Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.856344

53 (2015) 493–500
January

Taylor & Francis
Taylor & Francis Group

Degradation of 17β-estradiol by combined ultrasound/$KMnO_4$ in an aqueous system

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Received 14 April 2013; Accepted 20 August 2013

ABSTRACT

Estrogenic compounds in drinking water resources pose potential threats to human health. Treatment technologies are recommended to effectively remove these compounds in order to supply safe drinking water to the public. In this study, single ultrasound and combined ultrasound/$KMnO_4$ were adapted to reduce 17β-estradiol (E2) in aquatic systems. The effects of combined ultrasound/$KMnO_4$ were compared with ultrasound because $KMnO_4$ has an oxidative enhancement effect on ultrasound. The results showed that the E2 removal rate increased with increasing reaction time and power but decreased with solution temperature. The process of ultrasound could degrade small quantities of E2 by approximately 47.7% at the relatively optimal conditions of 270 W ultrasound power, 25°C, and 180 min reaction time. Compared with pure ultrasound, an obvious enhancement effect was observed after the introduction of $KMnO_4$. The residual E2 concentration decreased with increasing $KMnO_4$ dosage and irradiation time, and the removal efficiency of E2 was greater than 99.6% when the reaction reached 30 min with 5 $mg\,L^{-1}$ $KMnO_4$. A good correspondence with pseudo-first-order kinetics was found in each process. It was demonstrated that the degradation reaction rate constants of E2 in ultrasound, $KMnO_4$, and ultrasound/$KMnO_4$ treatment were 0.0037, 0.0247, and 0.0647 min^{-1}, respectively. Characterized by high efficiency and rapid effect, combined ultrasound/$KMnO_4$ treatment has great potential for future application. The non-purgeable organic carbon index indicated that the degradation products of E2 under ultrasound were mineralized.

Keywords: Estrogenic pollution; 17β-Estradiol; Ultrasound; $KMnO_4$; Water treatment

1. Introduction

Recently, more natural and synthetic chemical materials have been released into the environment, including some chemicals that may interfere with the normal function of the endocrine systems in humans and wildlife; these are referred to as Endocrine Disrupting Chemicals (EDCs) and have been a cause for concern for many years. The US Environmental Protection Agency (EPA) defines environmental EDCs as xenobiotics that interfere with the synthesis, secretion,

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transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior [1–3]. EDCs include natural estrogen, natural androgens, artificial synthetic estrogens or androgens, and phytoestrogens, as well as other industrial compounds [4]. They disrupt endocrine and other vital systems when present in the aqueous environment and increase the risk of cancer, even at nanogram levels [5–7]. Of the various categories, natural (estrone, estradiol, and estiol) and synthetic estrogens (17α-ethinylestradiol) exhibit much stronger estrogenic activity than phyto- and xeno-estrogen [8]. The many sources of estrogenic pollution include livestock wastes, biosolids, septic tanks, landfills, and effluent from municipal and industrial wastewater treatment plants, in which estrogens are insufficiently removed during treatment and end up in the natural aquatic environment [9,10].

17β-estradiol (E2) is responsible for development of female secondary and reproductive characteristics. E2 is one of the strongest natural estrogens, based on a yeast estrogenicity screening assay [11,12]. The exposure of fishes to 1–10 ng L^{-1} of E2 can provoke feminization in some species of wild male fishes [13]. Both estrone (E1) and E2 are excreted by women and are therefore ubiquitous in the aqueous environment receiving sewage inputs [14]. Recent surveys in North America, Europe, and Asia detected E2 in surface water and ground water, with concentrations up to 70 ng L^{-1} [15–18]. The US EPA recently added E2, along with two other natural estrogens, E1 and estriol (E3), onto its Contaminant Candidate List 3 [19].

However, conventional treatment plants are unable to effectively break down 17β-estradiol (E2) [20–23] because of its low Henry's Law coefficient (6.3×10^{-7} atm $\text{m}^3\,\text{mol}^{-1}$), high octanol–water partitioning coefficient ($\log K_{\text{ow}} = 3.9$), and low biodegradability. The accumulation of estrogens in the environment could pose a chronic risk to human health. It is therefore important to investigate and develop effective treatment technologies to destroy estrogens in the aquatic system. Studies of different ways to remove estrogens from water bodies have been carried out by scientists from all around the world, especially during the last decades [24–28]. In recent years, advanced oxidation processes (AOPs) have gained particular attention for the degradation of emerging micropollutants such as EDCs, pharmaceuticals, and personal care products in various aqueous matrices [29]. AOPs include sonocatalysis, O_3/H_2O_2, UV/H_2O_2, UV/TiO_2, and Fenton/photo-Fenton processes; sonocatalysis associated with UV, TiO_2, H_2O_2, ZnO, steel beads, and Al_2O_3 represents a relatively new and efficient technique for degrading contaminants [30–35]. AOPs are recognized for their potential to generate hydroxyl radicals (·OH) *in situ*, which react with a wide range of organic chemicals in water [36].

Ultrasonic irradiation has received considerable interest as an advanced oxidation process. The transmission of ultrasound waves through liquids at frequencies ranging from 20 kHz to a few MHz results in cavitation, which causes various physicochemical effects. Under the influence of an acoustic field, bubbles are generated from existing gas nuclei in liquids. These bubbles oscillate in a nonlinear manner, and they collapse violently under specific experimental conditions to generate high temperatures and pressures [37,38]. These cavitation bubbles, produced acoustically in a matter of microseconds upon implosion, result in extreme conditions (5,000 K and 500 bar in the gaseous phase [39]) at microscopic points in the solution. Cavitation produces high mechanical shear stresses that are exerted on the substances in the liquid. In general, sonochemical degradation in the aqueous phase involves several reaction pathways and zones, such as pyrolysis inside the bubble and at the bubble–liquid interface and hydroxyl radical-driven reactions at the bubble–liquid interface and in the liquid bulk [40,41].

The sonolytic degradation of micro-contaminants, including estrogen compounds, has been reported in recent studies [42,43], while other processes of assisted ultrasound are seldom discussed. In this study, the processes of ultrasound and combined ultrasound/$KMnO_4$ were employed, and their effects on the degradation of E2 were compared. The theoretical effect of ultrasound was defined by optimizing the main reaction conditions, such as ultrasonic power and solution temperature. In the combined process, the oxidative enhancement effect was evaluated.

2. Materials and methods

2.1. Chemicals

17β-estradiol (E2) was purchased from Sigma–Aldrich and used as received. Methanol (HPLC grade) was obtained from Tedia, and acetone (HPLC grade) was supplied by Merck. Pure water was produced by a Milli-pore pure water machine. The $KMnO_4$ and sodium thiosulfate were commercially available analytical-grade products.

2.2. Ultrasonic reactor

The ultrasonic generator FS-300 (Sonxi, Shanghai CN) can be operated either continuously or in pulse mode at a fixed frequency of 20 kHz and variable power output up to 300 W. Ultrasound irradiation was emitted through a 1 cm diameter tip, which was fixed on a tripod and positioned in the middle of a beaker. The beaker contained a solution of E2, and the tip was immersed to a depth of 1 cm from the bottom of the solution. To control the experimental temperature, the beaker was placed in a water bath.

2.3. Analysis methods

E2 was analyzed by a Shimadzu LC-20AB HPLC using a SPD-M20A detector set at 200 nm, a CTO-20A, and an ODS-SP column (250 mm × 4.6 mm × 5 μm). Sample injection was achieved with a SIJ-20A injection system. The mobile-phase solvent profile was 40% pure water and 60% acetonitrile at a constant flow rate of 0.7 mL min^{-1}, the column was maintained at 25℃, and the injection volume was 10 μL.

2.4. Experimental procedure

A stock E2 solution was prepared in 100 mL acetonitrile and stored at −18℃ in the dark. Appropriate sample solutions of E2 were made by dilution of the stock with Milli-Q water. Unless the effect of temperature was being specifically studied, experiments were proceeded at room temperature (25℃). Samples were periodically drawn from the reactor; sodium thiosulfate was immediately added to quench any reaction (to prevent the oxidative effect of residual $KMnO_4$) and samples were filtered through a 0.45 μm membrane. All experiments were performed in duplicate.

3. Results and discussion

3.1. Degradation of E2 by pure ultrasound

Ultrasound can remove a portion of E2 in aquatic systems by pyrolysis inside the bubble and/or at the bubble–liquid interface and hydroxyl radical-driven reactions at the bubble–liquid interface and/or in the liquid bulk, but low efficiency of pyrolysis and production of hydroxyl radical lead to low degradation. Because temperature and ultrasound power have a strong influence on the reaction [44], the effects of ultrasound were studied under different temperatures and ultrasound powers.

Temperature was considered to be one of the most important factors influencing the effect of ultrasound on the degradation of contaminants. The results in Fig. 1 shows that increased temperature led to decreased degradation efficiency. As the temperature was increased from 25 to 60℃, the total E2 degradation efficiency decreased from 30.0 to 5.8% after 180 min of sonication time. The E2 degradation efficiency was therefore 5.2 times greater at the lower temperature than at the higher temperature.

The temperature of the aqueous phase affects the viscosity, gas solubility, vapor pressure, and surface tension, which can influence the ultrasonic procedure. Increased temperatures are likely to facilitate bubble formation due to an increase of the equilibrium vapor pressure; on one hand, the bubbles contain more vapors which reduce the intensity of bubble collapse, but on the other hand, degassing of the liquid phase is promoted which reduces the number of gas nuclei available for bubble formation. The ultimate impact of temperature is a result of a number of complex interacting factors. This finding is in agreement with a study by Frontistis and Mantzavinos [45], who found that degradation of E2 is favored at a lower temperature where complete conversion is achieved after 30 min of reaction; however, the relative value for the run at the high temperature was only 70%. Usually, a decrease of degradation with increasing temperature is attributed to an increased vapor content of bubbles at higher temperatures which reduces the intensity of bubble collapse [40].

It has been reported that the maximum temperature ($T_{\max}$) obtained during bubble collapse is given as follows:

$$T_{\max} = (\gamma - 1)T_0 P/P_0$$

where T_0 is the liquid bulk temperature, P_0 is the vapor pressure of the solution, P is the liquid pressure during the collapse and γ is the gas polytropic ratio.

In certain reaction systems, the net effect of an increment in T_0 (and consequently $T_{\max}$) is an increase in degradation rates. This increase occurs up to the point at which the cushioning effect of the vapor begins to dominate the system, beyond which further increases in liquid temperature result in a reduced reaction rate. The fact that removal decreases with rising liquid temperature is believed to be associated with the effect of temperature on both the bubble formation energy threshold and the intensity of bubble implosion. Increased temperatures are compensated for by the fact that bubbles contain more vapor which cushions bubble implosion and consequently reduces $T_{\max}$. In addition, increased temperatures are likely to favor degassing of the liquid phase.

Ultrasonic power is one of three important parameters for sonochemical degradation. Varying levels of power, 90, 180, or 270 W, were used while maintaining

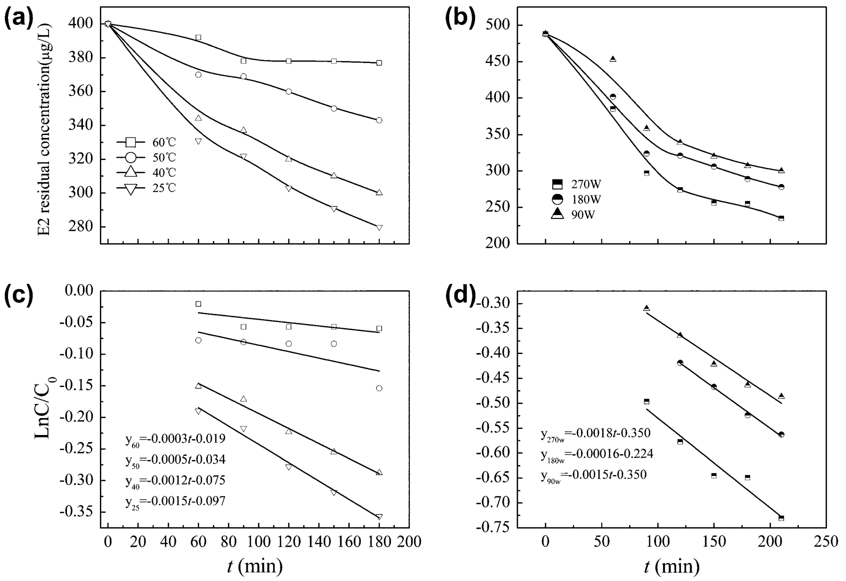

Fig. 1. Degradation of E2 by pure ultrasound process, and first-order kinetic models (frequency: 20 kHz; power: 180 W; volume: 200 mL; E2 initial concentration: 400 μg L^{-1}; pH: 7.05; (a), (c) temperature influence; and (b), (d) power influence).

other factors constant ([E2] = 488 μg L^{-1}, 20 kHz) in the ultrasound process. It is apparent that the degradation efficiency increased with increasing ultrasonic power because the quantity of active cavitation bubbles increases with increasing acoustic power, leading to greater generation of ·OH radical [46,47], which plays a key role in the E2 degradation reaction. In sonication, the production and implosion of cavities is dependent upon the ultrasound power intensity. Higher power intensity is thought to result in higher pressure which causes a more complete implosion of the cavities [48]. Previous studies [42,44] of the ultrasound degradation of 4-cumylphenol (4-CYP) and 17α-ethynylestradiol observed a similar effect of power. E2 degradation followed first-order kinetics; furthermore, at low levels, the degradation rate constants were similar.

Fig. 1 also showed that the reaction rate constants were very low; consequently, it would take a long time to reach the ideal degradation results. Therefore, sonication is relatively inefficient with respect to the total input energy and is not economically attractive or feasible alone. One of the most interesting topics in sonochemistry is the combination of cavitation and other remediation processes, such as advanced oxidation [49].

3.2. *Ultrasound/$KMnO_4$ degradation of E2*

In solution, the oxidation–reduction potential of $KMnO_4$ is essentially constant; hence, the removal efficiency of E2 is also effectively constant. Based on this assumption, further experiments focusing on the oxidative enhancement effect of $KMnO_4$ were carried out.

As shown in Fig. 2, three levels of $KMnO_4$ between 3.0 and 5.0 mg L^{-1} were investigated in the ultrasound/$KMnO_4$ process at 270 W and a frequency of 20 kHz. When more $KMnO_4$ was added into the solution, the degradation rate of E2 increased. At 20 min, the degradation efficiencies at 4.0 and 5.0 mg L^{-1} $KMnO_4$ were two and three times that at 3.0 mg L^{-1}, respectively.

The linear correlations of these first order kinetics equations were very good. The reaction rate constant increased with increasing concentration of $KMnO_4$. The highest and lowest rate constants differed by a factor of almost 71. Therefore, the oxidative enhancing effect of $KMnO_4$ is very significant.

3.3. *$KMnO_4$ oxidative promotional effect*

To compare the effects of $KMnO_4$, ultrasound, and ultrasound/$KMnO_4$, experiments were performed as follows: 1.2 mg L^{-1} $KMnO_4$ was added into the E2 solution in the $KMnO_4$ process, and the ultrasound/$KMnO_4$ process was conducted at a power of 270 W and a frequency of 20 kHz. Variations of degradation efficiency during a reaction time of 60 min are shown in Fig. 3. When the reaction time was extended to 20 min, the degradation efficiency of E2 by ultrasound/$KMnO_4$ was 72.3%, about two times that of $KMnO_4$ treatment, and approximately seven times that of ultrasound; the

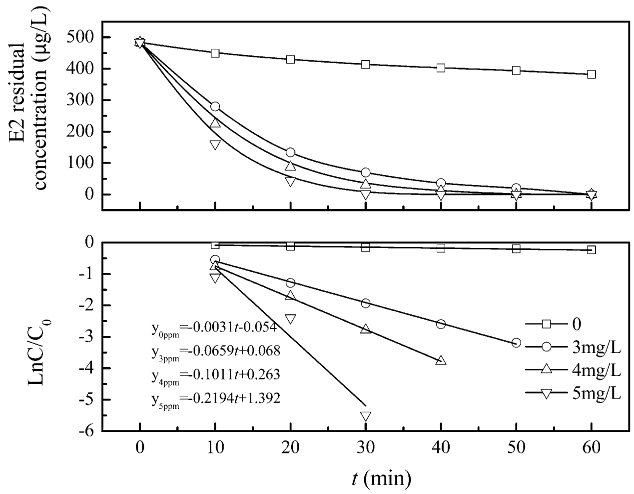

Fig. 2. Oxidative enhancing effect and first-order kinetics models of $KMnO_4$ on the degradation of E2 in the ultrasound/$KMnO_4$ process (frequency: 20 kHz; power: 270 W; volume: 200 mL; E2 initial concentration: 484 $\mu g\,L^{-1}$; pH: 7.38; and temperature: 25 ± 1℃).

maximum removal efficiency reached 97.8% when reaction time was extended to 60 min. The results showed that the ultrasound/$KMnO_4$ process was the most effective process among the three, followed by $KMnO_4$ and then ultrasound. It can be concluded that in the process of ultrasound/$KMnO_4$, $KMnO_4$ played a promotional action in the degradation of E2. To evaluate the enhancing effect of $KMnO_4$, a relevant curve to express $KMnO_4$-enhanced ultrasound was determined and is shown in Fig. 3. Before a reaction time of 20 min, the removal efficiency curve of ultrasound/$KMnO_4$ shows an increasing tendency and is enhanced by 33.3% compared to the ultrasonic process. After that time, the efficiency decreases. By the end of the reaction, the result is close to that of ultrasound. The mechanism of the synergetic effect of $KMnO_4$ and ultrasound could be explained as follows:

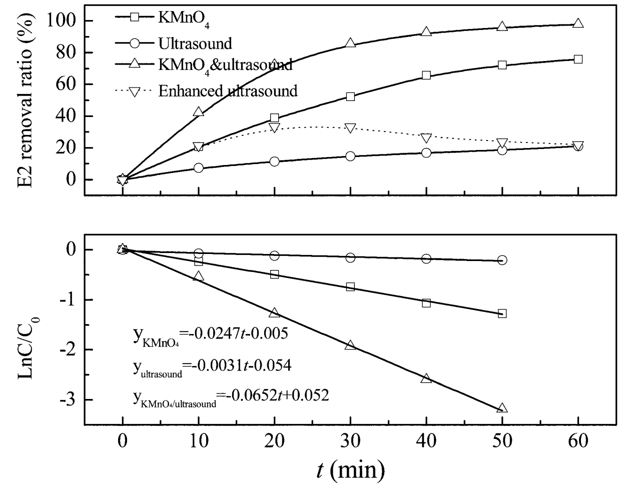

Fig. 3. First-order kinetics models and degradation efficiency of E2 by three processes: pure $KMnO_4$, pure ultrasound, and ultrasound/$KMnO_4$ (frequency: 20 kHz; power: 270 W; volume: 200 mL; E2 initial concentration: 484 $\mu g\,L^{-1}$; pH: 6.86; and temperature: 25 ± 1℃).

H_2O produces H_2O_2 which undergoes partial dissociation in the presence of ultrasound.

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+$$

Meanwhile, H_3O^+ makes the solution acidic. This condition improves the generation of ·OH from $KMnO_4$.

$$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + H_2O + 3O_2\uparrow$$

$$O_2 \rightarrow 2O^-$$

$$O^- + H_2O \rightarrow \cdot HO + \cdot HO$$

Furthermore, a redox reaction occurs between H_2O_2 and $KMnO_4$. Mn^{2+} and MnO_2, which are products of the reaction, are strong catalysts for cavitation, promoting further degradation of organic pollutants.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2\uparrow + 8H_2O$$

$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2\downarrow + 3O_2\uparrow + 2OH^- + 2H_2O$$

Enhanced ultrasound: relevant degradation efficiency of E2 in ultrasound/$KMnO_4$ process subtracts that in pure $KMnO_4$ process.

The degradation of E2 could be observed to follow first-order kinetics (Fig. 3). The rate constant for the process of ultrasound/$KMnO_4$ was much higher than that for the other processes.

3.4. *Non-purgeable organic carbon, alternative indicator of E2*

E2 is known to be a non-volatile substance. This section introduces the non-purgeable organic carbon (NPOC) index and discusses its behavior throughout the experiment. NPOC can represent the quantity of residual E2 because E2 is a type of NPOC; it can also precisely illustrate the safe transformation of E2 degradation because its degradation products can be completely mineralized or volatilized.

The NPOC index focuses not only on the removal efficiency of E2 but also on its degradation products.

The initial E2 concentration was 82 μg L^{-1}, and the relevant ultrasonic power and frequency were 270 W and 20 kHz. During the removal of E2, the NPOC in solution was also removed (Fig. 4). Before about 100 min, the degradation efficiency of NPOC is less than the degradation efficiency of E2. The reason for this is that the E2 working solution contains some acetonitrile, which increases the calculated base NPOC, that is the initial concentration of NPOC is greater than the concentration of E2. After 100 min, the degradation ratio of NPOC is greater than that of E2 which means degradation products of E2 were removal along with E2. When the reaction reached 360 min, both E2 and NPOC were completely removed. From the NPOC index, it can be easily speculate removal situation of E2 and its degradation products and indicate that it was safe and harmless or not.

4. Conclusion

The removal of the EDC E2 by 20 kHz ultrasonic irradiation was achieved. The extent of degradation was inversely proportional to the liquid temperature. The degradation rate increased with increasing ultrasonic power from 90 to 270 W. E2 degradation followed first-order kinetics. The removal rate was boosted in the presence of $KMnO_4$ because of the strong oxidizing effect of $KMnO_4$; together, these conditions promote the degradation of E2. By combining methods, the removal rate increased by 70.8 times over pure ultrasound treatment. Among the processes of pure $KMnO_4$, pure ultrasound, and ultrasound/$KMnO_4$, the latter was the most efficient. The degradation products of E2 under ultrasound were mineralized and harmless.

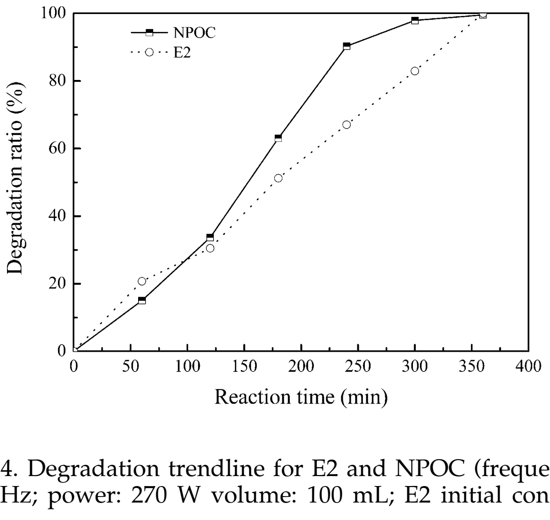

Fig. 4. Degradation trendline for E2 and NPOC (frequency: 20 kHz; power: 270 W volume: 100 mL; E2 initial concen-

Acknowledgments

This research is supported by National Natural Science Foundation of China (Grant Nos. 51208468 and 51008261), Natural Science Foundation of Zhejiang Province of China (Grant No. Q12E080063), Natural Science Foundation of Zhejiang University of Technology (Grant No. 1101106040408) and Outstanding Yong Scientific Talent Training Program of Xiamen University of Technology (No. JA11227).

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