Degradation of Paracetamol and Norfloxacin in Aqueous Solution Using Vacuum Ultraviolet (VUV) Process

Thunyalux Ratpukdi

Abstract—**The removal of pharmaceutical and personal care products (paracetamol and norfloxacin) in water by vacuum ultraviolet (VUV) process was studied. The effects of initial pharmaceutical concentrations (1, 5 and 10 mg/L), initial pHs (5, 7 and 9), VUV powers (30, 60 and 120 W) and bicarbonate concentrations (100 and 200 mg/L as $CaCO_3$) were investigated. The experiments under ultraviolet (UV) condition were performed for comparative purpose. The results showed that the VUV process exhibited superior degradation performance than that by the UV process. The rates of both paracetamol and norfloxacin removals were second order reaction. Higher concentrations resulted in the decrease of pharmaceutical degradation rate. The initial pH had slight impact on pharmaceutical removal efficiency and the neutral pH showed the highest degradation efficiency. Bicarbonate obviously decreased the pharmaceutical removal .This is due to from $OH^{\bullet}$ scavenging and the VUV light absorption of the bicarbonate. For the effect of VUV powers, removal efficiencies increased as the increase of VUV powers.**

Index Terms—**Paracetamol, Norfloxacin, PPCPs, Vacuum ultraviolet (VUV).**

I. Introduction

During the past few years, there has been a concern of the occurrence of pharmaceuticals in natural water resources. The presence of these pharmaceuticals poses the threat to aquatic organisms in terms of mutagenicity as well as the unknown effect to human. Pharmaceuticals are originally from human and feedstock wastewaters and often found their ways into surface water sources [1]-[3]. This because they were not be effectively removed by biological wastewater treatment plant. To prevent the release of pharmaceuticals to natural water sources, other techniques beside biological treatment should be applied. Advanced oxidation processes (AOPs) are the promising technologies employing hydroxyl radicals ($OH^{\bullet}$) to degrade the contaminants. Among AOPs, vacuum ultraviolet (VUV) process has gained a lot attention recently [4]-[6]. This because an advantage of VUV in that it generates $OH^{\bullet}$ without addition of chemicals [7] (Eq.1). In addition, the contaminants can be degraded by direct photolysis.

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

This work studied the removal of model pharmaceuticals (paracetamoal and norfloxacin) in aqueous solution by low pressure VUV (185 + 254 nm) lamps. The effect of operating parameters including initial concentrations, pH, and bicarbonate concentrations were investigated. Ultraviolet (UV, 254 nm) experiments was also conducted for comparative purpose.

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II. Materials and Methods

A. Water Sample

For preparing 10,000 mg/L of paracetamol stock solution, 10 g of paracetamol ($C_8H_9NO_2$, Tylenol®) was boiled with 100 mL of deionized water (DI) and 20 mL of 5 M H_2SO_4 for 30 min or until dissolved. The solution was filtered with 1.2 μm glass fiber filter and then made up volume to 1000 mL. Stock solution of norfloxacin was prepared by dissolving norfloxacin® ($C_{16}H_{18}FN_3O_3$) with deionized water. Specific concentrations of paracetamol norfloxacin were prepared from stock solutions. Sodium bicarbonate was used to prepare stock solution of 10,000 mg/L as $CaCO_3$. This stock solution will be diluted with DI water for experiment studying the effect of bicarbonate.

B. Experimental Setup and Procedure

The reactor of VUV process was a 10-L glass cylinder reactor which has a diameter of 23 cm and a height of 33 cm. Four VUV lamps (30W/lamp, model GPH383T5/VH/HO, Universal Light Source, Inc.) were immersed in water and placed evenly in the reactor. Mixing was provided using paddle motor at 60 rpm. UV process was setup in similar fashion like VUV process except that a UV lamp (30W/lamp, model GPH383T5/L/HO Universal Light Source, Inc.) was replaced. It is noted that the VUV lamps used in this research were the lamp that emit wavelength of 185 and 254 nm while UV lamps only emit the wavelength of 254 nm. Experiments were conducted in batch mode for 60 min. Samples were withdrawn from reactor at specific time interval of 0, 2, 5, 10, 20, 30, 45, and 60 min. For VUV process, the experiments were performed by varying paracetamol and norfloxacin concentrations (1, 5, and 10 mg/L), pH (5, 7, and 9), and VUV powers (30, 60 and 120 W). For UV process, only UV power of 120 W was used with various bicarbonate concentrations (0, 100, and 200 mg/L as $CaCO_3$).

C. Analyses

Analyses of paracetamol and norfloxacin concentrations

were performed by spectrophotometer (Pharma Spec UV-1700, SHIMADZU) at wavelength 242 nm and 272 nm, respectively. Calibration curve of paracetamol and norfloxacin were developed from known concentration of standards prepared in section II.A (data not shown).

III. Result and Discussion

A. Effect of Initial Concentrations

Degradation of paracetamol and norfloxacin at different initial concentrations is shown in Fig. 1a and Fig. 1b, respectively. From Fig. 1, the removal of both paracetamol and norfloxacin occurred rapidly during the first 10 min of reaction time and slower at later period. This could be explained that at the beginning of reaction time there were only parent compounds (parecetamol or norfloxacin) in the solution. Therefore, the parent compounds can react quickly with hydroxyl radicals or undergone photolysis. However at later period, the intermediates or byproducts were formed. These byproducts could compete with the parent compounds to react with hydroxyl radicals and absorb VUV. Degradation rates of paracetamol and norfloxacin were fitted with second order reaction. The second order reaction rates were 1.837, 0.836, 0.890 L/mg.min for 1, 5, 10 mg/L, respectively. It is noted that at higher concentration, degradation of paracetamol and norfloxacin was lower than low concentration. This was due higher mass of contaminant while the amount of hydroxyl radicals and photon remained the same. Plus more intermediates were formed at high concentration

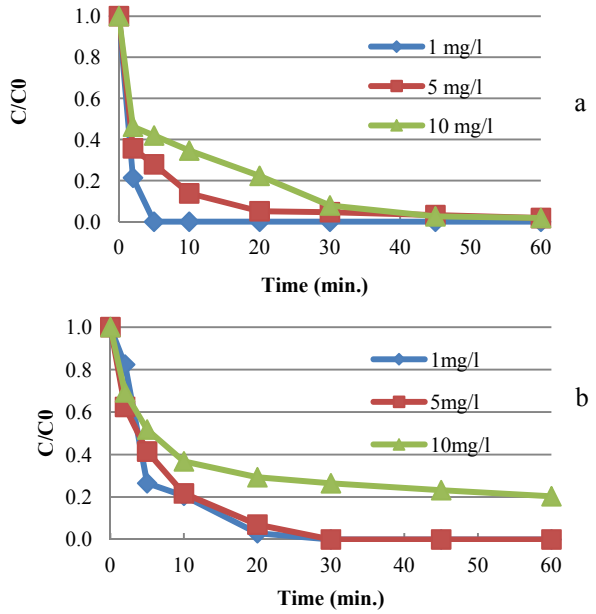

Fig. 1. Degradation of paracetamol (a) and norfloxacin (b) by VUV. Effect of initial concentrations.

B. Effect of pH

Fig. 2a and Fig. 2b show the effect of pH on degradation of paraetamol and norlfoxacin, respectively. Apparently, the optimum pH for degradation of paracetamol was at 7 while pH 5 and 9 exhibited the lower degradation rates (Table I). The optimum pH of norfloxacin degradation ranged from7 to 9. Tasaki et al. [8] also found that the optimum pH was at neutral range when studying the removal methyl orange by VUV. It was described that at too low pH, ozone generated by reaction of dissolved oxygen and VUV (Eq. 2) was stable and lead to less formation of hydroxyl radicals. However, at high pH hydroxyl radicals is dissociated to oxygen anion radical ($O^{\bullet-}$) which is less reactive than hydroxyl radicals (Eq.3).

$$1.5O_2 + h\nu(185\text{nm}) \rightarrow O_3 \quad (2)$$

$$OH^{\bullet} \rightarrow O^{\bullet-} + H^{\bullet+} \ (p\text{Ka}11.9) \quad (3)$$

TABLE I: Degradation Rate of Paracetamol and Norfloxacin by VUV and UV Processes

Run No.	Conc. (mg/L)	pH	VUV/UV power (W)	HCO_3^- mg/L as CaCO3	Second order rate constant (L/min-mg)
Paracetamol					
1	1	7	120	0	1.837
2	5	7	120	0	0.836
3	10	7	120	0	0.890
4	10	5	120	0	0.163
5	10	9	120	0	0.866
6	10	7	120	100	0.107
7	10	7	120	200	0.063
8	10	7	30	0	0.012
9	10	7	60	0	0.028
10	10	7	120*	0	0.008
Norfloxacin					
1	1	7	120	0	1.637
2	5	7	120	0	0.666
3	10	7	120	0	0.061
4	10	5	120	0	0.030
5	10	9	120	0	0.070
6	10	7	120	100	-
7	10	7	120	200	-
8	10	7	30	0	0.031
9	10	7	60	0	0.044
10	10	7	120*	0	0.055

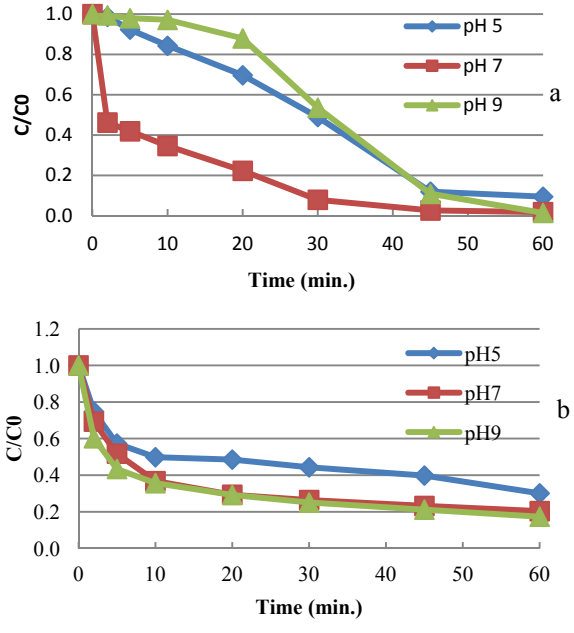

Fig. 2. Degradation of paracetamol (a) and norfloxacin (b) by VUV. Effect of pH. C_0= 10 mg/L.

C. Effect of VUV Power and UV

The degradation of paracetamol and norfloxacin under various VUV powers and comparison with UV is shown in Fig. 3a and Fig. 3b, respectively. Obviously, the increase of VUV power increased the of degradation rate. This was because more hydroxyl radicals generation and photolysis reaction by 185 and 254 nm wavelength to break down the contaminant [4]. UV performed less effective than VUV. This was due to the UV can emit only wavelength of 254 nm which can degrade contaminant via direct photolysis alone.

D. Effect of Bicarbonate Concentration

The effect of bicarbonate concentration of paracetamol and norfloxacin by VUV is described in Fig. 4a and Fig. 4b, respectively. Typically, the presence of bicarbonate could decrease the reaction rate of contaminant degradation because HCO_3^- acts as scavenger. This phenomenon was correct for paracetamol. However, for norfloxacin degradation, bicarbonate ions result in more rapid degradation. This discrepancy still needs further investigation.

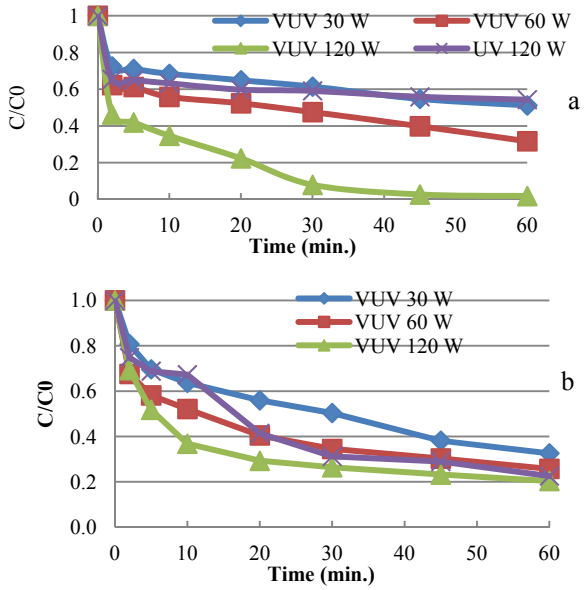

Fig. 3. Comparison of VUV and UV on degradation of paracetamol (a) and norfloxacin (b). C_0= 10 mg/L.

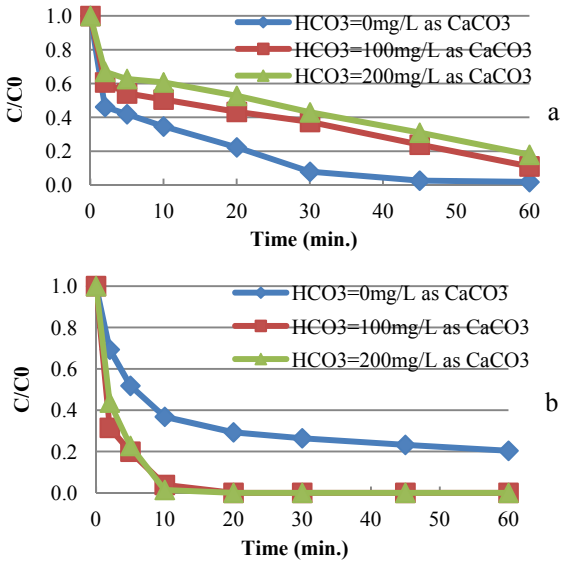

Fig. 4. Degradation of paracetamol (a) and norfloxacin (b) by VUV. Effect of bicarbonate concentration. C_0= 10 mg/L.

IV. Conclusion

From this research, the increase of concentrations of paracetamol and norfloxacin reduced the degradation rate. The pH was found to be optimum at neutral range. The increase of VUV power caused an increase of paracetamol and norfloxacin degradation due to more hydroxyl radicals formation and more photolysis reaction. UV exhibited the lower paracetamol and norfloxacin removal efficiency than VUV. Bicarbonate tended to lower degradation efficiency. The reduction of paracetamol and norfloxacin appeared to fit second order reaction kinetic. Paracetamol had higher degradation rates than norfloxacin. This could be the chemical structure of the paracetamol that is more susceptible to oxidation and photolysis compared to norfloxacin.

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