Enhanced sonochemical degradation of tetracycline by sulfate radicals
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ABSTRACT

Tetracyclines (TCs) are widely used antibiotics in human and veterinary medicine and as growth promoters in the world. Sulfate radical-based advanced oxidation processes have been of great interest due to the high oxidizing potential of sulfate radical to degrade refractory organic pollutants in aqueous solution. In this study, the degradation of antibiotic TC in aqueous solution by silver-activated persulfate (Na2S2O8) in the presence of ultrasound irradiation under various conditions has been investigated. The effects of several parameters such as Ag2SO4, Na2S2O8 concentration, temperature, ultrasonic (US) power, initial TC concentration and initial pH on the degradation of TC were investigated. More than 83% of TC removal was achieved within 120 min under optimal conditions. The optimum operational conditions were found to be as follows: Ag2SO4 dosage 3.5 mmol/L, Na2S2O8 concentration 70 mmol/L, reaction temperature 25°C, US power 120 W, initial TC concentration 50 mg/L, pH 3.0 and contact time 120 min. The degradation of TC in the persulfate/Ag+/US process followed the pseudo-first-order kinetics.

INTRODUCTION

A wide variety of antibiotics have been produced and consumed for disease prevention and health promotion since World War II (Jeong et al. 2010; Su et al. 2012). Due to the large use of antibiotics and their weak biodegradability, they are widely spread in the environment via sewage effluent and agricultural runoff (Hou et al. 2012). They are present in aquatic environments at trace amounts. They have been detected in surface water and groundwater and a major source of them is excretion (Jeong et al. 2010). Annually 100,000–200,000 tons of antibiotics are used in the world. Meanwhile, tetracycline (TC) is the second most commonly used antibiotic in the world (Gu & Karthikeyan 2005). TC is widely used for human and veterinary medicine and also as growth promoters in agriculture (Zhu et al. 2013). In the United States, TC residual has been detected in surface water, effluent and influent of wastewater treatment plants at 0.11 μg L⁻¹, 0.17 μg L⁻¹ and 0.52 μg L⁻¹, respectively. This study also has indicated that TC is the most dominant antibiotic, being present in 80% of the wastewater samples in several wastewater treatment facilities in Wisconsin, USA (Karthikeyan & Meyer 2006). TCs are poorly absorbed in human and animal bodies, with about 50–80% of their consumed value eventually discharged to sewer through feces and urine. Antibiotics are high environmental threats and have many side effects (Liu et al. 2012). The presence of antibiotics in the environment causes the increasing resistance of bacteria to the antibiotic, which ultimately causes damage to ecosystems and human health. Antibiotics have a weak biodegradability and high bioaccumulation, toxicity and chemical oxygen demand (COD) (Su et al. 2012). This is why we need efficient and effective techniques to remove these compounds from aqueous solutions. Conventional treatment processes could not effectively remove refractory organic compounds such as antibiotics (Zhu et al. 2013). So we need alternative techniques to effectively remove antibiotics from aqueous solutions. Various treatment techniques have been used for degradation of these compounds. One alternative is advanced oxidation processes (AOPs), which seem more effective compared with other techniques such as adsorption and reverse osmosis because these latter techniques do not destroy contaminants and only transfer them from one phase to another, while...
AOPs destroy and mineralize pollutants to CO₂ and H₂O (Schrank et al. 2004; Xiong et al. 2014). The conventional AOPs such as Fenton, UV/H₂O₂ and UV/O₃, are based on formation of hydroxyl radicals (•OH) that degrade pollutants effectively but non-selectively (Han et al. 2002; Yang et al. 2010). In recent years, an innovative AOP based on the sulfate radical (SR-AOP) has received great attention due to the higher redox potential and longer half-life of the sulfate radical (SO₄²⁻) (E₀ = 2.5–5.1 V vs. NHE (normal hydrogen electrode) and half-life = 10³–10⁴ μs) compared with the hydroxyl radical (E₀ = 1.89–2.72 V vs. NHE and half-life = 10⁻³ μs) (Yang et al. 2010; Olmez-Hanci & Arslan-Alaton 2013). Moreover, the sulfate radical has higher selectivity for reaction with the target pollutant via electron transfer than that of the hydroxyl radical (Yuan et al. 2011). The SO₄ radical is more able to participate in the electron transfer reaction whereas the OH radical participates in hydrogen addition and abstraction reaction for destruction of organic compounds (Olmez-Hanci & Arslan-Alaton 2013; Govindan et al. 2014). Several studies have been conducted on the effect of SR-AOP in the degradation of organic pollutants. The SO₄ radical is a strong oxidant and can degrade a variety of chemical contaminants in aqueous systems. Su et al. (2012) studied the degradation of amoxicillin by sulfate radicals and found that more than 98% of COD removal occurred under optimum operational conditions. Huang et al. (2005) successfully used sulfate radicals to degrade a great number of the 59 volatile organic chemicals listed in the US Environmental Protection Agency SW-846 method 8260B. Also Guan et al. (2013) successfully degrade more than 98% of atrazine with sulfate radicals within 15 min. Sulfate radicals were generated by peroxy-monosulfate (PMS) and persulfate (PS) (also named peroxydisulfate or peroxodisulfate) with standard redox potential E₀ = 1.81 and 2.01 V, respectively (Govindan et al. 2014). Activation of PS or PMS to generate SO₄²⁻ is done by UV radiation, thermal, sonication, base, radiolytic, electron, soil minerals and transition metal treatments (Yang et al. 2010; Hou et al. 2012; Zhu et al. 2013). Several studies have been conducted on the effectiveness of transition metals for activation of PS and PMS. Studies have shown that the best transition metals for the activation of PMS and PS are Co and Ag, respectively (Nfodzo & Choi 2011). With respect to the advantages of persulfate, such as oxidation power, high stability in surface environment, high aqueous solubility, low cost and producing safe final products of sodium and sulfate, it is a good choice for SR-AOPs (Huang et al. 2005). In the presence of transition metal (here Ag⁺), PS produced SO₄²⁻ as depicted by Equation (1) (Hou et al. 2012).

\[
\text{SO}_4^{2-} + \text{Ag}^+ \rightarrow \text{SO}_4^{+} + \text{SO}_4^{2-} + \text{Ag}^{2+} \quad (1)
\]

In recent years, sonolysis has been successfully used for degradation of persistent organic compound including dyes, phenolic compounds, trichloroethane, perfluorooctanoic acid and pharmaceutical compounds. Ultrasonic (US) treatment operates through cavitation. Cavitation in ultrasound treatment produces plasma in water that degrades molecules by pyrolysis directly. Cavitation also generates highly reactive hydroxyl radical and sulfate radical species that can enhance degradation of pollutants indirectly (Su et al. 2012; Hou et al. 2012). The formation of sulfate radical and hydroxyl radical by ultrasonication is shown in Equations (2) and (3).

\[
\text{H}_2\text{O}_8 \rightarrow \text{SO}_4^{+} + ^*\text{HO} \quad (2)
\]

\[
\text{SO}_4^{+} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + ^*\text{OH} + ^*\text{H} \quad (3)
\]

Sonochemical degradation of organic compounds can be accomplished along with the other activators such as transition metals (Su et al. 2012) and photocatalysis (Panchangam et al. 2009) in aqueous solution. The combination of transition metal and ultrasound irradiation is a good choice for the degradation of organic compounds. Relatively few studies have been conducted on the degradation of TC by SR-AOP with PS activated by Ag. There has been no study to investigate the degradation of TC by using sulfate radical activated by Ag ions under sonication. In this study we used Ag/US for activation of PS to degrade TC in different situations and to evaluate optimum pH, temperature, time and initial amount of oxidant, metal and pollutant.

**METHODS**

**Chemicals**

TC hydrochloride (C₂₂H₂₄N₂O₈×HCl) was purchased from Sigma-Aldrich and used without further purification (99% purity). The main relevant data for TC are shown in Table 1 (Jeong et al. 2010). De-ionized water used for preparation of aqueous solutions for use in experiments was purified by a Milli-Q system. The oxidant, sodium peroxysulfate (Na₂S₂O₈, 98%), was purchased from Sigma. Ag⁺ ion solution was prepared from Ag₂SO₄ and obtained from Sigma-Aldrich. Acetonitrile (high-performance liquid chromatography (HPLC) grade),
oxalic acid (HPLC grade) and methanol (HPLC grade) were obtained from Merck and used as received. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Merck and used for pH adjustment. All other chemicals were of reagent grade and were obtained from Sigma and used as received. Solutions were prepared daily prior to experiments.

**Procedures**

Prior to each experiment a stock solution of TC was prepared freshly in high purity water. A specific volume of TC was transferred into a 100 mL batch reactor and then a known amount of Ag and Na₂S₂O₈ was added to the solution and mixed by means of a magnetic stirrer. All solution reactors were covered with aluminum foil for prevention of light exposure. A US generator with 120 W power and 20 kHz frequency was used for sonication (model Kunshan Ultrasonic Instrument Co., Ltd). The vessel containing the solution was immersed into the US bath. Experiment temperature was controlled by a water circulating unit. At regular intervals, a specific aliquot of sample was withdrawn using a 0.45 μm syringe filter and mixed with the proper volume of methanol to quench further chemical reaction. The pH was measured by an S-25 pH meter.

**Analysis method**

The final concentration of TC was analyzed by HPLC: Agilent 1100 equipped with a Shimadzu LC-20 AB pump, Shim-Pack VP-ODS-C18 column (250 mm long, 4.6 mm i.d., 5 μm particle size) and UV detector (Shimadzu UV-1600 spectrophotometer). The wavelength of the detector was set at 359 nm for TC detection. The mobile phase was made of 0.01 M oxalic acid:methanol:acetonitrile (67:11:22) at a flow rate of 1.0 mL/min. The injection volume was 20 μL and the retention time was 4 min. Calibration was made with five standards, with good linearity ($R^2 > 0.999$).

**RESULTS AND DISCUSSION**

**Preliminary study for treatment method**

The preliminary experiments were conducted to compare the TC removal efficiency by different combinations of treatment systems. PS, Ag-activated persulfate (PS + Ag), ultrasound + persulfate (PS + US) and ultrasound coupled with Ag-activated persulfate (PS + US + Ag) were used in this experiment. Results are shown in Figure 1. The effect of each activator alone (US or Ag) or a combination of them (US + Ag) without oxidant was not examined because other studies have shown that, in the presence of activators without added oxidant, a little pollutant removal occurs (Lin et al. 2015). This is due to generation of a small amount of active radicals during the activator reactions in the absence of oxidant. For this study, the concentrations of TC, PS and Ag solution were taken as 70 mmol/L, 3.5 mmol/L and 50 mg/L, respectively. Also the ultrasound power was taken as 120 W.
In PS and PS + Ag systems mixing done by a magnet, whereas in the case of PS + US and PS + US + Ag systems mixing done by the turbulence generated by US waves. PS, PS + Ag, PS + US, PS + US + Ag had maximum TC degradation efficiency with increasing order of 20, 50, 54 and 83% at pH 3 and ambient temperature. In the case of Na2S2O8 alone, due to its stability, the chemical reaction and therefore the TC degradation rate are relatively slow in experimental condition (Hou et al. 2012). The activation of Na2S2O8 by Ag or ultrasound increased the chemical reaction rate and therefore the TC degradation efficiency reached 50 and 54% for Ag and US, respectively (Figure 1). The activators (Ag and US) catalyzed PS decomposition and generated more reactive radicals. In the PS + Ag system, TC can be degraded only by sulfate radicals generated by catalytic decomposition of PS; however, in presence of US, the additional generation of 'OH could increase the degradation of TC in aqueous solution. It was clearly seen that PS + US + Ag was the most efficient treatment system with the degradation efficiency of 83% for TC removal. This is due to the fact that more highly reactive hydroxyl and sulfate radicals will be generated by the synergistic effect of Ag and ultrasound during decomposition of PS according to Equations (1)–(3).

**Effects of solution pH**

To investigate the effect of solution pH on the degradation of TC, an experiment was conducted in the initial pH values of 3.0, 5.0, 7.0, 9.0 and 11.0. pH value was adjusted with dilute HCl and NaOH. As can be seen in Figure 2, the TC degradation rate increased as pH decreased. The highest TC degradation rate occurred in pH 3. In pH 9 and 11 TC removal efficiency was relatively equal. The lower removal efficiency at higher pH can be explained as follows. (1) 'SO4 would be scavenged by 'OH radicals in higher pH; in other words, reaction of sulfate and OH radicals and formation of 'O with a lower oxidation potential. (2) 'SO4 would be converted to 'OH under alkaline pH based on Equation (4). (Liang et al. 2007; Lin et al. 2015).

\[
\text{SO}_4^2^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{*OH} \tag{4}
\]

(3) The use of NaOH for pH adjustment in alkaline condition caused more 'OH formation, which has a lower oxidation potential than 'SO4 (Lin et al. 2015). (4) Another reason for the lower TC degradation rate in higher pH is also the presence of more ions under the alkaline conditions. As TC is naturally acidic, for adjustment of pH in alkaline conditions more NaOH was added to increase the ionic concentration of the solution. The higher concentration of ions may decrease the effect of ultrasound, which interferes in TC ability to adsorb to the bubble–water interface. These findings are in accordance with the results of Liang et al. (2007), Hou et al. (2012) and Lin et al. (2015). However, the pH effect on TC degradation efficiency was not appreciable in 100–120 minute reaction. The final removal efficiency was 83, 82, 80, 78 and 78% at pH 3.0, 5.0, 7.0, 9.0 and 11.0, respectively, after 120 min. According to the production of carboxyl acids in this experiment, it is expected that pH would drop during the reaction. So the relatively same removal efficiency in different initial pH can be due to the final acidic condition of solution at the end of the reaction (120 min) (Hou et al. 2012). Our results...
support those of previous studies, which also did not detect any appreciable effects of pH on decomposition of organic pollutant (Criquet et al. 2020). Finally, the initial pH of 3 was used as optimum pH in all the experiments in this study.

Effect of PS concentration

The effects of various PS concentrations from 2 to 100 mM on TC degradation were investigated and results are shown in Figure 3. The TC degradation rates increased with the increase of the concentration of PS, varying from 71 to 83% for PS concentration of 2 mM and 70 mM, respectively, at pH 3 and ambient temperature within 120 min. As the concentration of PS increased, more sulfate radicals were generated in the solution, which results in faster TC degradation. Therefore, it was concluded that the PS concentration causes positive effect on the degradation of TC. However, the removal efficiency was relatively equal in PS concentration of 70–100 mM within 100–120 min. So the use of a higher PS dosage has no economic justification for this reaction time. Moreover several previous studies reported that excess additional PS had adverse effect on TC degradation (Hori et al. 2005; Hou et al. 2012). This might be attributed to (1) generation of sulfate anions instead of sulfate radicals, (2) reactions of radicals with each other prior to the reactions of radical with organics according to Equation (5), (3) scavenging of sulfate radicals by S₂O₅²⁻ and the generation of less reactive S₂O₃⁻ based on Equation (6), and (4) prevention of 'OH generation by SO₄²⁻ (Madhavan et al. 2008).

\[ \text{SO}_4^{2-} + \text{S} \rightarrow \text{S}_2\text{O}_5^{2-} \quad k = 4.0 \times 10^8 1/(\text{mol} \cdot \text{s}) \quad (5) \]

\[ \text{S}_2\text{O}_5^{2-} + \text{SO}_4^{2-} \rightarrow \text{SO}_2\text{O}_4^{2-} + \text{S}_2\text{O}_8^{2-} \quad k = 6.1 \times 10^5 1/(\text{mol} \cdot \text{s}) \quad (6) \]

Therefore, the TC removal rate is reduced at higher concentration of PS. The optimum PS concentration is 70 mM with 83% removal efficiency in 120 min.

Effect of Ag ion concentration

For optimizing Ag ion concentration, different concentrations of Ag, from 0 to 6.4 mmol/L, were added at pH 3 and ambient temperature for degradation of TC. As depicted in Figure 4, the degradation of TC is strongly affected by the Ag concentration in aqueous solution. As shown, the degradation efficiency significantly increased with the Ag content in the solution from 0 to 3.5 mmol/L. However, a further increase of Ag content to 6.4 mmol/L, showed slight increase in the removal efficiency. As expected, the increase in the Ag amount would increase the rate of PS activation to generate the active sulfate radicals and then accelerate the TC removal. The Ag content of 3.5 mmol/L was chosen as an optimum dose for maximum TC degradation.

Effect of ultrasound power

The effect of ultrasound power on the degradation of TC was investigated. For this purpose, several experiments were conducted with different levels of ultrasound power from 0 to 150 W. The results are shown in Figure 5. As can be seen in Figure 5, increasing ultrasound power from 0 to 120 W could enhance the degradation efficiency from 50 to 83% after 120 min of reaction. Increase in the intensity of ultrasound to a certain level could accelerate the generation of hydroxyl and sulfate radicals (Neppolian et al. 2010). Therefore, the rate of TC degradation was enhanced.
with the increase in ultrasound power. However, with further increase in US power from 120 to 150 W, the TC removal efficiency decreased from 83 to 78%. When the US intensity exceeded the optimal value, it generated a large number of cavitation bubbles. These bubbles limited the transmission of sound through the solution by scattering the acoustic waves to the walls of the container or back to the transducer (Su et al. 2012). The removal efficiency of TC could reach to a maximum level when US intensity was the optimal value. The optimum intensity of ultrasound power was 120 W.

**Effect of initial TC concentration**

The effect of the initial TC concentration on process efficiency was determined. Concentration of TC was varied from 10 to 70 mg/L in the solution. Figure 6 presents the removal efficiency of TC at different initial concentrations. It can be seen that the removal efficiency decreased with the increase in TC concentration. However the total removal quantity was more at high concentration. The results can be explained in that higher concentration of TC would reduce the probability of collision and reaction between TC molecules and reactive radicals. Moreover intermediate products formed by the mineralization of TC would compete with parent pollutant in reaction with reactive radicals. Therefore, the degradation efficiency decreases with the increase in initial concentration of TC.

**Effect of temperature**

To evaluate the effect of temperature on degradation of TC, three temperatures (25, 40, and 70 °C) were provided for the PS + Ag + US process. As is shown in Figure 7, temperature had a positive synergistic effect on the PS + Ag + US process and TC decomposition increased with the increase of the temperature. This is due to the generation of sulfate and hydroxyl radicals under thermal activation of PS in aqueous solution; therefore higher efficiency of removal of pollutant was observed in high temperatures, as previously reported by some researchers (Jimenez et al. 2003; Liang & Bruell 2008). But the impact of temperature was not significant at the end of the experiment (120 min) and removal efficiency was approximately the same in 120 min. With regard to this issue and the practical operation of the system, the optimal condition for this experiment was ambient temperature.

**Kinetics of TC degradation**

The degradation of TC with the PS + Ag + US system is observed to follow a pseudo-first-order reaction and can be
efficiency in the increasing order of 20, 50, 54 and 83%. The PS + Ag + US process was proved to be an effective method for the degradation of TC in aqueous solution. The effect of several operational parameters on the degradation of TC was investigated. The result showed that the removal efficiency was strongly affected by initial concentration of TC, pH, ultrasound power, the concentration of persulfate, temperature and Ag ion. The degradation of TC in the PS + Ag + US process followed the first-order kinetics. This study has shown that the SR-based AOP is an effective and feasible technology for degradation of refractory organic compounds such as the antibiotic TC in aqueous solution.

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