

TOC and THMFP reduction by ultrasonic irradiation in wastewater effluent

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Abstract

Humic substances (HS) are amorphous organic macromolecules that are responsible for the color of natural water and wastewater effluents. They play an important role in the formation of disinfection by-products. The ultrasonic process is applied as a treatment method to investigate its effect on the TOC removal and the formation of trihalomethanes (THMs) during chlorination. It was observed that the metal ions such as Fe(II) and Mn(II) showed catalytic effects while Al(III), Ca(II), and Mg(II) had inhibitory effects on the TOC removal of humic substances in sonochemical reaction with hydrogen peroxide. Experimental results also showed hydrogen peroxide dose affected the formation of disinfection by-products. Chloroform and dichlorobromomethane were formed as major THMs during chlorination.

Keywords: Ultrasonic irradiation; Total organic carbon (TOC); Trihalomethane formation potential (THMFP); Humic substances; Hydroxyl radical

1. Introduction

The chlorine disinfection processes and other oxidation processes to inactivate harmful microorganisms are questioned by the potentially

toxic by-products formed during disinfection. In the 1970s, chloroform, a trihalomethane produced during chlorination, was shown to be a carcinogen for mice and rats [1]. Trihalomethanes were the first class of halogenated disinfection by-products identified in finished drinking water [2]. In 1975, the U.S. Environmental Protection

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Agency began preliminary investigations into the health threat posed by disinfection by-products, and these investigations led to the regulation of trihalomethanes in drinking water in US in 1979.

Since those initial regulations took effect, a great deal of research has been focused on finding the best balance the risk minimization from both waterborne pathogens and carcinogenic disinfection by-products. The initial efforts to control disinfection by-products fell into two categories. The first was the use of alternate disinfectants such as ozone. However, it was soon realized that each new disinfectant produced alternative disinfection by-products. The main focus now is on eliminating the disinfection by-product precursors like humic substances which contribute to major portion of organic matters in wastewater effluents [3]. In this study, ultrasonic process is selected as a treatment method owing to its several advantages. The advantages of the ultrasonic process include decomposition of volatile and semi-volatile organic compounds in aqueous phase, decomposition of semi-volatile organic compounds from soil, and transformation of the refractory compounds into highly degradable products [4]. Mainly, ultrasonic decomposition of organic compounds is brought by the formation and collapse of high-energy cavitation bubbles. Upon collapse, the solvent vapor is subjected to the enormous increases in both temperature (up to 5000 K) and pressure (up to several thousand atm). Under such extreme conditions the solvent molecules undergo homolytic bond breakage to generate radicals. When water is sonicated, H and OH radicals are produced, the latter being a strong oxidizing agent ($E_h = 2.33$ V) which can react with organic compounds. The aim of this study is to investigate effects of ultrasonic treatment on the decomposition of humic substances, and THM formation potential (THMFP) in the process of the ultrasonic treatment for humic substances has also been studied. Factors such as dose of

hydrogen peroxide, turbidity, and concentration of metals were examined as well.

2. Experimental

2.1. Materials

Hydrogen peroxide with a purity of 31.5% was obtained from the Fisher Scientific Company. A potable reverse osmosis (RO) system was used to collect and concentrate humic substances (HS) from a wastewater plant effluent. Effluent was first pumped through in-line filters (1 and 0.45 μm) to remove particulate matter and was then collected in a 40-L sample reservoir. A 1/16 HP submersible pump (Simer Pump, Model 2310, Kansas City, MO, USA) in the sample reservoir pumped the filtered samples through a cation exchanger (Dowex-50 cation exchange resin in the sodium form, Dow Chemical, Midland, MI, USA). The filtered and cation-exchanged sample was then delivered to the RO membrane by a high-pressure pump (Hypro, Model 2230B, New Brighton, MN, USA), which boosted the pressure to 150–200 psi. The RO membrane (Filmtec FT30, Dow Chemical) consisted of a 0.2- μm thick, highly crosslinked aromatic polyamide skin on a 35- μm polysulphone support and was designed for the desalination of tap water. The retentate solution from the RO system was collected into the sample reservoir and mixed with filtered sample. The recycling of the retentate solution to the sample reservoir was continued until the desired enrichment of HS was achieved.

Wastewater effluent samples were taken (pre-chlorination) from the W wastewater treatment plant (WWTP). The contents were evaluated using the methods described in “Standard Methods for the Examination of Water and Wastewater”, 18th edition, 1992. Results of this analysis are as follows; pH 7.8, Mn(II) 0.3 mg/L, Fe(II) 0.2 mg/L, Mg(II) 16 mg/L, Ca(II) 27 mg/L, Alkalinity 153 mg-CaCO₃/L, Br⁻ 220 mg/L, and Cl⁻ 167 mg/L.

2.2. Experiments

In order to get carbonate-free sample, bicarbonate was removed by acidifying the sample to pH 4 with perchloric acid and bubbling with pure nitrogen gas. Sonochemical treatments were conducted with an ultrasonic generator (Cole-Parmer 600-Watt, 20 kHz, ultrasonic homogenizer 4710) equipped with a titanium probe transducer (Cole Parmer, Model CV 17). Experiments were conducted in an open glass reactor (Sonics & Materials, 20 mL) in the batch mode. The reactor was filled with the wastewater effluent sample and immersed in a water bath (Frigomix 1495 Water Circulation and Temperature Control System). The temperature was kept at pre-selected value. Hydrogen peroxide was added at the starting point manually. The solution pH was adjusted to a pre-selected value at the last step before starting the sonochemical irradiation. The treated samples were immediately injected to TOC analyzer and adjusted to pH 7 with pH buffer solution. Sodium hypochlorite solution was added to samples, which were kept in sealed, zero-headspace, and amber bottles, then stored in darkness at 25°C.

Trihalomethanes in 0.5 mL samples from the reactor were extracted using the liquid–liquid extraction method and analyzed with gas chromatography (Hewlett–Packard model 5890) equipped with a Supelco-608 column ($L=30$ m, internal sampler injector, and an electron capture detector (ECD). The injector was in splitless mode. Nitrogen was the carrier gas set at a flow rate of 30 mL/min. The temperatures of the injection port and detector were 250°C and 300°C, respectively. The temperature program began at 50°C and was held for 3 min, followed by a 15°C/min ramp until a final temperature of 200°C was reached and held for 2 min. Total organic carbon (TOC) was determined using a Tekmar-Dohrmann DC-190 TOC analyzer (Rosemont Analytical Inc., Dohrmann Division, Cincinnati, OH).

The chlorine demand of the wastewater sample, appropriate dilution factor to prepare the chlorine dosing solution, volume of chlorine dosing solution per sample volume, and residual chlorine concentrations after THMFP tests were determined via titration using a Hach CN-65 test kit.

3. Results and discussion

The effect of hydrogen peroxide was tested at four different concentration levels of hydrogen peroxide (0 , 2.5×10^{-3} , 5.0×10^{-3} , 10×10^{-3} M). Hydrogen peroxide has long been recognized as a free radical producer. Although hydrogen peroxide can be produced by ultrasonic irradiation alone in aqueous solution, the amount may be not enough to be significant to decompose the humic substances in wastewater effluent. The addition of hydrogen peroxide is considered to initiate and promote the free radical reaction. Fig. 1 shows the effect of hydrogen peroxide on the TOC removal of humic substances in wastewater effluent. It shows the semi-log plot of rate constant vs. dose of hydrogen peroxide. The rate of TOC removal by ultrasonic irradiation increases with increasing dose of hydrogen

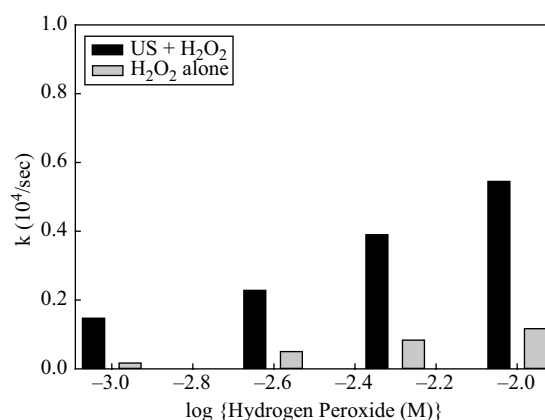


Fig. 1. Effect of hydrogen peroxide on decomposition rate of humic substances in wastewater effluent.

peroxide. Over 30% of TOC removal is achieved with 10^{-2} M of hydrogen peroxide concentration after 120 min of reaction time.

Fig. 2 shows the effect of turbidity on the decomposition of humic substances by ultrasonic irradiation with H_2O_2 in wastewater effluent. The effect of turbidity was tested at four different concentration levels of kaolinite (1, 10, 30, and 50 mg/L). The decomposition rate decreases as the turbidity increases in the range of 1–10 mg/L of kaolinite, then slightly decreases upon further increase in the turbidity above 10 mg/L.

Fig. 3 shows the effect of Al(III) on the decomposition of humic substances by ultrasonic irradiation with H_2O_2 in wastewater effluent. The effect of Al(III) was tested at four different concentration levels of Al(III) (0, 1, 5, and 10 mg/L). The extent of TOC removal decreases with increasing of Al(III) concentration. The decomposition rate decreases rapidly as the dose of Al(III) increases from 0 to 1 mg/L, then decreases slightly above 1 mg/L of Al(III) concentration.

Fig. 4 shows the effect of Ca(II) on the decomposition of humic substances in wastewater effluent. The effect of Ca(II) was tested at four different concentration levels of Ca(II) (0, 50, 100, and 200 mg/L). The decomposition

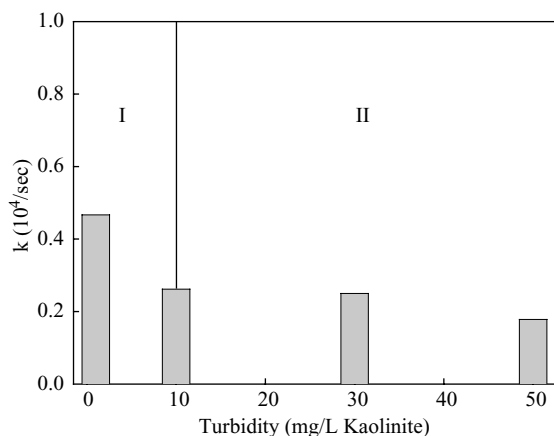


Fig. 2. Effect of turbidity on decomposition rate of humic substances in wastewater effluent.

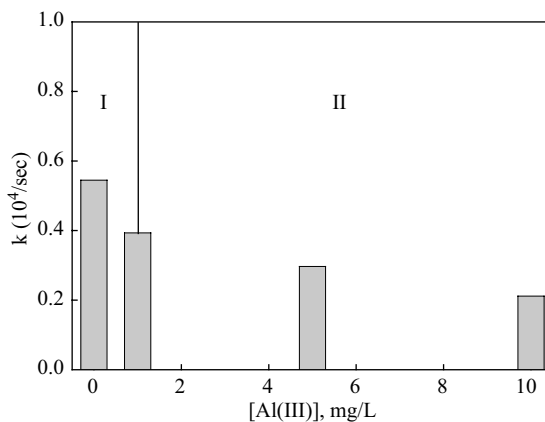


Fig. 3. Effect of Al(III) on decomposition rate of humic substances in wastewater effluent.

rate decreases as the Ca(II) concentration increases from 0 to 100 mg/L, then remains constant above 100 mg/L of Ca(II) concentration

Fig. 5 shows the effect of Mg(II) on the decomposition of humic substances in wastewater effluent. The effect of Mg(II) was tested at four different concentration levels of Mg(II) (0, 5, 20, and 50 mg/L). The decomposition rate decreases as the Mg(II) concentration increases from 0 to 5 mg/L, then decreases slightly above 5 mg/L of Mg(II) concentration.

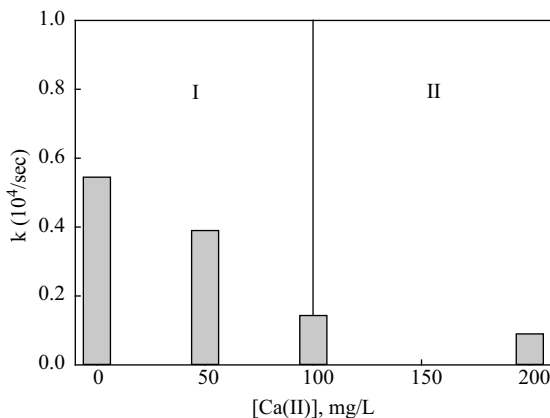


Fig. 4. Effect of Ca(II) on decomposition rate of humic substances in wastewater effluent.

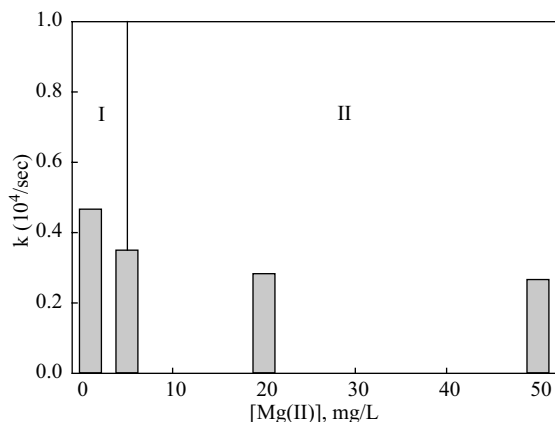


Fig. 5. Effect of Mg(II) on decomposition rate of humic substances in wastewater effluent.

Fig. 6 shows the effect of Fe(II) on TOC decomposition of humic substances in wastewater effluent. The effect of Fe(II) was tested at four different concentration levels of Mg(II) (0, 0.5, 1, and 5 mg/L). The extent of TOC removal increases with increasing of Fe(II) concentration. The decomposition rate has no significant change with small dose (0.5 mg/L). However, it increases rapidly from 0.5 to 2 mg/L, then increases slightly from 2 to 5 mg/L of Fe(II) concentration.

Fig. 7 shows the effect of Mn(II) on TOC decomposition of humic substances in wastewater

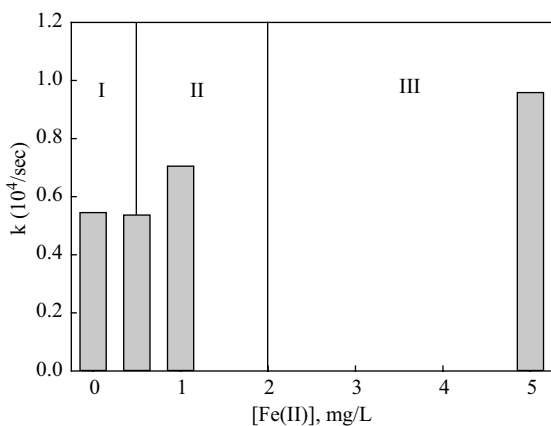


Fig. 6. Effect of Fe(II) on decomposition rate of humic substances in wastewater effluent.

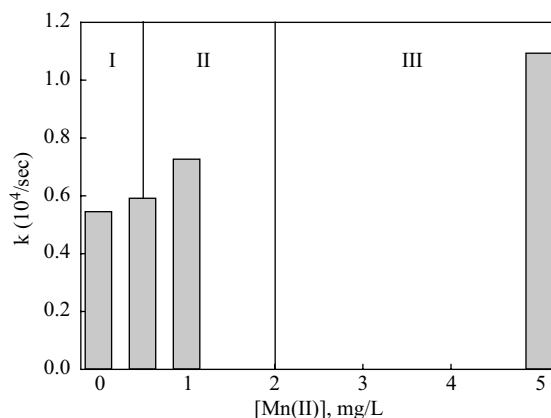


Fig. 7. Effect of Mn(II) on decomposition rate of humic substances in wastewater effluent.

effluent. The effect of Mn(II) was tested at four different concentration levels of Mn(II) (0, 0.5, 1, and 5 mg/L). The extent of TOC removal increases with increasing of Mn(II) concentration. The change of the decomposition rate shows a similar trend to that with Fe(II). The decomposition rate has small change with small dose (0.5 mg/L). However, it increases rapidly from 0.5 to 2 mg/L, then increases slightly from 2 to 5 mg/L of Fe(II) concentration. Fig. 8 illustrates the decrease in THMFP as a function of ultrasonic reaction time with different dose levels

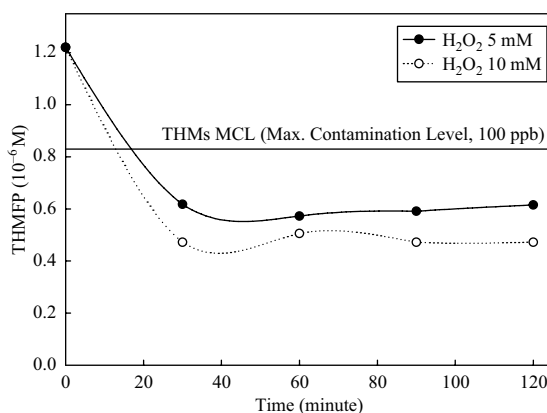
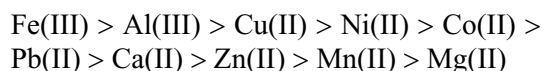


Fig. 8. Effect of US irradiation and hydrogen peroxide on THMFP of humic substances in wastewater effluent (Wilmington WW plant).

of hydrogen peroxide. It was observed that the extent of TOC removal of humic substances by the ultrasonic irradiation with 10 mM of hydrogen peroxide was over 30% after 120 min of reaction time. The ultrasonic irradiation combined with hydrogen peroxide reduces the THMFP. Several researchers have proposed that the combination of an ultrasonic process with an oxidant can enhance the decomposition of organic matter [5,6]. Since the ultrasonic process with hydrogen peroxide decreases the concentration of precursors (represented as TOC), the amount of chlorinated by-product formation can be decreased.

The weak acidic characteristic of humic substances is ascribed to complexation with free metals, such as Al(III), Mg(II), and Ca(II), and hydroxy-metals. Two significant modes of binding are as follows: (1) the formation complexes or chelates between the functional groups of the humic substances and metal, and (2) an association between the humic substances and colloidal particles of metal hydroxide (possibly through sorption on the surface of the particle) whereby the colloidal particles are stabilized in suspension. If two or more organic functional groups coordinate the metal ion, forming an internal ring structure, chelation, a form of complexation, occurs. It was also reported that adsorption of humic substances onto kaolinite took place to a large extent [7]. The above two mechanisms, complexation and sorption, appear to increase the degree of aggregation of humic substances and consequently, inhibit the transport of humic substances and their monomers produced through the depolymerization of HS polymers, then decrease the overall decomposition rate of humic substances. This trend is observed at the stage I in the Figs. 2–5. Beyond the complexation and sorption capacity of humic substances, the surplus dose of metal ions and kaolinite seems to have no more inhibitory effect on the reaction rate (Stage II). The determination of stability constants for HS-metal complexes provides information on the affinity of the metal for the organic ligand. Schmitzer

and Hansen [8] reported the stability constants for metal–HS complexes and found that the order of stability was



It was observed that Fe(II) and Mn(II) showed the catalytic effect combining with hydrogen peroxide [9]. The catalytic effect of transition metals (manganese and iron) was also found in ozonation processes for decomposition of humic substances [10]. The Mn(II) had larger extent of TOC removal of humic substances than that of Fe(II) in ozonation. The mechanism of the reaction of hydrogen peroxide with transition metals as catalysts consists of initiating the hydrogen peroxide decomposition chain producing OH radicals. For the start of radical chain reaction, transition metals as an initiator transfer an electron to hydrogen peroxide. It is known that ultrasonic irradiation can initiate and promote the hydrogen peroxide decomposition producing OH radicals. The larger extent of TOC removal of humic substances was previously obtained with a dose of hydrogen peroxide in combination with US irradiation in the experiments investigating the concentration effect of hydrogen peroxide. Consequently, the ultrasonic irradiation and the catalytic effect of transition metals initiates and promotes the radical reaction with hydrogen peroxide, which increases the extent and the decomposition rate of humic substances. It is observed that the ultrasonic reaction in the presence of transition metal has three different reaction stages (Figs. 6 and 7). At the first stage, the small dose of Fe(II) and Mn(II) has no significant catalytic effect. The abundant carboxylic and phenolic groups of humic substances appear to scavenge the OH radicals generated at this lag phase. The large amount of OH radicals produced by the increasing dose of transition metals decomposes the humic substances, then mineralize to carbon dioxide (Stage II). However, the

carbonate ions produced at stage II start to work as the competitive radical scavengers (Stage III).

4. Conclusion

The rate of TOC removal was proportional to dose of hydrogen peroxide while increasing of turbidity decreased the extent of TOC removal of humic substances. The metal ions such as Fe(II) and Mn(II) showed catalytic effect while Al(III), Ca(II), and Mg(II) had inhibition effect on the TOC removal of humic substances in sonochemical reaction with hydrogen peroxide. Experimental results also showed the dose of hydrogen peroxide affected the formation of disinfection by-products. Chloroform and dichlorobromomethane were formed as major THMs during chlorination.

Acknowledgement

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