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The contribution of free radicals in paracetamol degradation by UV/NaClO

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Abstract

UV/Chlorine is an emerging advanced oxidation process which forms several reactive species including $^\bullet$OH, $^\bullet$Cl, $^\bullet$OCl. This study investigated the contribution of three main free radicals: $^\bullet$OH, $^\bullet$Cl, $^\bullet$OCl on Paracetamol degradation under different conditions. Benzoic acid (BA), Nitro benzene (NB) and DMOB were used as probe compounds. The second rate constant of $^\bullet$OH, $^\bullet$Cl, $^\bullet$OCl with PRC were determined: 4.19 (±0.15) $\times 10^9$ $M^{-1}s^{-1}$; 3.71 10^{10} $M^{-1}s^{-1}$; 3.532×10^9 $M^{-1}s^{-1}$, respectively. The formation of free radicals depends on pH. In particular, at pH 5: the contribution of $^\bullet$OH and ($^{-\bullet}$OCl, $^\bullet$Cl) are 45 %, 41 %, respectively, at pH 8.5, the contribution of free radicals increases up to 63 %.

Keywords. Paracetamol, UV/Chlorine process, reactive species.

1. INTRODUCTION

Advanced oxidation processes (AOPs) are attracting many concerns from researchers in water treatment issues. Their capacity to degrade micro pollutants was demonstrated to be more effective than traditional methods such as: coagulation, filtration, bio-degradation…[1]. NaClO disinfection combined with UV irradiation is effective, low cost comsuption and widely applied. UV/NaClO generates primary free radicals $^\bullet$OH and $^\bullet$Cl [2] and secondary radicals such as: $^{-\bullet}Cl_2$, $HClO^{\bullet-}$ and $^\bullet$OCl [3, 4]. $^\bullet$OH is non-selective oxidation which has ability to react with micro pollutants in the rate constant from 10^8-10^{10} $M^{-1}s^{-1}$. Chlorine reactive radicals: $^{-\bullet}Cl_2$, $^\bullet$Cl and $^\bullet$OCl are selective oxidants. $^\bullet$Cl prefers to react with substituted aromatics such as : phenol, benzoic acid, toluene and aniline [5]. $^\bullet$OCl is selective for phenolate and methoxybenzene [5]. The diversity of reactive species in UV/Cl_2 process contributes to micropollutants degradation in water treatment [3, 4, 6-8]. UV/Cl_2 process has been applied for many micro pollutants degradation such as: atrazine, carbamazepine, ibuprofen, DEET and caffeine [8, 9], Metoprolol, Triclosan [10, 11]. PRC is a widely used drug all over the world for analgesic and antipyretic agent used for fever, headaches and other minor pain. PRC is one of top 5 most consumed drugs in the world so it presents in wastewater, surface and even drinking water through human excretion [12, 13]. However, there are no publications about PRC degradation by UV/NaClO.

This study was conducted to identify the kinetic and the relative contribution of 3 main free radicals: $^\bullet$OH, $^\bullet$Cl, $^\bullet$OCl in PRC degradation by UV/NaClO.

2. MATERIALS AND METHODS

2.1. Chemicals

Paracetamol (PRC) was purchased from Sigma Aldrich and NaOH, HCl, Na_2SO_4, NaCl, H_2O_2 from Merck, the water distilling machine from Arium Pro, pH measurement machine from Horiba, UV-2900 from Hitachi-Japan. The magnetic mixer and HPLC were obtained from Thermo, Ultra Aqueous C18 (250×3.2 nm×5 μm).

2.2. Experiment

All experiments were conducted in temperature of 25.0±0.5°C in 2 liters cylindrical reactor equipped with low pressure Hg lamp (UV 254 nm) in the center. UV lamp's photon flow determination was based on H_2O_2 degradation investigations.
The result was $I_0 = 3.41\times 10^{-6}$ Einstein/$M^{-1}s^{-1}$. PRC concentrations over time were monitored by HPLC.

3. RESULTS AND DISCUSSION

3.1. Determination the rate constant of PRC degradation with $^{\bullet}$OH

The rate constant of PRC with hydroxyl radical $^{\bullet}$OH was determined to evaluate the contribution of $^{\bullet}$OH generated in UV/NaClO process. The photolysis process of H_2O_2 was used to generate $^{\bullet}$OH following equation:

$$H_2O_2 + 2h\nu \rightarrow 2\ ^{\bullet}OH$$

The effects of pH to PRC degradation were observed and shown in figure 1.

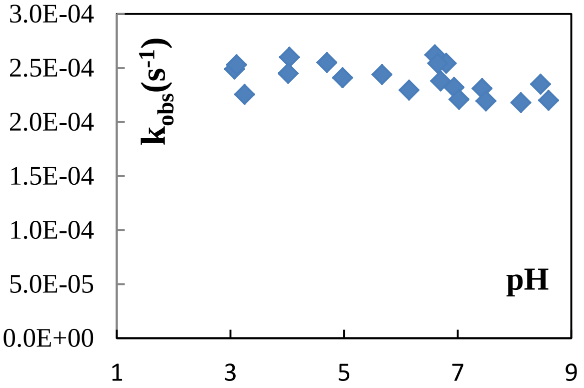

Figure 1: Effects of pH to the rate constant of PRC photolysis reaction

Due to the negligible effects of pH to degradation kinetic of PRC by H_2O_2/UV, so all experiments were conducts at unadjusted pH (pH 5). Samples were analysed PRC and H_2O_2 over time.

Based on the experiments conditions conducted, the PRC degradation pathways by hydoxyl radical $^{\bullet}$OH follow the pseudo first oder kinetic equation and the mechanism was calculated by following equation:

$$-\frac{d[\mathrm{PRC}]_T}{dt} = k_{\mathrm{HO^{\cdot}/PRC}}[\mathrm{HO^{\cdot}}]_{ss}[\mathrm{PRC}]_T = k_{obs}[\mathrm{PRC}]_T$$

$$-\ln\frac{[\mathrm{PRC}]_{T,t}}{[\mathrm{PRC}]_{T,0}} = k_{obs}t$$

Figure 2 shows that the decrease of PRC over time followed pseudo first order kinetic. Based on the average value of $k_{obs} = 5.31\times10^{-3} s^{-1}$ with the assumption that $^{\bullet}$OH generated is unvariable, we can calculate the second rate constant of $^{\bullet}$OH with PRC = 4.19 (±0.15)$\times10^{9}$ $M^{-1}s^{-1}$ at pH 5.5-6. This result is higher than in the investigation conducted by Andreozzi to degrade PRC at concentration of (5-20 10^{-6}M); $[H_2O_2]_0 < 15$ mM ($k_{\bullet OH}$/PRC = 2.2×10^{9} $M^{-1}s^{-1}$ [14, 15] and similar to the result published by Nasma ($k_{\bullet OH}$ /PRC = 4.94×10^{9} M^{-1} s^{-1}) [16].

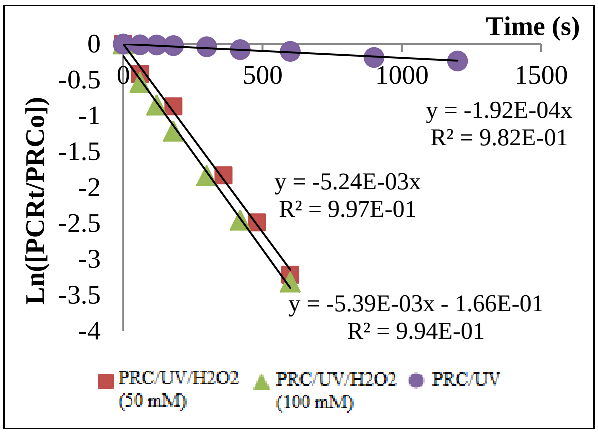

Figure 2: The pseudo first order rate constant of PRC/UV and PRC/UV/H_2O_2 processes

3.2. Determination the rate constant of PRC degradation with $^{\bullet}$Cl

To determine the contribution of free radical $^{\bullet}$Cl, some competitive dynamics experiments were conducted used nitrobenzene (NB) and Benzoic Acid (BA) as probe compounds. The decrease of NB concentration over time mainly caused by $^{\bullet}$OH (k^{*} $^{\bullet}$OH.NB = 3.9×10^{9} $M^{-1}s^{-1}$). NB does not react with $^{\bullet}$Cl, $^{\bullet}$OCl. Otherwise, BA reacts rapidly with $^{\bullet}$OH, $^{\bullet}$Cl with quite high rate constant (k^{*} $^{\bullet}$OH.BA = 5.9×10^{9} $M^{-1}s^{-1}$; k^{*} $^{\bullet}$Cl.BA = 1.8×10^{10} $M^{-1}s^{-1}$) and does not react with $^{\bullet}$OCl. All experiments were conducted at pH = 5.5-6 to make sure that the $^{\bullet}$OCl concentration is negligible, so we can ignore the contribution of $^{\bullet}$OCl in PRC degradation.

Thus, if the assumption of the free radicals $^{\bullet}$OH and $^{\bullet}$Cl is generated in the system is stable, we can calculate the concentration of $^{\bullet}$OH from the competitive kinetic experiment between PRC and NB. The $^{\bullet}$Cl concentration was calculated by the concentration reduction of BA in the simultaneous PRC, NB and BA experiments.

For the case of BA:

$k^{obs}_{BA} = k^{obs}_{UV.BA} + k^{obs}_{NaClO.BA} + k^{*}_{\bullet Cl.NB\times}[^{\bullet}Cl]_{ss} + k^{*}_{OH.NB\times}[^{\bullet}OH]_{s}$.

Based on the apparent rate constant obtained of PRC, NB and BA in the competitive kinetic reaction, we can calculate the second rate constant of PRC with $^{\bullet}$Cl = 3.71×10^{10} $M^{-1}s^{-1}$.

3.3. Determination the rate constant of PRC degradation with $^{\bullet}$OCl

To determine the competitive kinetic, dimethoxybenzene (DMOB) was used as probe compound due to reaction capacity with $^{\bullet}$OCl with the second rate constant quite high 2.1×10^{9} $M^{-1}s^{-1}$. To facilitate the formation of $^{\bullet}$OCl radicals, all experiments were conducted at pH 8.5, NaClO concentration 100 µM. HCO_3^- 100 mM was added to make sure that all free radicals such as: $^{\bullet}$OH, $^{\bullet}$Cl, $^{-\bullet}Cl_2$ are scavenged.

The rate constant of PRC with $^{\bullet}$OCl was calculated following this equation:

$$Ln\frac{PRC\ o}{PRC\ t} = Ln\frac{DMOB\ o}{DMOB\ t} \times \frac{k \bullet OCl \times PRC}{k \bullet OCl \times DMOB}$$

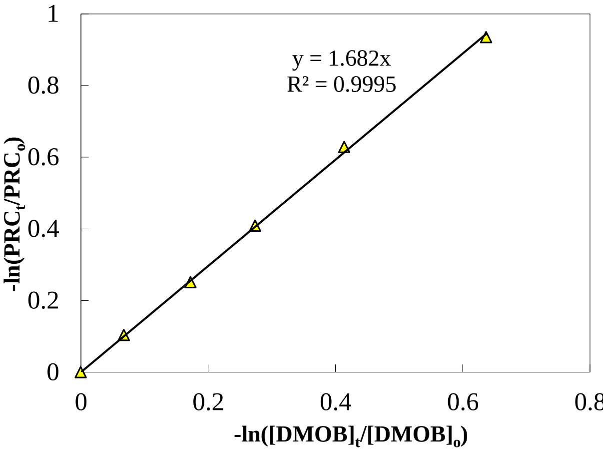

Figure 3: Relationship between degradation rate of PRC and DMOB probe compound

Based on the above results, we can calculate: $k_{\bullet OCl.PRC}$ = 1.682 × 2.1×10^9 = 3.532×10^9 M^{-1}s^{-1}

3.4. The contribution of free radicals on PRC degradation

Based on the results calculated above, we determined the relative contribution of each oxidizing agent on the PRC total degradation by UV/NaClO. The results were showed on figure 4.

Based on the results showed on figure 4, we can see that the contribution of free radicals on PRC degradation is high. Particularly, at pH 5: the contribution of $^{\bullet}$OH and ($^{-\bullet}$OCl, $^{\bullet}$Cl) are 45 %, 41 %, respectively. However, when pH increases, the concentration of $^{-\bullet}$OCl, $^{\bullet}$Cl increases. At pH 8.5, the contribution of free radicals increases up to 63 %.

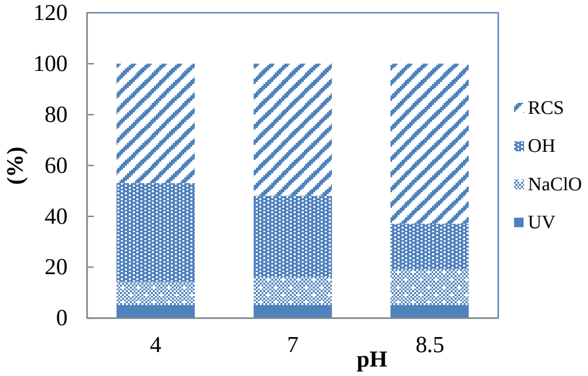

Figure 4: The relative contribution of free radicals to PRC degradation efficiency by UV/NaClO

4. CONCLUSION

AOPs processes are decided by the rate of free radicals formation. In this study, we determine the second rate constant of 3 main free radicals: $^{\bullet}$OH, $^{\bullet}$Cl, $^{\bullet}$OCl: 4.19 (±0.15) ×10^9 M^{-1}s^{-1}; 3.71×10^{10} M^{-1}s^{-1}; 3.532×10^9 M^{-1}s^{-1}, respectively. This investigation demonstrated that pH highly effects on the formation of free radicals, so their contribution on PRC degradation changes with pH. Particularly, at pH 5: the contribution of $^{\bullet}$OH and ($^{-\bullet}$OCl, $^{\bullet}$Cl) are 45 %, 41 %, respectively and at pH 8.5, the contribution of free radicals increases up to 63 %.

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