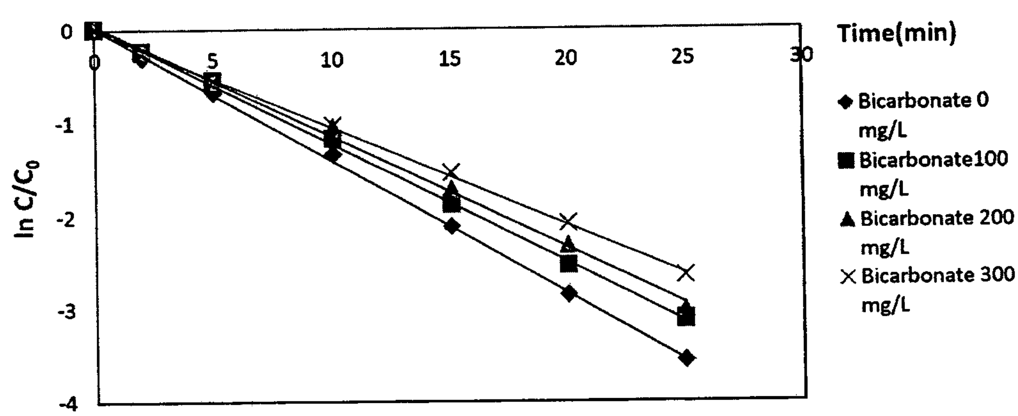

Figure 4. Profenofos removal by VUV process. Effect of bicarbonate.

3.4 Effect of aeration

The effect of the aeration on the degradation profenofos under VUV process was shown in Fig.5. From VUV process equipped with nitrogen and air purging had the first order degradation rate of profenofos higher than no aeration. It was found that aeration could enhance the degradation rate of profenofos. The aeration enhanced mixing [7] so that water can contact VUV light 185 nm and improve the photolysts of water. Because of the penetration of VUV light into water is limited due to its high absorption coefficients (1.8 cm^{-1} at 25°C;) [9], the intensity of 185 nm VUV light will decrease nearly 90% in 5 mm thickness of water. Hence, good mixing can improve the efficient of degradation. It is noticed that the first order degradation rates of aeration process with air was the same as that of with nitrogen. Tasaki et al. [4] studied the effect of type of microbubbles on the decolorization rate of methyl orange. They found that the type of gas in aeration and dissolved oxygen in aqueous solution did not affect the decolorization rate of methyl orange. Also, the type of gas in aeration was unaffected on degradation of profenofos.

Fig. 6 shows the effect of aeration on the mineralization of profenofos under VUV process. Unlike the degradation of profenofos itself, the type of gas in aeration had an effect on the mineralization. The VUV process with air provided 76% of profenofos mineralization while only 15% was observe with that of purging with nitrogen. Hence, purging air, which was increasing dissolved oxygen in aqueous solution, had great impact on profenofos mineralization. From Eq. 4-7 [12] described the process of mineralization that occurs in the VUV process. The peroxyl radicals are key intermediate on the way to the mineralization of organic compounds in aqueous solution. The recombination of carbon-centered radical following Eq.7 will happen under the condition of oxygen deficiency. For the VUV process with nitrogen the reactor was purging nitrogen about 10 min before start experiment. The initial dissolved oxygen concentration was at 0.39 mg/L and remained less than this level during the course of experimental run. This confirmed the condition of oxygen deficit took place. As a result, the VUV process purging with nitrogen gas had lower mineralization than VUV with air. In case of the reactor purging with air, the oxygen deficit is unlikely. Therefore, dissolved oxygen had important for efficient mineralization on profenofos in water.

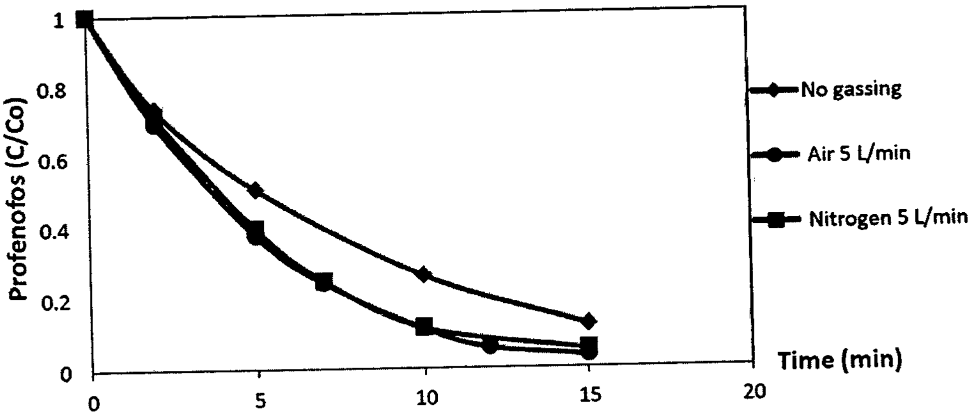

Figure 5. Profenofos removal by VUV processes. Effect of gas in aeration.

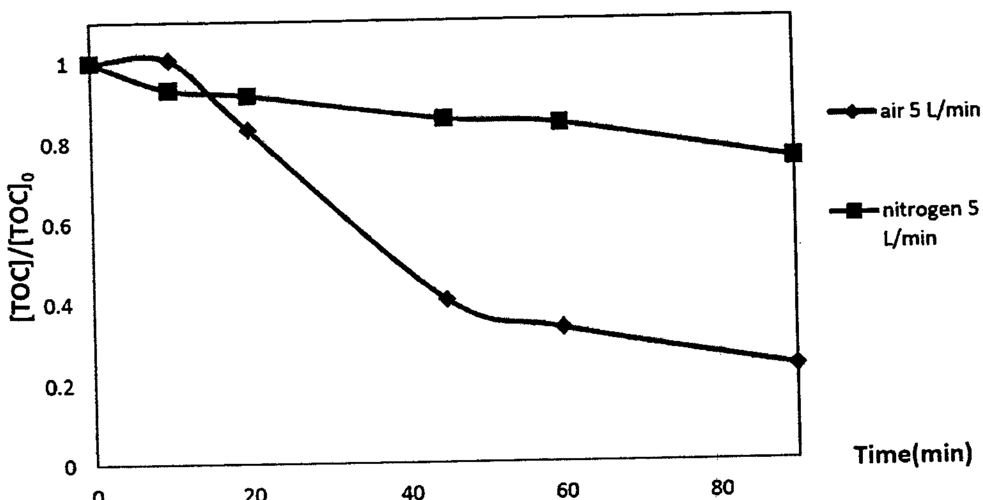

Figure 6. The mineralization of profenofos by VUV process. Effect of gas in aeration

$$R(\text{organic compound}) + OH^{\cdot} \longrightarrow R^{\cdot}(\text{carbon-centerea radias}) + H_2O \quad (Eq.4)$$

$$R^{\cdot} + {}_3O_2 \longrightarrow R\text{-}O^{\cdot}_2(\text{peroxl radicals}) \quad (Eq.5)$$

$$R\text{-}O^{\cdot}_2 + nO2 \longrightarrow CO_2 + H_2O + \ldots\ldots (\text{mineralization}) \quad (Eq.6)$$

$$R^{\cdot} + R^{\cdot} \longrightarrow R\text{–}R\ (\text{recombination of carbon-centered radicals}) \quad (Eq.7)$$

4. Conclusions

The findings of this research show that VUV process had potential to degrade profenofos in water. Increasing of profenofos concentrations resulted in decreasing of degradation rate. pH showed less impact to the process performance while bicarbonate has moderate impact. Gassing with air and nitrogen increased profenofos degradation rate significantly. Mineralization of profenofos in system purging with nitrogen gas decreased dramatically due to oxygen deficit.

Acknowledgments

This research was financially supported by Thailand Research Fund, Office of the Higher Education Commission, and Khon Kaen University, Thailand under New Researchers Grant (MRG5480184). This work was also conducted as a part of the research cluster "Fate and Removal of Emerging Micropollutants in Environment" granted by EHWM. Any opinions, findings, and conclusions or recommendations expressed in this research are those of the authors and do not necessarily reflect the views of The Thailand Research Fund.

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Effect of Nitrate on the Removal of Profenofos Pesticides by Vacuum Ultraviolet

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ABSTRACT

This research investigated effect of nitrate on the removal of profenofos (organophosphorous pesticide) in water using vacuum ultraviolet (VUV at wave lengths of 185 and 254 nm) and ultraviolet (UV at wave length of 254 nm). Nitrate concentrations (1, 10, and 50 mg/L) were varied. VUV degraded profenofos more rapidly than UV (99% vs 80% reduction in 15 min). VUV with low nitrate concentration had better profenofos degradation than VUV without nitrate. This was due to more $HO^{\bullet}$ formation. However, at high nitrate concentration, profenofos removal by VUV decreased. This could be because of the adsorption of VUV by nitrate molecules.

Keywords: organophosphorus pesticides, nitrate, hydroxyl radical, vacuum ultraviolet

INTRODUCTION

Profenofos is an organophosphorus pesticide that has been used in many counties to increase crop yields.. It is also used for several crops such as cotton, vegetable, fruit tree and tobacco (He *et al.*, 2010). Profenofos can inhibit acetyl cholinesterase enzyme (AChE) in the nervous system and breaks down signals between nerves and muscles on insects, however, profenofos also has similar effects on humans (USEPA, 1999). Consequently, profenofos has the potential to contaminate in surface and groundwater which are the sources of drinking water. Hence, the removal of profenofos from contaminated water sources is necessary.

Profenofos degradation can be achieved by the several methods. Current processes that can be used to remove profenofos and other organophosphorus peticides (OPs) include advance oxidation processes (AOPs). AOPs employ hydroxy radicals ($HO^{\bullet}$), which is non selective and strong oxidant, to degrade OPs or even mineralize them. UV based AOPs apply the principle of photolysis and photocatalysis that often require the addition of catalysts such as (H_2O_2), ozone (O_3), and TiO_2 to generate $HO^{\bullet}$ (Han et al., 2004). Vaccuum Ultraviolet (VUV) is one of AOPs that received much attention in the past decade. VUV was effectively degrade several contaminants in air and water such as indoor gaseous formaldehyde, pharmaceuticals, petroleums, and byproduct of industies (Yang et al.,2007; Drzewicz et al., 2010;Yu et al., 2012; and Arany et al., 2013). The advantage of VUV is that it does not require addtional chemicals for $HO^{\bullet}$ formation. Upon irradiation of VUV (λ< 190 nm), the molecule of water is splited to $HO^{\bullet}$ and $H^{\bullet}$ (equation 1 and 2) (Oppenländer et al., 2005)

$$H_2O + h\nu\ (<190nm) \longrightarrow H^{\bullet} + HO^{\bullet} \qquad (1)$$

$$H_2O + h\nu\ (<190\ nm) \longrightarrow HO^{\bullet} + H^{+} + e^{-} \qquad (2)$$

Nitrate, from inorganic fertilizer, is commonly present in natural water from agricultural area. NO_3^- could lead to the formation of $HO^\bullet$ when it is undergone UV photolysis from sun light (equation 3) (Zuo and Deng, 1998).

$$NO_3^- + H_2O + hv \longrightarrow NO_2 + OH^\circ + OH^- \qquad (3)$$

It has reported that nitrate can either promote or inhibit the degradation of organic compounds under UV process (Huang et al., 2013). Up-to-date, the information of how nitrate affect the contaminant degradation under VUV process is very limited. This research investigated effect of nitrate on the removal of profenofos at different conditions.

MATERIALS AND METHODS

Materials

Water sample was synthesized from profenofos (commercial grade 50%w/v) and deionized water (18.2 MΩ water, Millipore). NO_3^- prepared from KNO_3 (99.73%, RFCL limited, India). Samples were filtered through a 0.2 μm pore-size nylon syringe filter prior to analysis.

Experimental Setup and Procedure

The reactor was a 2-L glass cylinder reactor with diameter of 8 cm and equipped with a UV (model GPH383T5/L/HO universal Light Source, Inc.) or VUV lamp (model GPS383T5/VH/HO, Universal Light Source, Inc.) at the center of reactor. The volume of water sample in all experiments was 1.8 L. Mixing was provided by magnetic stirring system (> 50 rpm) and a glass tube in reactor for increasing the turbulence of water sample (Fig 1).

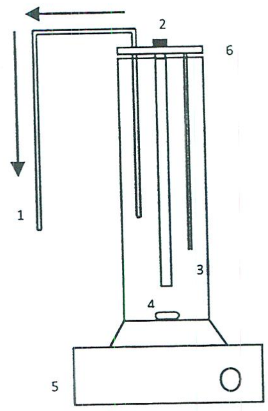

Fig.1 Reactor of UV and VUV process: (1) sampling tube, (2) lamp, (3) glass tube, (4) magnetic bar, (5) magnetic stirrer and (6) glass cylinder

Experimental Design

For the UV and VUV process, experiments were conducted with the initial profenofos concentration of profenofos 10 mg/L and pH at 7. The power of each UV (irradiation at 254nm) and VUV (irradiation at 185 and 254 nm) lamps in experiments were 30W. To study the effect of nitrate concentrations on the profenofos removal efficiency by VUV process, 1, 10 and 50 mg/L of NO_3^- were studied. UV experiment was conducted without nitrate addition. In each experiment, 40 mL of water sample was taken by siphoning at the reaction times of 0, 2, 5, 10, 15, 20 and 30 min for profenofos measurement. The diagram of experiment is shown in Fig 2.

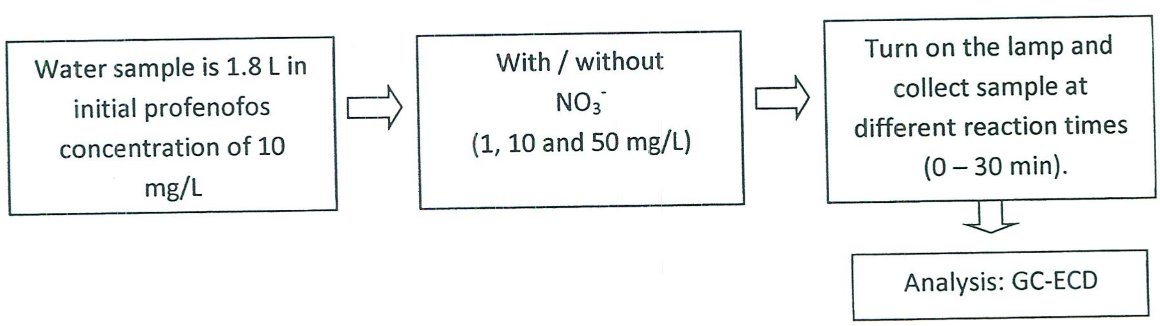

Fig. 2 Diagram of experiment

Profenofos Analysis

Profenofos solutions were extracted in n-hexane with 0.1% acetic acid using liquid-liquid extraction with the solvent and sample ratio of 1:1. Concentrations of sample were measured by gas chromatography with electron capture detector (GC-ECD, agilent) and column 4890/3100 (agilent). The temperature program was as the followings- initial temperature 120 °C, holding time 2 min, final temperatures 220 °C, and total runtime 4.5 min.

Electric Energy per Order (EE/O) calculation

EE/O can be calculated from the required electrical energy to degradation of a contaminant concentration by one order of contaminated water following equation 4 (Zoschke et al., 2012).

$$EE/O\ (kWh.m^{-3}) = \frac{P_{el} \cdot t \cdot 1000\ (\frac{L}{m^3})}{V \cdot 60\ (\frac{min}{h}) \cdot \log(\frac{C_0}{C})} \qquad (4)$$

Where P_{el} is electric power [kW], t is time [min], V is reactor volume [L], c_0 is initial concentration of the micropollutant and c is concentration of the micropollutant.

RESULTS AND DISCUSSION

Profenofos Removal with VUV and UV

The degradation rate of profenofos under UV and VUV irradiation were compared in Fig. 3. VUV had higher profenofos removal rate than UV. At 15 min VUV can remove nearly 99% of profenofos but UV only achieved 80% removal. This is because VUV lamp can emit wavelengths at 185 and 254 nm, which have more direct effect on photolysis than UV at wavelength of 254 nm. In addition, VUV has photon energy more than UV does. The high photon energy of VUV can induce water molecule to become hydroxyl radical which is strong oxidizing agent. Hydroxyl radical can directly react with profenofos; hence reaction of VUV is more rapid than UV.

For the effect of nitrate on profenofos removal, the initial profenofos concentrations of 1, 10 and 50 mg/L were studied. Nitrate serves as an additive to be a source of hydroxyl radical. Fig. 3 shows that the degradation rate of profenofos by VUV with nitrate was faster than without nitrate. As shown in Table 1, the first order kinetic constants of the profenofos removal at the higher concentrations of nitrate at 10 and 50 mg/L were slower than at 1 mg/L. This result was similar to report of Huang et al. (2013). It could be because the adsorption of VUV by nitrate molecules.

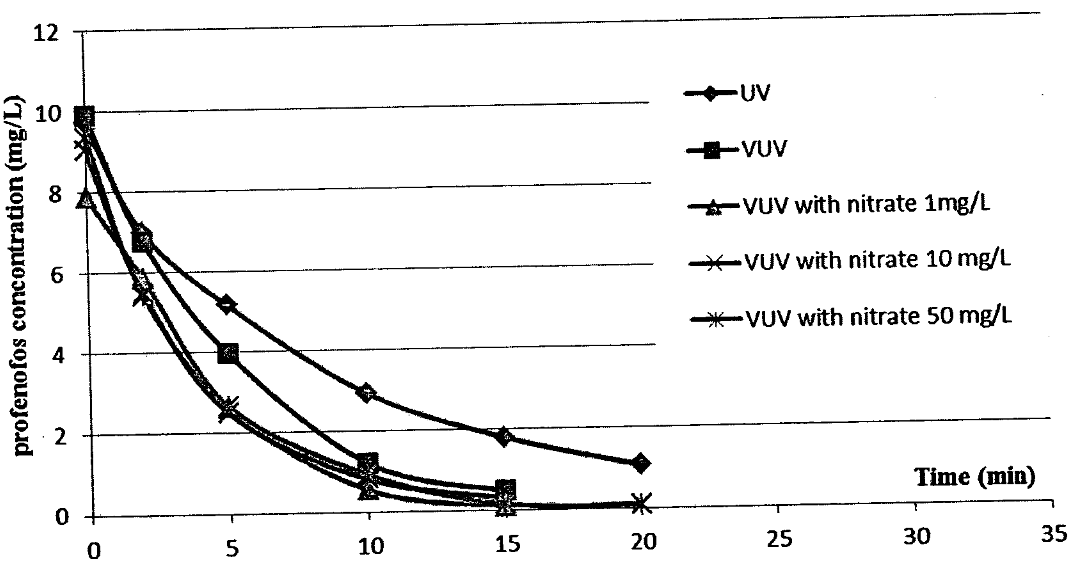

Fig. 3 Profenofos removal by UV and VUV

Table 1 Degradation rate of profenofos by UV and VUV

Process	Degradation rate (k, min^{-1}) (R^2)
UV	0.1136 (0.9939)
VUV	0.2036 (0.9975)
VUV with nitrate 1 mg/L	0.2777 (0.9849)
VUV with nitrate 10 mg/L	0.2334 (0.9958)
VUV with nitrate 50 mg/L	0.2434 (0.9794)

Electric Energy per Order (EE/O)

EE/O values for the degradation of 90% profenofos in water under different conditions are shown in Fig 4. The lowest EE/O was achieved by VUV with the nitrate concentration of 1 mg/L. At the high concentrations of nitrate, the EE/O values are slightly lower than only VUV irradiation. The EE/O information provided the economic costs for the electric energy of the operating process and can be used for process comparison. Hence, VUV irradiation is worth spending about energy more than UV irradiation.

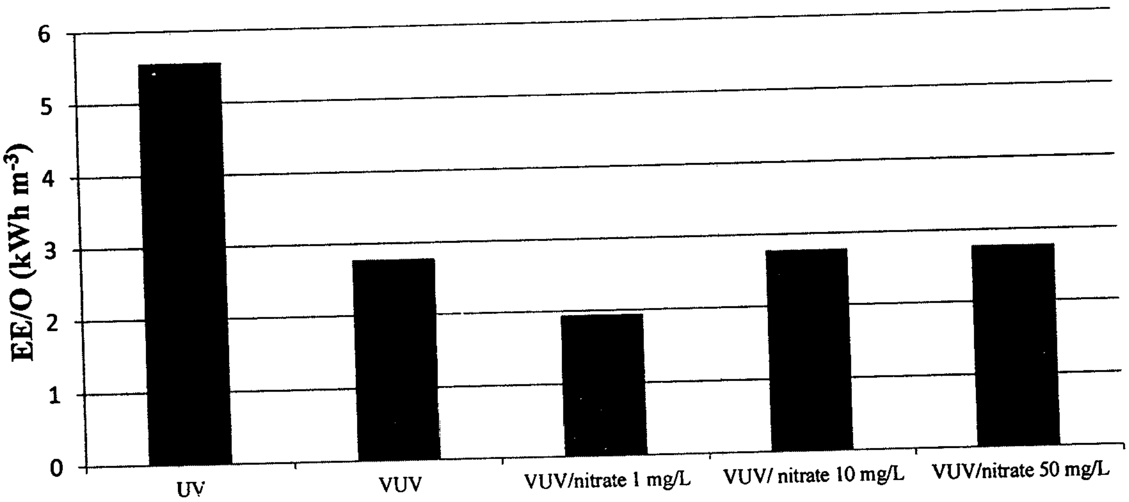

Fig. 4 EE/O by UV and VUV with/without the initial nitrate concentrations at 1, 10 and 50 mg/L for the degradation of 90% profenofos in water.

CONCLUDSION

The finding of this research shows that UV and VUV had ability to remove profenofos in water. The presence of nitrate resulted in the promotion of the degradation rate of profenofos under VUV irradiation. The kinetic of VUV with nitrate at the lower concentration of 1 mg/L is significantly more rapid than the higher concentrations of nitrate. This was due to more hydroxyl radical formation. The EE/O value showed that VUV is more economical than UV.

ACKNOWLEDGEMENTS

This research was financially supported by Thailand Research Fund, Office of the Higher Education Commission, and Khon Kaen University, Thailand under New Researchers Grant (MRG5480184) and also International Postgraduate Program in Environmental Management, Graduate School, Chulalongkorn University and a research program under Center of Excellence on Hazardous Substance Management (HSM), Thailand. Authors thanks staffs at Environmental Engineering laboratory, Khon Kaen University, Thailand for technical support. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of grant providers.

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