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Effect of H_2O_2 and Metals on The Sonochemical Decomposition of Humic Substances in Wastewater Effluent

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The sonochemical process has been applied as a treatment method and was investigated its effect on the decomposition of humic substances(HS). The reaction kinetics and mechanisms in the process of sonochemical treatment for humic substances(HS) in wastewater have also been discussed. 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 decomposition of humic substances in sonochemical reaction with hydrogen peroxide. Experimental results also showed factors such as hydrogen peroxide dose affected the formation of disinfection by-products. Two trihalomethanes, chloroform and dichlorobromomethane were formed as major disinfection by-products during chlorination. The mechanism of radical reaction is controlled by an oxidation process. The radicals are so reactive that most of them are consumed by HS radicals and hydroxyl radicals can be acted on organic solutes by hydroxyl addition, hydrogen abstraction, and electron transfer. The depolymerization and the radical reaction of HS radicals appear to occur simultaneously. The final steps of the reaction are the conversion of organic acids to carbon dioxide.

Key words : sonochemical, ultrasound, humic substances, advanced oxidation process, hydroxyl radical

1. Introduction

The excellent ability of a chlorine disinfection process(and other oxidation processes as well) to inactivate harmful microorganisms is clouded by the potentially toxic by-products formed during disinfection. In the 1970s chloroform, a trihalomethane(THM) possibly be produced during chlorination, was shown to be a carcinogen in mice and rats[1]. THMs were the first class of halogenated DBPs(disinfection byproducts) identified in finished drinking water[2]. In 1975 the U.S. Environmental Protection Agency(EPA) began preliminary investigations into the health effect posed by DBPs, and led to the regulation of THMs in drinking water in 1979.

Since those initial regulations took effect, a great deal of research has been focused on finding the best balance between the risk minimization from both waterborne pathogens and carcinogenic DBPs. The initial efforts to control DBPs 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 DBPs. The main focus now is on eliminating the DBP precursors like humic substances which contribute major portion of organic matters in wastewater effluents[3]. In this study, sonochemical process is selected as a treatment method owing to its several advantages. The advantages of the sonochemical 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]. The aim of this study is to investigate the effects of sonochemical treatment on the decomposition of humic substances, and reaction kinetics and mechanism have also been discussed. Factors such as the dose of hydrogen peroxide, turbidity, and concentration of metals were examined.

2. EXPERIMENTAL

2.1. Materials

Hydrogen peroxide with a purity of 31.5 % was obtained from the Fisher Scientific Company. Perchlorate salts of metals were obtained from the Aldrich Chemical Company(Milwaukee, WI).

A potable reverse osmosis(RO) system was used to collect and concentrate humic substances(HS) from Wilmington Wastewater Plant effluent. Effluent was first pumped through in-line filters(1 and 0.45 m) 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 to 200 psi. The RO membrane(Filmtec FT30, Dow Chemical) consisted of a 0.2 m thick, highly crosslinked aromatic polyamide skin on a 35 m polysulphone support and was designed for the desalination of tap water. The percent rejection of 0.2 % NaCl solution by Filmtec RO membrane ranged from 99.0 to 99.7 %, depending on operating pressure(E.M. Perdue, personal communication). 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.

2.2. Wastewater Characterization

Samples were taken(pre-chlorination) from the Gwangju wastewater treatment plant(GWTP) on two occasions. The Ca(II), Mn(II), Fe(II), and Mg(II) contents were evaluated using the direct air-acetylene flame method(method 3111 B)$^{5)}$. Bromide and chloride ion concentration was measured by Ion Chromatography(Dionex) equipped with a pulsed electrochemical detector and a Dionex AS-11 anion column. The eluent was a mixture of 90 % of deionized water and 10 % of 0.2N NaOH; the flow-rate was 1 mL/min and the injection loop was 50uL in volume. Results of this analysis are shown in Table 1. Also reflected in this table are the pH and alkalinity values. The alkalinity value was determined using the titration method(method 2320 B) and the pH value was measured using the electrometric method(method 4500-H$^+$ B)$^{5)}$.

2.3.Experiments

In order to get carbonate-free sample, bicarbonate was removed by acidifying the sample to pH 4 with perchlorate 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 using a manual method. 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 pH 7 with pH buffer solution. Sodium hypochloride solution was added to samples, which were kept in sealed, zero- head-space, and amber bottles, then stored in darkness at 25℃.

2.4. Analytical Methods

THMs in 0.5 mL sample 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 diameter=0.5 ㎛), a autosampler injector(Hewlett-Packard model 7376), and a electron capture detector(ECD). The injector was in splitless mode. Nitrogen was use

Table 1. Typical Characteristics of GWTP Samples

Items	Concentration of Pre-Chlorination Effluent
pH	7.8
Mn(II) (mg/L)	0.3
Fe(II) (mg/L)	0.2
Mg(II) (mg/L)	16
Ca(II) (mg/L)	27
Alkalinity (mg-$CaCO_3$/L)	153
Br^- (mg/L)	220
Cl^- (mg/L)	167

as a carrier gas set at a flow rate of 30 mL/min. The temperatures of the injection port and detector were 250 ℃ and 300 ℃, respectively. The temperature program began at 50 ℃ and was held for 3 min, followed by a 15 ℃/min ramp until a final temperature of 200 ℃ 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).

2.5. Chlorine Demand

The chlorine demand of the wastewater sample, appropriate dilution factor to prepare the chlorine solution, volume of chlorine solution per sample volume, and residual chlorine concentrations after THMFP tests were determined via titration using a Hach CN-65 test kit. The titration procedures are as follows: The sample volume was adjusted/diluted to 40 mL with the addition of deionized water(if the volume of original sample < 40 mL or the initial chlorine concentration > 20 mg/mL) and a sulfite 1 reagent powder pillow(Hach 2203-99) was added. A sulfamic acid powder pillow(Hach 1055-99) was then added and the sample was placed on the magnetic stirrer(VWR Magnestir)and mixed; a blue color developed is indicating the presence of chlorine. The prepared sample was reduced in volume to 30 mL(6 mL for high Cl_2 samples) and titrated with 2.46×10^{-3} N sodium thiosulfate standard solution(Hach 24085-37) until the sample became colorless. Each drop of titrant used to bring about the color change represented 0.2 mg/L(2.0 mg/L for high Cl_2 samples) chlorine(after correcting for appropriate dilution factors).

The chlorine dosing solution was prepared in the following manner. 1 mL of 5 % aqueous sodium hypochlorite solution(stock hypochlorite) was added to 25 mL of deionized water, and titrated to a starch-iodide endpoint using a sodium thiosulfate solution. Chlorine concentration was determined as outlined above(stock hypochlorite solutions with less than 20 mg Cl_2/mL were discarded). A chlorine dosing solution(5 mg Cl_2/mL) was prepared using the following formula:

$$\text{mL required} = \frac{1250}{\text{stock hypochlorite conc.mg } Cl_2/\text{mL}} \quad (1)$$

This calculated volume(22.2 mL) was added by the appropriated volume of deionized water to generate a 250 mL dosing solution. This solution was stored in an amber bottle at 4 ℃ and was discarded if the chlorine concentration dropped below 4.7 mg-Cl_2/mL.

The chlorine demand of the wastewater was determined to be 60 mg/L using the following procedure: 2.5 mL of chlorine dosing solution was pipetted into a 125 mL amber bottle and completely filled with deionized water, capped with a TFE-lined screw cap and shaken. The initial chlorine concentration of the sample was determined to be 95 mg/L(C_I). A second sample was prepared in the same fashion with the exception that 2.5 mL of phosphate buffering solution was also added and the sample was stored in the dark for over 4 hrs prior to titration. The residual chlorine concentration of the wastewater sample measured by titration was 35 mg/L(C_R). The volume of chlorine dosing solution(0.45 mL) need to chlorinate each sample for the THMPF test was determined using the following formula:

$$V_d = \frac{D_{Cl}+3}{5} \times \frac{V_s}{1000} \quad (2)$$

Where, V_d = volume of dosing solution,
V_s = volume of sample(35 mL)
D_{Cl} = C_I - C_R(60 mg/L).

3. Results and Discussion

The effect of hydrogen peroxide was tested at 4 different concentration levels(0, 2.5×10^{-3}, $5.0 \times$

10^{-3}, and 10×10^{-3} M). Hydrogen peroxide has long been recognized as a free radical producer. Although hydrogen peroxide can be produced by sonochemical irradiation alone in aqueous solution, the amount may not be enough to decompose the humic substances in wastewater effluent. The addition of hydrogen peroxide is considered to initiate and promote the free radical reaction. Figure 1 shows the effect of hydrogen peroxide on the TOC removal of humic substances in wastewater effluent. The extent of TOC removal increases with increasing dose of hydrogen peroxide. While little extent of removal is observed with the ultrasound alone, over 30 % of TOC removal is achieved with 10^{-2} M of hydrogen peroxide concentration after 120 minutes of reaction time. In the experiments without sonochemical irradiation, the rate constant of decomposition remains at low levels. Figure 2 shows the semi-log plot of rate constant and dose of hydrogen peroxide for both methods.

Figure 3 shows the effect of turbidity on the decomposition of humic substances in wastewater effluent. The effect of turbidity was tested at 4 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 to 10 mg/L of kaolinite, then slightly decreases upon further increase in the turbidity above 10 mg/L.

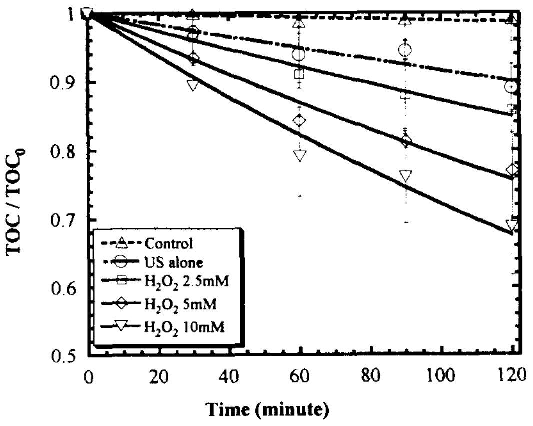


Fig. 1. Effect of Hydrogen Peroxide on Decomposition of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity=283 watts/cm^2, total volume = 10 mL, C_0 =TOC 10 mg/L, pH_0 = 7, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

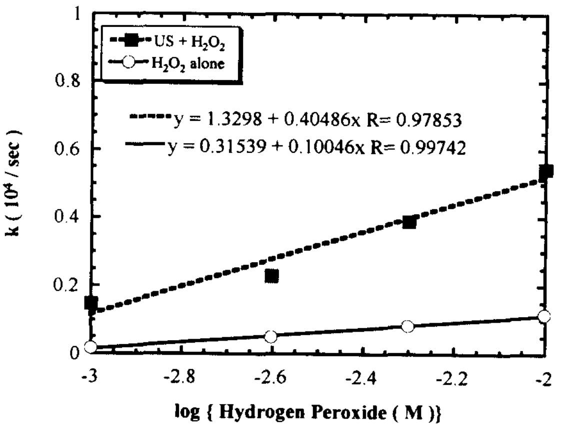


Fig. 2. Effect of Hydrogen Peroxide on Decomposition Rate of Humic Substances in Wastewater Effluent(semi-log plot). Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, C_0 = TOC 10 mg/L, pH_0 = 7, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

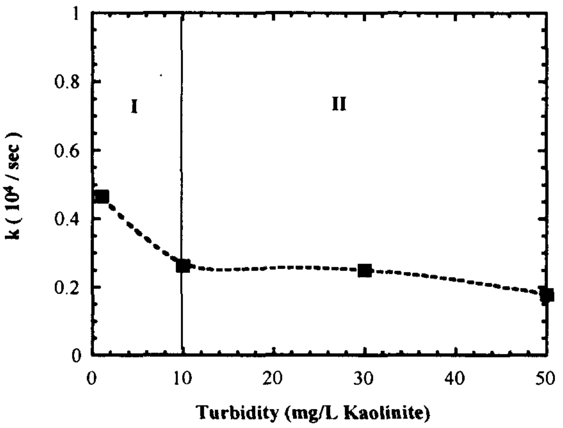


Fig. 3. Effect of Turbidity on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

Figure 4 shows the effect of Al(III) on the decomposition of humic substances in wastewater effluent. The effect of Al(III) was tested at 4 different concentration levels of Al(II) (0, 1, 5, and 10 mg/L). The extent of TOC removal decreases with increasing of Al(II) 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.

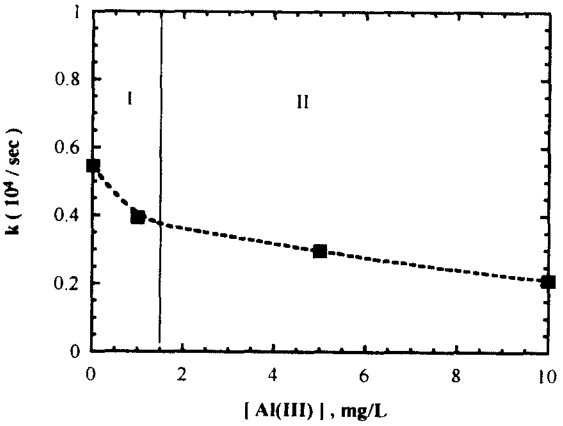


Fig. 4. Effect of Al(III) on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

Figure 5 shows the effect of Ca(II) on the decomposition of humic substances in wastewater effluent. The effect of Ca(II) was tested at 4 different concentration levels of Ca(II) (0, 50, 100, and 200 mg/L). The decomposition 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.

Figure 6 shows the effect of Mg(II) on the decomposition of humic substances in wastewater effluent. The effect of Mg(II) was tested at 4 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.

Figure 7 shows the effect of Fe(II) on TOC decomposition of humic substances in wastewater effluent. The effect of Fe(II) was tested at 4 different concentration levels of Fe(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). But it increases rapidly from 0.5 to 2 mg/L, then increases slightly from 2 to 5 mg/L of Fe(II) concentration.

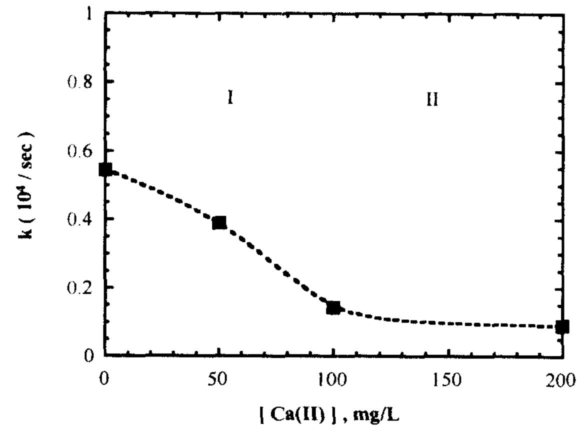


Fig. 5. Effect of Ca(II) on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

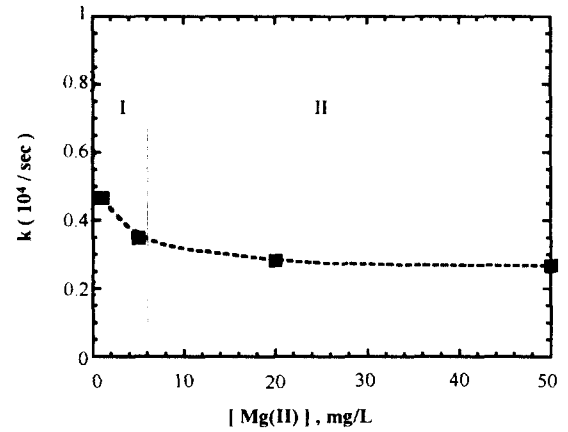


Fig. 6. Effect of Mg(II) on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

Figure 8 shows the effect of Mn(II) on TOC

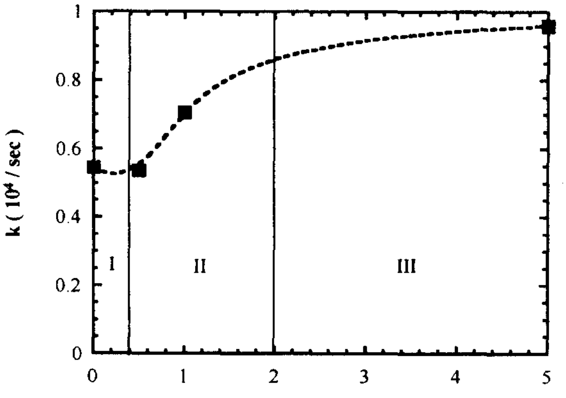


Fig. 7. Effect of Fe(II) on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

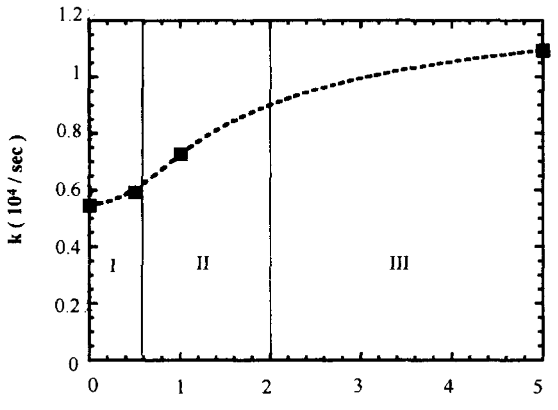


Fig. 8. Effect of Mn(II) on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

decomposition of humic substances in wastewater effluent. The effect of Mn(II) was tested at 4 different concentration levels of Mn(II) (0, 0.5, 1, and 5 mg/L). The extent of TOC removal increases with increasing of Fe(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). But it increases rapidly from 0.5 to 2 mg/L, then increases slightly from 2 to 5 mg/L of Fe(II) concentration.

Figure 9 illustrates the decrease in THMFP as a function of sonochemical reaction time with different dose levels of hydrogen peroxide.

The pseudo-first order rate constants6-7 were normalized to the degradation rate constant of the 20kHz probe system by

$$k_{nom} = k_{obs} \frac{1}{PD_{reactor}} PD_{20kHz(probe)} \qquad (3)$$

where k_{norm} is the rate constant normalized for the ultrasonic power density under specific conditions. k_{obs} is the observed rate constant in the reactor under specific conditions, and PD is the power input per volume of solution sonicated(i.e., power intensity). Normalized rate constant are the degradation rate constant normalized to the same energy input per volume of solution degraded in each reactor. Although other factor such as power intensity and reactor geometry and composition play a role in degradation efficiencies, normalization to energy input per volume provides a rough

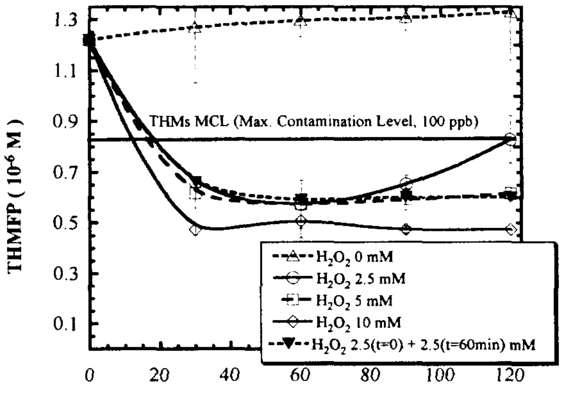


Fig. 9. Effect of US Irradiation and Hydrogen Peroxide on THMFP of Humic Substances in Wastewater Effluent(Wilmington WW Plant). Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

basis for comparison[8)]. The reactors used in experiments by Petrier et al.[9)] have the same area for emitting ultrasound as well as the same power density. In addition, other studies of the frequency effect with organic compounds have observed enhancement at 500 KHz over 20 KHz[10~11)]. In this study, the frequency of ultrasonic process is constantly controlled as a 20 kHz. And then the effects of metals and H_2O_2 added in the sample solution have been investigated.

When an aqueous solution is sonicated, a phenomena called cavitation takes place. This phenomena can be described as a formation of cavities(or bubbles) filled with gas or vapor. The diameter of these bubbles get a critic value and start to collapse. The pressure and temperature of these collapsing bubbles are estimated to get very high values[12)].

Figure 9 was observed that the extent of TOC removal of humic substances by the sonochemical irradiation in the presence of 10 mM of hydrogen peroxide was over 30 % after 120 minutes of reaction time. The sonochemical irradiation combined with hydrogen peroxide reduces the THMFP, while the irradiation without hydrogen peroxide slightly increases the THMFP of humic substances. The increasing trend is also observed by the sonochemical reaction of 60 minutes in the presence of small dose(2.5 mM) of hydrogen peroxide. The hydrogen peroxide appears to be consumed completely during the initial stage of reaction period. The second dose of hydrogen peroxide at 60 minutes of reaction time reduces the increasing trend, then keep the constant concentration of THMFP in low level(Figure 9). Several researchers have proposed that the combination of a sonochemical process with an oxidant can enhance the decomposition of organic matter3-14. Since the sonochemical process with hydrogen peroxide decreases the concentration of precursors(represented as TOC), the amount of chlorinated by-product formation can be decreased.

When H_2O_2 in introduced into this system, the oxidation process can be improved since hydrogen peroxide as an initiator to increase the concentration of free radicals in solution. This phenomena is also shown in Figure 1-2, and Figure 9. H_2O_2 is known by-product of sonolysis. However, the concentration of this by-product is very little. So H_2O_2 should be added into the solution as a initiator in order to enhence the degradation of humic substances. At pH values above 5.0, H_2O_2 accelerates the degradation of organic compounds such as humic substances by resulting in bulk phase · OH formation.

If O_2 is present in the vapor phase of the bubble, it can undergo thermolysis as follows:

$$O_2 \rightarrow 2\ O\cdot \qquad (4)$$

Cleavage of the O-O bond during sonolysis has been demonstrated by isotopic exchange experiment[15)]. Because the dissociative bond energies in the gas phase for water and oxygen are 119 kcal mol-1 [16)], thermolysis of these molecules in the cavitation bubbles is an important process during sonication of O_2-saturated solutions.

Since H_2 is not detected during sonolysis of an O_2-saturated solution[17)], it appears that O_2 efficiently scavenges · H according to the following standard reaction:

$$\cdot H + O_2 \rightarrow HO_2\cdot \qquad (5)$$

An alternate pathway for production of · OH in an O_2-saturated solution is as follows:

$$\cdot H + O_2 \rightarrow \cdot OH + \cdot O \qquad (6)$$

The H_2O_2 and · OH are strong oxidants and have aqueous reduction potentials at pH 7 of 1.35 and 2.31 V(Eo, V vs NHE)[18)], respectively. The kinetics of · OH reaction with organic compounds have been studied extensively both in the gas phase[19)] and aqueous phase[20)].

The weak acid character of humic substances is ascribed to complexation with free metals, such as Al(III), Mg(II), and Ca(II), and hydroxymetals[21)]. Two significant modes of binding are as following; (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, chelate, occurs. It was also reported that adsorption of humic substances onto kaolinite took place to a large extent[22)].

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 Figure 10. 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).

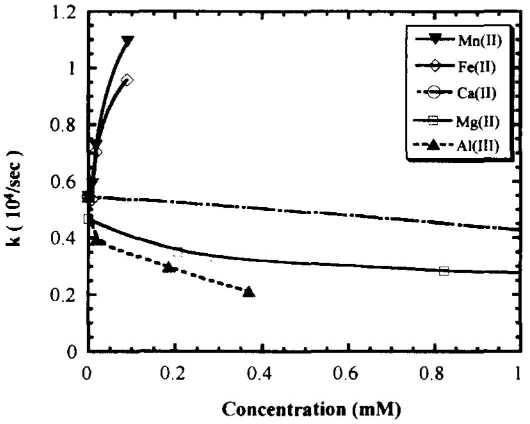


Fig. 10. Effect of Different Metal Ions on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions : ultrasonic energy intensity = 283 watts/cm^2, total volume = 10 mL, H_2O_2 10 mM, pH_0 7, C_0 = TOC 10 mg/L, temperature = 25 ℃, ionic strength = 0.05 M $NaClO_4$.

The determination of stability constants for HS-metal complexes provides information on the affinity of the metal for the organic ligand. Schmitzer and Hansen[23)] reported the stability constants for metal-HS complexes and found that the order of stability was:

Fe(III) > Al(III) > Cu(II) > Ni(II) > Co(II) > Pb(II) > Ca(II) > Zn(II) > Mn(II) > Mg(II)

Figure10 shows the variation of decomposition rate of humic substances versus the dose of 5 different metal ions. The decomposition rates increase significantly with increasing dose of Fe(II) and Mn(II), while the rates decrease with increasing dose of Al(III), Ca(II), and Mg(II). Fe(II) and Mn(II) show an important catalytic effect promoting the decomposition of humic substances in wastewater effluent. It was observed that Fe(II) and Mn(II) showed the catalytic effect combining with hydrogen peroxide[24)]. The catalytic effect of transition metals(manganese and iron) was also found in ozonation processes for decomposition of humic substances[25)]. 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 sonochemical process can initiate and promote the production of · OH radicals by decomposing hydrogen peroxide using the ultrasonic radiation. The larger extent of TOC removal of humic substances was previously obtained with a dose of hydrogen peroxide in the experiments investigating the concentration effect of hydrogen peroxide. Consequently, The transition metals introduced in the sonochemical irradiation show the catalytic effect, and hydrogen peroxide promotes the radical reaction, which increases the decomposition rate of humic substances. The Fenton' s reagent is characterized by a chain reaction between ferrous iron and H_2O_2 to generate hydroxyl radicals. Fenton's reaction is summarized by the following equations :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (7)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad (8)$$

$$\cdot H + O_2 \rightarrow \cdot OH + \cdot O \quad (9)$$

$$\cdot OH + R(:HS) \rightarrow \cdot ROH \quad (10)$$

$$\cdot OH + R \rightarrow \cdot R + H_2O \quad (11)$$

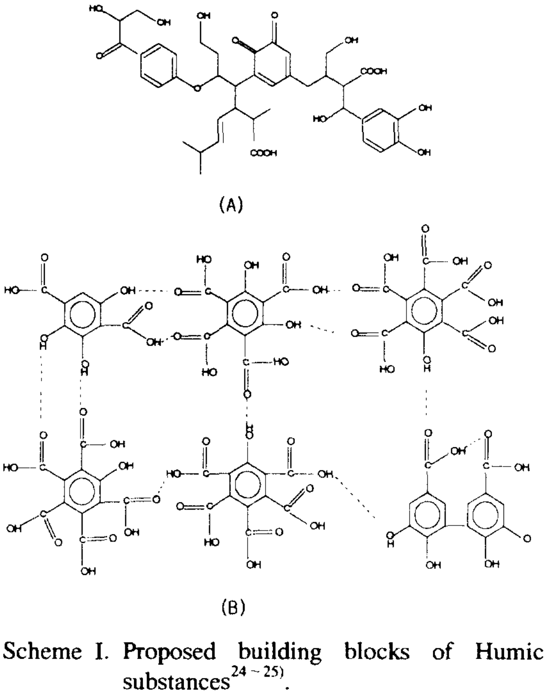
$$Fe^{3+} + \cdot R \rightarrow Fe^{2+} + \text{Products} \quad (12)$$

Reactions between ferrous iron and hydrogen peroxide promote a powerful and fast degradation of the organic contaminant[26)]. Likewise, Mn^{2+} can be also explained by the same meaning such as equation (7)-(12). It is observed that the sonochemical reaction in the presence of transition metal has 3 different reaction stages(Figure 7 and Figure 10). 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 leg phase. The large amount of OH radicals produced by the increasing dose of the transition metals used in this experiment enhance the decomposition of humic substances, then mineralize to carbon dioxide(Stage II). But the catalyst activity in this sonochemical reaction was substantially inhibited by the presence of typical elements such as Al(III), Ca(II), and Mg(II). The carbonate ions produced at stage II start to work as the competitive radical scavengers(Stage III).

Humic substances(HS) are ubiquitous, heterogeneous polymers that are isolated from many types of terrestrial and aqueous environments. They are amorphous organic materials that possess a variety of physical and chemical properties that make them unique to other types of environmental substances.

The functional groups of HS are amine, carboxylic, carbonyl, phenol, catechol, and quinone ect. These groups are on the HS surface or are chemically combined to cross link the molecular backbone. So far, the structure for HS is unknown, only proposed building blocks exist in Scheme I [27~28].

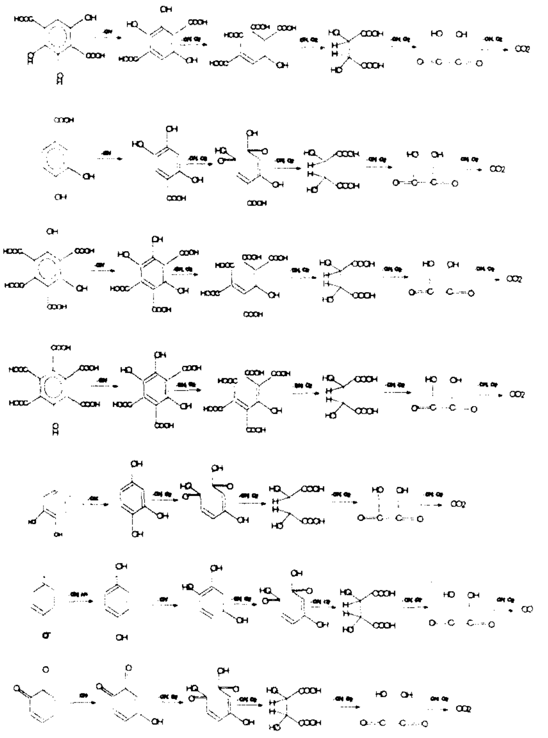


(A)

(B)

Scheme I. Proposed building blocks of Humic substances[24~25].

Cleavage of a covalent bond can occur in two ways, homolytically, resulting in one electron from the bond going to each fragment to produce radical species, or heterolytically, with both electrons going to one fragment, leading to formation of an ion pair. Both of these possibilities have been observed during polymer degradation(Scheme II). The production of macromolecular radicals is perhaps the most common breakdown mechanism and has been observed for many carbon skeleton polymers[29~30]. The radical species and ion pairs of HS undergo further chain scission, reaction with other radicals, and stabilization by water molecules. The heterolytic bond cleavage of polymers and the stabilization mechanism of ion pairs by water molecules was studied[31]. Consequently, the monomers can be formed as intermediates of HS, shown in Scheme II.



Scheme II. Proposed decomposition pathways of HS monomers.

The radical reaction is conducted by the radicals produced from the decomposition of hydrogen peroxide and water molecules by sonochemical irradiation.

The mechanism of radical reaction is rapid oxidation. The radicals are so reactive that most of them are consumed by HS. The OH radicals can act as organic solutes by hydroxy addition, hydrogen abstraction, and electron transfer. In other words, the radical reaction can open aromatic rings and form carbonyl compounds and organic acids [31, 32]. The depolymerization and radical reaction of HS appears to occur simultaneously. The final step(s) of the reaction is the conversion of organic acids to carbon dioxide.

4. Conclusion

The extent of TOC removal was proportional to a factor such as 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 factor such as dose of hydrogen peroxide affected the formation of disinfection by-products. Chloroform and dichlorobromomethane were formed as major THMs during chlorination.

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