

## Sonochemical Decomposition of Humic Substances in Wastewater Effluent

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The sonochemical process is applied as a treatment method to investigate its effect on the TOC removal of humic substances. The extent of TOC removal was proportional to factors such as ultrasonic energy intensity and hydrogen peroxide concentration while increasing of total carbonate, pH, and temperature decreased the extent of TOC removal of humic substances. The Langmuir-Hinshelwood model provided a good fit of the experimental data. 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.

**Keywords :** Sonochemical decomposition, Humic substances, Trihalomethane, Reaction kinetics, Mechanisms.

### 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) produced during chlorination, was shown to be a carcinogen in mice and rats.<sup>1</sup> THMs were the first class of halogenated DBPs identified in finished drinking water. In 1975 the U.S. Environmental Protection Agency (EPA) began preliminary investigations into the health threat posed by DBPs, these investigations 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.<sup>2</sup> 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.<sup>3</sup> The objectives of this study are to investigate effects of sonochemical treatment on the decomposition of humic substances. Reaction kinetics and mechanism in the process of the sonochemical treatment of the humic substances have been discussed. Factors such as total carbonate concentration, ultrasonic energy intensity, dose of hydrogen peroxide, solution pH, and solution temperature were also examined.

### Experimental Section

**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  $\mu\text{m}$ ) 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  $\mu\text{m}$  thick, highly crosslinked aromatic polyamide skin on a 35  $\mu\text{m}$  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.

**Experiments.** In order to get carbonate-free sample, bi-carbonate was removed by acidifying the sample to pH 4 with perchlorate acid and bubbling with pure nitrogen gas. Sonochemical treatments were conducted with a 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

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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 hypochlorite solution was added to samples, which were kept in sealed, zero-headspace, and amber bottles, then stored in darkness at 25 °C.

**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 =  $0.5 \mu\text{m}$ ), a Hewlett-Packard model 7376 autosampler 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).

**Chlorine Demand.** 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. The titration procedures are as follows: The sample volume was adjusted/diluted to 40 mL with the addition of distilled, deionized water (if original sample < 40 mL or if 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 a VWR Magne stir and mixed; a blue color developed indicating the presence of chlorine. The prepared sample was reduced in volume to 30 mL (6 mL for high  $\text{Cl}_2$  samples) and titrated with  $2.46 \times 10^{-3}$  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  $\text{Cl}_2$  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 distilled, deionized water and titrated to a starch-iodide endpoint using a sodium thiosulfate titrant. Chlorine concentration was determined as outlined above (stock hypochlorite solutions with less than 20 mg  $\text{Cl}_2$ /mL were discarded). A chlorine dosing solution (5 mg  $\text{Cl}_2$ /mL) was prepared using the following formula:

$$\text{mL required} = \frac{120}{\text{stock hypochlorite conc. mgCl}_2/\text{mL}} \quad (1)$$

This calculated volume (22.2 mL) was added to the appropriated volume of distilled, deionized water to generate a 250 mL dosing solution. This solution was stored in an amber bottle at 4 °C and was discarded if the chlorine concentration dropped below 4.7 mg  $\text{Cl}_2$ /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 distilled, 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. This titration indicated that the residual chlorine concentration of the wastewater sample 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:

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

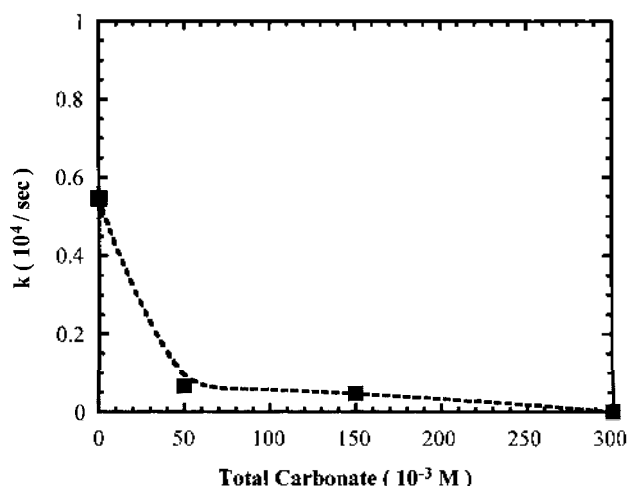
Where:  $V_d$  = volume of dosing solution.  $V_s$  = volume of sample (35 mL) and  $D_{Cl} = C_I - C_R$  (60 mg/L).

## Results and Discussion

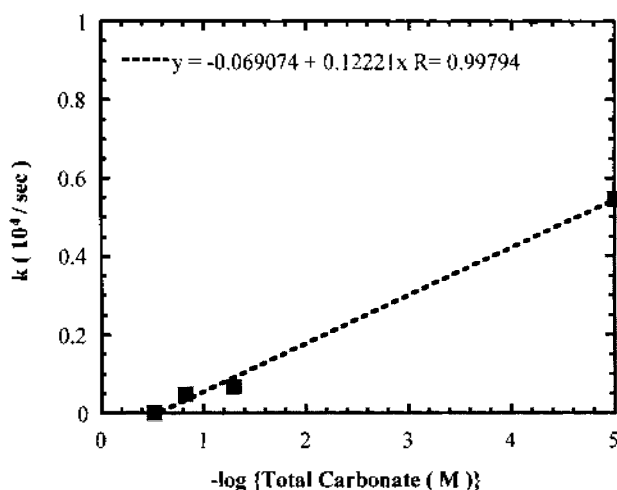
Figure 1 shows the effect of total carbonate on decomposition of humic substances in wastewater effluent. The effect of total carbonate was tested at 4 different concentration levels of sodium carbonate (0, 50, 150, and 300 mM sodium carbonate). The extent of TOC removal decreases as the concentration of total carbonate increases. After 120 minutes of reaction time, the extent of TOC removal without addition of sodium carbonate reaches 31%, while the removal extents with sodium carbonate concentrations of 50, 150, 300 mM are below 10% in the given experimental condition. The decomposition trend of humic substances without carbonate appears to follow the first-order kinetics in the initial stage of the reaction. It is examined in the later section (discussion).

The carbonate and bicarbonate are well-known radical scavengers. That means that hydroxyl radical scavengers are effective competitors for hydroxyl radicals, then inhibit the reaction between the humic substances and hydroxyl radicals. Then it decreases the sonochemical decomposition rate of humic substances (Figure 1). Figure 2 shows the semi-log plot of the total carbonate concentration and the reaction rate constant.

Figure 3 shows the effect of ultrasonic energy intensity on decomposition of humic substances in wastewater effluent. The effect of energy intensity was tested at 4 different energy intensity levels (0, 142, 283, and 340  $\text{watts/cm}^2$ ). Figure 3 displays 3 different reaction stages. At the first stage, the rate constant remains at low values. The ultrasonic energy seems to be not high enough to break the backbone of humic substances. Over 120  $\text{watts/cm}^2$  of energy intensity,



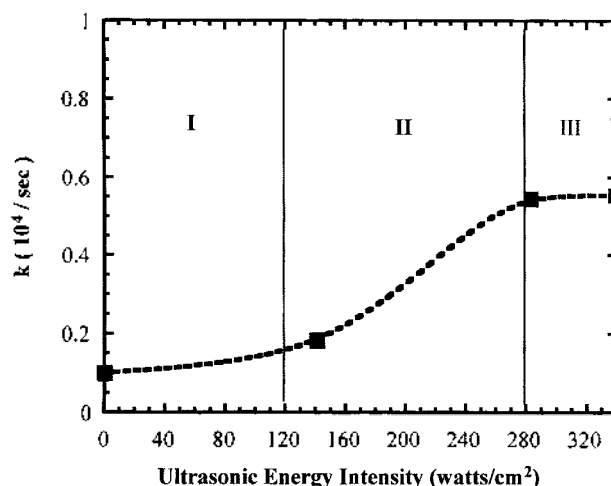
**Figure 1.** Effect of Total Carbonate on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, H<sub>2</sub>O<sub>2</sub> 10mM, C<sub>0</sub> = TOC 10 mg/L, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.



**Figure 2.** Effect of Total Carbonate on Decomposition Rate of Humic Substances in Wastewater Effluent (semi-log plot). Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, H<sub>2</sub>O<sub>2</sub> 10 mM, C<sub>0</sub> = TOC 10 mg/L, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

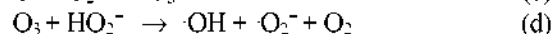
apparently, the higher the ultrasonic energy intensity, the larger the reaction rate constant in the range of 120 to 283 watts/cm<sup>2</sup> (Stage II). But there is no further increase in the reaction rate above 283 watts/cm<sup>2</sup> of energy intensity. Since the energy intensity determines the number of cavitation bubbles and their size in unit volume of liquid,<sup>4</sup> the number of bubbles and their size appear to reach their maximum values (Stage III).

The effect of hydrogen peroxide was tested at 4 different concentration levels of hydrogen peroxide ( $0.25 \times 10^{-3}$ ,  $5.0 \times 10^{-3}$ ,  $10 \times 10^{-3}$  Molar). Hydrogen peroxide has long been recognized as a free radical producer.<sup>5</sup> H<sub>2</sub>O<sub>2</sub> is a known byproduct of sonolysis and the rate of H<sub>2</sub>O<sub>2</sub> formation at 500 KHz has been shown to be a factor of 6.2 greater than that at

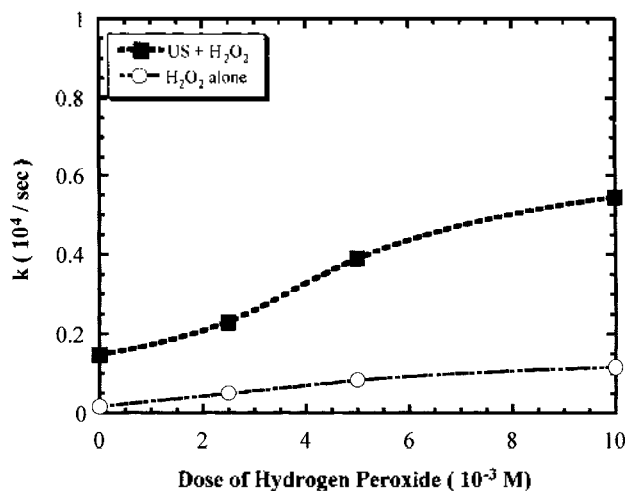


**Figure 3.** Effect of Ultrasonic Energy Intensity on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: H<sub>2</sub>O<sub>2</sub> 10 mM, C<sub>0</sub> = TOC 10 mg/L, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

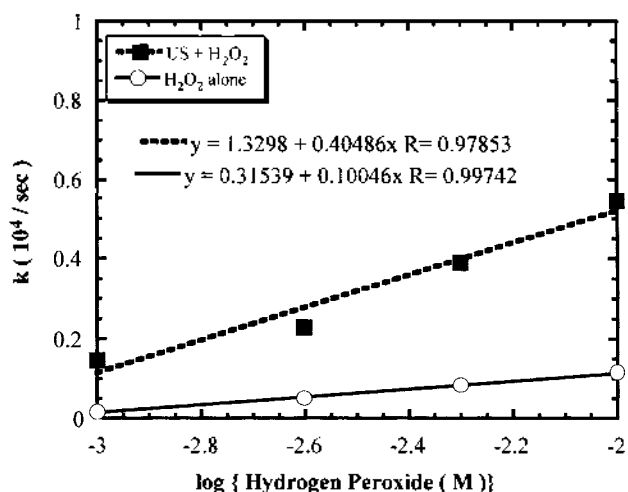
20 KHz.<sup>6</sup> Although hydrogen peroxide can be produced by sonochemical irradiation alone in aqueous solution, the amount may be not enough to be significant to decompose the humic substances in wastewater effluent. Therefore, the sonochemical irradiation is suggestive of HO<sub>2</sub><sup>-</sup> reacting with O<sub>3</sub> and subsequent ·OH formation. At pH values above 5, H<sub>2</sub>O<sub>2</sub> accelerates the decomposition of O<sub>3</sub> (peroxide process) resulting in bulk phase ·OH formation as follows<sup>7</sup>:



The addition of hydrogen peroxide is considered to initiate and promote the free radical reaction. Figure 4 shows the



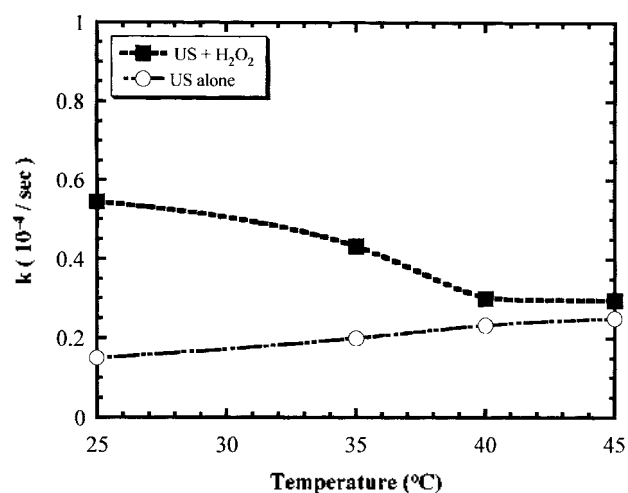
**Figure 4.** Effect of Hydrogen Peroxide on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, C<sub>0</sub> = TOC 10 mg/L, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.



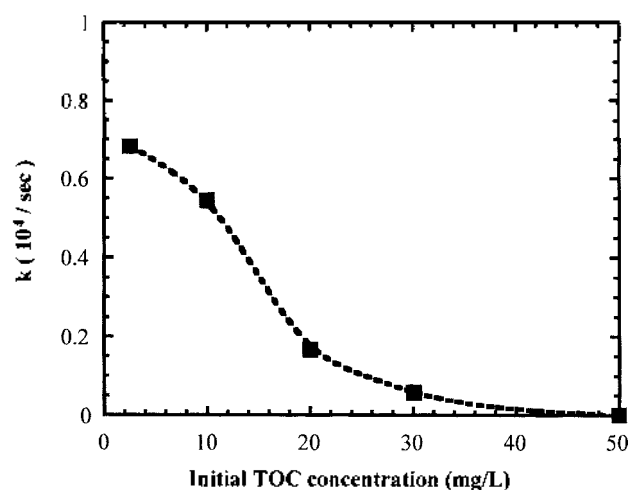
**Figure 5.** Effect of Hydrogen Peroxide on Decomposition Rate of Humic Substances in Wastewater Effluent (semi-log plot). Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, C<sub>0</sub> = TOC 10 mg/L, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

effect of hydrogen peroxide on the decomposition 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<sup>-2</sup> M of hydrogen peroxide concentration after 120 minutes of reaction time. Figure 4 shows the relationship between the reaction rate constant and the dose of hydrogen peroxide. In the experiments without sonochemical irradiation, the rate constant of TOC decomposition remains at low levels. Figure 5 shows the semi-log plot of rate constant and dose of hydrogen peroxide for both of methods.

Figure 6 shows the effect of steady-state solution temperature on the decomposition of humic substances in wastewater effluent. The effect of temperature was tested at 4 different levels (25, 35, 40, and 45 °C). The extent of TOC



**Figure 6.** Effect of Temperature on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, H<sub>2</sub>O<sub>2</sub> 10mM, C<sub>0</sub> = TOC 10 mg/L, pH<sub>0</sub> = 7, ionic strength = 0.05 M NaClO<sub>4</sub>.

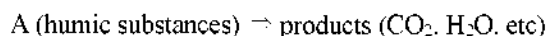


**Figure 7.** Effect of Initial TOC Concentration on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, H<sub>2</sub>O<sub>2</sub> 10mM, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

removal decreases as the temperature increases. The extent of TOC removal was largest at 25 °C in the temperature range of 25 to 45 °C. It was observed that the decomposition rate of hydrogen peroxide increased with increasing of temperature. Figure 6 shows the relationship between the temperature and the decomposition rate constant for two sonochemical systems. In the system of sonochemical reaction without hydrogen peroxide, the rate constant remains at low levels and slightly increases as temperature increases.

Figure 7 shows the effect of initial TOC concentration of humic substances on the decomposition of humic substances in wastewater effluent. The effect of initial TOC concentration was tested at 5 different levels (2.5, 10, 20, 30, and 50 mg/L). The decomposition rate decreases as the initial TOC concentration increases (Figure 7). The decomposition rate was found to be dependent on the initial TOC concentration of humic substances.

In order to explain the effect of initial TOC concentration on the sonochemical reaction rate, the Langmuir-Hinshelwood model was introduced and modified with the assumptions; (1) the bubble-liquid interfacial area is regarded as a surface. (2) The main decomposition reaction of humic substances takes place in the interfacial surface, that is, the decomposition of humic substances inside cavitation bubbles and in the bulk solution is ignoble.



The decomposition rate is taken to be proportional to the quantity of A in the interfacial surface. Then

$$-\frac{dC_A}{dt} = k\theta_A \quad (3)$$

The value of  $\theta_A$  is given by Langmuir isotherm:

$$\theta_A = \frac{KC_A}{(1 + KC_A)} \quad (4)$$

Combining these two equations,

$$-\frac{dC_A}{dt} = \frac{kKC_A}{(1 + KC_A)} \quad (5)$$

where,  $\theta_A$ : the occupied fraction of the interfacial surface,  $A$ : Humic substances,

$C_A$ : TOC concentration of humic substances,  $k$ : Overall decomposition reaction rate constant, and  $K$ : ratio of  $k_1$  and  $k_2$  ( $= k_1/k_2$ ).

The constants  $k_1$  and  $k_2$  are obtained as follows;

The rate of occupying sites on interfacial surface  $dN_A/dt$  is proportional to the fraction of unoccupied sites and the TOC concentration of humic substances in solution,

$$\left(-\frac{dN_A}{dt}\right)_{\text{association}} = k_1(1 - \theta_A)C_A \quad (6)$$

The rate of unoccupying sites on interfacial surface is proportional to the number of molecules on the interfacial surface.

$$\left(-\frac{dN_A}{dt}\right)_{\text{dissociation}} = k_2\theta_A \quad (7)$$

At equilibrium, the rate of association equals the rate of dissociation, so that

$$\theta_A = \frac{k_1C_A}{(k_2 + k_1C_A)} = \frac{KC_A}{(1 + KC_A)} \quad (8)$$

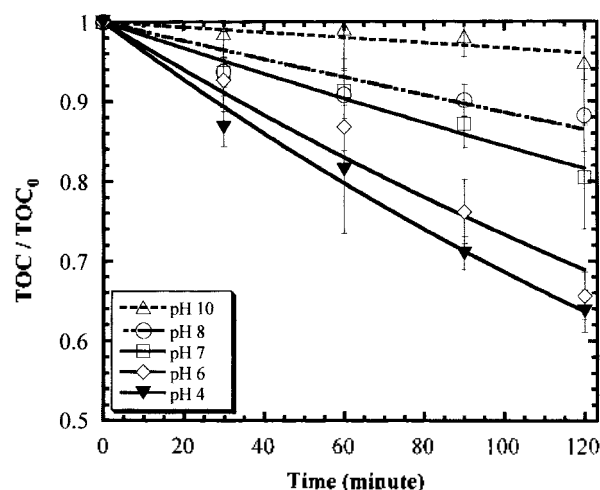
Combining with equation 3, then we can get the equation 5.

If the system follows the Langmuir-Hinshelwood model, the reaction rate should be first order at sufficiently low values of  $C_A$ . As  $C_A$  increases, the order of reaction should gradually drop and become zero order.

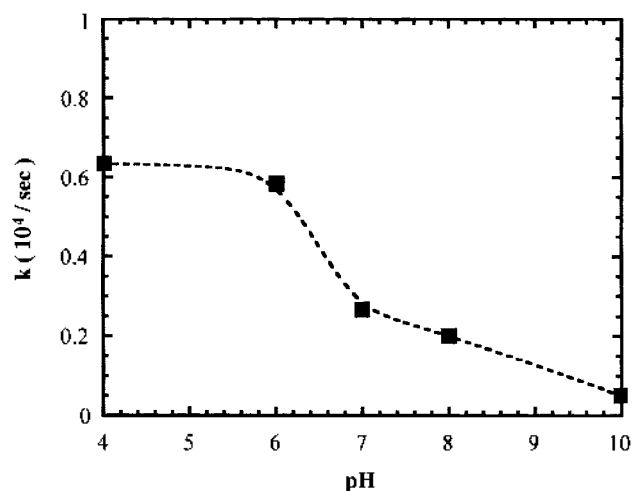
Results of the kinetic studies for TOC removal of humic substances were fitted with the kinetic model described above (equation 3), and fitted values along with correlation coefficients are shown in Table 1. Figure 11 shows the fitted kinetic curves for TOC removal with different initial TOC concentration of humic substances. The calculated concentration versus time profiles are obtained by numerical integration with a fourth-order Runge-Kutta routine. These fitted results indicated that the Langmuir-Hinshelwood model provided a good fit of the experimental data. Figure 8 shows the effect of solution pH on TOC decomposition of humic substances in wastewater effluent. The effect of solution pH

**Table 1.** Fitted Parameters  $K$ ,  $k$ , and Coefficient of the Langmuir-Hinshelwood Model for Decomposition of Humic Substances. Conditions for Experimental Data: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, H<sub>2</sub>O<sub>2</sub> 10 mM, pH<sub>0</sub> 7, C<sub>0</sub> = TOC 10 mg/L, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>

Run	TOC <sub>0</sub> (mg/L)	$K$ (mg <sup>-1</sup> L)	$k$ (mg L <sup>-1</sup> min <sup>-1</sup> )	R
1	2.5	10	0.004	0.9487
2	10	10	0.0032	0.9698
3	20	10	0.0011	0.9589
4	30	10	0.00035	0.9778
5	50	10	0.00015	0.9682



**Figure 8.** Effect of pH on Decomposition of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, H<sub>2</sub>O<sub>2</sub> 10 mM, C<sub>0</sub> = TOC 10 mg/L, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

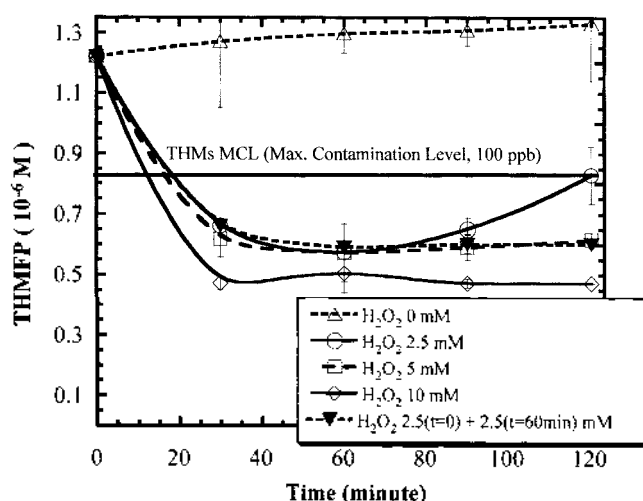


**Figure 9.** Effect of pH on Decomposition Rate of Humic Substances in Wastewater Effluent. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, H<sub>2</sub>O<sub>2</sub> 10 mM, C<sub>0</sub> = TOC 10 mg/L, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

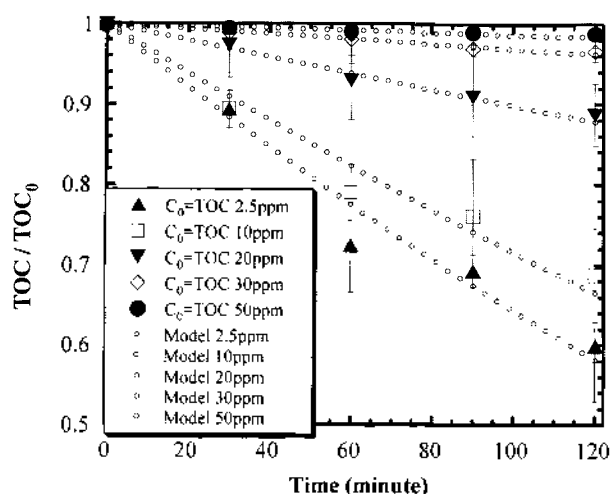
was tested at 5 different levels (4, 6, 7, 8, and 10). The extent of TOC removal increases as the solution pH decreases. Figure 9 shows the relationship between the solution pH and the decomposition rate constant. The decomposition rate slightly decreases in the pH range of 4 to 6 and rapidly decreases as pH becomes greater than 6.

The functional groups of humic substances, particularly the acidic groups. The main acidic groups are carboxyl (R-C=O-OH) and acidic phenolic OH groups.<sup>8</sup> Similar results for humic substances from the Wilmington wastewater plant were observed.<sup>9</sup>

Humic substances have variable charge components. Since their points of zero charge (pzc) are low, about 3, humic substances are negatively charged at pH values greater than



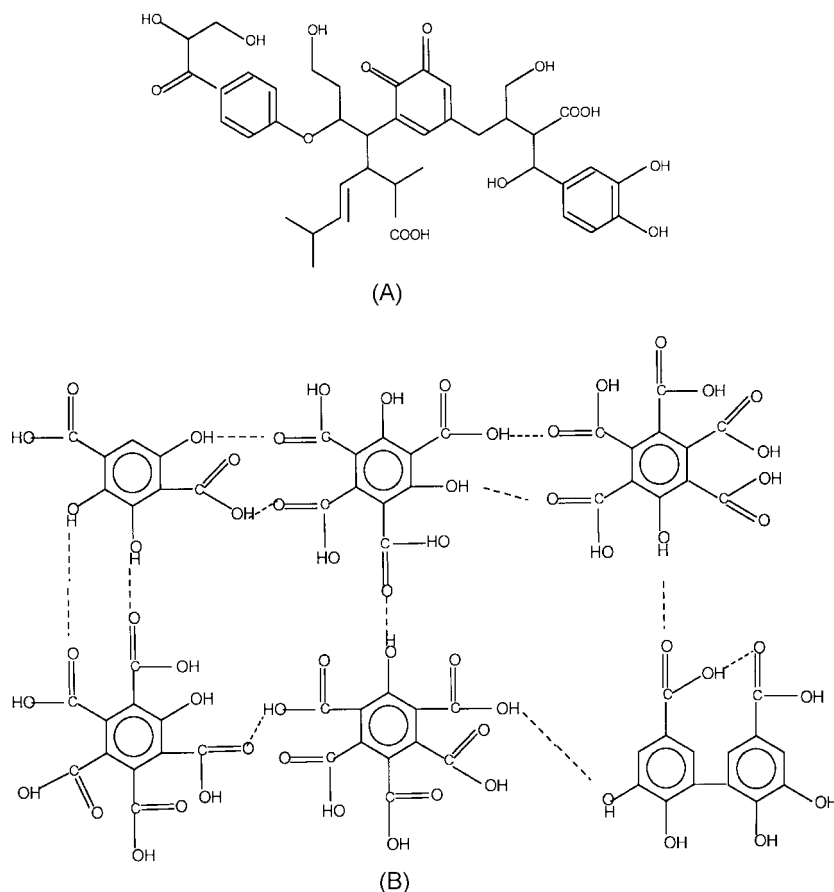
**Figure 10.** Effect of US Irradiation and Hydrogen Peroxide on THMFP of Humic Substances in Wastewater Effluent (Wilmington WW Plant). Experimental Conditions : ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, pH<sub>0</sub> = 7, C<sub>0</sub> = TOC 10 mg/L, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.



**Figure 11.** Kinetics of HS Decomposition with Different Initial TOC Concentrations. Experimental Conditions: ultrasonic energy intensity = 283 watts/cm<sup>2</sup>, total volume = 10 mL, H<sub>2</sub>O<sub>2</sub> 10 mM, pH<sub>0</sub> = 7, temperature = 25 °C, ionic strength = 0.05 M NaClO<sub>4</sub>.

3.<sup>10</sup> As pH increases, the degree of negative charge increases due to the deprotonation or dissociation of H<sup>+</sup> from functional groups. Many researchers found the sonochemical decomposition rate decreased with increasing solution pH values.<sup>11</sup>

It was also observed that the sonochemical decomposition rates of polar organic compounds were smaller than those of nonpolar compounds when the similar organic compounds were tested.<sup>12</sup> Since it is well-known that the majority of decomposition reaction takes place in bubble-liquid inter-

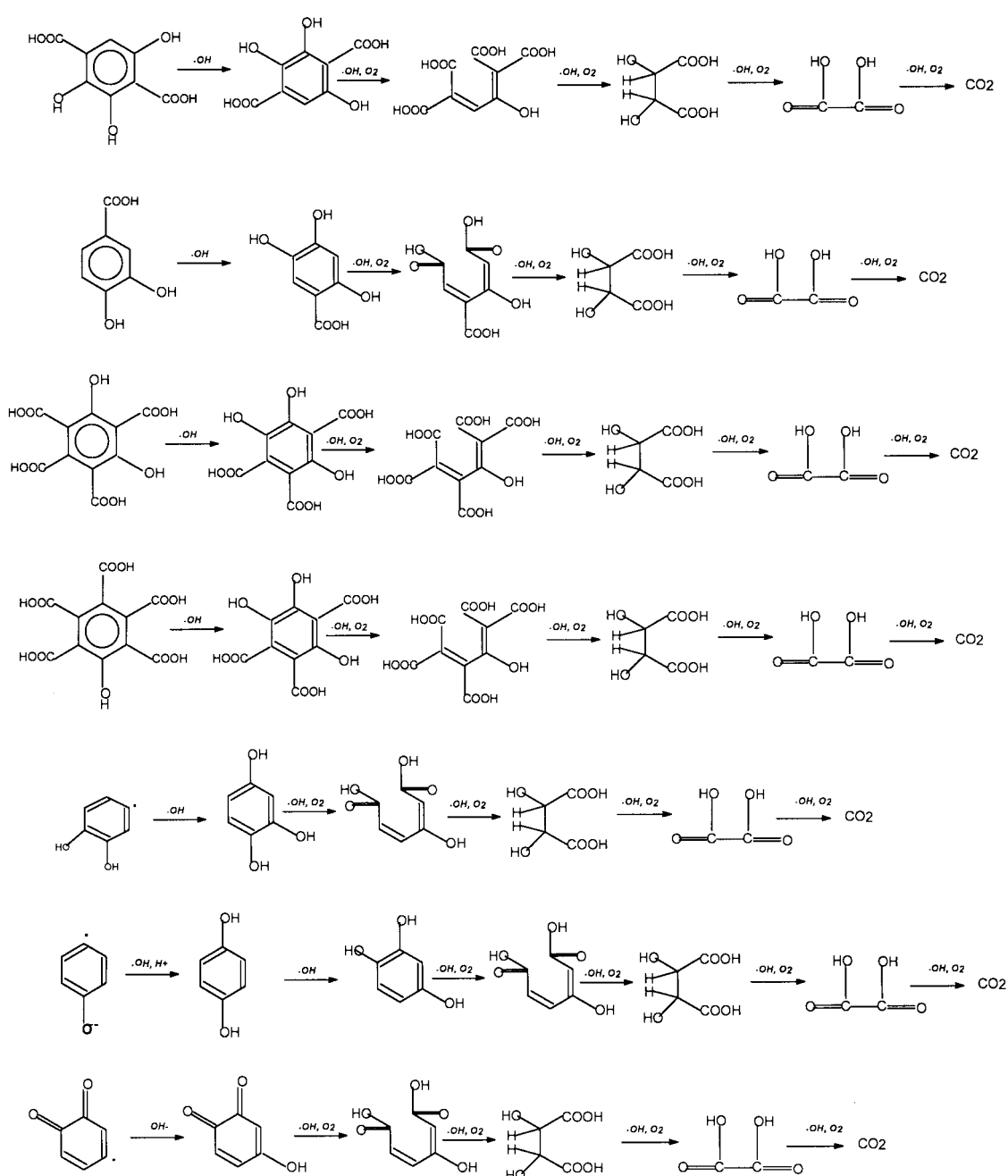


**Scheme 1.** Proposed building blocks of Humic Substances.<sup>9</sup>

face,<sup>13</sup> the enhanced accessibility and subsequently increased amount of less polar compound in the interface can increase the sonochemical reaction rate. Consequently, decreasing solution pH decreased the negative charge of humic substances and, hence, enhanced the sonochemical decomposition in the interface.

Figure 10 illustrates the decrease in THMFP as a function of sonochemical reaction time with different dose levels of hydrogen peroxide. It was observed that the extent of TOC removal of humic substances by the sonochemical irradiation with 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 in the reaction with small dose (2.5 mM) of hydrogen peroxide after 60 minutes of reaction time. 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 THMFP at low level (Figure 10). Several researchers have proposed that the combination of a sonochemical process with an oxidant can enhance the decomposition of organic matter.<sup>14</sup> Since the sonochemical process with hydrogen peroxide decreases the concentration of precursors (represented as TOC), the amount



Scheme 2. Proposed decomposition pathways of HS monomers.

of chlorinated by-product formation can be decreased.

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. 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 1.<sup>15</sup>

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 2). The production of macromolecular radicals is perhaps the most common breakdown mechanism and has been observed for many carbon skeleton polymers.<sup>13</sup> 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.<sup>16</sup> Consequently, the monomers can be formed as intermediates of HS, shown in Scheme 2.

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 on 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.<sup>17</sup> 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.

### Conclusion

The extent of TOC removal was proportional to factors such as ultrasonic energy intensity and hydrogen peroxide

concentration while increasing of total carbonate, pH, and temperature decreased the extent of TOC removal of humic substances. The Langmuir-Hinshelwood model provided a good fit of the experimental data of decomposition of humic substances by sonochemical processes. 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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