2Pb4-7

Proceedings of Symposium on Ultrasonic Electronics, Vol. 32 (2011) pp. 245-246
8-10 November, 2011

Sonophotolytic Degradation of Estriol at Various UV Wavelength in Aqueous Solution

Seungmin Na[1†], Jinhua Cai[1], Beomguk Park[1] and Jeehyeong Khim[1]
([1]School of Civil Env. Archi. Eng., Korea Univ.)

1. Introduction

Estriol is an estrogenic chemical that cause of endocrine disruption in humans, even at low concentration[1,2]. Estriol is present at concentrations ranging from 1.0 to 100 ng L^{-1} in environment including surface water and wastewater effluents [2,3]. Therefore, to obtain safe drinking water, complete degradation of estriol in surface water is needed. Various advanced oxidation processes (AOPs) have been applied to contaminated systems to effectively treat micro-pollutants, such as estriol [2]. Generation of hydroxyl radicals is the critical step for AOPs. Therefore, reaction conditions must be optimized to maximize hydroxyl radical generation in order to effectively degrade pollutants.

When aqueous solutions with organic pollutants are exposed to ultrasound (US) waves, pollutants can be degraded by thermal and chemical (hydroxyl radical) effect generated during cavitation process. However, ultrasound-mediated degradation is more effective when combined with other oxidative approaches, such as Ultraviolet (UV) irradiation. UV irradiation can be used for the direct and indirect photolysis of pollutants, as well as for disinfection. In particular, vacuum ultraviolet (VUV) at a wave length of 185nm effectively degrades pollutants and has been to generate ultrapure water. VUV irradiation results in a high rate of hydroxyl radical formation by water homolysis (Eq.1) and water ionization (Eq. 2) [4].

$$H_2O \xrightarrow[\text{185 nm(vuv)}]{} \cdot H + \cdot OH \quad \text{---------} \quad [1]$$

$$H_2O \xrightarrow[\text{185 nm(vuv)}]{} H^+ + \cdot OH + e^- \quad \text{---------} \quad [2]$$

UV irradiation also shows better results when combined with a photocatalyst, such as titanium dioxide (TiO_2), oxidants, such as hydrogen peroxide (H_2O_2) or ozone (O_3) or with acustic wave, such as ultrasound[2,5]. One advantage of sonophotolysis is that there is no need to remove the photocatalyst or add additional chemicals to effectively degrade pollutant. US irradiation generates hydrogen peroxide. Direct UV photolysis of hydrogen peroxide generated by US exposure can also generate hydroxyl radicals that could degrade pollutants (Eq.3) [5].

$$H_2O_2 \text{ (}H_2O_2\text{ generated by US process) } \xrightarrow{hv} \cdot OH + \cdot OH \quad \text{---------} \quad [3]$$

Sonophotolysis at various UV wavelength have not been investigated. Therefore, this study examined the kinetics of the sonolytic, photolytic and sonophotolytic degradation of estriol using UVA, UVC and VUV irradiation. In addition, synergistic effect of sonophotolytic degradation also was determined at different UV wavelength.

2. Experimental Methods

The degradation of estriol (Aldrich, 99.5 % pure grade, initial concentration 34 μM) was carried out in a capped cylindrical glass batch reactor. The reactor had an inner diameter of 12.5 cm and a height of 22 cm. The aqueous volume was 1L. VUV, UVC and UVA lamps (Han Sung Ult. Co. LTD) with main emission wavelengths of 185nm, 254nm and 365nm, respectively, and output powers of 10±5 W were centered axially and immersed in the reactor. The applied total intensity of UV irradiation in solution was approximately 40±2 W L^{-1}. The US of 283 kHz and powers of 29.5, 45, 85 and 115.5 W L^{-1} was applied from a cup horn type single transducer located beneath the reactor. The reaction temperature was kept within 15-18°C using a water jacket placed around the reactor. The pH was uncontrolled but was measured and remained between 5.2 and 6.0 during the reactions. The concentration of estriol was determined by high performance liquid chromatography (HPLC) using a system equipped with a 335 LC photo diode array detector (Varian Prostar) and a reversed phase column (Phenomenex XRs, C18, 250 mm × 4.6 mm inner diameter, 5μm beads). The mobile phase was acetonitrile:orthophosphoric acid (0.02mM) (35:65). The flow rate was 1 ml min^{-1}. The total sample volume withdrawn from the reactor for each experiment was less than 5% of the initial volume.

---

hyeong@korea.ac.kr

The molar absorption coefficient of estriol was determined using the Lambert Beer law 6).

3. Results and Discussion

Fig.1 shows the effect of the applied US power (283 kHz; 29.5-115.5 WL^{-1}) on the sonolytic degradation constants of estriol. The degradation rate of estriol increased linearly with increasing applied power. The degradation rates were approximately 3.0×10^{-4}, 7.0×10^{-4}, 3.5×10^{-3} and 6.1×10^{-3} min^{-1} at 29.5, 45.0, 65.0 and 115.5 W L^{-1}, respectively. This increase in estriol degradation is due to the increase in cavity activity and the number of cavitation bubble generated, and the increased production of hydroxyl radical as the applied power increases 1,7).

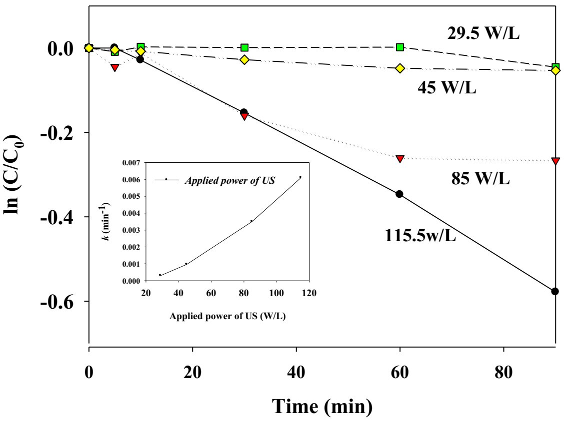

Fig. 1 Sonolytic estriol degradation at various applied US powers (29.5, 45, 65, 115.5 W/L).

Fig.2 shows the photolytic and sonophotolytic degradation rates of estriol at different UV wavelength. The photolytic degradation rate constants were 1.7×10^{-1}, 1.1×10^{-2} and 1.0×10^{-4} min^{-1} for VUV, UVC and UVA irradiation, respectively. The difference in degradation rates is due to differences in the energy (647, 471.5 and 327.7 KJ mol^{-1}) of the UV irradiation 8) and molar absorption coefficient ($\varepsilon_{estriol}$) of estriol at the different UV wavelengths, such as 2.6, 0.12 and 0.002 L mol^{-1} cm^{-1}.

For sonophotolysis, the greatest estriol degradation rate was observed for US/VUV, followed by US/UVC and US/UVA, as for the photolytic degradation of estriol (**Fig.2**). The synergistic effect between sonolysis and photolysis was quantified as the normalized difference between the sonophotolysis rate constant and the sum of the individual sonolysis and photolysis rate constant 5,9). Small synergistic effect of 1.29 and 1.11 were observed for US/UVC and US/UVA sonophotolysis, respectively. No synergism was observed for US/VUV sonophotolysis.

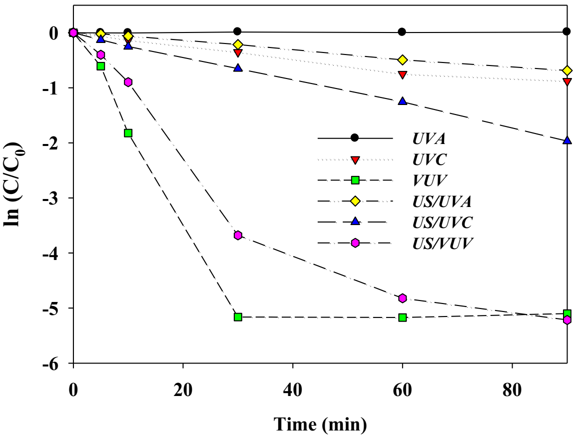

Fig.2 Photolytic and sonophotolytic estriol degradation rate at different UV wavelengths.

The synergistic effects for US/UVC and US/UVA sonophotolysis can be explained by the direct photolysis of hydrogen peroxide produced during US exposure by UVC and UVA radiation to form hydroxyl radicals (Eq. 3).

Acknowledgment

This work was supported by the Mid-career Researcher Program through NRF grant funded by the MEST (KRF-2009-0092799).

References

1. R.J. Emery, M. Papadaki, L.M. Freitas dos Santos and D. Mantzavinos: Env. Int. **31** (2005) 207.
2. Y. Ohko, K. I. Iuchi, C. Niwa, T. Tatsuma, T. Nakashima, T. Iguchi, Y. Kubota and A. Fujishima: ES&T. **36** (2002) 4175.
3. S.D. Kim, J. Cho, I. S. Kim, B. J. Vanderford and S.A. Snyder: Wat. Res. **41** (2007) 1013.
4. D. Wnag, T. Oppenländer, M. G. Ei-Din and J. R. Bolton: Photo. & Photocio. **86** (2010) 176.
5. C. Wu, X. Liu, D. Wei, J. Fan and L. Wang: Wat. Res. **35** (2001) 3927.
6. D. F. Swinehart: J of Chem Edu. **39** (1962) 333.
7. F. Méndez-Arriaga, R. A. Torres-Palma, C. Pétrier, S. Esplugas, J. Gimenez and C. Pulgarin: Wat. Res. **42** (2008) 4243.
8. M. A. Tarr: New York Basel, Marcel Dekker, Inc. (2003)
9. R. Kidak and N. H. Ince : J. of Haz. Mat. **146** (2007) 630.