Direct US/O₃ combination treatment of hormones in aqueous solutions

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1. Introduction

Worldwide, researchers are discovering trace levels of pharmaceuticals and human hormones in water that is associated with wastewater treatment plant (WWTP) effluents[1-3].

A growing body of scientific research indicates that many exogenous chemicals, both natural and synthetic, have the potential of interfering with the endocrinal activity of natural hormones in both animals and humans. These chemicals are called endocrine disrupting chemicals (EDCs) or endocrine disruptors (EDs)[4,5] Besides industrial chemicals such as DDT, bisphenol, methoxychlor, chlordecone, alkylphenols, PCBs, and phthalic esters, some natural estrogens, such as estradiol (E2) and estrone, and synthetic pharmaceuticals, such as diethylstilbestrol (DES) and 17a-ethinylestradiol (EE2), are found to be the most potent EDs.[6] Desbrow[6] detected these estrogens in municipal wastewater treatment effluents in UK at concentrations from less-than-detectable values to more than 100 ng L^{-1}; the effluents were released into natural environments. Research has further revealed that even at extremely low concentrations, these estrogens and not alkylphenols or their derivatives cause adverse effects, such as the feminization of male fish.[7]

Colucci and Topp[8] studied the dissipation and persistence of estrogenic hormones in soils and indicated that E2, estrone, and EE2 were readily biodegradable under a range of conditions that were typical of a temperate growing environment. These estrogens are difficult to remove totally from wastewater through primary and secondary treatments.[9] New methods are needed for removing these estrogens from wastewaters prior to their release into the environment. Yoshihisao and Ken-Ichiroiuchi[10] have studied the degradation of 17-estradiol through TiO₂ photocatalysis. Activated carbon can remove nearly all organic contaminants; however, the removal capacity is limited by the duration of contact, competition from natural organic matter, contaminant solubility, and carbon type.[11, 12, 13]

The purpose of this study is to overview the mineralization, kinetics, and the impact of the pH value in relation to the US/O₃ treatment of estrone and estriol aqueous solutions at high concentrations.

**Table1.** Summary of concentrations for six selected micropollutants in effluents.[3]

Compound	Class	Effluents	NOD	Conc.
Estriol	Hormone		**3**	**8.9-25**
Estrone			**5**	**2.2-36**
17α-ethynylestradiol			1	1.3
17β-estradiol			0	<1.0
Testosterone			1	1.1
Androstenedione			3	1.0-3.5

NOD: Number of samples detected among a total of seven samples for effluents (unit: ng L^{-1}).

2. Experimental procedures

The system, which is illustrated schematically in Fig.1, consists of a 2L stainless-steel pentagon reactor, a generator with a maximum power of 500 W, piezoelectric transducers (emitting at 35 kHz) mounted on three lateral walls, and three quartz windows. Ozone was generated in the gaseous phase by passing pure dry oxygen through the ozone generator(a LAB 2B model). Arrangements were made for applying this gaseous mixture to the bottom of the reactor, where it bubbled through a porous ceramic plate and moved upwards through the reactor. The ozone concentration in the gaseous influent to – and effluent from – the reactor was measured using an online ozone monitor (Ozone Instrumentation; Model: H1-S; USA).
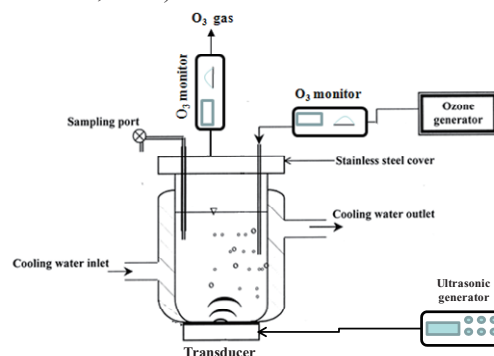
Fig.1. Schematic of the experimental apparatus for the US/O₃ setup.

Estriol ($C_{18}H_{24}O_2$) and estrone ($C_{18}H_{22}O_2$) (see Fig. 2 for the molecular structure) were purchased from Sigma (USA). Henry' Law constant 1.33×10^{-12} and 3.8×10^{-10} atm m^3 mole^{-1}, respectively. 0.01 M HCl and 0.1 M NaOH were used to adjust the pH of the estrogen solutions.
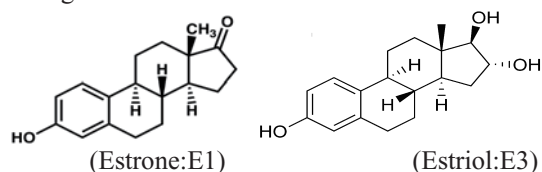

(Estrone:E1)   (Estriol:E3)
Fig. 2. Molecular structure of estriol and estrone.

For the total organic carbon (TOC) determination, the samples were analyzed using a TOC analyzer (a Model Sievers 5310C TOC analyzer and a Sievers 900 auto sampler GE Jena USA). The absorbed ozone concentration was analyzed using an ozone analyzer meter (Model H1 Analyzer USA). The solution pH was measured using a pH meter (Thermo Orion Model-420A$^+$).

3. Results and discussion

3.1 Mineralization

Fig. 3 shows the estrone and estriol TOCs under a combination of an ultrasound process and ozonation. In the US/O_3 process, the removal efficiencies of the estrone and estriol TOCs after an hour-long operation were 79.5% and 81.3%, respectively. However, the ultrasound process could enhance the removal efficiency significantly when it was combined with ozonation. This might be due to the physical and chemical effects of ultrasound. Physical effects, including micro-jets, shock waves, and micro-streaming, enhance the ozone mass transfer through micro mixing and the fragmentation of ozone bubbles. Chemical effects, including pyrolysis and radical generation, intensify the radical chain reactions through various, highly reactive radicals.
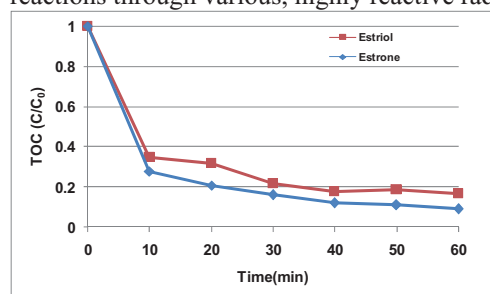
Fig.3. Comparison of the effect of US/O_3 on aliquots of estrol and estrone. 25℃ . Gaseous application rate: 4.8 g hr^{-1}. US frequency: 35 kHz. Power: 400 W (intensity of 1.6 W cm^{-2}). Several estrol and estrone aliquots of 500 mL volume. Initial TOC values in mg L^{-1} are (estrol 5.1) and (estrone 5.12)

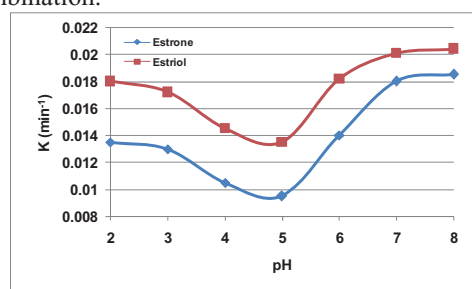### 3.2 US/O_3 kinetics of estrogens in aqueous solutions

The results of kinetic analysis are listed in Table 2. The results indicate that the US/O_3 reactions of the two estrogens in aqueous solutions were all Pseudo-first-order. The US/O_3 degradation of organic compounds is usually complex. In fact, the kinetics we studied in our work are apparent kinetics since the reaction is not a simple one in which the reaction kinetics are clearly defined. Therefore, the equation, $\ln(C/C_0)=-kt$, is apparently tenable, where k varies with C_0.

Table 2 US/O_3 kinetics analysis

Estrogens	C_0 (mg L^{-1})	pH	Pseudo-first-order rate constants (min^{-1})
Estrone	10	6.82	0.0178
Estriol	10	7.32	0.025

3.3 Effect of the pH value on the US/O_3 of the estrogens in aqueous solutions

To study the effect of the pH value on the US/O_3 of estrogens in aqueous solutions under irradiation, pH values ranging from 2 to 8 were chosen for conducting US/O_3 experiments for 10 mg L^{-1} estrone and estrol solutions, respectively. Fig. 4 shows that both the estrogens have similar pH dependencies under radiation in aqueous solutions for they have very similar molecular structures. The US/O_3 performs the worst at a pH value of approximately 5, while higher pH values of 7-8 benefit the US/O_3 combination.

Fig.4. Effects of the pH value on the US/O_3 of estrogens in aqueous solutions.

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