



EFFECT OF PRE-SONICATION ON REMOVAL OF ORGANIC MATTERS RESULTING FROM CHLORINATED HUMIC ACIDS

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ABSTRACT

Humic acids are amorphous organic macromolecules that are responsible for the color of natural water. They play an important role in the formation of disinfection by-products, the stabilization of wastewater sludge, and the treatment of wastewater. An ultrasonic process is applied as a pretreatment method for the purpose of reducing the risk of chlorinated by-products. Experimental results indicate that the initial pH, ionic strength, and chlorine demand affect the amount of total organic carbon removal and Cl_2 consumption significantly. The formation of chlorinated by-products depends on both the initial pH and ionic strength. Experimental results also propose a good agreement that the humic acid can be removed efficiently by ultrasonic pretreatment under aerobic conditions. In this study, when the ultrasound/ O_2 process is used as a pretreatment method, the biodegradability which is defined as the formation of BOD_5 increases with sonication time. © 1998 Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Biodegradability; chlorination; humic acid; pretreatment; sonication.

INTRODUCTION

Aquatic humic substances (HS) are responsible for 40-80% of the dissolved organic carbon (DOC) in many surface waters and these are primarily responsible for the color of natural water (Watt *et al.*, 1996; Hintelmann *et al.*, 1997). Yeh and Huang (1993) have proposed that the organics in natural water are fractionated into humic acid, fulvic acid, hydrophilic-acid, and a neutral fraction. However, the structure of humic substances is still not well known. But the major functional groups present in humic acid are carboxylic acids, phenolic and alcoholic hydroxyl groups, keto groups, and quinonoid groups (Rook, 1977; Lou and Chiang, 1991; Hintelmann *et al.*, 1997). The following four reasons explain why HS must be removed: (1) the yellow color of HS is incompatible with the requirement that drinking water is colorless; (2) HS have a potential for bacterial regrowth; (3) when disinfectants are used in water treatment processes, they lead to the formation of toxic disinfection by-products; and (4) HS can form complexes with heavy metals present in the water, as a consequence, they reach the consumer since they cannot be precipitated in the water treatment plant (Scheck and Frimmel, 1995).

Sodium hypochlorite (NaOCl) is used as a reagent for disinfection, bleaching, and decolorisation of drinking water and wastewater treatment (Chang *et al.*, 1995; Chang and Ma, 1995; Mascolo *et al.*, 1995). The chlorinated by-products, which were produced by chlorination of humic acid, have caused problems not only of odor, but also of taste and of human health (Muftikian *et al.*, 1995). Smeds *et al.* (1995) also found that mutagenic activity of human beings seem to increase with an increasing number of chlorine atoms in the by-products. Therefore, it is a very important task to reduce the formation of chlorinated compounds efficiently. A number of methods have been investigated to minimize the formation of chlorinated by-products during chlorination of humic acids (Edwards *et al.*, 1993; Lin *et al.*, 1996a, b). The advanced oxidation processes such as ozonation, UV irradiation, and ultrasound treatments are all effective on the decomposition of chlorinated compounds. In this study, we select the ultrasonic process as a pretreatment method owing to its several advantages. The advantages of the ultrasound process include decomposition of semivolatile organic compounds from soil, remediation of groundwater, and transformation of the undegraded compounds into highly degraded products (Orzechowska *et al.*, 1995). The objectives of this study are (1) to determine the effects of reaction parameters on TOC removal and chlorine consumption during the chlorination of synthetic humic acid samples (2) to determine the efficiencies of several pretreatment processes on humic acid decomposition and (3) to study the effect of pretreatment methods on TOC removal, chlorine consumption and biodegradability enhancement.

EXPERIMENTAL SECTION

Materials

Commercial humic acid (Tokyo Chem. HO161) was directly used as the target compound in chlorination test without purification. Stock solution of humic acid of concentration 1,000 mg/l was prepared using the deionized and distilled water from a Millipore purification system under alkaline conditions, and preserved in a brown Pyrex bottle. Sodium hypochlorite solutions were prepared from the stock solution (Hayashi, JCL07710) after proper dilution and were estimated using iodometric titration. All other chemicals were of analytical grade manufactured by Riedel-de Haën and Merck. In each experiment, humic acid stock solution was diluted with deionized water to a concentration of 50 mg/l.

Extraction of semi-volatile compounds

The extraction and analytical procedures were carried out according to the Standard Method (18th Ed). The samples were taken at appropriate time intervals and extracted immediately by a liquid-liquid extraction procedure. 5-ml of chlorinated humic acid solution was taken in a 10-ml bottle, and to this approximately 0.4 gram of anhydrous potassium carbonate was added followed by 1-ml of anhydrous acetic acid. The bottle was shaken vigorously using an orbital shaker (Yih Der Ltd. Company, Taiwan, ROC) for 6 hours. After this stage, 1-ml of n-hexane was added into the bottle, then extracted vigorously for another 6 hours. The upper layer of the extracted sample was injected into a GCD (HP 1800A GCD, USA).

Experimental set-up

The duration of chlorinated compounds incubation experiment is 7-days. The reaction temperature is maintained at 20°C by means of a thermostatically controlled water jacket. NaClO₄ is used to adjust the ionic strength at 0.001, 0.01, 0.05, 0.1, and 0.2 N. The pH values are maintained at 3, 5, 7, 9, and 11 using HClO₄ and NaOH. The reaction is initiated by the addition of 50 and 500 mg/l of NaOCl. All solutions are prepared using deionized water from a Millipore purification system. The profiles of pH and ORP values are monitored using pH and ORP meters respectively. Ultrasonic pretreatment conducted with a Microson XL2020 sonicator (Heat system, Ltd., USA) operated at 20 kHz (the power output equals to 160 W) is described below. The double amplitude at the titanium tip (Part. No. 419) of the standard horn (Part. No. 200, 1/2" d) is adjusted to 120 μm (126.5 W/cm² of tip).

Instrumental analysis

The sample is analyzed with a gas chromatograph equipped with mass spectrometry detector (HP 1800A GCD). The analysis of chlorinated compounds is performed with a 30 m x 0.25 mm I.D. DB-5 capillary column (J and W Scientific, Folsom, CA, U.S.A.) in which Helium (1 ml/min) is used as the carrier gas. The column is heated from 50°C (holding time 3 min) to 250°C (holding time 3 min) at the rate of 5°C/min. The temperatures of the injector and detector are 250°C and 280°C respectively. Electron impact (70 eV, voltage 1649 V) mass spectrometry is used for the detection. The acquisition is performed from 30 to 425 amu at 1 scan/s. Profiles of TOC are measured by a TOC analyzer (ASTRO 2001, USA). The DPD ferrous titrimetric method is used for the analysis of chlorine.

RESULTS AND DISCUSSION

The reaction between humic acid and chlorine or NaOCl is well-documented (Långvik and Holmbom, 1994; El-Rehaili and Weber, 1987; Lou and Chiang, 1991). However, there is no report on the decomposition of humic acid with ultrasound application to reduce the formation of chlorinated compounds. We are interested in the change of TOC removal and chlorine consumption by ultrasonic pretreatment using various reaction conditions as discussed below. The analytic result shows that 50 mg/l humic acid represents 18.6 ± 0.4 mg/l TOC (7 measurements).

Effect of pH and chlorine demands on TOC removal and chlorine consumption

The effect of various pH values on TOC removal and chlorine consumption during the chlorination of humic acids are shown in Figure 1. Apparently, in Figure 1, the pH value plays an important role during chlorination of humic acids. With the addition of 50 mg/l humic acids and 50 mg/l NaOCl, the removal of TOC decreased with increasing pH value. This phenomenon shows that the NaOCl can provide a higher oxidizing tendency in a low pH solution and there occurs a large removal of TOC. Many recent studies have revealed that the NaOCl can be dissociated into Na^+ and OCl^- . In an acidic medium, OCl^- can react with H^+ and HOCl, a high oxidation potential product is formed. Therefore, a large amount of TOC can be removed under an acidic condition (Pourmoghaddas *et al.*, 1993; Mascolo *et al.*, 1995). When the concentration of NaOCl is increased to 500 mg/l, the amount of TOC removal is also increased.

The consumption of chlorine is also dependent on the pH value adjusted by the addition of 500 mg/l NaOCl. The ratios of NaOCl consumption are between 49 and 58%. However, the initial ratio of chlorine demand per unit TOC with the additions of 50 mg/l NaOCl and 50 mg/l humic acid is 2.72. This value is less than 3 and this is the least ratio of chlorine consumed per unit TOC removal (Rook, 1977; Chang and Ma, 1995; Chang *et al.*, 1995). Therefore, the amounts of chlorine consumption at different pH values with 50 mg/l NaOCl addition are approximately 47 mg/l NaOCl (94% NaOCl consumed) as shown in Figure 1. In addition, the minimal amount of chlorine required to react with 50 mg/l humic acid is greater than 47 mg/l NaOCl at various pH values.

Effect of ionic strength on TOC removal and chlorine consumption

Our previous studies have revealed that the ionic strength also plays an important role during the decomposition of organics just like the pH value (Lin *et al.*, 1996a, b). According to the results discussed in the above section, the humic acid solutions at different ionic strengths are prepared and a constant pH value of 3 is maintained. The effect of ionic strength on TOC removal and chlorine consumption resulting from chlorination of humic acids solution is shown in Figure 2. James *et al.* (1995) proposed that the humic acid molecule could either be a rigid or flexible sphere, or a rod-like, or a flat plate depending on ionic strength. The higher ionic strength favors a spherical molecule of humic acid, so that, the other compounds or oxidants can react with humic acid more easily due to its large surface area (James *et al.*, 1995; Bose and Reckhow, 1997). Therefore, it is observed that the removal of TOC and consumption of chlorine increased with increasing ionic strength (Figure 2). After the reaction period of 7 days, the ratio of TOC removal is 45% with an ionic strength of 0.001 N, 61% with 0.1 N, and 67% with 0.2 N. The results of chlorine

consumption resemble TOC removal. The ratio of chlorine consumption is 60% with an ionic strength of 0.001 N, 93% with 0.1 N, and 99% with 0.2 N. These observations are plotted in Figure 2 and the results are similar to the reports of James *et al.* (1995) and Bose and Reckhow (1997).

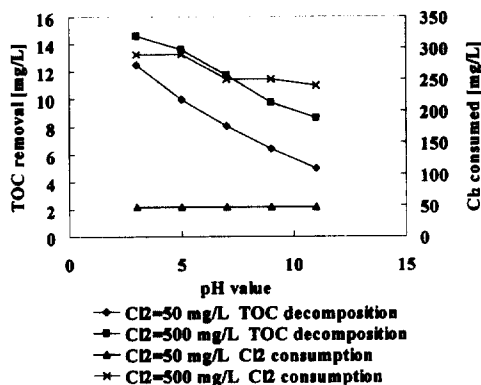


Figure 1. The effects of different pH values and chlorine demands on TOC removal and chlorine consumption. (Humic acids 50 mg/l, ionic strength 0.1 N, and reaction temperature 20°C)

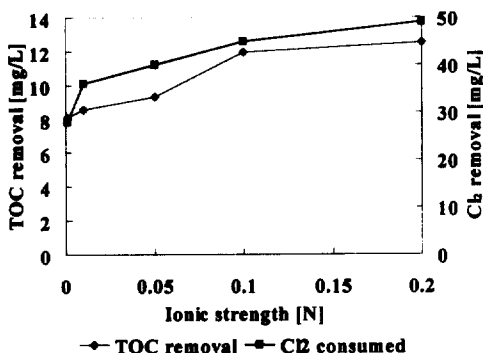
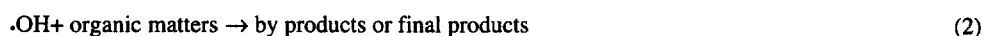


Figure 2. The effects of different ionic strength on TOC removal and chlorine consumption (Humic acids 50 mg/L, chlorine demand 50 mg/l, pH 3, and reaction temperature 20°C).

In the previous discussion, we have found out the initial ratio of chlorine demand per unit TOC with the addition of 50 mg/l NaOCl and 50 mg/l humic acid (2.72). The experimental results indicate that 50 mg/l NaOCl is sufficient to decompose 50 mg/l humic acids. Therefore, we summarize the variation of the chlorine consumption per unit TOC (Cl_2/TOC) at different initial pH values and ionic strengths in Table 1. The ratios of Cl_2/TOC are between 3.5 and 9.4. That is, 3.5-9.4 units of chlorine is necessary to decompose each unit of TOC. It is an accurate result which can be used to verify the least ratio of chlorine consumption per unit TOC removal, and is 3, as reported in Rook (1977), Chang and Ma (1995) and Chang *et al.* (1995). In Table 1, we also summarize the changes of biodegradability (BOD_5) at various pH values and different ionic strengths. The larger formation of BOD_5 represents the greater biodegradability. Therefore, it is obvious that the biodegradability is increased with a decreasing pH value, and increasing ionic strength. Based on these results, we set up the reaction condition in which the pH value is 3 and ionic strength is 0.1 N for the pretreatment processes shown below.

Influence of various pretreatment methods on ORP profiles

The oxidation-reduction reaction is known to be taken place by the transfer of an electron from oxidant to substrate. Moreover, the ORP values can be considered as an indicator of the oxidation power or potential. In this study, the profiles of the ORP values are monitored during the pretreatment. Figure 3 demonstrates the profiles of ORP values for different pretreatment methods, i.e., ultrasound, O₂, and ultrasound/O₂ methods. The initial ORP value at each reaction condition is 203 mV. Figure 3 shows the variation of ORP values for various pretreatment methods are different. With ultrasonic pretreatment alone, ORP values decline gradually during the course of reaction. As shown in the Eq. (1) and (2) H₂O is decomposed in the collapsing cavitation bubbles to yield OH radicals with sonication, and then the OH radicals thus formed react with organic matters (Kotronarou *et al.*, 1992; Wu *et al.*, 1992). Therefore, the consumption of OH radicals results in the decrease of ORP values.



With the O₂ pretreatment alone, the ORP values remain almost constant. This fact indicates that the O₂ introduced into the solution alone can not provide enough oxidizing power to decompose the organic matters. Therefore, there is no change in the ORP value. However, with the incorporation of ultrasound and O₂, the ORP value increases in the first 10 min, then decreases gradually (Figure 3). Also, the ORP values of humic acids decomposition by ultrasound/O₂ method are greater than that by ultrasound or O₂ alone. Okouchi *et al.* (1992) have proposed that the rate of decomposition of organic compounds can be enhanced by introducing pure oxygen. Therefore, from Figure 3, it is understood that the incorporated method, i.e., ultrasound/O₂ is more effective on humic acids decomposition.

Influence of various pretreatment methods on biodegradability

In this study, we represent the BOD₅ value as the biodegradability. An increase in the concentration of BOD₅ denotes the enhancement of the biodegradability. Figure 4 illustrates the profiles of BOD₅ in the decomposition of humic acids with three different pretreated processes. The advantages of the ultrasonic process such as the high efficiency of decomposition of semivolatle organic compounds, profitable remediation of groundwater, and effective transformation of the undegraded compounds to highly degraded products have been reported (Orzechowska *et al.*, 1995). The concentration of BOD₅ of the untreated humic acid after chlorination for 7-days is 32.9±0.4 mg/l. In Figure 4, it is clear that both the ultrasound and O₂ processes can not enhance the biodegradability of the chlorinated humic acids. However, by means of the incorporated process, the biodegradability increases with the sonication time. Therefore, it is better to use the ultrasound/O₂ process as the pretreatment for the chlorination of humic acids.

Table 1. The effects of different initial pH values and ionic strength on the changing of (BOD₅) and Cl₂/TOC TOC (Humic acids 50 mg/l, chlorine demand 50 mg/l, and reaction temperature 20°C)

	Initial pH values				
	3	5	7	9	11
BOD ₅ (mg/L)	32.7	26.7	20.7	20.7	17.7
Cl ₂ /TOC (mg/mg)	3.8	4.7	5.9	7.4	9.4
	Ionic strength (N)				
	0.001	0.01	0.05	0.1	0.2
BOD ₅ (mg/L)	14.5	23.5	23.5	32.5	44.5
Cl ₂ /TOC (mg/mg)	3.5	4.2	4.3	3.8	3.9

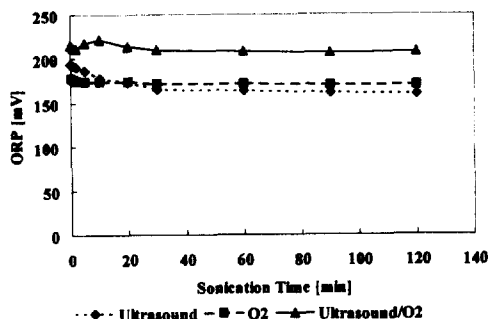


Figure 3. The effects of different pretreatment methods on ORP (Humic acids 50 mg/l, pH 3, ionic strength 0.1 N, and reaction temperature 20°C).

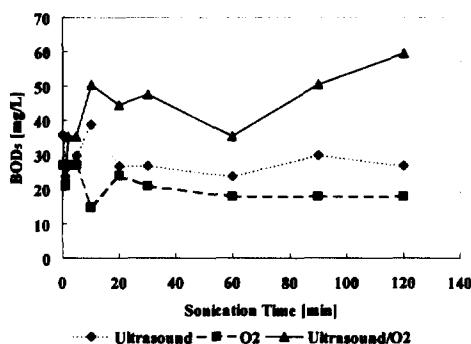


Figure 4. The effects of different pretreatment methods on biodegradability (Humic acids 50 mg/l, pH 3, ionic strength 0.1 N, and reaction temperature 20°C).

Influence of various pretreatment methods on TOC removal

In the previous discussion, it is clear that the ultrasound/O₂ process is the best pretreatment method resulting in the enhancement of biodegradability. In addition, we also examine the amounts of mineralization of the humic acids with the ultrasound, O₂, and ultrasound/O₂ processes, respectively. Figure 5 shows the residual amount of TOC with different pretreatment methods. The initial concentration of TOC is 18.6±0.4 mg/l. After 120 minutes pretreatment, the amount of TOC removal is 26.5% with ultrasonic method, 27.4% with O₂, and 52.6% with ultrasound/O₂ method. Several authors have proposed that the combination of the chemical method with O₂ can enhance the decomposition ratios of organic matters (Lin *et al.*, 1996a, b; Petrier *et al.*, 1992; Okouchi *et al.*, 1992; Serpone *et al.*, 1992). The initial concentration of precursor represented as TOC decreases significantly with the pretreatment process. Hence, the amount of chlorinated by-products formation can be decreased.

Influence of various pretreatment methods on chlorine consumption

The pretreatment processes not only enhance the removal of TOC but also reduce the consumption of chlorine. The profiles of chlorine consumption after 7 days incubation of the pretreated sample collected at different sonication time are plotted in Figure 6. Figure 6 shows the chlorine consumption using ultrasound or O₂ pretreatment process remains constant. However, when the humic acids pretreated with the ultrasound/O₂ process is chlorinated, the chlorine consumption decreases with time. Therefore, the ratio of chlorine consumed per unit TOC is decreased. This result verifies the assumption that the amount of chlorinated by-products formation can be decreased, as described in the above section. Figure 4 shows that

the biodegradability also can not be enhanced by these two methods. On the basis of TOC removal, biodegradability enhancement and the low consumption of NaOCl, the best pretreatment method in the study is the incorporated process, i.e., ultrasound/O₂.

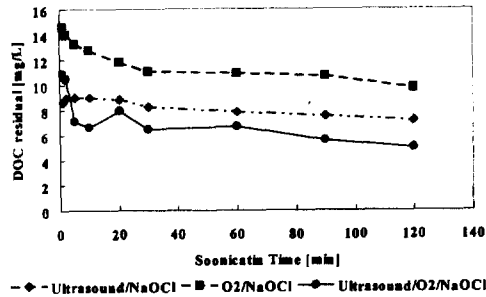


Figure 5. The effects of different pretreatment methods on TOC removal (Humic acids 50 mg/l, pH 3, ionic strength 0.1 N, and reaction temperature 20°C).

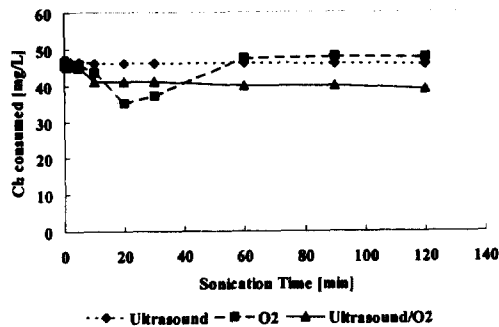


Figure 6. The effects of different pretreatment methods on chlorine consumption (Humic acids 50 mg/l, pH 3, ionic strength 0.1 N, and reaction temperature 20°C).

CONCLUSIONS

This study shows that the reaction parameters such as initial pH value, ionic strength, and chlorine demand play an important role in the chlorination of humic acid. After 7 days of incubation, the amounts of TOC removal and chlorine consumption depend on the initial pH value with high chlorine demand (500 mg/l NaOCl). In low chlorine demand (50 mg/l NaOCl), the amounts of TOC removal and chlorine consumption increase with an increasing ionic strength. But, in this condition, the consumption of chlorine remains constant at different pH values. By means of the incorporated ultrasound/O₂ method as the pretreatment of a 50 mg/l humic acid sample, the experimental result gives an effective increase of TOC removal and BOD₅ biodegradability, and the incorporated pretreatment process decreases the consumption of chlorine.

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