EFFECT OF NITRITE AND NITRATE ON THE REMOVAL OF PROFENOFOS BY VACUUM ULTRAVIOLET

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ผลกระทบของไนไตรท์และไนเตรทต่อการย่อยสลายโพรฟีโนฟอสด้วยแวคคูอัมอัลตราไวโอเลต

นางสาวปวันกร หนองสูง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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ปวันกร หนองสูง : ผลกระทบของไนไตรท์และไนเตรทต่อการย่อยสลายโพรฟีโนฟอสด้วยแวคคูอัมอัลตราไวโอเลต (EFFECT OF NITRITE AND NITRATE ON THE REMOVAL OF PROFENOFOS BY VACUUM ULTRAVIOLET) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ดร. ธัญลักษณ์ ราษฎร์ภักดี, 94 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาผลกระทบของไนไตรท์และไนเตรทต่อการย่อยสลายโพรฟีโนฟอส (สารกำจัดศัตรูพืชออร์แกโนฟอสฟอรัส) ที่ปนเปื้อนในน้ำด้วยแวคคูอัมอัลตราไวโอเลต (วียูวี ที่ความยาวคลื่น 185 และ 254 นาโนเมตร) เปรียบเทียบกับอัลตราไวโอเลต (ยูวี ที่ความยาวคลื่น 254 นาโนเมตร) โดยการเติมไนไตรท์ (0.1 0.5 และ 1 มก./ล. ของ ไนไตรท์) และไนเตรท (1 10 50 และ 100 มก./ล. ของไนเตรท) ที่ค่าความเป็นกรดด่าง (พีเอช) 5 7 และ 9 นอกจากนั้นยังวัดการสัมผัสของอนุมูลไฮดรอกซิล ผลการทดลองแสดงให้เห็นว่าวียูวี (ร้อยละ 87.9) มีประสิทธิภาพในการกำจัดโพรฟีโนฟอสได้สูงกว่ายูวี (ร้อยละ 72.1) ที่ความเข้มข้นโพรฟีโนฟอสเริ่มต้น 10 มก./ล. (พีเอช 7) และเวลาในการทำปฏิกิริยา 10 นาที จากผลของความเข้มข้นของไนไตรท์พบว่าที่เข้มข้นของไนไตรท์ที่ 0.1 มก./ล. มีการย่อยสลายโพรฟีโนฟอสได้สูงที่สุดเมื่อเปรียบเทียบกับความเข้มข้นอื่นๆของไนไตรท์ สำหรับไนเตรทอัตราในการย่อยสลายสูงสุดเกิดขึ้นความเข้มข้นของไนเตรทที่ 1 มก./ล. ซึ่งผลการทดลองสอดคล้องกับการเกิดขึ้นของอนุมูลไฮดรอกซิล การสัมผัสของอนุมูลไฮดรอกซิลยืนยันว่าไนไตรท์และไนเตรทในน้ำสามารถทำให้เกิดอนุมูลไฮดรอกซิลได้ สำหรับผลกระทบจากพีเอชพบว่าพีเอช 9 ส่งผลต่ออัตราการลดลงของโพรฟีโนฟอสมากที่สุด ผลที่ได้จากงานวิจัยนี้คือไนไตรท์และไนเตรทมีความสำคัญต่อการย่อยสลายของโพรฟีโนฟอสภายใต้กระบวนการยูวีและวียูวี ไนไตรท์และไนเตรทที่ความเข้มข้นน้อยสามารถกระตุ้นการเกิดของอนุมูลไฮดรอกซิลในขณะที่ความเข้มข้นสูงกลับดูดซับแสงวียูวีส่งผลให้ยับยั้งการเกิดปฏิกิริยา

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This research investigated effect of nitrite and nitrate on the removal of profenofos (organophosphorous pesticide) in water using vacuum ultraviolet (VUV, wavelengths of 185 and 254 nm) in comparison with UV (254 nm). Effects of initial nitrite concentrations (0.1, 0.5, and 1 mg/L as NO_2^-) initial nitrate concentrations (1, 10, 50, and 100 mg/L as NO_3^-), and initial pH of 5, 7, and 9 were studied. Also hydroxyl radical exposure was determined. The results showed that the VUV (87.9%) had superior degradation performance than that by the UV (72.1%) for the initial concentration of profenofos 10 mg/L (pH7) at 10 minute. Nitrite at 0.1 mg/L yielded the highest profenofos removal rate constant comparing to other nitrite concentrations. In case of nitrate, the highest removal rate constant of profenofos was at 1 mg/L. These results were agreeable to the formation of hydroxyl radical ($OH^\bullet$). The $OH^\bullet$ exposure confirmed that the presence of nitrite and nitrate can generate $OH^\bullet$. pH 9 was found to have the highest profenofos removal rate constant. The finding of the work suggests that nitrite and nitrate play important role in profenofos degradation under UV and VUV processes. At low concentration, nitrite and nitrate can induce $OH^\bullet$ formation. However, high concentration resulted in adsorption of VUV which in turn inhibit the reaction.

Field of Study:	Environmental Management	Student's Signature	....
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CHAPTER I
INTRODUCTION

1.1 Background

Organophosphorus pesticides (OPs) were developed in Germany in the 1940s and soon became the most widely used defense against agricultural, garden, and in the home pests to replace organochlorine pesticides (USEPA, 1998). OP structure consists of a phosphorus atom and bond of phosphoric (P=O) or phosphorothioates (P=S) (Gupta, 2006). Profenofos, *O*-(4-bromo-2-chlorophenyl) *O*-ethyl *S*-propyl phosphorothioate, is one of organophosphorus pesticide (Pehkonen and Zhang, 2002). Profenofos can inhibit acetyl cholinesterase enzyme (AChE) in the nervous system that breaks down signals between nerves and muscles on insects which also has similar effects on humans (USEPA, 2006a). Moreover it can cause nausea, dizziness and confusion when exposures at low level. At very high exposures, it causes respiratory paralysis and death. Following oral and dermal administration, profenofos has a moderate order of acute toxicity (USEPA, 2006a). In addition, World Health Organization classified profenofos as a moderately hazardous (toxicity class II) pesticide (WHO, 2011).

Profenofos was found in environment as a result of agricultural activities. Profenofos were distributed in different environmental fates, especially in soil and water. Since it has high sorption coefficient (Koc = 2000, Kow = 2.75×10^4), it is likely retained in soil or sediment (Lu, 2010; Malghani et al., 2009). In Pakistan, profenofos residue in soil was found at 2-520 μg/kg (Anwar et al., 2012). Profenofos contamination also was found in surface water and groundwater (Jaipieam et al., 2009; Laabs et al., 2007; Tasaki et al., 2009). In Thailand, profenofos had been detected in deep well drinking water during rainy and summer seasons in Songkla Province at 0.46 and 1.32 μg/L, respectively (Jaipieam et al., 2009). In Pathum Thani Province, Thailand, profenofos was found at concentration range from 0.11 to 1.11 mg/L in vegetable farm drained water as well (Tethgatuk et al., 2001). Moreover profenofos were detected and found in fish tissues at 12.6 and 2.1 ppb in autumn and winter, respectively (Abdel-Halim et al., 2006) and it is causing harmful on aquatic life (Ismail et al., 2009). Due to the toxicity of profenofos that post the threat to human, standard has been set in certain countries. The Australian Drinking Water Guidelines for pesticides had standard of profenofos concentration in water at 0.3 μg/L. Nowadays, profenofos has been used in many countries for increased crops yield from the attack of pests. It is also used in several agricultures such as cotton, vegetable, fruit tree and tobacco (He et al., 2010). In 2012, Thailand imported profenofos 380,862 kg for agricultural application (AED, 2014). Due to high consumption of this chemical, there is the potential of profenofos contamination in surface or groundwater which are the sources of drinking water. Hence, the removal of profenofos from contaminated water sources is extremely necessary.

Profenofos degradation can be achieved by the several methods. Current processes that can be used to remove profenofos and other OPs are such as biodegradation, adsorption, and advanced oxidation processes (AOPs). Biodegradation process used becteria and fungi to degrade OPs (Harish et al., 2013; Salunkhe et al., 2013), however, it took long time to degrade with removal efficiciencies around 70-85%. Removal of OPs by adsorption was accomplished using zeolite (Meng et al., 2011), α-Al_2O_3 (nanoparticle) (Wei et al., 2012), and humic fraction immobilize on silica gel (Lai and Chen, 2013) as adsorbents. Nevertheless, the spent adsorbents required further treatment. AOPs employ hydroxy radicals ($OH^{\bullet}$), which is non selective and strong oxidant, to degrade OPs or even mineralize them. The AOPs are such as fenton, ozone and UV based processes. For fenton reaction, ferrous ions and H_2O_2 are used to generate $OH^{\bullet}$. But it has some disadventages for practical application because of iron sludge production and low pH operation (required pH adjustment before and after reaction) (Badawy et al., 2006). Ozonation is effective oxidizing agent in water disinfection and contaminant degradation, dissolve ozone of 1.4 mg/L could degrade OPs 60-90 % in 30 min (Wu et al., 2007). However, ozonation requires complicate unit setup for gas feed prepration and potential of carcinogen formation such as bromate. UV based AOPs applies the principle of photolysis and photocatalysis that are often added the catalyst such as (H_2O_2), ozone (O_3), and TiO_2 to generate $OH^{\bullet}$ (Han et al., 2004). Vaccuum Ultraviolet (VUV) is another AOPs that recieved a lot of attention during the past decade. VUV has been studied to degrade several contaminants in air and water such as indoor gaseous formaldehyde, pharmaceuticals, petroleums, and byproduct of industies (Arany et al., 2013; Drzewicz et al., 2010; Yang et al., 2007; Yu et al., 2012). The advantage of VUV is that it does not require addtional chemicals for $OH^{\bullet}$ formation. Upon irradation of VUV (λ< 190 nm), molecule of water is splited to $OH^{\bullet}$ and $H^{\bullet}$ (detail of VUV chemistry is provided in literature review session).

1.2 Problem Statement

In natural water from agricultural area where pesticides often applied, nitrate and nitrite are commonly present (mainly from inorganic fertilizer). It was reported that both nitrate and nitrite could be undergone photolysis and generate $OH^{\bullet}$ (Sharpless et al., 2003). Several studies had investigated the effect of nitrate and nitrite upon UV irradiation (wavelength of 254 nm). It was found that the present of nitrate and nitrite could either promote (Huang et al., 2013; Keen et al., 2012) or inhibit (Ko et al., 2009) the degradation of contaminants. Keen et al. (2012) found that the formation $OH^{\bullet}$ in water under UV irradiation with nitrate (5 mg/L) was similar to that of UV-H_2O_2 (5 mg/L) (Keen et al., 2012). In contrast, nitrate was found to inhibit the photodegradation of 2,4-dichlorphenol (Ko et al., 2009). As a result, the presence of nitrate and nitrite could influence the photodegradation of organic contaminants. Up-to-date, the information of how nitrate and nitrite affect the contaminant degradation under VUV process is very limited. Also the formation of $OH^{\bullet}$ at the presence of nitrate and nitrite in VUV process has never been explored. This research aims to investivate the affect of nitrate and nitrite concentrations on the removal of profenofos by VUV process and formation of $OH^{\bullet}$ at different conditions.

1.3 Objectives

The main objective of this research is to investigate effect of nitrite and nitrate on profenofos removal by vacuum ultraviolet (VUV). The sub-objectives are as following:

1. To determine the effect of nitrite and nitrate concentrations on the profenofos removal by VUV in comparison with UV.
2. To determine the formation of $OH^{\bullet}$ under the presence of nitrite and nitrate under VUV

1.4 Hypothesis

1. The degradation of profenofos by VUV under the presence of nitrite and nitrate can be enhanced because of more $OH^{\bullet}$ generation.

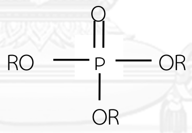
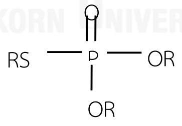
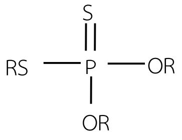
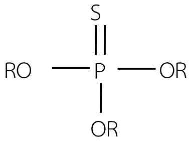
CHAPTER II

LITERATURE REVIEWS

2.1 General Information of Profenofos

Structures of organophophorus can be classified into 4 types: phosphates, phosphorothioates, phosphorodithioates, and phosphorothiolates (Pehkonen and Zhang, 2002) (Table 2.1). Phofenofos are categorized to phosphorothioates. Its structures and properties are shown in Figure 2.1 and Table 2.2, respectively.

Table 2.1 Type of organophosphorus (OP) (Gupta, 2006)

Type of organophosphorus	Structure	Example
Phosphates	 $\mathrm{RO}-\underset{\mathrm{OR}}{\overset{\mathrm{O}}{\mathrm{P}}}-\mathrm{OR}$	Chlorfenvinphos Monocrotophos Tri-*o*-cresylphophat
phosphorothioates	 $\mathrm{RS}-\underset{\mathrm{OR}}{\overset{\mathrm{O}}{\mathrm{P}}}-\mathrm{OR}$	Echothiophate Profenofos
phosphorodithioates	 $\mathrm{RS}-\underset{\mathrm{OR}}{\overset{\mathrm{S}}{\mathrm{P}}}-\mathrm{OR}$	Dimethoate Disulfoton Malathion
phosphorothiolates	 $\mathrm{RO}-\underset{\mathrm{OR}}{\overset{\mathrm{S}}{\mathrm{P}}}-\mathrm{OR}$	Bromophos Fenthion Parathion

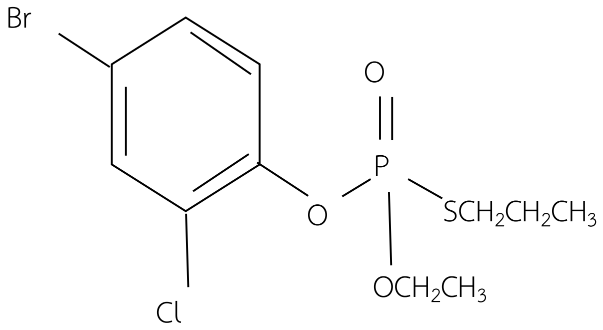


Figure 2.1 Chemical structure of profenofos

Table 2.2 Properties of profenofos (MSDS, 2014)

Properties	**Information**
Description	Pale yellow liquid
Empirical Formula	$C_{11}H_{15}O_3PSBrCl$
Molecular Weight	373.6 g/mole
Density	1.42±0.02 gm/cm^3
Solubility in water	28 mg/L at 25°C *Completely Soluble in organic solvent ethanol, (acetone, toluene, n-octanol, and n-hexane)
Vapor Pressure	1.24 x 10^{-4} Pa at 25 °C
boiling point	100°C (1.8 Pa)

Profenofos half-life are related on pH for example, at pH 5, 7, and 9 profenofos half-life are 104-108, 24-62 and 0.33 days, respectively (USEPA, 1998). It is noted that profenofos is unstable in high pH (alkali condition) and undergone hydrolysis (Malghani et al., 2009).

2.2 Profenofos Contamination in Environments

Nowadays, profenofos has been used in many counties for increased crops yield from the attack of pests. It is also used in several agricultures such as cotton, vegetable, fruit tree and tobacco (He et al., 2010). Lu (2010) detected several pesticide residue of agricultural soil in Philippine and found that profenofos was the third predominance pesticide (8.9 % or 0.003 mg/kg) in soil. In southern Caspian Sea basin, Haraz River, Iran, found profenofos contamination in surface water during May and April as well as in sediment were 0.2-0.5 μg/L, 0.1-0.4 μg/L and 0.1-0.6 mg/kg, respectively (Nasrabadi et al., 2011). In Mekong Delta, Vietnam, profenofos was found in surface water 0.35 μg/L (Toan et al., 2013). Profenofos contamination was found in groundwater (Jaipieam et al., 2009; Laabs et al., 2007; Tethgatuk et al., 2001). In Thailand, profenofos had been detected in deep well drinking water during rainy and summer seasons in Songkla Province at 0.46 and 1.32 μg/L, respectively (Jaipieam et al., 2009). In Pathum Thani Province, profenofos was found at concentration ranged from 0.11 to 1.11 mg/L in vegetable farm drained water as well (Tethgatuk et al., 2001). In Khonkaen province, profenofos contaminant in vegetable growing area during summer in ambient air, water and soil sediment are 0.0347 mg/m^3, 0.9520 mg/L and 41.8080 mg/kg, respectively. During winter, in Khonkaen province found profenofos 0.0020 mg/m^3, 0.3186 mg/l and 16.5956 mg/kg in ambient air, water and soil sediment, respectively (Harnpicharnchai et al., 2013). Moreover, profenofos were detected in fish tissues at 12.6 and 2.1 ppb in autumn and winter, respectively (Abdel-Halim et al., 2006). In 2012, Thailand imported profenofos 380,862 kg for agricultural application (AED, 2014). The information of profenofos contamination in environments was summarized in Table 2.3. Due to high consumption of this chemical, there is the potential of profenofos contamination in surface or ground waters which are the sources of drinking water.

Table 2.3 Summary of profenofos contamination

Environmental Fate		**Profenofos concentration**	**Reference**
Philippine			Lu (2010)
soil		0.003 mg/kg	
Iran			Nasrabadi et al. (2011)
surface water	(May)	0.0002-0.0005 mg/L	
	(April)	0.0001-0.0004 mg/L	
sediment		0.0001-0.0006 mg/kg	
Vietnam			Toan et al. (2013)
surface water		0.00035 mg/L	
Songkla, Thailand			Jaipieam et al. (2009)
groundwater	(rainy)	0.00046 mg/L	
	(summer)	0.00132 mg/L	
Pathum Thani, Thailand			Tethgatuk et al. (2001)
surface water		0.11-1.11 mg/L	
Khon Kaen, Thailand			Harnpicharnchai et al.,2013
ambient air	(summer)	0.0347 mg/m^3	
	(winter)	0.0020 mg/m^3	
water	(summer)	0.9520 mg/L	
	(winter)	0.3186 mg/L	
sediment	(summer)	41.8080 mg/kg	
	(winter)	16.5956 mg/kg	
fish tissues		0.000126-0.00021 mg/L	Abdel-Halim et al., 2006

2.3 Toxicity of Profenofos

Profenofos can inhibit acetyl cholinesterase enzyme (AChE) in the nervous system that breaks down signals between nerves and muscles on insects which also has similar effects on humans (USEPA, 1998). Profenofos can absorb into the human body from oral, inhalation and skin expose. Symptoms usually appear within 24 hours after exposure or at high exposure it can cause of respiratory paralysis and death only in 5 minute (USEPA, 2006a). Profenofos was great generators of free radicals like reactive oxygen species that can damage on cell for example: damage of DNA, oxidations of polydesaturated fatty acids in lipids, oxidation of amino in proteins, and oxidatively inactivate specific enzymes by oxidant of co-factors (Greish et al., 2011). These free radicals could be the causes of cancer, Alzheimer, cardiac reperfusion abnormalities, kidney disease, fibrosis, etc. (Greish et al., 2011). Because of profenofos is highly toxicity for human health then the standard was set. The Australian Drinking Water Guidelines for pesticides had standard of profenofos concentration in water at 0.3 μg/L. U.S. Geological Survey (USGS) has set guideline value of profenofos for The Health-Based Screening level (HBSL) on drinking water quality at 0.4 μg/L (Greish et al., 2011). Additionally, the acute and chronic recommendation by EPA chronic reference dose were 0.002 mg/kg body weight (bw) and 0.0002 mg/kg bw for females and 0.00031 mg/kg bw and 0.000031 mg/kg bw for males.

2.4 Vacuum Ultraviolet

Vacuum Ultraviolet (VUV) refers to ultraviolet wavelength between 140 to 190 nm (Gonzaleza et al., 2004). Under VUV irradiation (wavelength < 190 nm), water is homolysis into hydrogen ion, hydrogen radical and $OH^{\bullet}$ (equation 2.1 and 2.2) (Oppenländer et al., 2005)

$$H_2O + h\nu\ (<190\text{nm}) \rightarrow H^{\bullet} + OH^{\bullet} \qquad (2.1)$$

$$H_2O + h\nu\ (<190\text{ nm}) \rightarrow OH^{\bullet} + H^{+} + e^{-} \qquad (2.2)$$

The light sources of VUV irradiation include excimer lamp and low pressure mercury lamp. The excimer lamp can emit photon in various wavelengths depending on excimer gas (Ne, Ar, Kr, and Xe) or gas mixture (F, Cl, Br, and I) that contain in the lamp (Oppenländer, 2003). Another VUV light source is low pressure mercury (Hg) lamp which emits the wavelength at 254 nm and 185 nm. The lamp was enveloped with high purity quartz that transmits the radiation of mercury fluorescence at 185 nm. The radiant power of 185 nm is approximately 10 % of the radiation of 254 nm (Oppenländer, 2003). Low pressure Hg lamp as VUV light source was used in this research because it emits wavelength only 185 nm and 254 nm which can be controlled and compared efficiency.

2.5 Factor Affecting VUV Process

2.5.1 pH

pH is one of important factor that have effect on the performance of VUV process. Huang et al. (2013) studied on 4-tert-octylphenol degradation under VUV process and reported that at the removals of 4-tert-octylphenol were about 70% pH 3 and 6 while 40.7% removal was achieved at pH 10. Their finding was consistent with Tasaki et al. (2009) who found that pH nearly 7 had highest methyl orange degradation than very low or high pH (90% removals for pH 4.0-6.9 and 20% removals for pH 2.9 and 10.8). Furthermore, Ratpukdi et al. (2010) reported that pH 7 had the highest dissolved organic carbon (DOC) mineralization rate (37.01%) comparing to pH 9 and 11 which removal efficiency were 18.05 and 18.89 %, respectively. This was because at high pH, $OH^{\bullet}$ can decay into O^{-}. The disappearance of $OH^{\bullet}$ caused the decrease of removal rate (Huang et al., 2013). However, effect of pH on some compound was not predictable because of compound specific (Moussavi et al., 2014; Shemer and Linden, 2006).

2.5.2 Temperature

During irradiation experiment, the light source (lamp) generates heat. Da-Zhang et al. (2008) compared temperature effect (15, 25 and 40 °C) on the degradation of quinoline by VUV process and reported the degradation rates increased as the temperature increased by 0.18±0.01 min^{-1}, 0.45±0.02 min^{-1} and 0.66±0.02 min^{-1}, respectively. Similar the study of Abdel-Gawad et al. (2010) point out temperature effect on the hydrolysis of ^{14}C-ethyl prothiofos (organophosphorus pesticide) at 25°C, 40°C, and 55°C at pH 5, 7, 8 and 9 found that at pH 9 and 55°C hydrolysis rate is higher than other temperature. The low pressure Hg lamp that used in this study can be operated temperature approximately 40 °C during light emission (USEPA, 2006b).

2.5.3 Bubbling gas

The type of gas bubbling into the solution affected the degradation of contaminants. Da-Zhang et al. (2008) reported the rate of degradation of quinoline was in the order $O_2 >$ air $> N_2$. Under VUV process, O_2 promoted removal rate (100% after 40 min) better than N_2 (100% after 60 min) on the degradation of methyl orange (Tasaki et al., 2009). This could be explained that the present of O_2 can be the source of $OH^{\bullet}$ in VUV process (Hochanadel, 1962).

$$O_2 + H \rightarrow HO_2 \tag{2.3}$$

$$H + HO_2 \rightarrow H_2O_2 \tag{2.4}$$

$$H_2O_2 + hv_{185nm} \rightarrow 2OH^{\bullet} \tag{2.5}$$

$$H_2O_2 + hv_{254nm} \rightarrow 2OH^{\bullet} \tag{2.6}$$

$$H_2O_2 + OH^{\bullet} \rightarrow OH_2^{\bullet} + H_2O \tag{2.7}$$

$$OH_2^{\bullet} + HO_2^{\circ} \rightarrow H_2O_2 + O_2 \tag{2.8}$$

$$H_2O_2 + O_2^{\bullet} \rightarrow OH^{\bullet} + O_2 + HO^{-} \tag{2.9}$$

2.5.4 Additional oxidants

Additional oxidants (e.g. O_3, H_2O_2, Fe_2O_3 or TiO_2) under light irradiation can enhance $OH^{\bullet}$ formation in which it reacts with target contaminants and intermediate species (Han et al., 2004). $OH^{\bullet}$ is powerful, effective, non-specific oxidizing agent because it has high electronegative oxidation potential that show in Table 2.4 (Goi, 2005).

Table 2.4 Relative oxidation power of some oxidants.

Oxidant	**Oxidation potential, eV**
Hydroxyl radical	2.80
Nascent oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.77
Perhydroxyl radical	1.70
Hyprochlorus acid	1.49
Chlorine	1.36

Han et al. (2004) studied photolysis and photocatalysis degradation of p-chlorobenzoic acid in water. The result showed that the removal efficiencies were in the order of VUV/ TiO_2 > VUV > UV/TiO_2 > UV.The equations below explain some mechanisms of $OH^{\bullet}$ formation with additional oxidants in VUV process.

$$O_3 + H_2O + hv_{185nm} \rightarrow O_2 + H_2O_2 \quad (2.10)$$

$$TiO_2 + H_2O \rightarrow TiO_2 + OH^{\bullet} + H^{+} \quad (2.11)$$

2.6 Profenofos and Organophosphorus Degradation by UV based AOPs

Over the last two decades, UV based AOPs for water contaminant degradation has been studied extensively. The UV based AOPs is the combinations of photolysis from ultraviolet irradiation, oxidation and catalysis to generate $OH^{\bullet}$ (Badawy et al., 2006). OPs is the one of hazardous substance that likely degraded by UV process. In general, OPs can be degraded by direct photolysis under irradiation from sunlight (280-320 nm) and/or combine with photosensitize as iron, nitrate ion and organic matter (Zamy et al., 2004). AOPs based on UV frequently applied wavelength at 254 nm to degrade compounds. It can completely degrade pesticides to water carbon and mineral salts (Badawy et al., 2006). Many studies found products of OPs under photodegradation process are simple ions as PO_4^{3-}, SO_4^{2-}, NH_3 and Cl^- (Pehkonen and Zhang, 2002).

A number of studies investigated the removal OPs in water combine UV process with hydrogen peroxide (H_2O_2) and ions in natural water as sulfate (SO_4) and bicarbonate (HCO_3). Fadaei et al. (2012) reported H_2O_2 (10 and 30 mg/L) enhanced ability of contaminant degradation reaction but increasing of SO_4 and HCO_3 inhibited the reaction. Pehkonen and Zhang (2002) reviewed the degradation of OPs. They reported attested that adding H_2O_2 and TiO_2 can promote the removal of OPs under UV process. In addition, light power is the one of factors that has affected on system. Da-Zhang et al. (2008) reported that when increased the power of lamp (40, 80 and 200 W) the degradation became faster as the removal efficiencies at 10 min were 20%, 30% and 99.9%, respectively. Recently, VUV process has gained lots of attention and was used to degrade hazardous substances because of it has more powerful than UV and can generate $OH^{\bullet}$. It was reported that the degradition of 4-tert-octyphenol by VUV was more effective than UV by 49.5% (Huang et al., 2013).

2.7 Nitrite and Nitrate in Natural Water

Nitrite and nitrate can be forms with nitrogen, which is necessary for all living things, by nitrogen-cycle. It are generally known that can be found contaminate in water in several sources as runoff from fertilizer use, leaching from septic tank, sewage, livestock and naturally occurring source of nitrogen (Agency for Toxic Substances and Disease Registry (ATSDR) 2013). The nitrite and nitrate may cause health problem by breath shortness and blue baby syndrome. The contamination of nitrite and nitrate in drinking water source was important. Then USEPA was set maximum contaminant levels goal (MCLG) by 1 and 10 mg-N/L for nitrite and nitrate, respectively.

Nitrate likely soluble in water and willingly migrate with groundwater. ATSDR (2013) also review the detection of water contamination by nitrate, in agricultural areas, nitrogen based on fertilizers are major source of contamination for shallow groundwater that supply drinking water. Table 2.5 summarized nitrate contamination in water. In Thailand, farmers apply nitrogen fertilizers in rate close to 1000 kg-N ha^{-1} $year^{-1}$. Shockingly, only 5% of this nitrogen is recovered by the plant, the lack being lost to the soil, water and air (Tirado, 2007). In Kanchanaburi and Suphanburi province, which are areas in the central plain, water pollution with nitrate was found up to 150 mg/L (Tirado, 2007). The concentration of nitrate found more than WHO (2011) drinking water safety limit of 50 mg/L as NO_3^- up to 3 times.

Table 2.5 Summary of nitrite and nitrate contamination in water.

Area	**Contamination (mg/L as N)**	**Reference**
Columbia, Wisconsin (1998)		Knobeloch et al. (2000)
tap water	NO_3^- = 22.00	
well (42 ft)	NO_3^- = 30.50	
Grant, Wisconsin (1999)		Knobeloch et al. (2000)
Tap water	NO_3^- = 27.40	
South-Eastern, Nigeria		Okafor and Ogbonna (2003)
bore-hole	NO_3^- = 0.27-1.05	
	NO_2^- = 0.06-0.47	
stream/river	NO_3^- = 0.13-0.48	
	NO_2^-= 0.05-0.20	
well	NO_3^- = 0.11-4.84	
	NO_2^- = 0.1-0.37	
tap water	NO_3^- = 0.17-1.00	
	NO_2^- = 0.03-0.25	
central sewage effluent	NO_3^- = 0.52-28.62	
	NO_2^- = 5.49-6.00	
Angat, Philippines		Tirado (2007)
groundwater	NO_3^- = 24.83	

2.8 Role of Nitrite and Nitrate on Contaminant Degradation by UV Photolysis and UV Based AOP

Nitrite and nitrate are commonly found in natural water due nitrification reaction of ammonia. In agricultural area the excessive use of nitrogen fertilizer and pesticides could lead to the contamination of NO_2^- /NO_3^- and residual of pesticides in groundwater and surface water. The range of NO_2^- and NO_3^- concentrations were widely in the range of 0.08-3.66 mg NO_2^--N/L and 10-55.44 mg NO_3^--N/L, respectively (Díaza et al., 2012). The level of nitrate ion (NO_3^-) in natural water is usually higher than nitrite since nitrate is more stable form of combined nitrogen for oxygenated systems. The presence of NO_2^- and NO_3^- could lead to formation of $OH^\bullet$ when they are undergone UV photolysis from sun light (equation 2.13 and 2.14) (Zuo and Deng, 1998). Sharpless et al. (2003) reported that the presence of $OH^\bullet$ from NO_3^- photolysis increased degradation rate of atrazine (ATZ). NO_3^- also was reduced to NO_2^- but the presence of NO_2^- inhibited ATZ degradation rate.

$$NO_3^- + H_2O + hv \longrightarrow NO_2 + OH^\bullet + OH^- \qquad (2.12)$$

$$NO_2^- + H_2O + hv \longrightarrow NO^\bullet + OH^\bullet + OH^- \qquad (2.13)$$

Figure 2.2 shows the light adsorption of nitrite and nitrate. The absorption spectra of NO_2^- and NO_3^- are dominated by intense ¶ ⟶¶* bands at 200 nm (ε= 5500 M^{-1} cm^{-1} and ε= 9900 M^{-1} cm^{-1}, respectively) (Mack and Bolton, 1999). However, at wavelength > 250 nm the light adsorption of nitrite and nitrate was relatively small within the magnitude between 5-25 M^{-1} cm^{-1}.

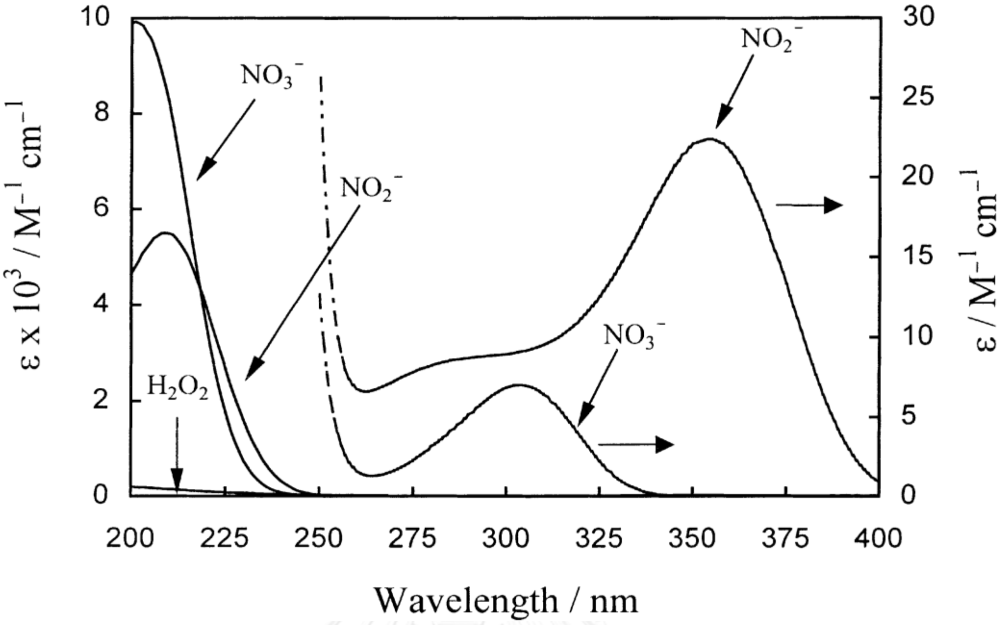


Figure 2.2 Nitrite and nitrate light absorption (Mack and Bolton, 1999)

The photolysis of nitrite in the 200 – 400 nm is decribed as the following equation:

$NO_2^- + h\nu \rightarrow [NO_2^-]^*$ (2.14)

$[NO_2^-]^* \rightarrow NO^\bullet + O^{\bullet -}$ (2.15)

At pH<12, $O^{\bullet -}$ protonates to form the $OH^\bullet$ (pKa = 11.9)

$O^{\bullet -} + H_2O \leftrightarrow OH^\bullet + OH^-$ $k=1.7 \times 10^6\ M^{-1}s^{-1}$

$K= 1.2\times 10^{10}\ M^{-1}s^{-1}$ (2.16)

$NO^\bullet + OH^\bullet \rightarrow HNO_2$ $k= 1.0 \times 10^{10}\ M^{-1}s^{-1}$ (2.17)

$OH^\bullet + NO_2^- \rightarrow NO_2^\bullet + OH^-$ $k = 1.0 \times 10^{10}\ M^{-1}s^{-1}$ (2.18)

$NO^\bullet + NO_2^\bullet \rightarrow N_2O_3$ $k = 1.1 \times 10^{9}\ M^{-1}s^{-1}$ (2.19)

N_2O_3 hydrolyses to regenerate NO_2^-

$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^-$ $k = 5.3 \times 10^{2}\ s^{-1}$ (2.20)

Two $NO_2^\bullet$ radicals can be combined during flash photolysis experiments to form N_2O_4.

$2NO_2^\bullet \rightarrow N_2O_4$ which hydrolyses to form NO_2^- and NO_3^-

$k = 4.5 \times 10^{8}\ M^{-1}s^{-1}$ (2.21)

$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+$ $k = 1 \times 10^{3}\ M^{-1}s^{-1}$ (2.22)

In solutions containing dissolved O_2, $NO^\bullet$ is competitively oxidized to form NO_3^- via N_2O_4

$NO^\bullet + NO^\bullet \rightarrow N_2O_2 + O_2 \rightarrow N_2O_4$ (2.23)

Nitrate also degrade under UV then photolysis of nitrate illustrated by

$NO_3^- + hv \rightarrow NO_2^- + ½O_2$ (2.24)

$NO_3^- + hv \rightarrow [NO_3^-]^*$ (2.25)

$[NO_3^-]^* \rightarrow NO_2^- + O$ (2.26)

$[NO_3^-]^* \rightarrow NO_2^\bullet + O^{\bullet-}$ (2.27)

$NO_2^{\bullet} + O^{\bullet-} + H_2O \rightarrow NO_2^{\bullet} + OH^{\bullet} + OH^{-}$ (2.28)

$[NO_3^{-}]^* \rightarrow ONOO^{-} \leftrightarrow HOONO$ (peroxynitrous acid) (2.29)

$OH^{\bullet} + NO_2^{\bullet} \rightarrow HOONO$ (2.30)

$HOONO \rightarrow NO_3^{-} + H^{+}$ (2.31)

UV photolysis of nitrite (NO_2^{-}) and nitrate (NO_3^{-}) efficiently triggers the fission of O–N bonds to produce reactive oxidizing intermediates, which may contribute to photochemical transformation of chemical substances in the aquatic environment and the oxidative treatment of organic/inorganic contaminants and pathogenic microorganisms in water (Kim et al., 2014).

Photolysis of aqueous NO_3^{-} with λ 195 nm is known to induce the formation of NO_2^{-} and O_2 as the only stable products. The mechanism of NO_3^{-} photolysis, however, is complex, and there is still uncertainty about the primary photoprocesses and subsequent reactions. This is, in part, due to photoisomerization of NO_3^{-} to $ONOO^{-}$ at $\lambda < 280$ nm, followed by the formation of $OH^{\bullet}$ and $NO_2^{\bullet}$ through the decomposition of ONOOH.

$NO_3^{-} + h\nu \rightarrow NO_2^{\bullet} + O^{\bullet-}$ (2.32)

$O^{\bullet-} + H_2O \leftrightarrow OH^{\bullet} + OH^{-}$ (2.33)

$NO_3^{-} + h\nu \rightarrow ONOO^{-}$ (2.34)

$$NO_3^- + h\nu \rightarrow NO_2^- + O^\bullet \qquad (2.35)$$

Upon increasing the pH, nitrite and O_2 at a ratio 2:1 are formed at the expense of nitrate.At pH 9-10, the yield of nitrite amounts to about 80% of the initial peroxynitrite (ONOOH/$ONOO^-$) (Goldstein and Rabani, 2007). Overall of nitrite and nitrate photolysis pathway has been summarized by Keen et al. (2012) in Figure 2.3.

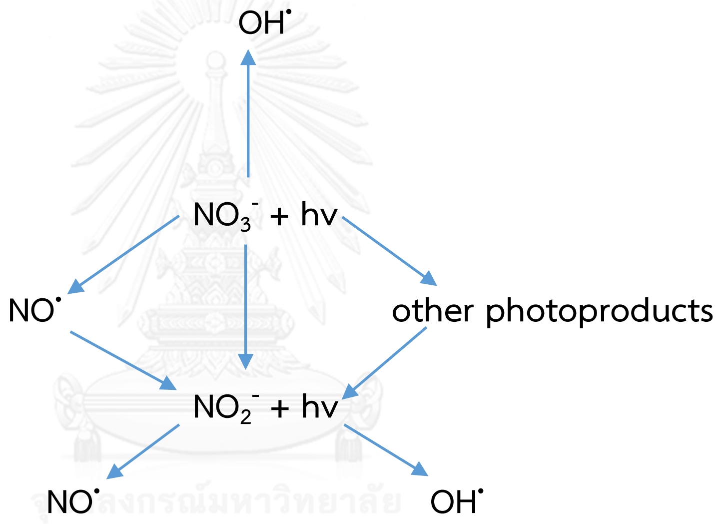


Figure 2.3 Photolysis pathway of nitrite and nitrate to generate hydroxyl radical (Keen et al., 2012).

Several studies reported that nitrite and nitrate can either promote or inhibit the degradation of organic compounds under UV process. The effect of NO_2^- and NO_3^- on the photodegradation rate and removal efficiency of compounds depended upon their concentrations. The concentration of NO_2^- at 0.1 and 1 mg/L exhibited no different in the degradation rate of monoliuron while NO_3^- at 1 and 10 mg/l provided significantly different result (Nelieu et al., 2004). Table 2.3 summarized the studies of effect of NO_3^- under UV process. At concentration of nitrate 5 mg/L on the degradation of 2, 4-dichlorphenol was promoted and achieve 40% in 2 minute by Ko et al. (2009). The study of Niu et al. (2013) on the removal of tetracycline reported that concentration of nitrate (0-50 mg/L) concentration was inversely proportional to photolysis. Keen et al. (2012) found that nitrate 5 mg/L produced hydroxyl radical more than nitrate 10 mg/L by UV irradiation on the degradation of wastewater from biological treatment plant. Another research of Huang et al. (2013) illumined nitrate enhance removal rate of 4-tert-octylphenol by UV (after 20 minute) and VUV (after 5 min) was achieve 68% and 60% respectively. At high concentration of nitrate could inhibit the removal rate because the adsorption light by nitrate molecules.

Table 2.6 Summary of previous studies on effect of nitrate on contaminants removal by UV based AOPs

Compound	**Light source descriptions**	**Additional oxidant**	**Removal**	**Reference**
2,4-dichlorphenol	UV lamp(67W)	H_2O_2(10mg/L), NO_3^- (5 mg/L)	After 2 min 15 % by UV 40 % by UV-NO_3^- 90 % by UV-H_2O_2 88 %by UV-H_2O_2-NO_3^-	Ko et al. (2009)
Tetracycline	Solar light Xenon lamp (500w) UV-365 lamp UV-254 lamp	NO_3^- (0-50mg/L) Humic acid (HA)	Removal efficiency: UV-254 > UV-365 > solar > xenon HA inhibits removal under UV-254 and UV-365 but promotes under solar and xenon lamp NO_3^- promotes removal under solar and xenon lamp. NO_3^- promotes and inhibit remove rate under UV-254 and UV-365, depending on concentrations.	Niu et al. (2013)

Table 2.6 Summary of previous studies on effect of nitrate on contaminants removal by UV based AOPs (continued)

Compound	**Light source descriptions**	**Additional oxidant**	**Removal**	**Reference**
Wastewater from biological treatment plant	UV lamp (1kW)	H_2O_2 NO_3^-	NO_3^- more effective than H_2O_2 to produce OH° when present similar level at 5 mg/L but at 10 mg/L H_2O_2 is better than NO_3^-.	Keen et al. (2012)
4-tert-octylphenol	UV lamp (20W) VUV lamp (20W)	NO_3^- SO_4^- CO_3^{2-}	After 20 min 50 % by UV 68 % by UV- NO_3^- 51 % by UV- SO_4^- 40 % by UV-CO_3^{2-} After 5 min 49 % by VUV 60 % by VUV- NO_3^- 52 % by VUV- SO_4^- 30 % by VUV- CO_3^{2-}	Huang et al. (2013)

CHAPTER III

MATERAILS AND METHODS

3.1 Water Sample

Water samples following Figure 3.1 were synthesized from profenofos (commercial grade, YUSA; China) and deionized water (18.2 MΩ water, Millipore) to achieve concentration approximately of 10 mg/L. NO_3^- and NO_2^- stock solutions of 1000 mg/L were prepared by KNO_3 and $NaNO_2$, respectively and then spiked in water sample to desired concentrations, respectively. Concentration rang of nitrite and nitrate that varying in this study chosen from contamination rang of nitrite and nitrate in agricultural area (discuss in chapter 2).

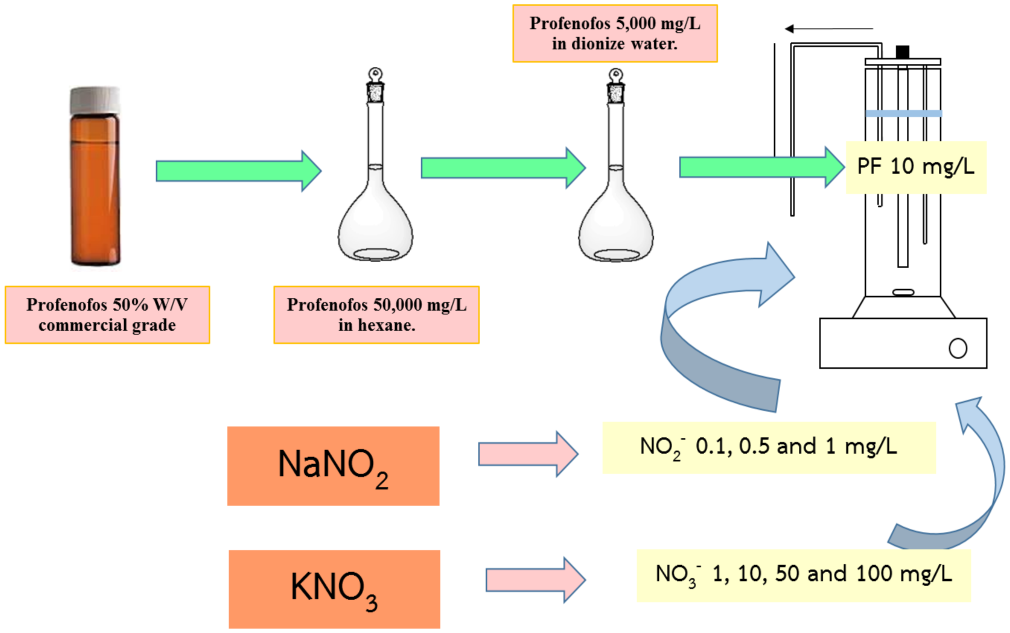


Figure 3.1 Water sample preparation

3.2 Experimental Framework

The experimental frame work of this research is shown in Figure 3.2. The detail of this research was separated into 4 stages which are: 1) water sample used in this research were synthesized, 2) experimental set up and procedure (light sources: UV and VUV lamp), 3) experimental design (study effect of nitrite, nitrate concentrations and hydroxyl radical exposure), 4) analyses.

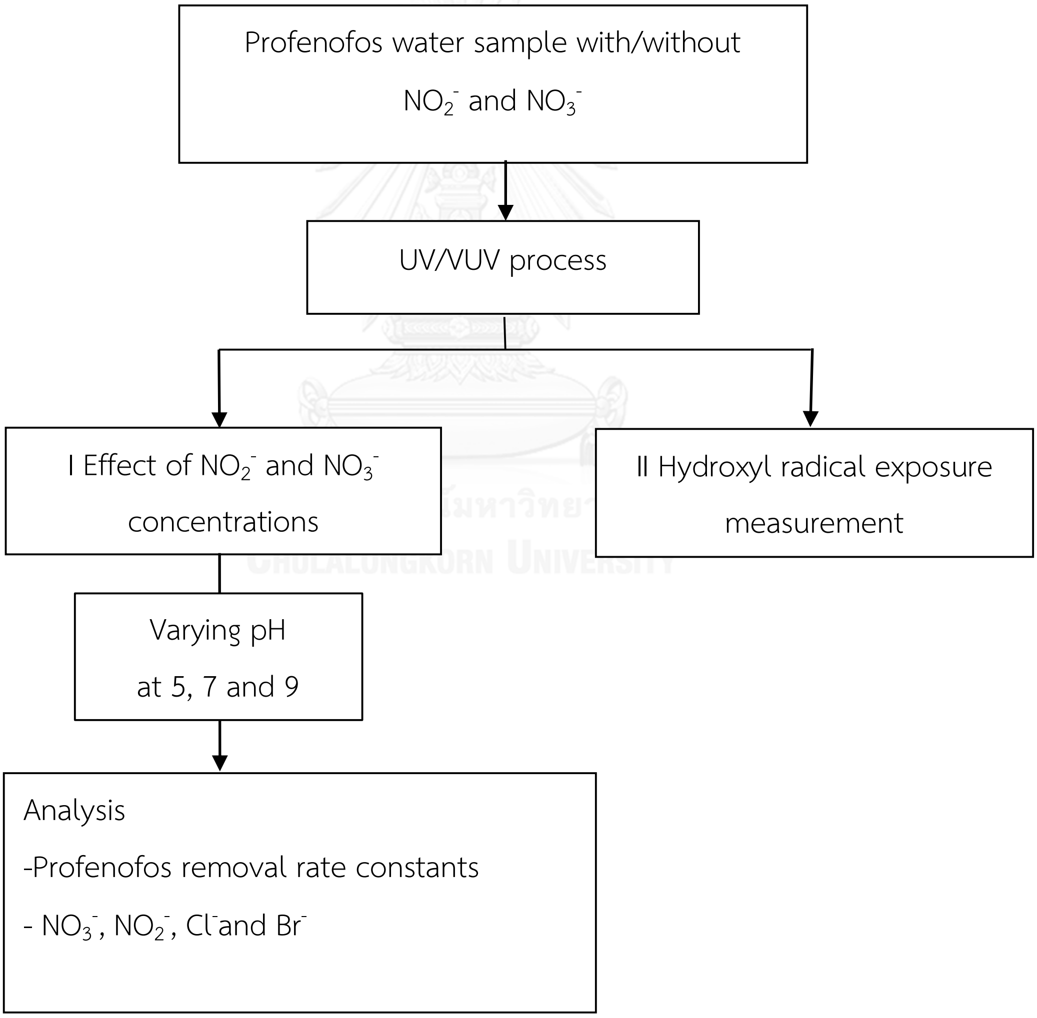


Figure 3.2 Research framework

3.3 Experimental Set Up and Procedure

The volume of water sample of all the experiments were used 1.8 L. The reactor was a 2-L glass graduate cylinder which has a diameter of 8 cm and equipped with a UV (model GPH383T5/L/HO universal Light Source, Inc.) or VUV lamp (model GPH383T5/VH/HO, Universal Light Source, Inc.) at the center of reactor. Mixing was provided by magnetic stirring system (> 50 rpm) and has glass tube in reactor to prevent vortex current (Figure 3.3).

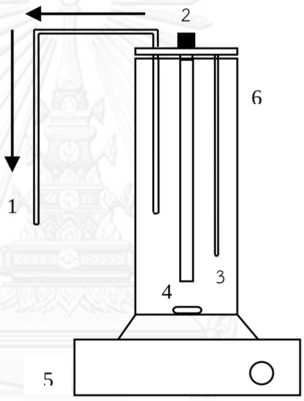


Figure 3.3 Reactor of UV and VUV process: (1) sampling tube, (2) lamp, (3) glass tube, (4) magnetic bar, (5) magnetic stirrer and (6) glass cylinder.

For the UV and VUV process, experiments were conducted by fixing initial concentration of profenofos at 10 mg/L and varying pH at 5, 7, and 9, respectively. The power of UV (irradiation at 254 nm) and VUV (irradiation at 185 and 254 nm) in experiments was 30W. The effect of concentrations of NO_3^- (1, 10, 50 and 100 mg/L as NO_3^-) and NO_2^- (0.1, 0.5 and 1 mg/L as NO_2^-) on profenofos removal by UV and VUV processes were investigated as shown in Table 3.1.

The formation of hydroxyl radical was measured to determine the role of NO_3^- and NO_2^- on VUV process. Para-chlorbenzoic acid (pCBA) as probe compound was spiked in the reactor at 400 µg/L. To observe the effect of VUV irradiation only, tert-butanol (5 mmol/L) was added into reactor as a hydroxyl radical scavenger (Ratpukdi et al., 2010).

During each experiment condition, 40 mL of sample was taken by siphoning at the reaction time 0, 2, 5, 10, 15, 20, and 30 min for measurement of profenofos, hydroxyl radicals, NO_3^-, NO_2^- and byproducts (Br^- and Cl^-) concentrations. Samples were filtered through a 0.2 µm pore-size nylon syringe filter (Vertical, Thailand) before taken to analysis.

Table 3.1 Experimental conditions

Run	UV/VUV	pH	NO_3^- (mg/L as NO_3^-)	NO_2^- (mg/L as NO_2^-)	$OH^\bullet$ exposure
1	UV	7	0	0	/
2	UV	7	1	0	/
3	UV	7	10	0	
4	UV	7	50	0	
5	UV	7	100	0	
6	UV	7	0	0.1	
7	UV	7	0	0.5	
8	UV	7	0	1	/
9	VUV	7	0	0	/
10	VUV	7	1	0	/
11	VUV	7	10	0	/
12	VUV	7	50	0	/
13	VUV	7	100	0	/
14	VUV	7	0	0.1	
15	VUV	7	0	0.5	
16	VUV	7	0	1	/
17	VUV	5	0	0	
18	VUV	5	1	0	
19	VUV	5	10	0	
20	VUV	5	50	0	
21	VUV	5	100	0	
22	VUV	5	0	0.1	
23	VUV	5	0	0.5	
24	VUV	5	0	1	
25	VUV	9	0	0	/
26	VUV	9	1	0	/
27	VUV	9	10	0	/
28	VUV	9	50	0	/
29	VUV	9	100	0	/
30	VUV	9	0	0.1	
31	VUV	9	0	0.5	
32	VUV	9	0	1	

3.4 Experimental Analyses

3.4.1 Measurement of Profenofos

Prepare profenofos solution 10 mL in centrifuge tube (50 mL) and add 10 mL n-hexane with acetic acid 0.1% in solution. After that shake this solution with vortex mixer then centrifugation with centrifuge 5,000 rpm for 5 min. Draw 1.5 mL of hexane that separation from water to amber vial (2 mL). Concentrations of sample were determined by Gas Chromatography with electron capture detector (GC-ECD, Agilent 4890 D). The column was used a SPE-608 fused silica capillary column (15 m × 0.53 nm × 0.5µm). The analyze condition, initial temperature is 120 °C hold 2 min, final temperatures is 220 °C and total runtimes of 4.5 min.

3.4.2 Measurement of Nitrite, Nitrate, Chloride and, Bromide

Concentrations of nitrate, nitrite, chloride and bromide were analyzed using an ion chromatography (IC, Dionex). The IC column was IonPac CG12A (4 × 250 mm). The mobile phase was N_2 gas. The analyze condition, 20 µL of water samples were inject to IC by auto sampler, flow rate is 1 mL/min, temperature is 30 °C and total runtime is 17 min.

3.4.3 Measurement of Hydroxyl Radicals

To determine hydroxyl radicals ($OH^{\bullet}$) generated in the oxidation reaction, $OH^{\bullet}$ exposure was measured. In this way, *p*-chlorobenzoic acid (*p*CBA, Acros Organics, Belgium) was used as a probe compound to measure $OH^{\bullet}$ indirectly of oxidation kinetic following the equation (3.1).

$$\int_0^t [OH^{\circ}]dt = \frac{(k_{obs} - k_d)}{\mathrm{k_{OH^{\circ},pCBA}}} t \qquad (3.1)$$

Where t is reaction time (s), k_{obs} is an observed pseudo first order of *p*CBA removal rate (1/s), k_d is pseudo first order constant by direct photolysis of *p*CBA removal, and $k_{OH^{\circ},pCBA}$ is a second order rate constant of *p*CBA with $OH^{\bullet}$ (5×10^9 L/(mol·s) (Ratpukdi et al., 2010). Two milliliter of sample were taken to measure concentration of *p*CBA by high performance liquid chromatograph (00G-4252-E0), the column was used a Luna 5u C18 column (250 × 4.6 mm, Phenomenex). The mobile phase was composed of acetronitrile (50%) and water added with formic acid at 0.66 mL/L (50%). The flow rate was 0.8 mL/min and injection volume was 20 µL. The wavelength of UV-detector was 236 nm.

3.4.4 Electrical 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 using equation (3.2) (Zoschke et al., 2012).

$$\text{EE/O (kWh.m}^{-3}) = \frac{\mathrm{P_{el}} \cdot \mathrm{t} \cdot 1000\ (\frac{\mathrm{L}}{\mathrm{m^3}})}{\mathrm{V} \cdot 60\ (\frac{\mathrm{min}}{\mathrm{h}}) \cdot \log(\frac{\mathrm{C_0}}{\mathrm{C}})} \qquad (3.2)$$

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.

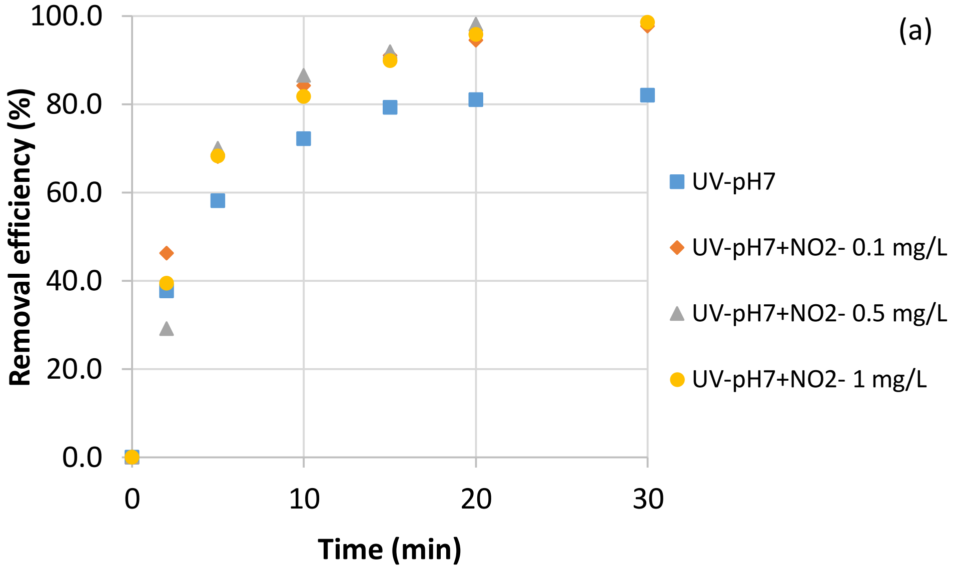
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Removal Efficiency of Profenofos by UV and VUV

The removal efficiencies of profenofos by UV (pH 7) and VUV (pH 5, 7, and 9) processes under the presence of nitrite and nitrate are illustrated in Figure 4.1, 4.2, 4.3, and 4.4, respectively. In overall, most of profenofos removal (70-90%) occurred in the first 10 min of reaction. Then degradation of profenofos began to level off at around 10-20 min. The slow degradation after 10 min was due to formation of intermediate products that competed with mother compound (profenofos) for light adsorption (UV and VUV) or reacting with hydroxyl radicals. Similar trend of result was observed by Huang et al. (2013) who investigated the degradation of 4-tert-octylphenol in water by UV and VUV. When comparing the profenofos removal by UV and VUV (same experimental condition), it was found that VUV performed better than UV. For example, at pH 7 (Figure 4.1 (b) and Figure 4.3(b)), removal efficiencies of UV and VUV at 10 min were 70% and 90 %, respectively. The substantial reduction of profenofos by UV process indicated that profenofos was susceptible to UV irradiation at 254 nm. Thus, direct photolysis at 254 nm is main mechanism of profenofos degradation. The application of VUV was found to moderately enhance the removal efficiency by 20%. The photons at wavelength 185 nm can degrade profenofos by direct photolysis or induce the formation of hydroxyl radicals which react directly with profenofos. In contrast, some compounds may not strongly adsorb UV wavelength at 254 nm. Therefore, VUV could dramatically enhance the removal efficiency and the direct photolysis at 185 nm and reaction with hydroxyl radicals could be main degradation mechanism. For example, Cao et al. (2010) reported that degradations of perfluorooctanoic acid by UV (254 nm) and VUV (185 and 254 nm) were 9% and 87%, respectively.

The presence of nitrite and nitrate obviously affected with the removal efficiency of profenofos. Figure 4.1(a) and Figure 4.1 (b) showed that the removal efficiencies increased with nitrite or nitrate addition. For example, the comparing with no nitrite in UV process at pH 7, prefenofos removal efficiencies increased by 15.6%, 16.1% and 16.4% for the concentration of nitrite (0.1, 0.5, and 1 mg/L, respectively). In VUV process at pH 7, the presence of nitrate slightly increased profenofos removal efficiencies by 5.2%, 3.1% and 2.3% for nitrate concentration of 1, 10, and 50 mg/L, respectively. This was because nitrite and nitrate can be sources of hydroxyl radicals during indirect photolysis reaction which for profenofos degradation. The initial concentrations of nitrite and nitrate also affected the profenofos removal efficiencies. The pH was one of parameters influencing the profenofos degradation by UV and VUV. At pH 5 and pH 7 (Figure 4.2 and 4.3) profenofos removal efficiencies were relatively similar. However, at pH9 (Figure 4.4) profenofos removal efficiencies were dramatically increased. The details of the effect of nitrite, nitrate and pH on profenofos degradation will be discussed in subsection of this chapter. Notice of all experiment in this study have effect of temperature increase from initial temperature at 30°C to 35°C. It can mention that effect of temperature can be account the same in all experiment.



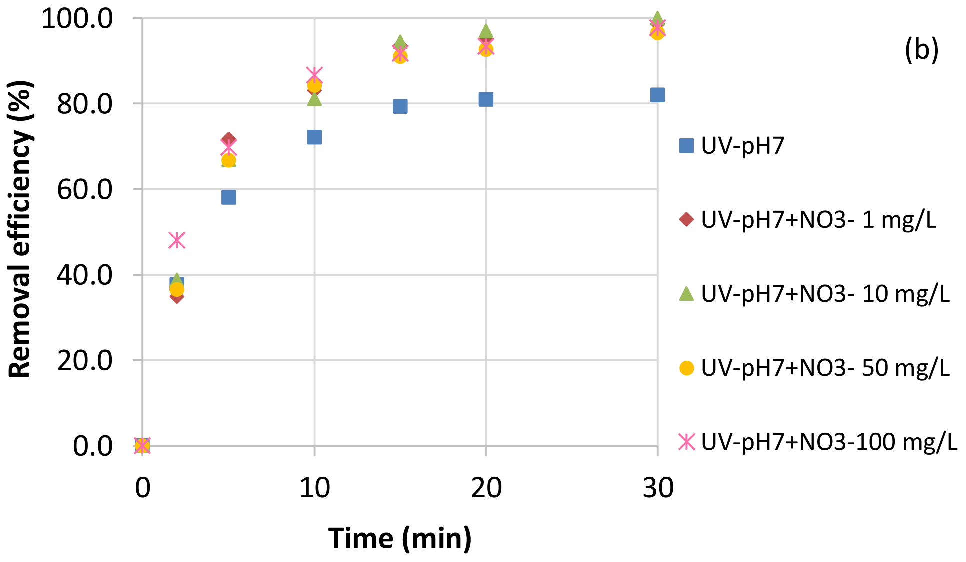
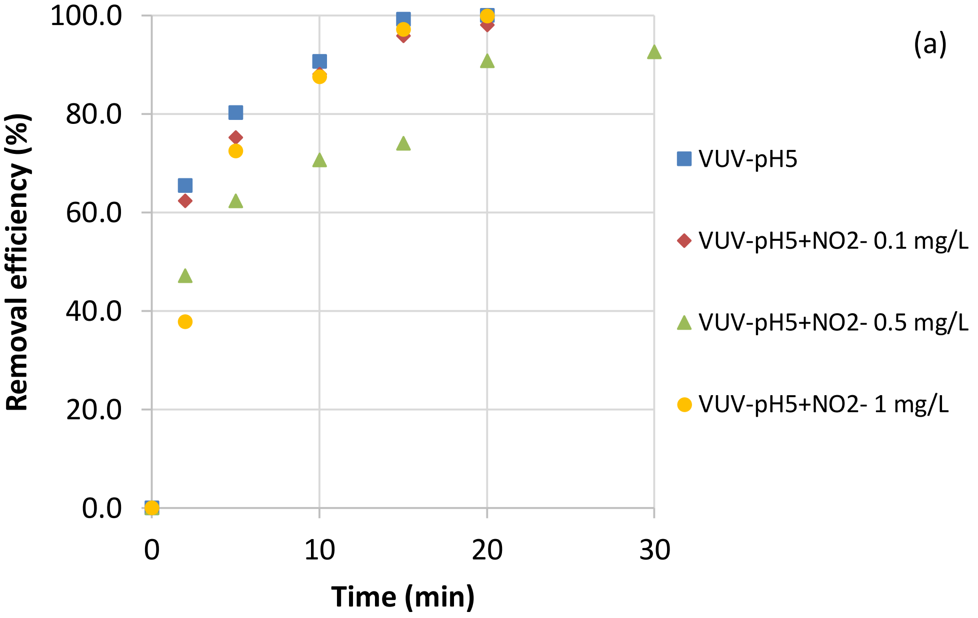


Figure 4.1 Removal of profenofos at initial concentration 10 mg/L by UV process at pH 7 (a) with nitrite, (b) with nitrate.



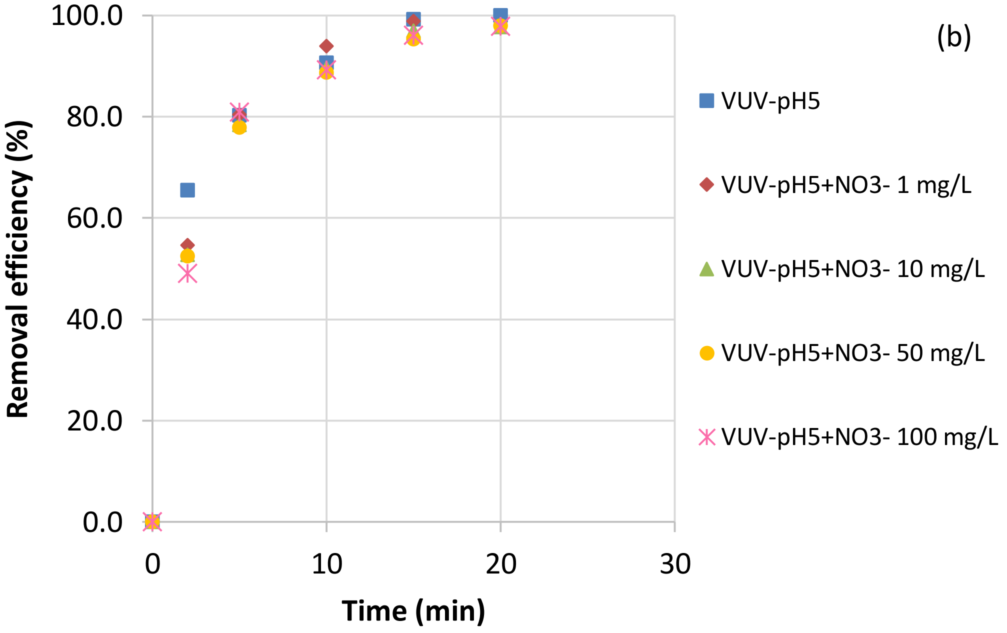


Figure 4.2 Removal profenofos at initial concentration 10 mg/L by VUV process at pH 5. (a) with nitrite, (b) with nitrate.

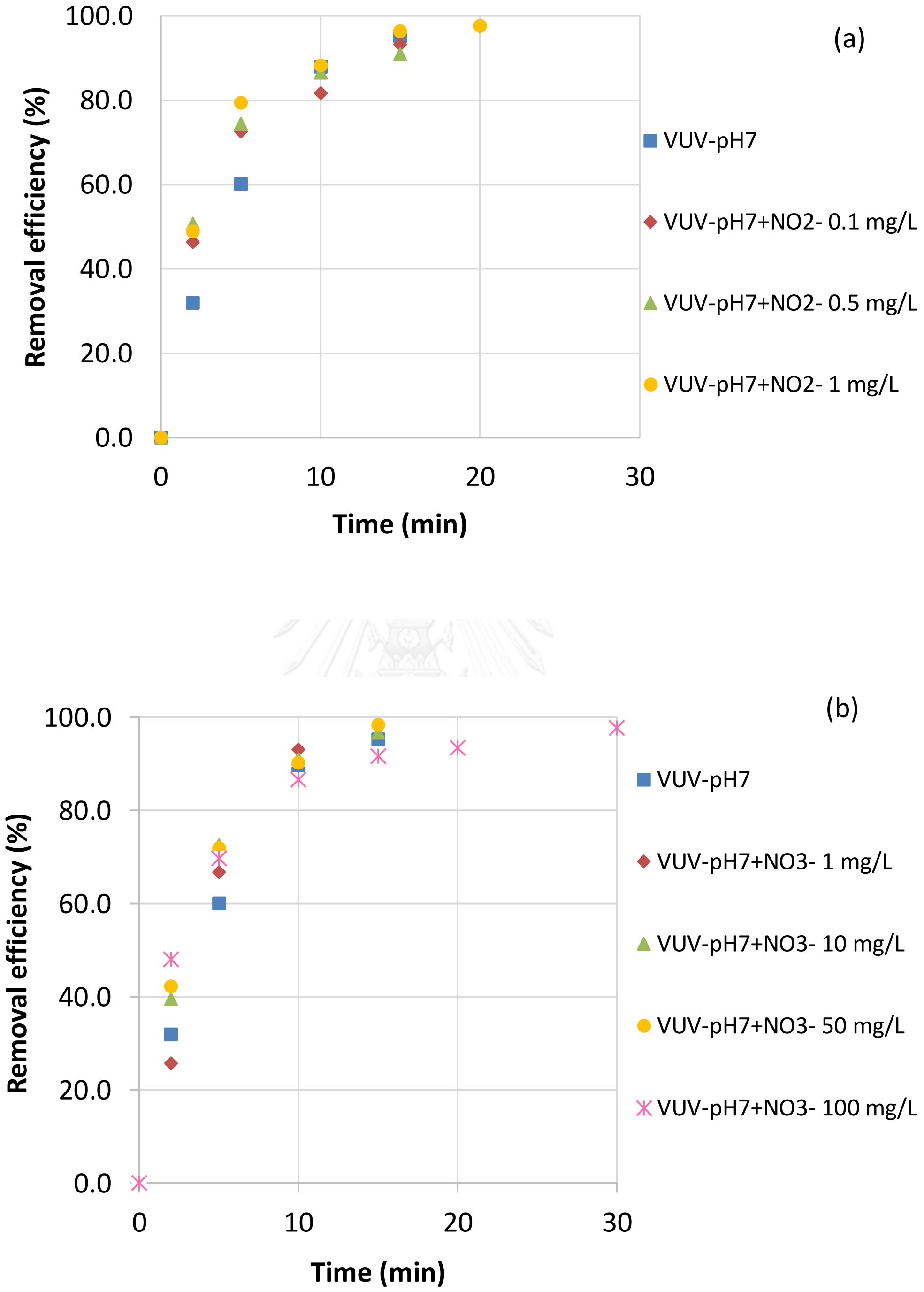


Figure 4.3 Removal of profenofos at initial concentration 10 mg/L by VUV process at pH 7. (a) with nitrite, (b) with nitrate.

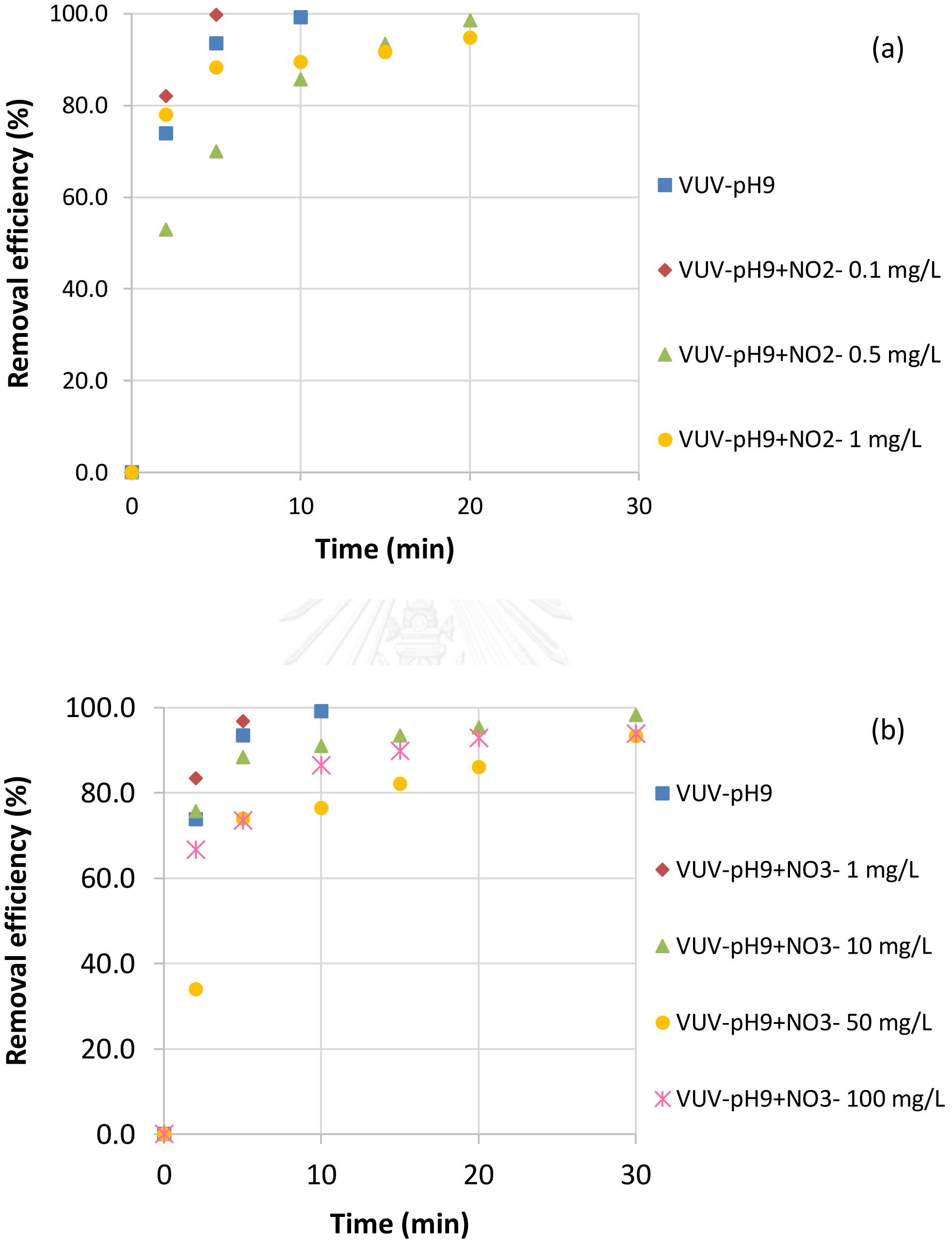


Figure 4.4 Removal of profenofos at initial concentration 10 mg/L by VUV process at pH 9. (a) with nitrite, (b) with nitrate.

4.2 Degradation Kinetic of Profenofos by UV and VUV

Degradation kinetics of profenofos by UV and VUV without nitrite and nitrate are shown in Figure 4.5. The initial degradation rate of profenofos follows first order reaction (determine during the first 10 min of experiment). The first order kinetic rate constants of profenofos degradation by UV and VUV were 0.0994 and 0.2063min^{-1}, respectively (Table 4.1). It was observed that the profenofos degradation rate constant of VUV was 2 times higher than that of UV. This is because VUV lamp can emit wavelengths at 185 and 254 nm while UV lamp emit only wavelength of 254 nm. The wavelength of 185 nm from VUV is strong wavelength which enhancing the direct photolysis reaction. In addition, the high photon energy of VUV can induce water molecule to become hydroxyl radical which is strong oxidizing agent. Hydroxyl radicals can directly react with profenofos; hence reaction of VUV is more rapid than UV. For the effect of pH, it was found that the degradation rate constants of pH5 and pH7 were not quite different both on UV and VUV processes (Table 4.1). However, the profenofos degradation rate constants of UV (0.2978 min^{-1}) and VUV (0.5635 min^{-1}) at pH9 were very high comparing to pH 5 and 7. Although, the influence of pH on the degradation of compounds can be compound specific (Moussavi et al., 2014; Shemer and Linden, 2006), high degradation rate at pH 9 can be explained by few possible reasons. At high pH, the profenofos was subjected to hydrolysis reaction (Malghani et al., 2009). USEPA (1998) reported that profenofos half-life depended on pH. At pH 5, 7 and 9, profenofos half-lives are 104-108, 24-62 and 0.33 day, respectively. Effect of hydrolysis can be calculated by 1st order degradation kinetic rate constant. At pH 9 half-life is 0.33 day or 7.92 hr. This equals to kinetic rate constant of 1.458×10^{-3} min. From the calculation, effect of hydrolysis accounted for profenofos degradation around 2 %. The initial profenofos concentration of this study achieved at 10 mg/L then effect of hydrolysis after 10 min could remove concentration of profenofos 0.2 mg/L, approximately. This pointed out that the fast degradation of profenofos at pH 9 during first 10 min was not mainly from reaction of hydrolysis.

In case of VUV, high degradation of profenofos can be attributed from hydroxyl radicals' reaction from ozone generation under VUV process. Under VUV irradiation with oxygen, the series of reactions by water homolysis causes the formation of $OH^{\bullet}$ and ozone (Eq. 4.1-4.4). At high pH (>9), there are more available hydroxide ions to dissociate ozone molecules, to form $OH^{\bullet}$ (Eq 4.5-4.6). Similar result was reported by Moussavi et al. (2014) who investigated the degradation diazinon, organophosphate pesticides in which its structure has similarity to profenofos, by VUV process.

$$H_2O + h\nu\ (185\ \text{nm}) \rightarrow OH^{\bullet} + H^{\bullet} \qquad (4.1)$$

$$H_2O + h\nu\ (185\ \text{nm}) \rightarrow OH^{\bullet} + H^{+} + e_{eq}^{-} \qquad (4.2)$$

$$O_2 + h\nu\ (185\ \text{nm}) \rightarrow 2O^{\bullet} \qquad (4.3)$$

$$O^{\bullet} + O_2 \rightarrow O_3 \qquad (4.4)$$

$$O_3 + OH^{-} \rightarrow OH_2^{-} + O_2 \qquad (4.5)$$

$$O_3 + OH_2^{-} \rightarrow OH^{\bullet} + O_2^{\bullet -} + O_2 \qquad (4.6)$$

Table 4.1 Removal efficiency and the first order kinetic rate constant of profenofos degradation by UV and VUV

Experimental condition **VUV or UV** **with NO_2^- or NO_3^- (mg/L)**	**pH**	**% Removal (at 10 min)**	**Degradation rate constant (k, min^{-1}) (R^2)**
UV	5	73	0.1390 (0.9616)
VUV	5	90.6	0.2627 (0.8476)
VUV+ NO_2^- (0.1)	5	88.0	0.2336 (0.8481)
VUV+ NO_2^- (0.5)	5	70.7	0.1429 (0.7241)
VUV+ NO_2^- (1)	5	87.5	0.2187 (0.9791)
VUV+ NO_3^- (1)	5	93.9	0.2918 (0.9798)
VUV+ NO_3^- (10)	5	89.5	0.2459 (0.9309)
VUV+ NO_3^- (50)	5	88.6	0.2385 (0.9199)
VUV+ NO_3^- (100)	5	89.1	0.2467 (0.9065)
UV	7	72.1	0.1399 (0.9104)
UV+ NO_2^- (0.1)	7	84.1	0.1965 (0.9499)
UV+ NO_2^- (0.5)	7	86.5	0.1838 (0.9456)
UV+ NO_2^- (1)	7	81.7	0.1838 (0.9456)
UV+ NO_3^- (1)	7	83.1	0.1935 (0.9411)
UV+ NO_3^- (10)	7	81.1	0.1796 (0.9511)
UV+ NO_3^-(50)	7	84.3	0.1934 (0.9849)
UV+ NO_3^-(100)	7	86.7	0.2127 (0.9617)
VUV	7	87.9	0.2052 (0.9938)
VUV+ NO_2^-(0.1)	7	81.6	0.1909 (0.8692)
VUV+ NO_2^-(0.5)	7	86.5	0.2192 (0.9203)
VUV+ NO_2^- (1)	7	88.5	0.2373 (0.9076)

Table 4.1 Removal efficiency and the first order kinetic rate constant of profenofos degradation by UV and VUV (continued)

Experimental condition		**% Removal**	**Degradation rate constant**
VUV or UV with NO_2^- or NO_3^- (mg/L)	**pH**	**(at 10 min)**	**(k, min^{-1}) (R^2)**
VUV+ NO_3^- (1)	7	93.1	0.2543 (0.9791)
VUV+ NO_3^- (10)	7	91.0	0.2446 (0.9979)
VUV+ NO_3^- (50)	7	90.2	0.2377 (0.9951)
VUV+ NO_3^- (100)	7	86.7	0.2183 (0.8392)
UV	9	80.0	0.2978 (0.9574)
VUV	9	99.1	0.5635 (0.9859)
VUV+ NO_2^- (0.1)	9	>99.7(at 5 min)	1.1374 (0.9804)
VUV+ NO_2^- (0.5)	9	85.6	0.2596 (0.9145)
VUV+ NO_2^- (1)	9	89.4	0.4730 (0.8463)
VUV+ NO_3^- (1)	9	96.8 (at 5 min)	0.7186 (0.9748)
VUV+ NO_3^- (10)	9	91.0	0.4689 (0.8888)
VUV+ NO_3^- (50)	9	76.4	0.2602 (0.9861)
VUV+ NO_3^- (100)	9	86.5	0.3045 (0.7221)

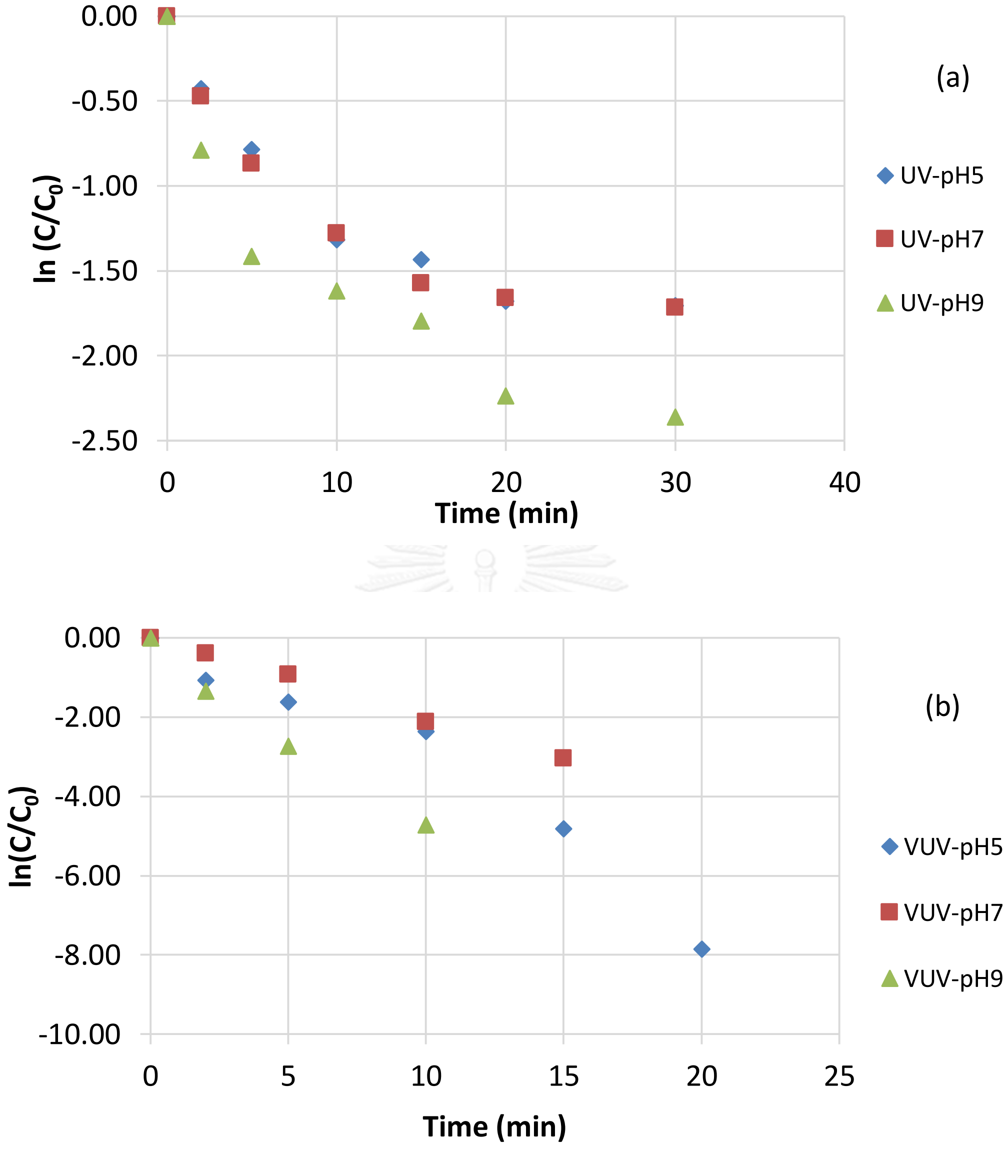


Figure 4.5 Normalized concentration of profenofos (C_0 = 10 mg/L) treated by (a) UV and (b) VUV

4.2.1 Effect of Nitrite

Figure 4.6 and 4.7 show the degradation of profenofos by UV and VUV under the presence of nitrite, (1, 0.5 and 0.1 mg/L), respectively. The degradation rate constants summarized in Table 4.1. In UV process (Figure 4.6), the presence of nitrite obviously promoted the degradation rate of profenofos by 40.46%, 31.38% and 31.38% (at nitrite concentration 0.1, 0.5 and 1 mg/L, respectively) comparing to that of without nitrite addition. However, the increase of nitrite concentrations (from 0.1 to 1.0 mg/L as NO_2^-) did not much improve on profenofos degradation rate. The degradation rate constants ranged from 0.1838 to 0.1965 min^{-1}. Effect of nitrite on profenofos degradation by VUV at pH 5, pH 7 and pH 9 are presented in Figure 4.7. From the results, the concentration of nitrite appeared to have slight effect on the profenofos degradation for pH 5 and pH 7. Nitrite concentration of 0.1 mg/L tended to have the highest the degradation rate constant (Table 4.1). The improvement of profenofos degradation might be due to the formation of $OH^•$ from irradiation of nitrite as shown in Eq. 2.13.-2.17

$$NO_2^- + H_2O + h\nu \longrightarrow NO^• + OH^• + OH^- \qquad (2.13)$$

$$NO_2^- + h\nu \longrightarrow [NO_2^-]^* \qquad (2.15)$$

$$[NO_2^-]^* \longrightarrow NO^• + O^{•-} \qquad (2.16)$$

At pH<12, $O^{•-}$ protonates to form the $OH^•$ (pKa = 11.9)

$$O^{•-} + H_2O \leftrightarrow OH^• + OH^- \qquad (2.17)$$

Figure 4.8 summarized the profenofos degradation rate constant at different pH (5, 7 and 9). It was found that pH 5 and 7 had similar trend of results. However, at pH 9, it was found that profenofos degradation rate constant increased 5 to 6 times for VUV without and with nitrite 0.1 mg/L, respectively. At higher nitrite concentrations (0.5 and 1.0 mg/L), the profenofos degradation rate constants decreased to the level lower than that of without nitrite. Although the initial degradation rate constant of profenofos at pH by VUV at nitrite 1.0 mg/L was greater than 0.5 mg/L, more inhibition effect of nitrite 1.0 mg/L was observed at later period after 5 min. These results suggested that high nitrite concentration could lead to inhibition of profenofos degradation. Nelieu et al. (2004) also observed the slight decrease of photodegradation rate of monolinuron as nitrite concentration increased from 0.1 to 1×10^{3} M. This might be because of two reasons. First, nitrite at higher concentration could act as inner filter to absorb the VUV wavelength at 185 nm. Second, the $OH^{\bullet}$ generated by VUV could combind with $NO^{\bullet}$ and NO_2^- (Eq. 4.7 and 4.8, respectively) (Mack and Bolton, 1999). Thus, $OH^{\bullet}$ were scavenged.

$$NO^{\bullet} + OH^{\bullet} \longrightarrow HNO_2 \text{ , } k = 1.0\times10^{10}\ M^{-1}s^{-1} \qquad (4.7)$$

$$NO_2^- + OH^{\bullet} \longrightarrow NO_2^{\bullet} + OH^-,\ k = 1.0\times10^{10}\ M^{-1}s^{-1} \qquad (4.8)$$

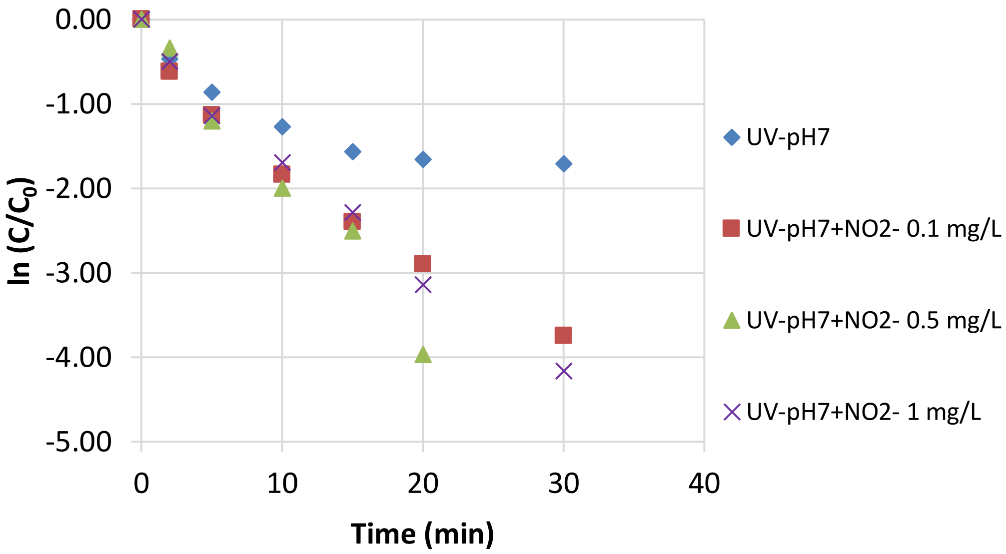


Figure 4.6 Degradation rate of profenofos by UV with nitrite (0.1, 0.5 and 1 mg/L) at pH 7

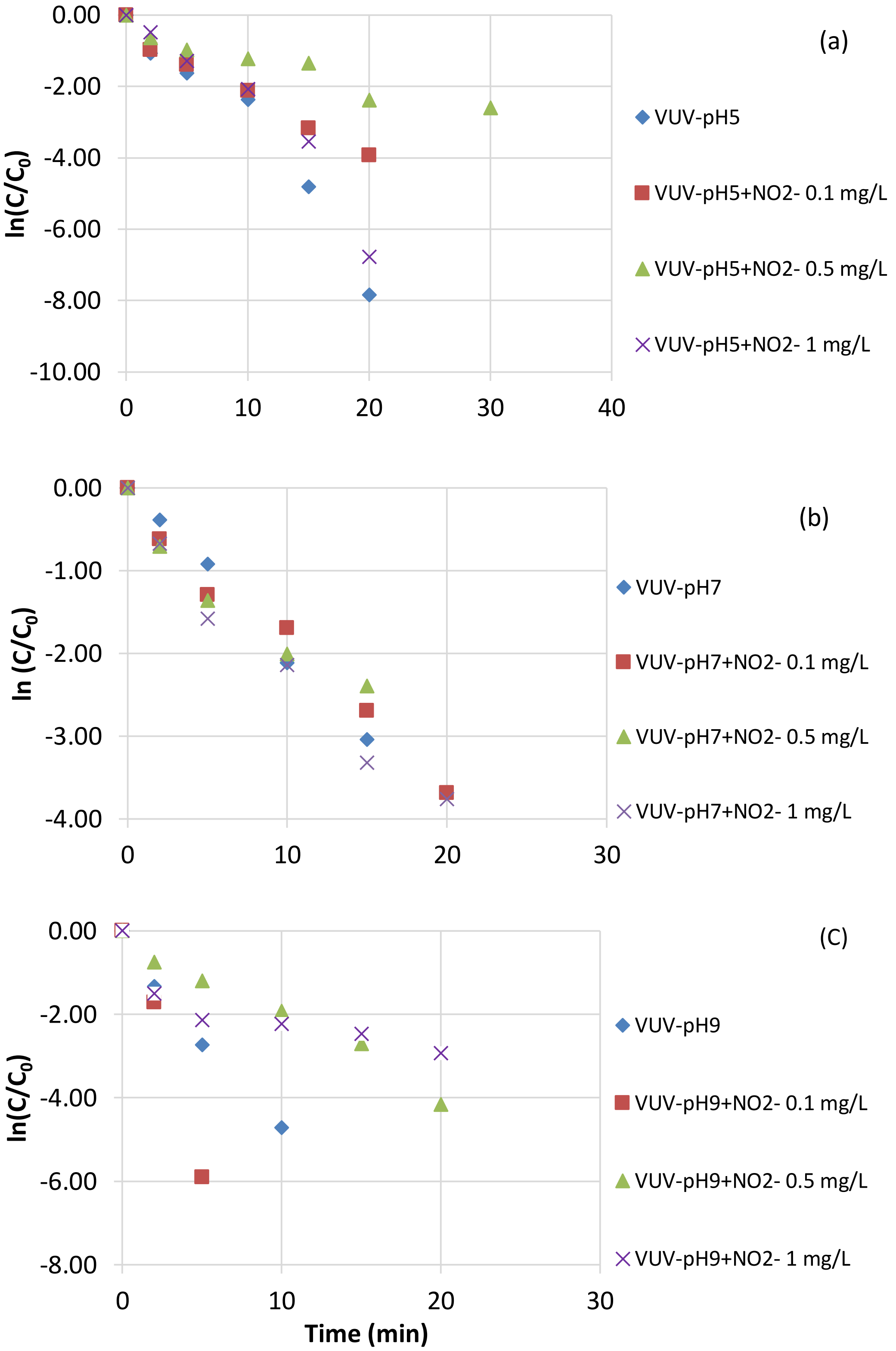


Figure 4.7 Degradation rate of profenofos by VUV with nitrite (0.1, 0.5 and 1 mg/L) at (a) pH 5, (b) pH 7 and (c).pH 9

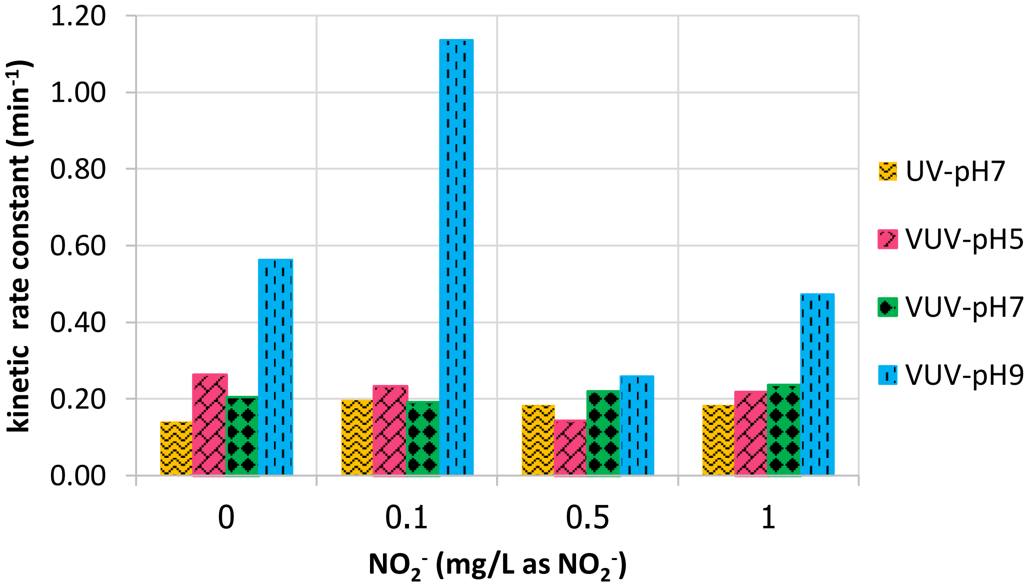


Figure 4.8 Profenofos degradation rate constant by UV and VUV. Effect of nitrite concentrations.

4.2.2 Effect of Nitrate

Profenofos degradation by UV and VUV with nitrate were presented in Figure 4.9 and Figure 4.10, respectively. The results show that profenofos degraded rapidly during the first 10 minute for UV (Figure 4.9). For UV at pH 7, comparing with no nitrate, the profenofos degradation rate constant slightly increased by 38.31%, 28.38%, 38.24% and 52.04%, for nitrate concentration of 1, 10, 50 and 100 mg/L, respectively. For VUV, profenofos concentration decreased sharply and achieved 90% at 10 minute excepting the condition of VUV with nitrate 100 mg/L that profenofos decreased sharply in 5 min and gradually decreased in later period (Figure 4.10).

In VUV process at pH 7, the presence of nitrate slightly increased profenofos rate constant by 23.92%, 19.20%, 15.84% and 6.38% for nitrate concentration of 1, 10, 50 and 100 mg/L, respectively. The result showed that the highest profenofos degradation rate constant was achieved at nitrate concentration of 1 mg/L and increasing of nitrate concentration higher than this level inhibit profenofos degradation. The increase of profenofos degradation rate constant can be contributed from nitrate photosensitization that was known to produce hydroxyl radicals as previously described in Eq. 2.12 and Eq. 2.24-2.28 in chapter 2 (Gonzaleza et al., 2004).

$$NO_3^- + H_2O + hv \longrightarrow NO_2 + OH^\bullet + OH^- \qquad (2.23)$$

$$NO_3^- + hv \longrightarrow NO_2^- + \tfrac{1}{2}O_2 \qquad (2.24)$$

$$NO_3^- + hv \longrightarrow [NO_3^-]^* \qquad (2.25)$$

$$[NO_3^-]^* \longrightarrow NO_2^- + O \qquad (2.26)$$

$$[NO_3^-]^* \longrightarrow NO_2^\bullet + O^{\bullet-} \qquad (2.27)$$

$$NO_2^\bullet + O^{\bullet-} + H_2O \longrightarrow NO_2^\bullet + OH^\bullet + OH^- \qquad (2.28)$$

Huang et al. (2013) also reported that the present of nitrate of 5.0×10^{-4}mol/L (31 mg/L as NO_3^-) enhanced the removal of 4-tert-octylphenol under UV and VUV irradiation by 18% and 11%, respectively. However, too high concentration of nitrate reduced profenofos degradation rate and efficiencies. This was because nitrate at high level could act as inner filter for UV or VUV (Mack and Bolton, 1999). It was noticed that the inhibition of profenofos degradation by VUV process with the presence of high nitrate concentration was more pronounced than that of UV process. This was because at wavelength below 200 nm, nitrate strongly absorb UV with the molar adsorption coefficient ($\mathcal{E}$) of 9000 $M^{-1}cm^{-1}$ while that of UV wavelength of 254 nm (for UV process) was 5 $M^{-1}cm^{-1}$ (Mack and Bolton, 1999; Sharpless and Linden, 2001). In addition, high concentration of nitrate could lead to more nitrite formation in which it scavenges $OH^{\bullet}$ (Eq. 2.35).

$$NO_3^- + hv \longrightarrow NO_2^- + O^{\bullet} \qquad (2.35)$$

Figure 4.11 summarized the profenofos degradation rate constant under the presence of nitrate (1, 10, 50 and 100 mg/L) by UV and VUV, respectively. For the effect of pH (5, 7 and 9), the rate of profenofos removals are very high that supporting profenofos is unstable in high pH (alkali condition) and undergone hydrolysis (Malghani et al., 2009) or attributed from hydroxyl radicals' reaction from ozone generation (Moussavi et al., 2014) similar to the experiment of UV or VUV with nitrite addition.

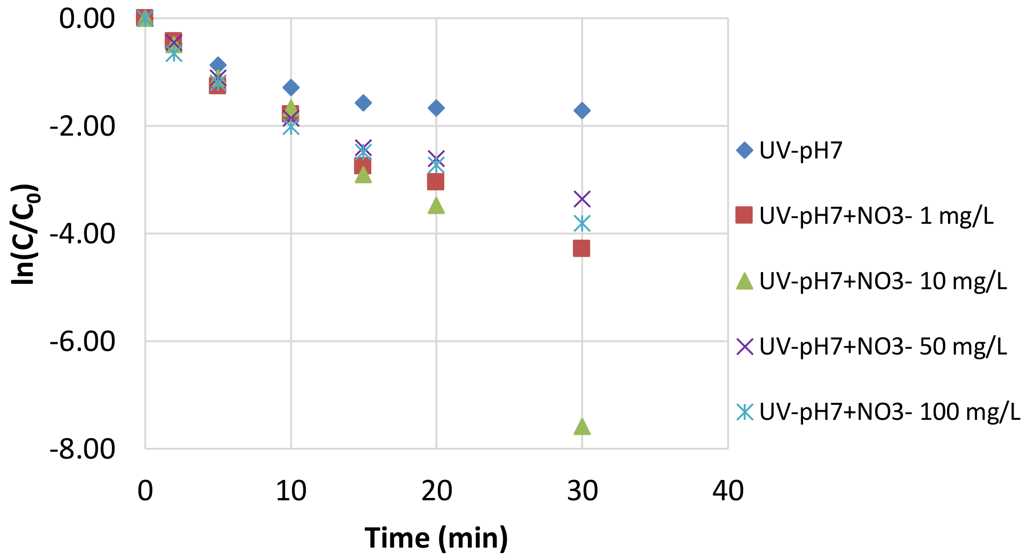


Figure 4.9 Degradation rate of profenofos by UV with nitrate (1, 10, 50 and 100 mg/L) at pH 7.

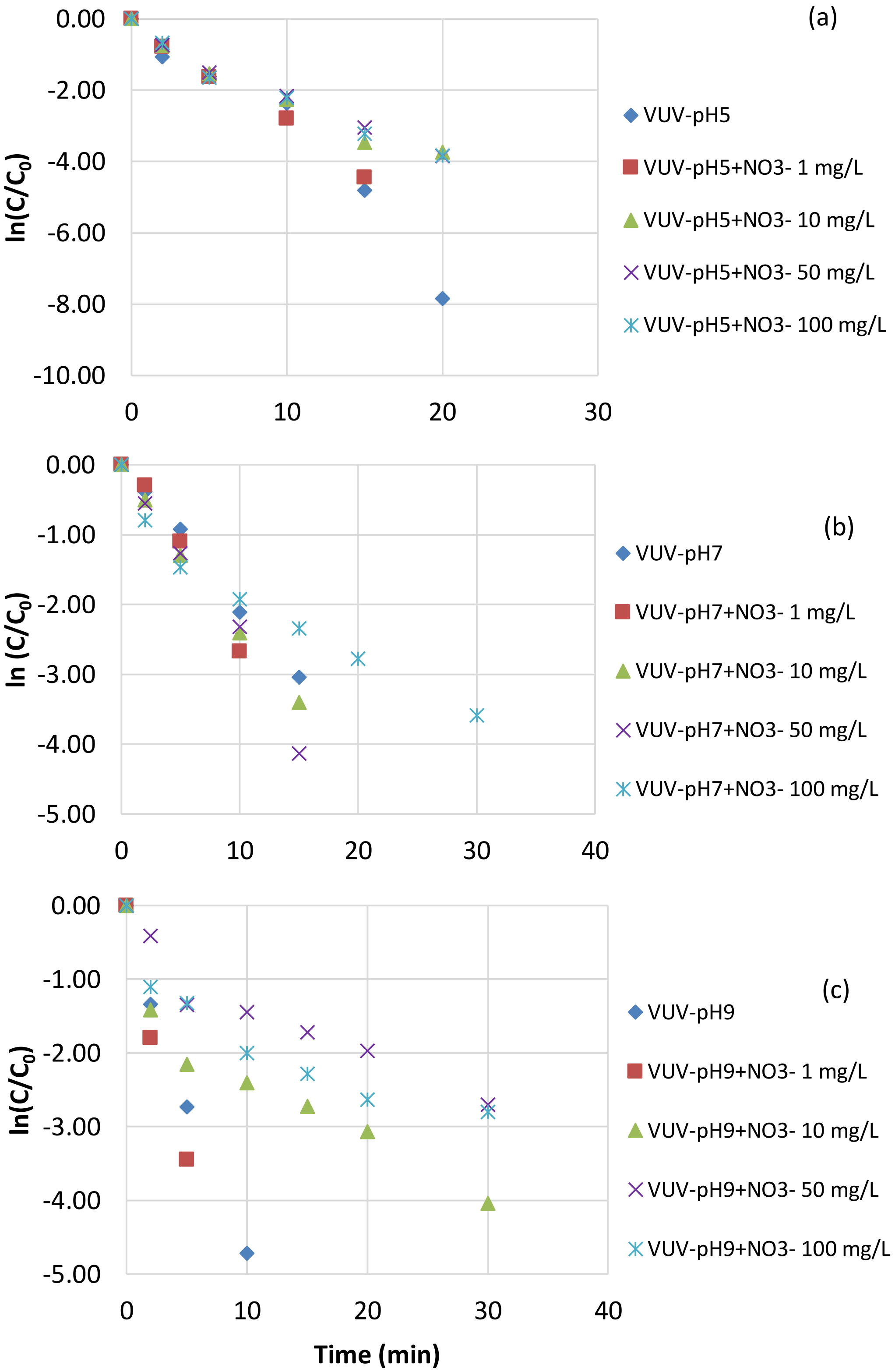


Figure 4.10 Degradation rate of profenofos by VUV with nitrate (0.1, 10, 50 and 100 mg/L) at (a) pH 5, (b) pH 7 and (c) pH 9

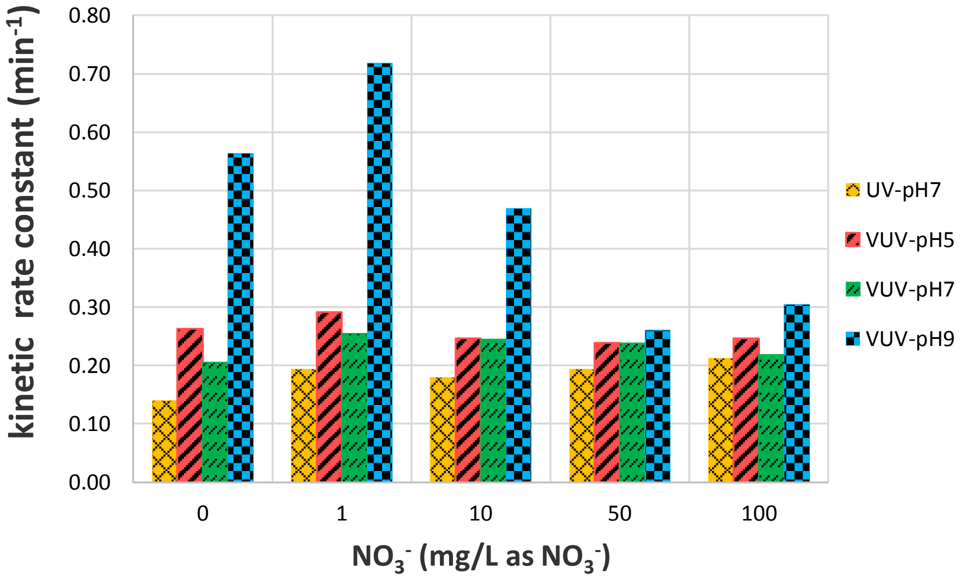


Figure 4.11 Profenofos degradation rate constant by UV and VUV. Effect of nitrate concentrations.

4.3 Role of Hydroxyl Radicals

Profenofos degradation by VUV process was subjected to direct photolysis and indirect photolysis. The indirect photolysis degradation was based on the reaction of profenofos and OH$^\bullet$. To account for the effect of OH$^\bullet$, the term "hydroxyl radicals exposure", which are product of the concentration of OH$^\bullet$ and reaction time ([OH$^\bullet$]*t), was determined. Since OH$^\bullet$ is reactive oxygen species, measurement of OH$^\bullet$ was performed by the reaction between OH$^\bullet$ and a probe compound, para-chlorobenzoic acid. The effect of direct photolysis was determined by adding tert-butyl alcohol (t-BuOH) as OH$^\bullet$ scavenger. Calculation of hydroxyl radical exposure was described in Appendix C. Table 4.2 shows values of OH$^\bullet$ exposure at the different conditions of profenofos removal by UV and VUV with or without nitrite and nitrate. From the results, removal rate constant of pCBA by direct photolysis of UV ($k_{d, UV}$, s^{-1}) and VUV ($k_{d, VUV}$, $^{-1}$) were 0.0007 and 0.0016 respectively (Table 4.2). It can be seen that the removal of pCBA with and without t-BuOH were very close to by that of UV. This means that UV generate $OH^{\bullet}$ at very small concentration. Obviously, $OH^{\bullet}$ can be formed by VUV alone and UV or VUV with nitrite and nitrate. The result of $OH^{\bullet}$ exposure was agreeable to the profenofos degradation in that VUV with 1mg/L of nitrate had highest profenofos degradation rate constant. Hydroxyl radical exposure confirmed that the present of nitrite and nitrate can generate $OH^{\bullet}$. When the concentration of nitrate increased the formation of $OH^{\bullet}$ was decreased similar to the value of kinetic rate constant. The experimental condition of VUV at pH7 was found to have higher $OH^{\bullet}$ exposure than that of VUV at pH 9. This could support that fast kinetic rate constant of VUV at pH 9 might be compound specific (Moussavi et al., 2014; Shemer and Linden, 2006) or hydrolysis (Malghani et al., 2009).

Table 4.2 Formation of $OH^{\bullet}$ on UV (pH7) and VUV (pH 7 and pH 9).

Experimental condition	*p*CBA degradation rate const.(k_{obs}, s^{-1})	OH exposure (mol·sec/L)
VUV-pH7	0.0024	2.84×10^{-10}
VUV-pH7+NO_3^- 1 mg/L	0.0030	4.84×10^{-10}
VUV-pH7+ NO_3^- 10 mg/L	0.0027	3.82×10^{-10}
VUV-pH7+ NO_3^- 50 mg/L	0.0027	3.83×10^{-10}
VUV-pH7+ NO_3^- 100 mg/L	0.0022	2.16×10^{-10}
VUV-pH7+NO_2^- 1 mg/L	0.0029	4.43×10^{-10}
UV-pH7	0.0010	5.46×10^{-11}
UV-pH7+NO_3^- 1 mg/L	0.0013	1.88×10^{-10}
UV+pH7+NO_2^- 1 mg/L	0.0018	3.71×10^{-10}
VUV-pH9	0.0020	9.78×10^{-11}
VUV-pH9+NO_3^- 1 mg/L	0.0020	7.02×10^{-11}
VUV-pH9+NO_3^- 10 mg/L	0.0020	7.08×10^{-11}
VUV-pH9+NO_3^- 50 mg/L	0.0017	NA
VUV-pH9+NO_3^- 100 mg/L	0.0015	NA

Note: Removal rate constant of pCBA by direct photolysis of UV ($k_{d,\ UV}$, s^{-1}), VUV pH7 ($k_{d,\ VUVpH7}$, s^{-1}), and VUV pH9 ($k_{d,\ VUVpH9}$, s^{-1}) were 0.0007, 0.0016 and 0.0017, respectively.

NA = Not available

4.4 Ion Byproducts from Profenofos Degradation by UV and VUV

During profenofos degradation by UV and VUV, nitrate can be reduced to nitrite. Bond of profenofos can be broken down eventually to ion such as chloride and bromide. Figure 4.12 showed the concentration of nitrite, nitrate, chloride and bromine under the degradation of profenofos 20 mg/L (5.35×10^{-5} mol/L) by UV and VUV at 1 mg/L of NO_3^- (1.6×10^{-5} mol/L). Nitrate was slightly decreased but nitrite was increased by UV irradiation (Figure 4.12(a)). This is because when nitrate react with UV irradiation, it was reduced to nitrite and oxygen or nitrite radical and oxygen radical. Moreover, nitrite radical can reform to nitrate when react with hydroxyl radicals in water (Keen et al., 2012). Under VUV irradiation nitrate was reduced rapidly and nitrite also increased constantly during the course of experiment. It was observed that more nitrate reduction and more nitrite formation was found in VUV compared to UV. The result suggested that VUV irradiation reacts with nitrate better than UV irradiation. Chloride ion was increased during reaction time similar as nitrite. This indicated that bond of chloride has been destroyed. Bromide ion was not detected from this experiment suggesting that the bond of bromide in profenofos structure may not be degraded.

Table 4.3 shows concentration of nitrite that formation from nitrate versus time provided by UV and VUV at pH7. At 10 and 100 mg/L of NO_3^-, nitrite formation was relatively small comparing with the disappearance of nitrate. During the photolysis, nitrate could convert to peroxynitrite ($ONOO^-$) and peroxynitrous acid (HOONO) (Eq. 2.20-2.21 described in section 4.2.2). Moreover, nitrite, which is unstable compound, could be also photolyzed to form nitrogen oxide ($NO_2^{\bullet}$), nitric oxide ($NO^{\bullet}$), dinitrogen trioxide (N_2O_3) and nitrous acid (HNO_2) (Eq.2.6-2.10). This illustrated that the loss of concentration nitrate provide by UV and VUV process may not necessary to be converted to nitrite. Note that at the present level of nitrite after UV or VUV irradiation did not exceed the maximum contaminant level of 1 mg NO_2^--N/L (USEPA, 2012). Therefore the removal of profenofos using UV or VUV at the presence of nitrate does not create the problem of nitrite contamination.

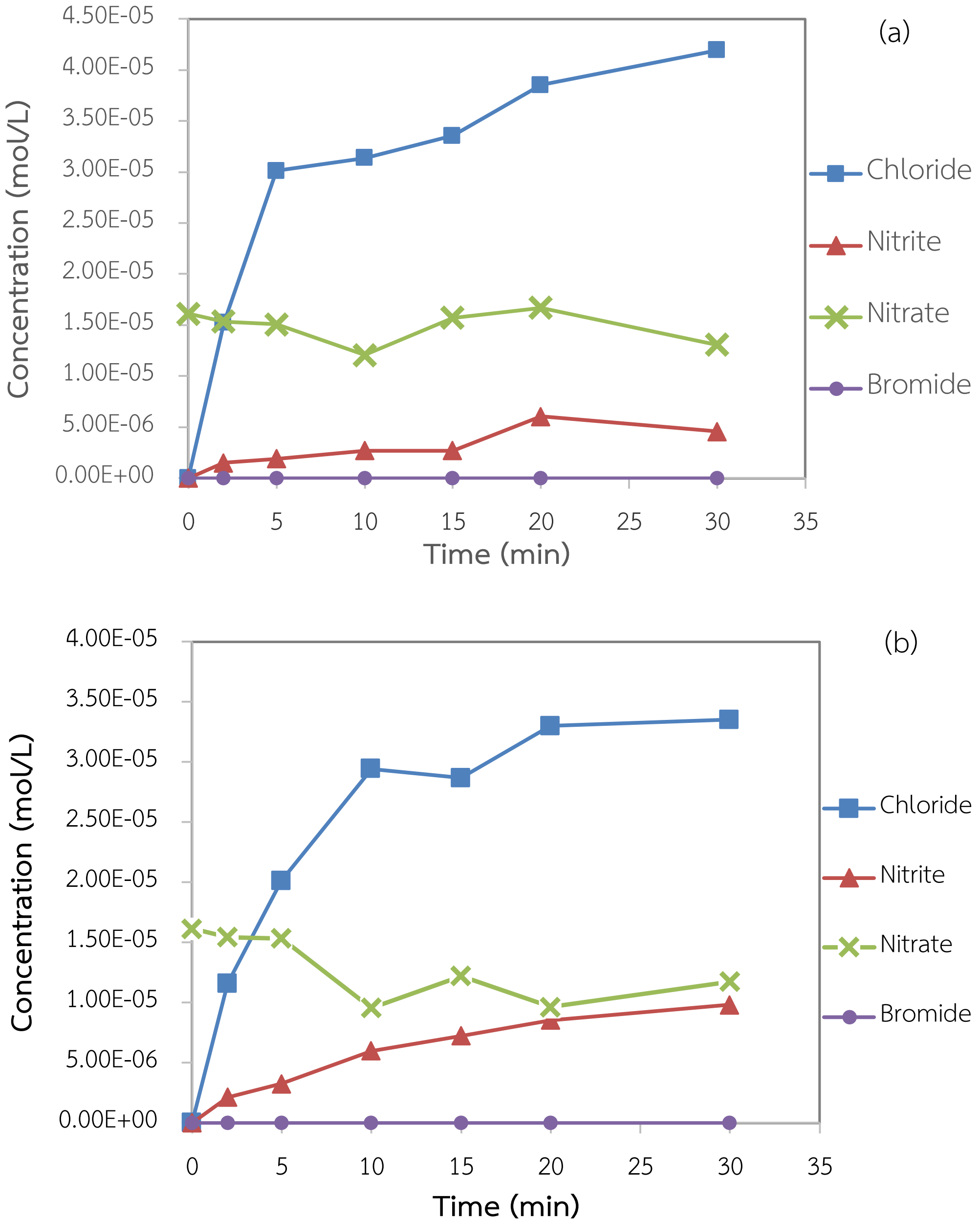


Figure 4.12 Formation of ions on profenofos removal by (a) UV and (b) VUV.

Table 4.3 Formation of NO_3^- and NO_2^-

Experiment condition	Time (min)	NO_3^- (mol/L)	NO_2^- (mol/L)
UV-pH7+ NO_3^- 1 mg/L or 1.61E-05 mol/L	0	1.61×10^{-5}	0.00
	2	1.54×10^{-5}	1.52×10^{-6}
	5	1.51×10^{-5}	1.89×10^{-6}
	10	1.21×10^{-5}	2.70×10^{-6}
	15	1.57×10^{-5}	2.70×10^{-6}
	20	1.67×10^{-5}	6.04×10^{-6}
	30	1.31×10^{-5}	4.58×10^{-6}
VUV-pH7+ NO_3^- 1 mg/L or 1.61E-05 mol/L	0	1.61×10^{-5}	0.00
	2	1.54×10^{-5}	2.13×10^{-6}
	5	1.53×10^{-5}	3.26×10^{-6}
	10	9.55×10^{-6}	5.99×10^{-6}
	15	1.22×10^{-5}	7.23×10^{-6}
	20	9.64×10^{-6}	8.53×10^{-6}
	30	1.17×10^{-5}	9.82×10^{-6}
VUV-pH7+ NO_3^- 10mg/L or 1.61E-04 mol/L	0	1.66×10^{-4}	0.00
	2	1.04×10^{-4}	1.71×10^{-6}
	5	9.09×10^{-5}	4.11×10^{-6}
	10	7.72×10^{-5}	6.71×10^{-6}
	15	8.18×10^{-5}	6.91×10^{-6}
	20	6.16×10^{-5}	6.28×10^{-6}
	30	5.55×10^{-5}	6.25×10^{-6}
VUV-pH7+ NO_3^- 100 mg/L or 1.61E-03 mol/L	0	1.71×10^{-3}	0.00×10^{-8}
	2	1.68×10^{-3}	6.83×10^{-6}
	5	1.14×10^{-3}	1.26×10^{-5}
	10	4.04×10^{-4}	1.76×10^{-5}
	15	1.71×10^{-3}	2.53×10^{-5}
	20	1.55×10^{-3}	2.77×10^{-5}
	30	1.45×10^{-3}	3.16×10^{-5}

4.5 Electrical Energy per Order (EE/O)

Electrical energy per order (EE/O) is the term describing the electrical energy consumption per order of contaminant removed for a volume of 1 m^3 of solution. For this work, EE/O values at 90% profenofos degradation in water under different conditions are shown in Figure 4.13. 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. Low concentration of nitrate (< 1 mg/L) will benefit for energy consumption for profenofos removal by VUV.

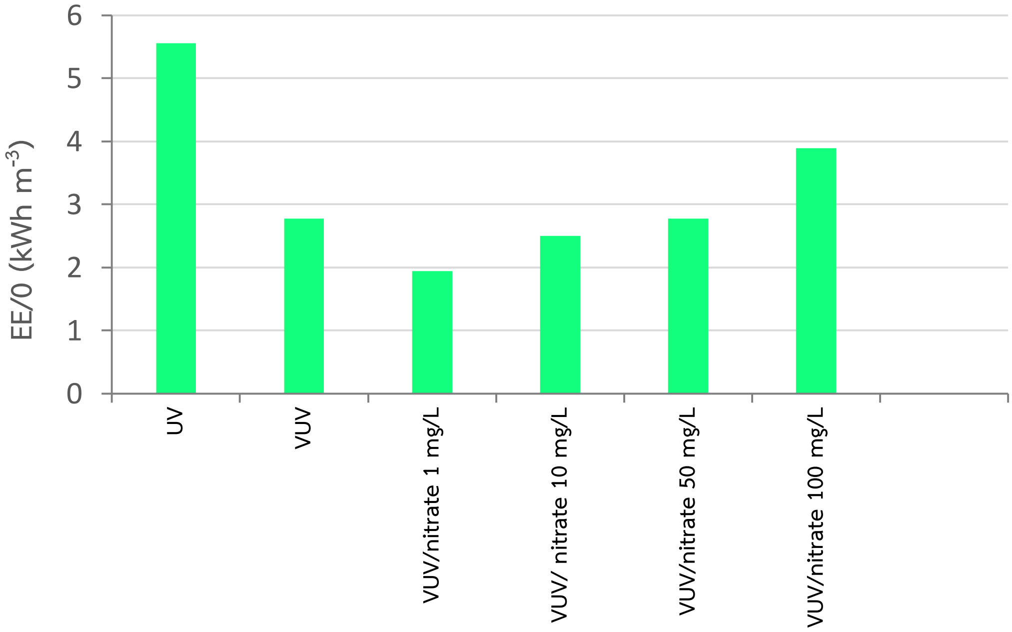


Figure 4.13 Electrical Energy per order (EE/O) by UV and VUV with/without the initial nitrate concentrations at 1, 10 and 50 mg/L for the degradation of 90% profenofos in water

CHAPTER V

CONCLUSIONS AND RECOMMENTDATIONS

5.1 Conclusions

The finding of this research shows that UV and VUV had ability to remove profenofos in water. The presence of nitrite and nitrate resulted in the promotion of the degradation rate of profenofos under VUV irradiation. The result confirmed that hypothesis. Clearly profenofos removal rate constant of VUV with nitrite at 1 mg/L was higher than those of 0.1 mg/L. The kinetic of profenofos degradation by VUV with nitrate at low concentration of 1 mg/L was significantly more rapid than the higher concentrations of nitrate. This was due to more hydroxyl radical formation. Effect of initial pH at 5, 7 and 9 strengthen the theory that profenofos unstable at high pH value. High profenofos degradation rate constants were observed for solution of pH 9 for UV and VUV. This because profenofos was unstable at high pH. At pH 9, profenofos removal was 90% in 10 min by VUV.

Hydroxyl radical exposure of UV experiment confirmed that the removal of profenofos was mainly by direct photolysis. The present of nitrate and nitrite results in the formation of hydroxyl radicals. The hydroxyl exposure of VUV with nitrate 1 mg/L was the highest.

For the byproduct under the degradation of profenofos by UV and VUV, chloride concentration increased during reaction time similar as nitrite but bromide concentration was not detected.

The EE/O value showed that VUV is more economical than UV. The lowest EE/O was achieved by VUV with the nitrate concentration of 1 mg/L. The present of nitrate at low concentration decreased value of EE/O and high concentration tend to increased EE/O value that correspond with degradation rate of profenofos.

5.2 Recommendations

1. The byproduct toxicity and pathway of profenofos degradation under VUV and UV should be determined.
2. In natural water, there are several other inorganic species of both cation and anion besides nitrate and nitrite. These ions may influence the performance of VUV process. Therefore, the effect of other major ions such as Ca^{2+}, Mg^{2+}, Na^{+}, Fe_2^{+} and SO_4^{2-} in the water to profenofos degradation by UV and VUV should be investigated.
3. In real situation where profenofos may not be as high as 10 mg/L, the removal efficiency would be a different from this study. The treatment efficiency at low concentration of profenofos and electrical energy per order of contaminant removed in natural water matrices should be evaluated.

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APPENDIX A

CALIBRATION CURVE

Analysis concentration of profenofos by Gas Chromatography with electron capture detector (GC-ECD)

Laboratory Equipment and chemical regent

1. Gas Chromatography with electron capture detector (GC-ECD, Agilent)
2. Stock solution of profenofos concentration 100 mg/L
3. Volumetric flask
4. Pipette
5. Hexane

Preparation of stock solution of profenofos

Profenofos 100 mg/L was dissolved in hexane by amber vial and was stored in the dark at 4 °C.

Preparation of standard solution of profenofos

Pipette stock solution of profenofos followed Table A.1 into volumetric flask 25 mL by calculation from Equation 1 due to standard solution was serial dilution.

$$C_1V_1 = C_2V_2 \tag{1}$$

Example Preparation of standard solution of profenofos at 10 mg/L from stock solution 100 mg/L in 25 ml of volumetric flask

$$C_1V_1 = C_2V_2$$

$$100 \text{ mg/L} \times V_1 = 10 \text{ mg/L} \times 25 \text{ mg/L}$$

$$V_1 = 2.5 \text{ mL}$$

∴ Pipetted stock solution of profenofos 2.5 mL into 25 mL of volumetric flask and adjusted volume of solution by hexane until final volume was 25 mL

Table A.1 Volume of stock solution

Concentration of profenofos (mg/L)	Stock solution (mg/L)	Volume of stock solution (mL)
0.1	1	2.5
1	10	2.5
5	10	12.5
10	100	2.5

Standard curve

The concentrations of standard solution of profenofos were analyzed by GC-ECD. Standard curve was potted between area of chromatogram and concentration of standard solution of profenofos.

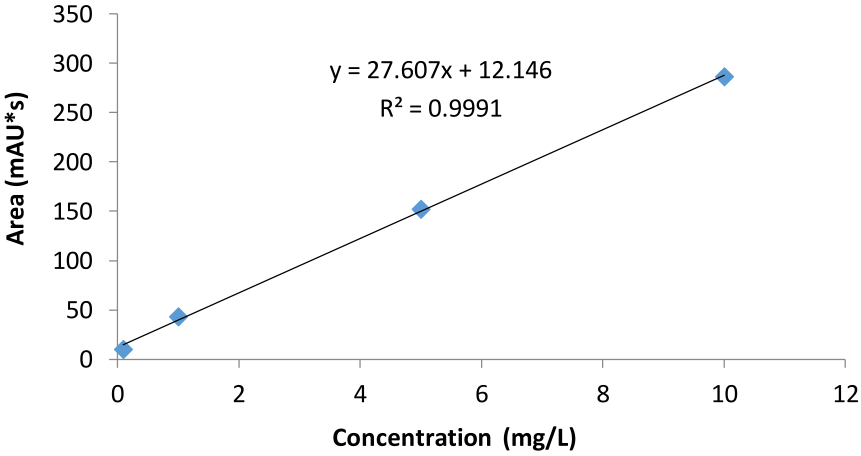

Figure A.1 Standard curve of profenofos analyzing by GC-ECD

After we had standard curve, the concentration of profenofos was calculate by using equation from standard curve substituted by area of chromatogram from GC-ECD.

APPENDIX B

EXPERIMENTAL RESULT OF PROFENOFOS REMOVAL

Table B.1 Result of profenofos removal by UV and VUV at initial concentration 10 mg/L

Time (min)	Concentration of profenofos (mg/L)					
	pH5		pH7		pH9	
	UV	VUV	UV	VUV	UV	VUV
0	8.19	8.03	8.22	9.93	9.41	9.57
2	5.34	2.77	5.13	6.76	4.28	2.98
5	3.74	1.58	3.45	3.96	2.29	0.35
10	2.2	0.75	2.29	1.2	1.87	-
15	1.95	0.07	1.7	0.47	1.57	-
20	1.53	-	1.56	-	1	-
30	1.49	-	1.48	-	0.89	-

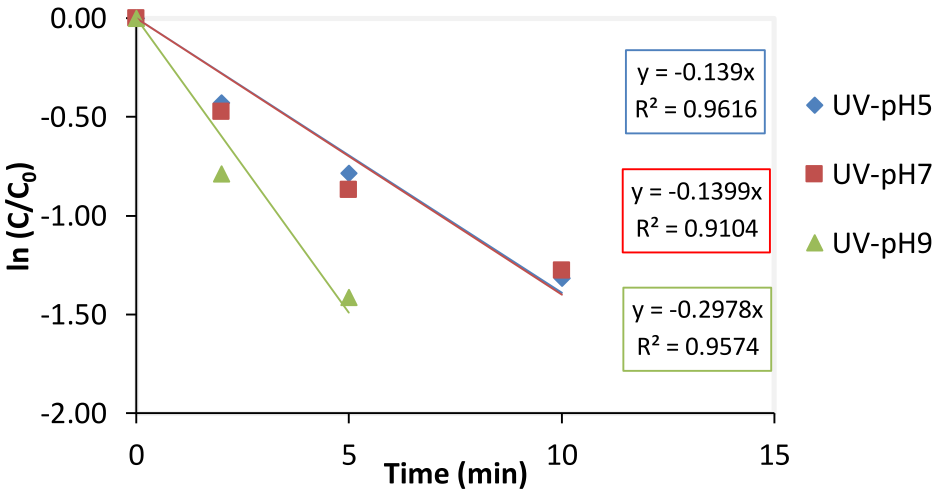

Figure B.1 Plotted profenofos removal first order kinetic rate constant at initial concentration of profenofos 10 mg/L under UV irradiation at pH 5, 7 and 9.

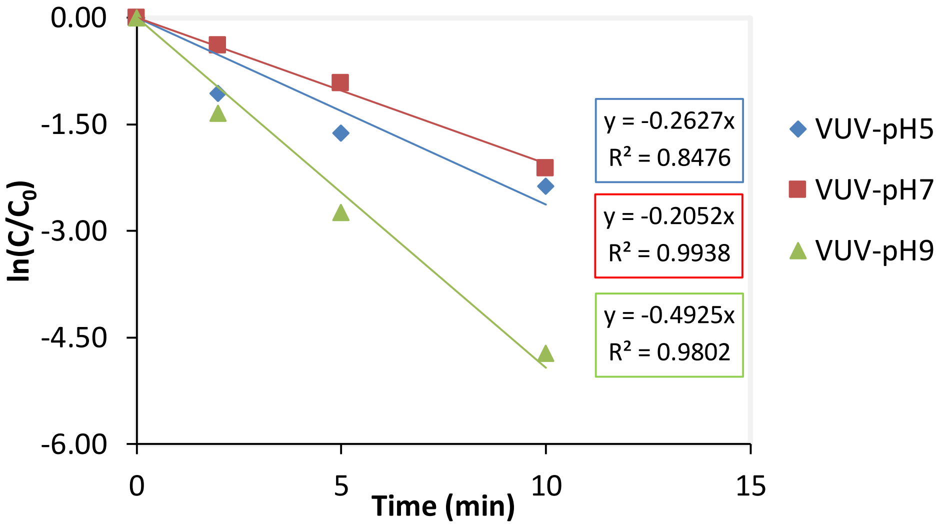

Figure B.2 Plotted profenofos removal first order kinetic rate constant at initial concentration of profenofos 10 mg/L under VUV irradiation at pH 5, 7 and 9.

APPENDIX C

EFFECT OF NITRITE AND NITRATE

Table C.1 Result of profenofos removal by UV with nitrite (0, 0.1, 0.5 and 1 mg/L) at pH 7.

Time (min)	Concentration of profenofos (mg/L)			
	NO_2^- = 0 mg/L	NO_2^- = 0.1 mg/L	NO_2^- = 0.5 mg/L	NO_2^- = 1 mg/L
0	8.22	9.57	10.94	8.84
2	5.13	5.15	7.76	5.36
5	3.45	3.06	3.28	2.80
10	2.29	1.52	1.48	1.62
15	1.7	0.86	0.89	0.90
20	1.56	0.53	0.21	0.38
30	1.48	0.23	-	0.14

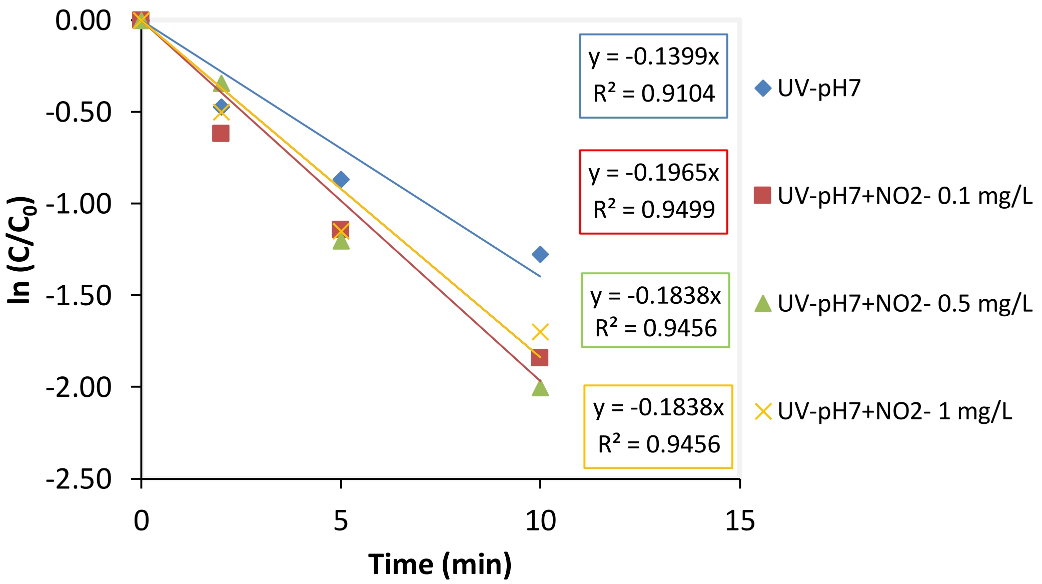

Figure C.1 Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrite 0.1, 0.5 and 1 mg/L under UV irradiation at pH7

Table C.2 Result of profenofos removal by UV with nitrate (0, 1, 10, 50 and 100 mg/L) at pH7.

Time (min)	Concentration of profenofos (mg/L)				
	NO_3^- = 0 mg/L	NO_3^- = 1 mg/L	NO_3^- = 10 mg/L	NO_3^- = 50 mg/L	NO_3^- = 100 mg/L
0	8.22	8.72	8.50	9.83	8.45
2	5.13	5.68	5.21	6.24	4.38
5	3.45	2.47	2.81	3.27	2.55
10	2.29	1.47	1.61	1.55	1.13
15	1.70	0.56	0.47	0.90	0.70
20	1.56	0.42	0.26	0.73	0.56
30	1.48	0.12	0.00	0.35	0.19

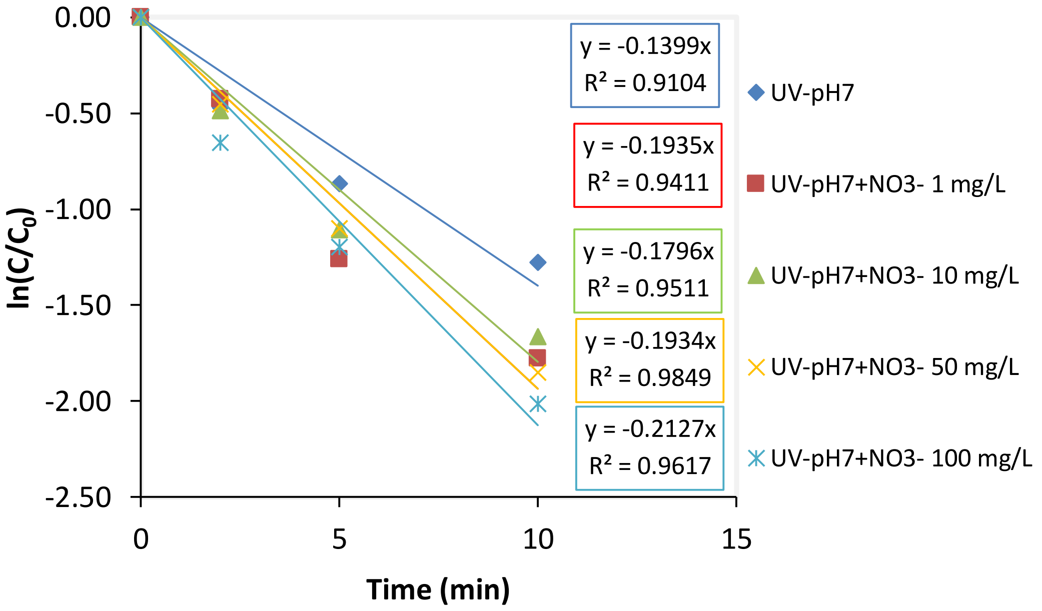

Figure C.2 Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrate 1, 10, 50, and 100 mg/L under UV irradiation at pH7.

Table C.3 Result of profenofos removal by VUV with nitrite (0, 0.1, 0.5 and 1 mg/L) at pH5.

Time (min)	Concentration of profenofos (mg/L)			
	NO_2^- = 0 mg/L	NO_2^- = 0.1 mg/L	NO_2^- = 0.5 mg/L	NO_2^- = 1 mg/L
0	8.03	10.62	9.95	11.89
2	2.77	4.00	5.26	7.39
5	1.58	2.63	3.74	3.27
10	0.75	1.27	2.92	1.49
15	0.07	0.45	2.58	0.34
20	0.003	0.21	0.91	0.01
30	-	-	0.73	-

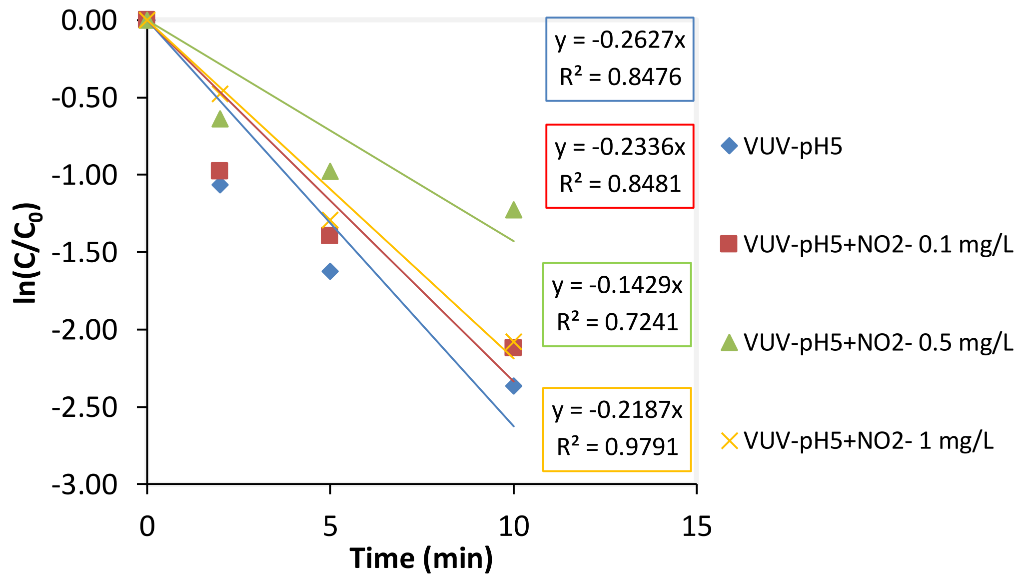

Figure C.3Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrite 0.1, 0.5 and 1 mg/L under VUV irradiation at pH5.

Table C.4 Result of profenofos removal by VUV with nitrate (0, 1, 10, 50 and 100 mg/L) at pH5.

Time (min)	Concentration of profenofos (mg/L)				
	NO_3^- = 0 mg/L	NO_3^- = 1 mg/L	NO_3^- = 10 mg/L	NO_3^- = 50 mg/L	NO_3^- = 100 mg/L
0	8.03	8.52	8.90	9.12	10.28
2	2.77	3.87	4.21	4.34	5.23
5	1.58	1.67	1.93	2.02	1.97
10	0.75	0.52	0.93	1.04	1.12
15	0.07	0.10	0.28	0.43	0.41
20	0.00	-	0.21	0.19	0.22
30	-	-	-	-	-

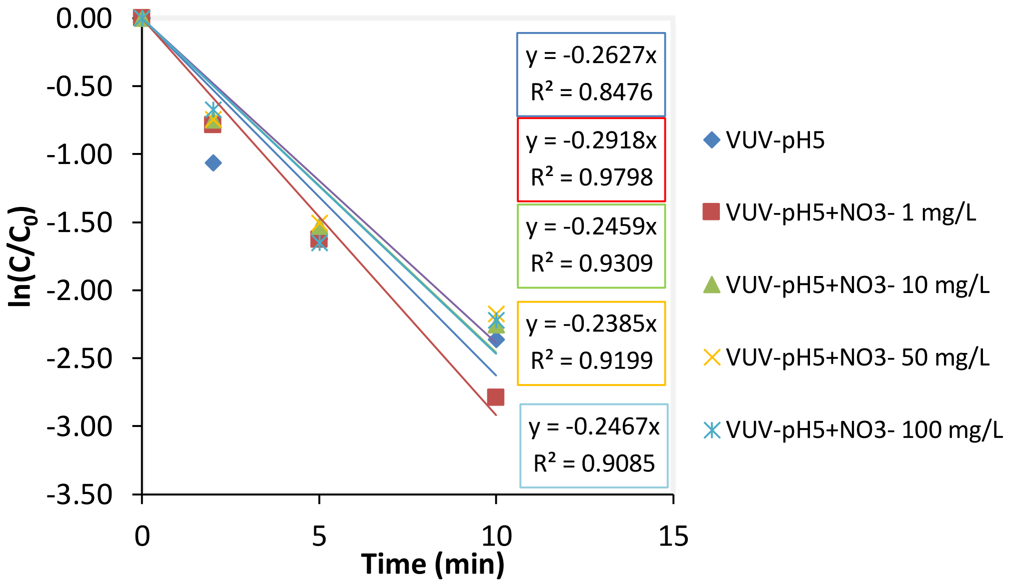

Figure C.4Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrate 1, 10, 50 and 100 mg/L under VUV irradiation at pH5.

Table C.5 Result of profenofos removal by VUV with nitrite (0, 0.1, 0.5 and 1 mg/L) at pH7.

Time (min)	Concentration of profenofos (mg/L)			
	NO_2^- = 0 mg/L	NO_2^- = 0.1 mg/L	NO_2^- = 0.5 mg/L	NO_2^- = 1 mg/L
0	9.93	8.65	8.07	10.16
2	6.76	4.65	3.97	5.20
5	3.96	2.38	2.07	2.09
10	1.20	1.59	1.09	1.20
15	0.47	0.59	0.74	0.37
20	-	0.22	-	0.24
30	-	-	-	-

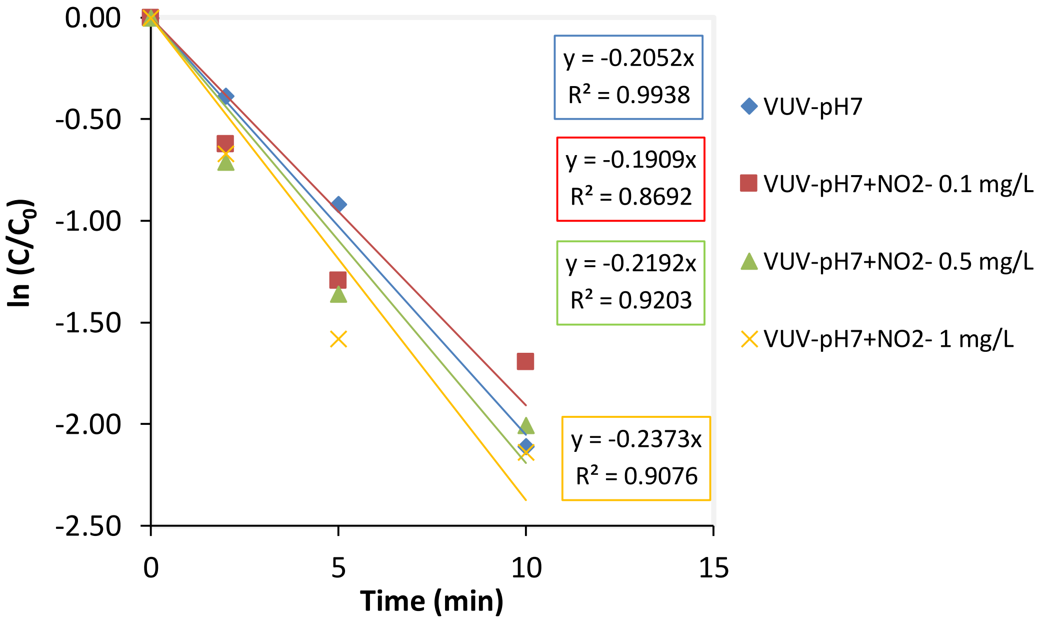

Figure C.5 Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrite 0.1, 0.5 and 1 mg/L under VUV irradiation at pH7

Table C.6 Result of profenofos removal by VUV with nitrate (0, 1, 10, 50 and 100 mg/L) at pH7.

Time (min)	Concentration of profenofos (mg/L)				
	NO_3^- = 0 mg/L	NO_3^- = 1 mg/L	NO_3^- = 10 mg/L	NO_3^- = 50 mg/L	NO_3^- = 100 mg/L
0	9.93	7.87	9.04	9.37	8.44
2	6.76	5.84	5.47	5.41	3.81
5	3.96	2.62	2.47	2.63	1.95
10	1.20	0.55	0.81	0.92	1.23
15	0.47	-	0.30	0.15	0.81
20	-	-	-	-	0.52
30	-	-	-	-	0.23

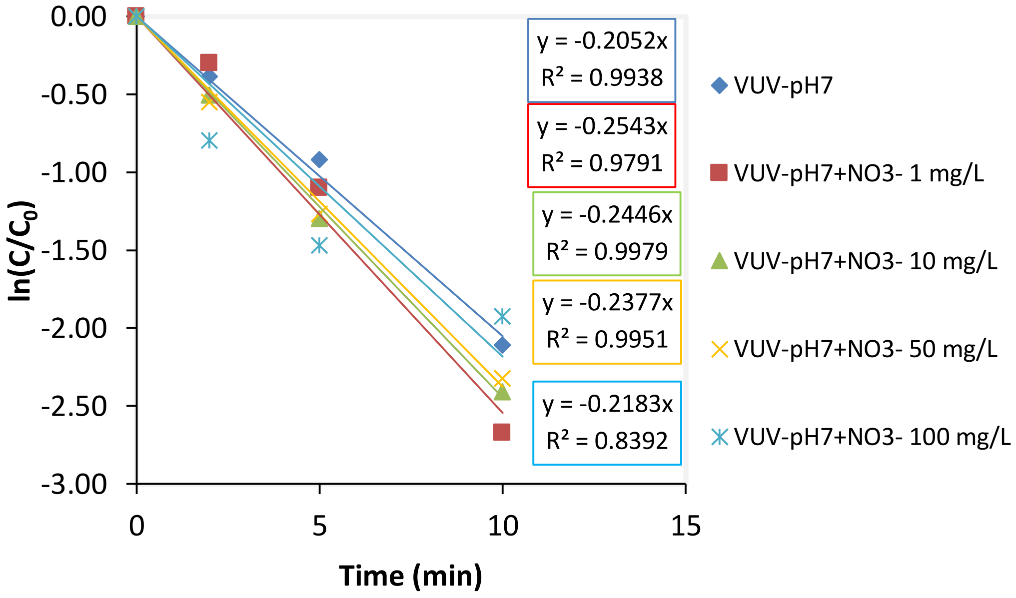

Figure C.6 Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrate 1, 10, 50 and 100 mg/L under VUV irradiation at pH7.

Table C.7 Result of profenofos removal by VUV with nitrite (0, 0.1, 0.5 and 1 mg/L) at pH9.

Time (min)	Concentration of profenofos (mg/L)			
	NO_2^- = 0 mg/L	NO_2^- = 0.1 mg/L	NO_2^- = 0.5 mg/L	NO_2^- = 1 mg/L
0	9.57	8.14	11.38	11.95
2	2.98	1.46	5.36	2.63
5	0.35	0.02	3.41	1.41
10	-	-	1.64	1.27
15	-	-	0.75	1.01
20	-	-	0.18	0.63
30	-	-	-	-

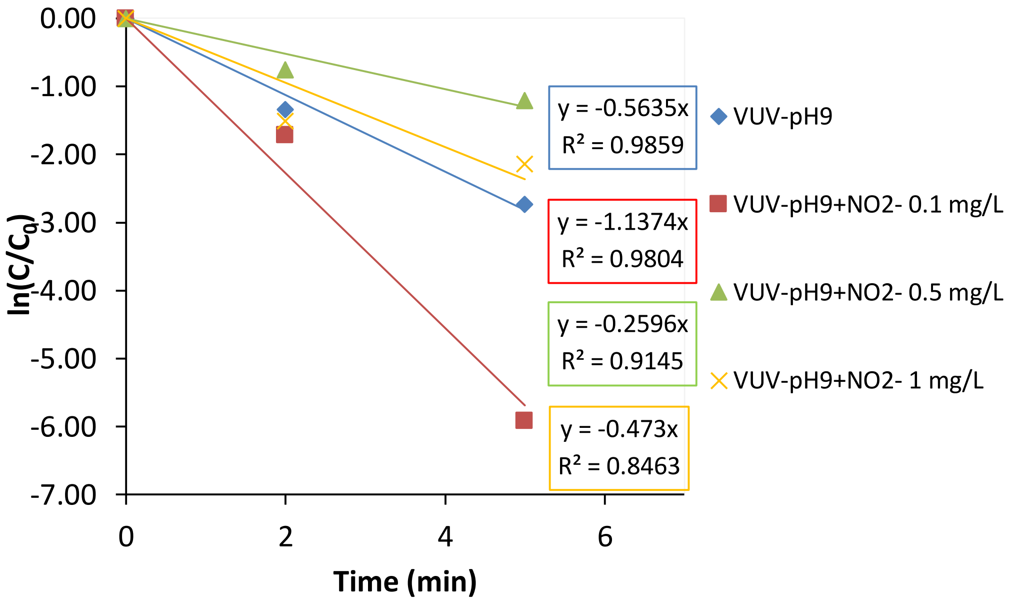

Figure C.7 Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrite 0.1, 0.5 and 1 mg/L under VUV irradiation at pH9

Table C.8 Result of profenofos removal by VUV with (0, 1, 10, 50 and 100 mg/L) at pH9.

Time (min)	Concentration of profenofos (mg/L)				
	NO_3^- = 0 mg/L	NO_3^- = 1 mg/L	NO_3^- = 10 mg/L	NO_3^- = 50 mg/L	NO_3^- = 100 mg/L
0	9.57	10.14	8.68	9.85	7.04
2	2.98	1.68	2.10	6.51	2.34
5	0.35	0.32	1.01	2.57	1.87
10	-	-	0.78	2.32	0.95
15	-	-	0.57	1.77	0.72
20	-	-	0.41	1.38	0.51
30	-	-	0.15	0.66	0.43

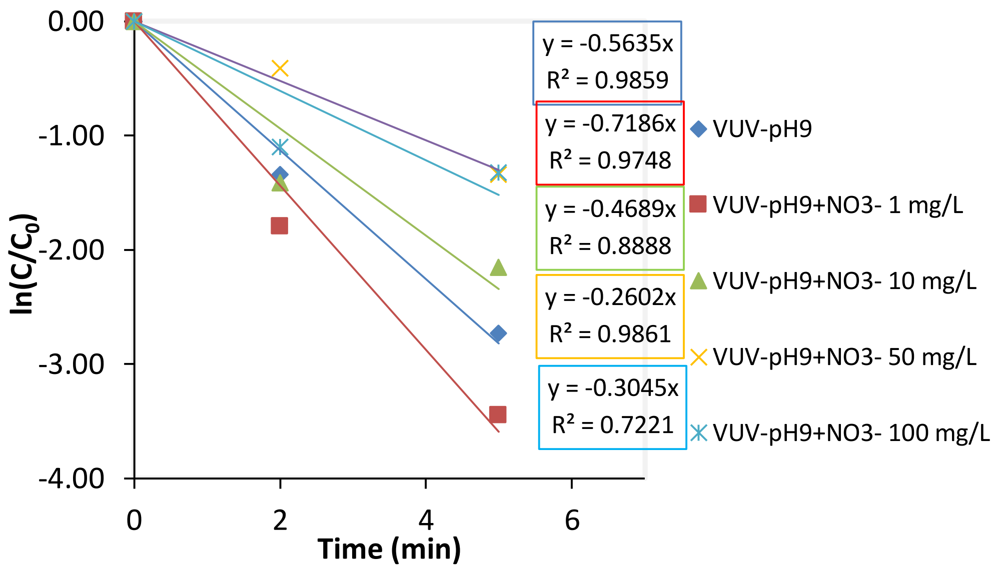

Figure C.8.Plotted profenofos removal first order kinetic rate constant at initial concentration of nitrate 1, 10, 50 and 100 mg/L under VUV irradiation at pH9.

APPENDIX D

THE FORMATION OF HYDROXYL RADICAL

Table D.1 Result of pCBA removal by UV at pH 7.

Time (min)	concentration of pCBA (µg/L)			
	UV	UV w/ t-BuOH	UV + NO_2^- 1 mg/L	UV + NO_3^- 1 mg/L
0	135.67	126.71	168.77	173.01
2	118.35	116.56	143.02	132.45
5	99.85	103.62	79.96	123.46
10	77.91	76.77	61.51	77.66
15	27.88	18.18	28.30	32.26
20	0.23	4.04	5.31	0.58
30	-	-	-	-

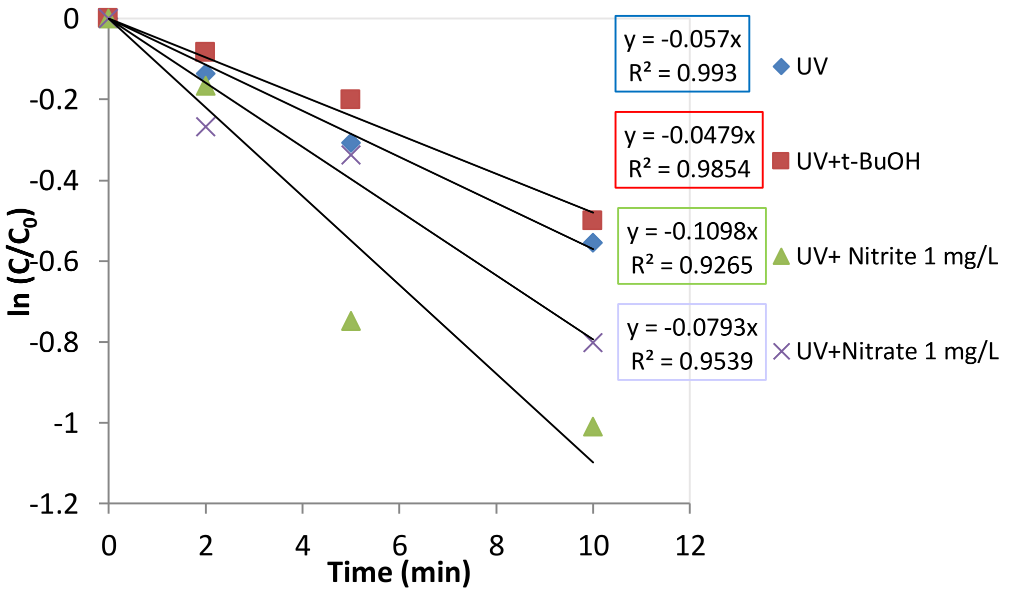

Figure D.1 Observed pseudo first order of pCBA removal rate and pseudo first order constant by direct photolysis of *p*CBA removal by UV at pH7

Table D.2 Result of pCBA removal by VUV at pH7.

Time (min)	concentration of pCBA (μg/L)					
	VUV	VUV w/ t-BuOH	VUV + NO$_3^-$ 1 mg/L	VUV + NO$_3^-$ 10 mg/L	VUV + NO$_3^-$ 50 mg/L	VUV + NO$_3^-$ 100 mg/L
0	164.85	103.28	392.37	404.17	375.78	443.33
2	128.52	89.11	299.30	298.17	263.17	367.08
5	68.80	67.61	170.67	189.78	201.74	285.63
10	39.81	36.97	62.47	77.54	68.04	121.65
15	-	-	-	10.70	16.85	59.71
20	-	-	-		-	27.41
30	-	-	-	-	-	2.65

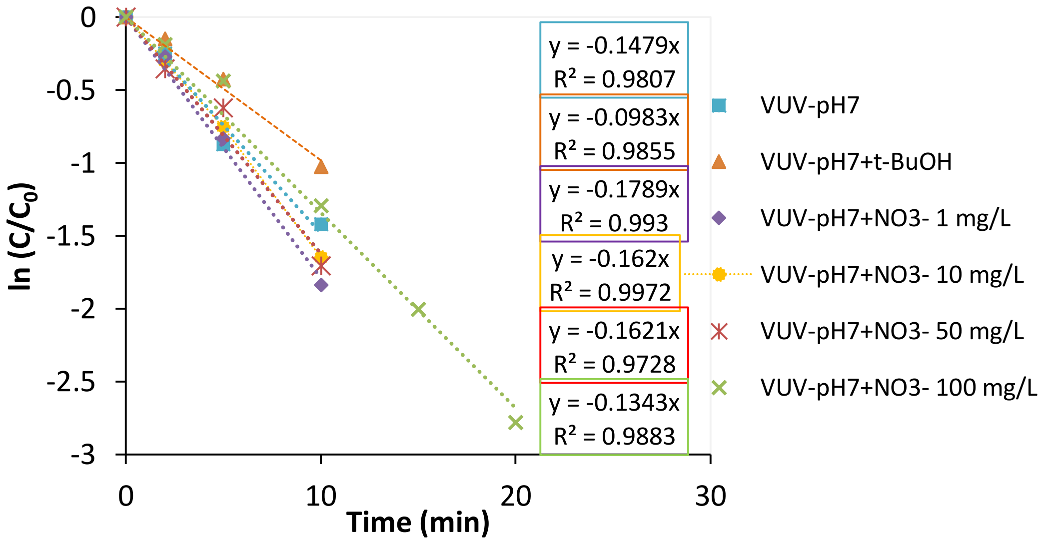

Figure D.2 Observed pseudo first order of pCBA removal rate and pseudo first order constant by direct photolysis of pCBA removal by VUV at pH7.

Table D.3 Result of pCBA removal by VUV at pH9

Time (min)	concentration of pCBA (µg/L)					
	VUV	VUV w/ t-BuOH	VUV + NO3- 1 mg/L	VUV + NO3- 10 mg/L	VUV + NO3- 50 mg/L	VUV + NO3- 100 mg/L
0	320.82	399.59	373.65	382.96	404.25	338.27
2	251.28	341.22	299.25	287.85	313.40	263.98
5	140.81	230.43	217.07	233.02	241.66	208.73
10	48.94	75.53	112.53	114.04	143.38	137.70
15	-	24.04	20.12	28.79	94.20	84.05
20	-	-	11.98	21.48	35.09	60.20
30	-	-	-	-	6.49	8.32

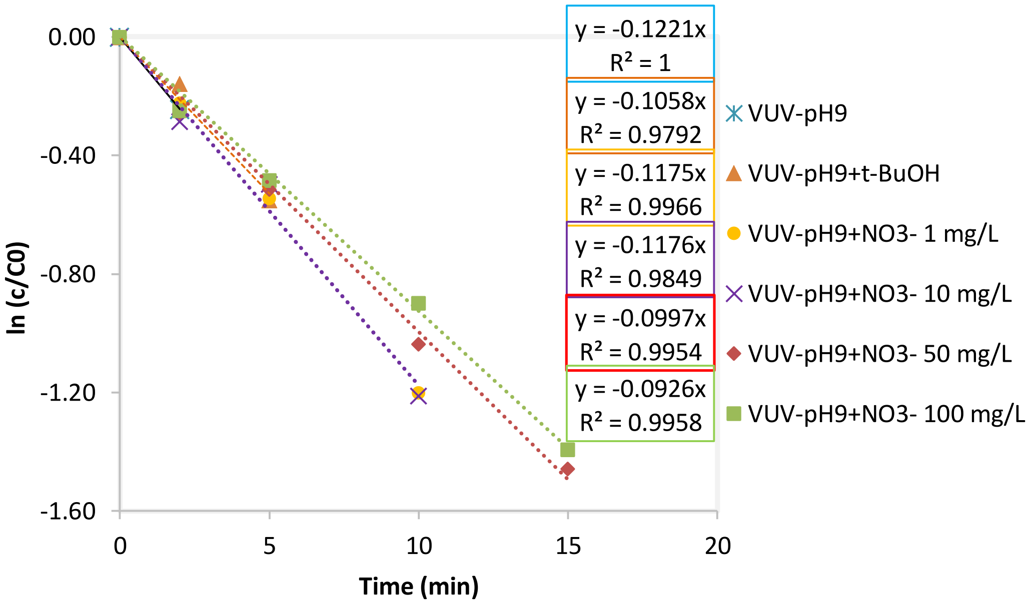

Figure D.3 Observed pseudo first order of pCBA removal rate and pseudo first order constant by direct photolysis of pCBA removal by VUV at pH9.

APPENDIX E

ELECTRICAL ENERGY PER ORDER

Electrical energy per order (EE/O) calculation from Equation below

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

Where P_{el} is 30×10^{-3} [kW]

t is time [min]

V is 1.8 [L]

C_0 is initial concentration of the profenofos

C is concentration of the profenofos

For this work, EE/O values at 90% profenofos degradation in water under different conditions are shown in Table D.1

Table D.1 Electrical energy per order data

Experimental condition	Time (min) at 90% profenofos degradation	EE/O (kWh m^{-3})
UV	20	5.56
VUV	10	2.78
VUV + NO_3^- 1 mg/L	7	1.94
VUV + NO_3^- 10 mg/L	9	2.5
VUV + NO_3^- 50 mg/L	10	2.78
VUV + NO_3^- 100 mg/L	14	3.89

VITA

Miss Pawankorn Nongsung was born on February 25, 1990 in Roi-ET province. She graduated Bachelor's degree of Engineering of environmental from Khonkaen University. After that she continued study in Master's degree of science in Environmental management, Chulalongkorn University

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