Effects of UV irradiation on humic acid removal by ozonation, Fenton and Fe^0/air treatment: THMFP and biotoxicity evaluation

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ABSTRACT

Effects of UV irradiation on humic acid (HA) removal by Fe^0/air, ozonation and Fenton oxidation were investigated. The trihalomethane forming potential (THMFP) and toxicity of treated solutions were also evaluated. The experimental conditions were ozone of 21 mg min^{-1}, H$_2$O$_2$ of 8×10^{-4} M, Fe^0 of 20 g L^{-1}, air flow of 5 L min^{-1}, and UVC of 9 W. Results indicated that Fe^0/air rapidly removed HA color (>99%) and COD (90%) within 9 min. 51–81% of color and 43–50% of COD were removed by ozonation and Fenton oxidation after 60 min. Both UV enhanced ozone and Fenton oxidation removed HA, but the Fe^0/air process did not. Spectrum results showed all processes effectively diminished UV–vis spectra, except for ozonation. The THMFP of Fe^0/air-treated solution (114 µg L^{-1}) was much lower than those of Fenton- (226 µg L^{-1}) and ozonation-treated solutions (499 µg L^{-1}). Fe^0/air with UV irradiation obviously increased the THMFP of treated solution (502 µg L^{-1}). The toxicity results obtained from *Vibrio fischeri* light inhibition test indicated that the toxicity of Fe^0/air-treated solution (5%) was much lower than that of ozonation- (33%) and Fenton-treated solutions (31%). Chlorination increased the solution toxicity. The correlation between biotoxicity and chloroform in the chlorinated solution was insignificant.

1. Introduction

Humic substrates are mixtures of organic matters that often occur in surface waters. Humic acid (HA) is a major component of humic substrates. It comes from different sources including nature, landfill leachate, and pulp wastewater [1,2]. HA can react with active chlorine in water treatment plants, resulting in the formation of trihalomethanes (THMs). THMs are carcinogenic and toxic to human life and, more specific, the kidneys [3]. Besides, HA causes membrane fouling [4] and scavenges the free radicals in advanced oxidation processes [5].

Many approaches have been applied to remove HA, including GAC adsorption [1], membrane filtration [1], coagulation [6], ozonation [5], and advanced oxidation processes [5,7]. However, either their low removal efficiency or high costs often limit their application. To increase the degradation ability, UV irradiation is often employed to enhance HA removal by chemical oxidation and AOPs [5]. Besides, chlorine reacts with the intermediates in the treated solution and generates toxic byproducts during disinfec-

tion processes. Factors that influence trihalomethane formation potentials (THMFPs) during disinfection processes include humic acid content [8,9] and properties like aromaticity, unsaturated bonds [10,11], molecular weight [8,12], and hydrophobicity [9,13]. Because each technique has its own specific removal mechanisms, the organic contents, intermediate properties, toxicity, and THMFP of the treated HA solutions might be different.

Zero-valent iron (Fe^0) has received wide attention recently because it is low-cost and effective for various pollutant removals [14–17]. Iron erodes in Fe^0/H$_2$O system and removes pollutants through coagulation of iron corrosion products [18–20]. In addition, zero-valent iron under oxic condition can generate Fenton-like reaction and degrade organic pollutants [21–23]. Fe^0/air methods have been applied to remove various pollutants including EDTA [14], chlorinated organic compounds [15], and dyes [16,17]. Recently, it has been reported that Fe^0 irradiated with UV can produce Fenton-like reaction which enhances organic removal [24]. However, studies on HA removal by Fe^0/air and UV/Fe^0/air process are limited. Studies on the biotoxicity and THMFP of Fe^0/air- and UV/Fe^0/air-treated HA solutions are also rare.

In this study, humic acid (HA) was selected as the model humic substrate. The aims of this study were to investigate (1) HA removal by ozonation, Fenton oxidation, and Fe^0/air processes, (2) effects

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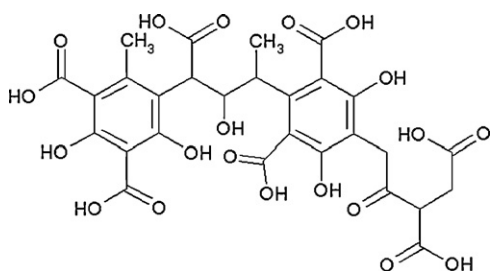*E-mail address:* shchang@csmu.edu.tw (S.-H. Chang).

Fig. 1. Molecular structure of humic acid.

of UV irradiation on HA removal by above three processes, and (3) the trihalomethane forming potential and biotoxicity of treated solutions.

2. Materials and methods

2.1. Chemicals

Humic acid (60% purity) was obtained from Sigma–Aldrich and was used as received (Fig. 1). H_2O_2 (30% purity) was purchased from Hayashi Pure Chemical Ind. Ltd., Japan) and $FeSO_4$ ($FeSO_4 \cdot 7H_2O$, >99% purity) was obtained from Showa (Japan). The zero-valent iron (analytical grade, 99% purity, 300 mesh) was purchased from Shimakyu Chemical Osaka, Japan). NaOCl (5% purity) was obtained from Hayashi Pure Chemical Ind. (Japan).

2.2. Humic acid treatment

2.2.1. Ozonation and UV/ozone treatment

The ozonation and UV/ozone experiments were conducted in a 275 mL glass reactor (5 cm diameter, 13 cm high) containing 100 mL of HA solution. The initial HA solution in this study was 50 mg L^{-1}. Ozone was provided by ozone generator (CHYF-3A, Company, Ltd., Taiwan). The ozone flow rate and ozone dose were 3 L min^{-1} and 21 mg min^{-1}, respectively. To obtain the desired pH, the solution was adjusted using diluted H_2SO_4 and NaOH solutions and measured by pH meter (Cyberscan 510, Taiwan). For the UV/ozonation experiments, the UVC light (9 W, Philips) was placed in the center of the rector (7 cm depth). All experiments were conducted at room temperature (20 ± 2 °C). Samples were withdrawn at specific time intervals during the ozonation. The concentration of the treated HA solution was measured based on the constructed calibration curves at absorption wavelength of 400 nm. The UV–vis spectrum during HA degradation was measured at 200–800 nm using a UV–vis spectrophotometer (Shimadzu, UV-mini 1240, Japan). The sample was diluted with distilled water when the absorbance exceeded the range of calibration curve. COD was determined according to standard method for examination of water and wastewater [25].

2.2.2. Fenton and UV/Fenton

Appropriate amounts of stock HA solution and ferrous ion were added to a 300 mL beaker and diluted with distilled–deionized water to 100 mL. The initial solution pH was adjusted using diluted H_2SO_4 and NaOH solutions. H_2O_2 was then added to initiate the Fenton reaction. The H_2O_2:Fe^{2+} molar concentration ratio was kept at 10:1. The applied H_2O_2 doses were 0, 2, 4, and 8 × 10^{-4} M. The initial solution pH was 3 and the reaction time was 60 min. The air flow rate was 5 L min^{-1}. For the UV/Fenton experiment, a UVC light tube (9 W, Philips) was inserted in the solution (7 cm depth). The sample was withdrawn at 60 min, centrifuged at 13,000 rpm for 5 min and then analyzed.

2.2.3. Fe^0/air and UV/Fe^0/air treatment

The Fe^0/air experiments were conducted in a 275-mL glass reactor (5 cm diameter, 13 cm high) containing 100 mL of HA solution. An air flow rate of 5 L min^{-1} was used to maintain the suspension of iron powder in the solution. The initial pH of the solution was adjusted with H_2SO_4 and NaOH solutions. For the UV/Fe^0/air experiment, a UVC light tube was inserted in the solution (7 cm depth). Samples were withdrawn at specific time intervals during the Fe^0/air and UV/Fe^0/air treatment.

2.3. THMFP

The THMFP test was conducted according to Standard Method 5710B [26]. The samples were adjusted to 7 by phosphate buffer. The concentrated sodium hypochlorite was dosed and the final NaOCl concentration was 50 mg L^{-1}. The sample was kept at 25 °C and placed in a dark place. After 7 days, THMs of the samples were measured using purge and trap and GC/MS (Agilent-6890 GC/5973N MS).

2.4. Vibrio fischeri light inhibition test

The marine luminescent bacterium, V. fischeri (NRRL B-11117, obtained from DSMZ Germany), was employed to evaluate the biotoxicity of treated solutions. The cultivation of luminescent bacteria and toxicity evaluation procedure were according to ISO 11348-1 standard protocol (ISO, 1998). The solution sample was adjusted to pH 7.0 ± 0.2. V. fischeri was exposed to the solution samples for 5 min as determined by a luminometer at 15 °C. Phenol was used as the positive control with EC$_{50}$ ranging from 13 to 26 mg L^{-1}. Toxicity was expressed as the light inhibition ratio and was calculated as follows (Eq. (1)) [27]:

$$\text{Light inhibition} \ (\%) = \frac{I_0 \times f_{kt} - I_f}{I_0 \times f_{kt}} \times 100 \tag{1}$$

where f_k is the correction factor at t = 5 min, $f_k = I_{kc}/I_{0c}$. I_{0c} and I_{kc} are the luminescence intensity of the control sample at t = 0 and 5 min, respectively, and I_0 and I_f the luminescence intensity of the sample at t = 0 and 5 min, respectively. The bioluminescence intensity of V. fischeri may decrease with exposure time. The correcting factor f_k is used to correct the luminescence intensity of the test sample at t = 0 min. Therefore, in this study, the inhibition ratio (percentage) was used to represent the biotoxicity of pollutants instead of inhibition percentage of the bioluminescence. A toxicity experiment was conducted to investigate the effectiveness of $Na_2S_2O_3$ of 20 g L^{-1} in eliminating the residual H_2O_2 and chlorine in Fenton-treated and chlorinated solution, respectively [28]. The selected doses of H_2O_2 (8 × 10^{-4} M) and NaClO (6.7 × 10^{-4} M) were based on doses used for Fenton oxidation and chlorination treatments in this study. Experimental results showed that without $Na_2S_2O_3$ addition, the light inhibition ratio was 53% and 32% for 8 × 10^{-4} M of H_2O_2 and 6.7 × 10^{-4} M of Cl_2, respectively. After addition of $Na_2S_2O_3$ of 20 g L^{-1}, the light inhibition ratios of both solutions were 0%. This suggests that the addition of $Na_2S_2O_3$ of 20 g L^{-1} could effectively reduce the residual H_2O_2 and chlorine in both Fenton-treated and chlorinated solution.

3. Results and discussion

3.1. Ozonation and UV/ozone treatment

HA decolorization by ozonation and the UV/ozone process were investigated. The operating conditions were humic acid of 50 mg L^{-1}, flow rate of 3 L min^{-1}, and ozone dose of 7 mg L^{-1}. First, the initial solution pH (pH$_0$) was evaluated. Fig. 2 indicates that at pH$_0$ of 3, 77% color removal was obtained after 60 min. An increase
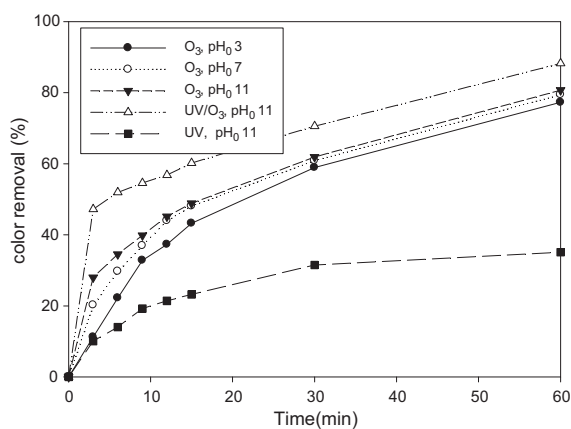
**Fig. 2.** Effects of UVC on humic acid decolorization by ozonation. Humic acid of $50\,mg\,L^{-1}$, O_3 dose of $7\,mg\,L^{-1}$, ozone flow rate $3\,L\,min^{-1}$, and UVC of 9 W.

in initial solution pH slightly increased decolorization. At solution pH_0 of 11, 81% decolorization was achieved after 60 min. Influences of UV irradiation on HA decolorization by ozonation was also assessed. Fig. 2 indicates that at pH_0 of 11, UV alone decolorized less HA than ozonation. However, UV rapidly enhanced HA removal by ozonation; 47% of HA was rapidly decolorized by UV/ozone at 3 min. After that, the HA decolorization became slow and 88% of color removal was achieved after 60 min.

In this study, HA color removal increased with an increase in solution pH_0. This is because at acidic or neutral conditions, most of the ozone is in molecular phase ($E^0 = 2.08\,V$) [29], which decolorizes HA by breaking the unsaturated carbon–carbon bonds [9]. At alkaline solution, ozone reacts with OH^- to generate strong oxidants like hydroxyl radical ($OH^\bullet$, $E^0 = 2.80\,V$) (Eq. (2)) [29,30]. Free radicals can destroy aromatic sites and unsaturated components of HA and increase HA decolorization [5,11,31].

$$O_3 + OH^- \rightarrow OH^\bullet + (O_2^\bullet \leftrightarrow HO_2^\bullet) \tag{2}$$
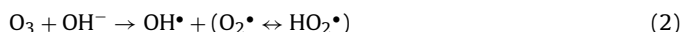
In this study, UV/ozone had higher HA decolorization than ozone-alone. This is because UV can enhance production of free radicals through UV photolysis of ozone (Eqs. (3) and (4)) and increase HA decolorization [30,32].

$$O_3 + H_2O + h\nu \rightarrow O_2 + H_2O_2 \quad h\nu < 310\,nm \tag{3}$$

$$O_2 + H_2O_2 \rightarrow 2OH^\bullet + 3O_2 \tag{4}$$
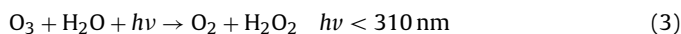
3.2. Fenton and UV/Fenton treatment

HA decolorization by Fenton oxidation was evaluated. The experimental conditions were $H_2O_2:Fe^{2+}$ molar ratio of 10, pH_0 of 3, and reaction time of 60 min. Fig. 3 shows that 40% color removal was obtained after 60 min at H_2O_2 of $2 \times 10^{-4}\,M$. The HA decolorization increased with the increase of H_2O_2 concentrations. 51% color removal was achieved at $8 \times 10^{-4}\,M$ at 60 min. Fig. 3 also illustrates that UV noticeably enhanced HA decolorization by Fenton oxidation. For example, 93% of HA decolorization was obtained by photo-Fenton at 60 min.

It has been reported that H_2O_2 ($E^0 = 1.776\,V$) can react with catalyst Fe^{2+} to generate free radicals like hydroxyl radical ($OH^\bullet$) (Eqs. (5)–(7)) [7,33], which can effectively destroy HA chromophore groups [11,31]. Wu et al. [7] also indicates that anions (Fe^{2+} and Fe^{3+}) in the Fenton solution also act as coagulants to remove HA.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \tag{5}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^\bullet + H^+ \tag{6}$$
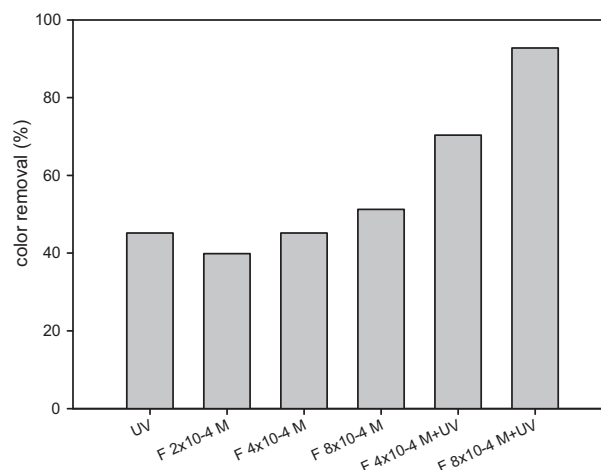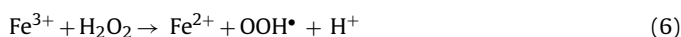
Fig. 3. Effects of UVC on decolorization of humic acid by Fenton oxidation. Humic acid of $50\,mg\,L^{-1}$, $H_2O_2:Fe^{2+}$ molar ratio of 10:1, and pH_0 of 3, flow rate of $5\,L\,min^{-1}$, UVC of 9 W. F: Fenton.

$$Fe^{3+} + {}^\bullet OOH \rightarrow Fe^{2+} + H^+ + O_2 \tag{7}$$
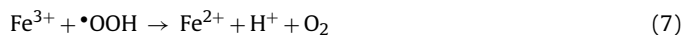
In this study, HA color removal by photo-Fenton was much higher than by Fenton oxidation. This is because H_2O_2 reacts with ferrous iron oxide to form complex compound $Fe(H_2O)_5(OH)_2{}^+$ (Eq. (8)), which can be irradiated by UV, producing hydroxyl radicals, which decolorize HA (Eq. (9)) [7].

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH^\bullet \tag{8}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^\bullet \tag{9}$$

3.3. Fe^0/air and UV/Fe^0/air treatment

HA decolorization by Fe^0/air and UV/Fe^0/air processes was investigated. First, the effects of pH_0 on HA color removal were evaluated at Fe^0 of $10\,g\,L^{-1}$. Fig. 4a shows that when pH_0 decreased from 11 to 3, HA decolorization increased from 19% to 63% at 9 min. Acidic solution is suitable for HA decolorization by the Fe^0/air process. Fig. 4b illustrates the effects of Fe^0 doses on HA decolorization at pH_0 3. HA color removal increased with Fe^0 doses. Greater than 99% of HA color was removed after 9 min at Fe^0 of $20\,g\,L^{-1}$. A further increase of the Fe^0 dose to $30\,g\,L^{-1}$ did not obviously enhance HA decolorization. Effects of UV irradiation on HA decolorization by Fe^0/air process were also evaluated. The operating conditions were Fe^0 of $20\,g\,L^{-1}$ and pH_0 of 3. Fig. 4c shows that UV enhanced HA decolorization by Fe^0/air process and >99% HA decolorization was achieved at 7 min.

In this study, Fe^0/air rapidly decolorized HA. This is possibly because iron corrodes in Fe^0/H_2O system and generates iron corrosion products, like $Fe(OH)_2$, $Fe(OH)_3$, $FeOOH$, Fe_2O_3, and Fe_3O_4 or green rusts (Eqs. (10)–(13)) [18].

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{10}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{11}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{12}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{13}$$

During Fe^0/air treatment, iron corrodes and a layer of iron oxides/hydroxide forms on the Fe^0 surface [34]. The layer of iron oxides/hydroxide can rapidly sorb the humic acid through electrostatic attraction. Humic acid has been reported to generate complexes with iron and iron oxide through various types of carboxylate, phenolic, and carbonyl functional groups in the humic acid [35,15]. Thus, the humic acid decolorization may also be caused
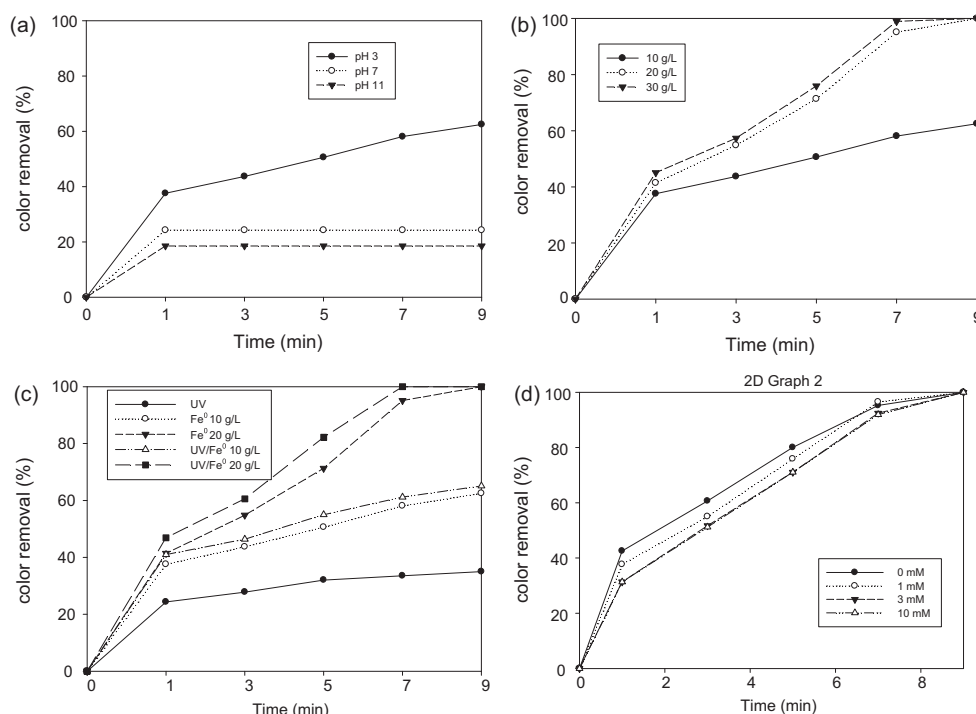
Fig. 4. Decolorization of humic acid by Fe^0/air method, (a) effects of pH_0, Fe^0 of $10\,g\,L^{-1}$, (b) effects of Fe^0 dose, (c) effects of UVC irradiation at different Fe^0 doses, (d) effects of t-butanol, Fe^0 dose of $20\,g\,L^{-1}$. If not mentioned otherwise, the experimental conditions were humic acid of $50\,mg\,L^{-1}$, pH_0 of 3, UVC of 9 W, air flow rate of $5\,L\,min^{-1}$.

by the adsorption of HA onto the layer of iron oxides/hydroxide formed on the Fe^0 surface. Especially, since the dose of Fe^0 is high ($20\,g\,L^{-1}$) in this study, the fast elimination of humic acid may result from the adsorption of humic acid on the Fe^0 surface, which can also lead to significant COD removal and a low concentration of THMFPs.
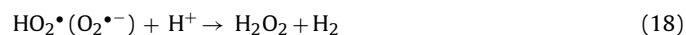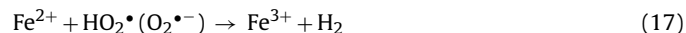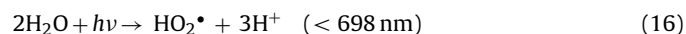
Besides, production of strong oxidants by Fe^0 under oxic condition was also responsible for the enhancement of HA decolorization. Several studies have indicated that iron corrosion in the presence of dissolved oxygen can produce H_2O_2 [22] (Eq. (14)). The H_2O_2 can react with the Fe^{2+} to produce strong oxidants such as hydroxyl radical ($OH^\bullet$) (Eq. (5)) and ferryl (iron (IV) iron species) [14] which can oxidize HA.

$$Fe^0 + O_2 + 2H^+ \rightarrow H_2O_2 + Fe^{2+} \qquad (14)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$$
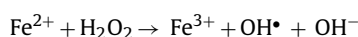
An experiment with addition of t-butanol (0–10 mM), an $OH^\bullet$ scavenger, into the reaction solution was conducted to investigate the HA oxidation by hydroxyl radical ($OH^\bullet$) during Fe^0/air treatment. Fig. 4d shows that an increase of t-butanol doses from 0 to 10 mM did not obviously inhibit the HA decolorization by Fe^0/air treatment. This suggests that the HA oxidation by hydroxyl radicals only played a minor role in humic acid removal by Fe^0/air treatment.

In this study, the HA decolorization by Fe^0 was faster under acidic solution than under alkaline solution. This is because the thickness of the iron oxide/hydroxide layer might obviously affect the HA decolorization rate. Mielczarski et al. [34] indicate that the iron oxide/hydroxide layer on Fe^0 surface is thin and most iron oxides exist in the solution at pH of 3. However, when solution pH increases, most of the iron oxides accumulate on the Fe^0 surfaces and reduce HA decolorization rates. In this study, HA decolorization by UV/Fe^0/air process was faster than that by Fe^0/air process. This might be because UV accelerates iron corrosion and enhances Fe^0 to produce Fenton-like reaction. Son et al. [24] applied the UVC/Fe^0 process to remove 1,4 dioxane. They indicated that UVC/Fe^0 removed 1,4 dioxane through two mechanisms: (1) UVC

irradiates iron to produce iron corrosion coagulants (Eq. (15)), which remove 1,4 dioxane. (2) UVC photolyzes H_2O to generate H_2O_2, which reacts with Fe^{2+} to produce Fenton-like reaction (Eqs. (16)–(18)) [24].

$$Fe^0 + h\nu \rightarrow Fe^{2+} + 2e^- \qquad (15)$$

$$2H_2O + h\nu \rightarrow HO_2^\bullet + 3H^+ \quad (< 698\,nm) \qquad (16)$$

$$Fe^{2+} + HO_2^\bullet (O_2^{\bullet-}) \rightarrow Fe^{3+} + H_2 \qquad (17)$$

$$HO_2^\bullet (O_2^{\bullet-}) + H^+ \rightarrow H_2O_2 + H_2 \qquad (18)$$

3.4. Comparisons of COD removal and spectrum change

The COD removals of humic acid solution by different processes were compared. Experimental conditions were ozonation: pH_0 11, ozone of $21\,mg\,min^{-1}$, $t = 60\,min$; Fenton oxidation: H_2O_2 of 8×10^{-4} M and pH_0 3, $t = 60\,min$; Fe^0/air treatment: Fe^0 dose of $20\,g\,L^{-1}$, air flow $5\,L\,min^{-1}$, $t = 9\,min$. The UVC light was 9 W. Fig. 5 indicates that ozone-alone and Fenton treatments removed 43% and 50% COD, respectively, after 60 min. Fe^0/air treatment rapidly removed 91% COD at 9 min. Fig. 5 also shows that UV obviously enhanced COD removal by the ozonation and Fenton processes. COD removal by UV/ozone and photo-Fenton were 83% and 87%, respectively. However, UV did not obviously increase COD removal by Fe^0/air treatment.

The UV–vis spectrum changes of HA solution during different treatments were also investigated. For HA solution, characteristic absorption peaks at wavelength 400 nm and 254 nm are attributed to chromophore groups and benzene components, respectively [10,11]. Fig. 6a shows that the A_{400} and A_{254} of the original HA were 0.539 and 1.983, respectively. Although ozonation could decolorize HA, absorption spectrum still remained after 60-min treatment ($A_{400} = 0.146$ and A_{254} of 1.096).

Fig. 6b illustrates the spectra of UV, ozone, and UV/ozone-treated HA solutions after 60-min treatment. UV alone only slightly reduced the UV–vis absorption bands. UV/ozone treatment
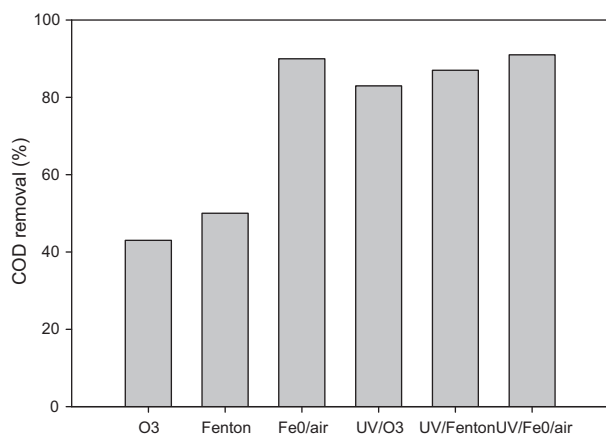
Fig. 5. COD removal of humic acid solution by ozonation, Fenton, and Fe^0/air treatments. If not mentioned otherwise, conditions are humic acid of 50 mg L^{-1}, flow rate of 5 L min^{-1}, UVC of 9 W, t = 60 min. Ozonation: pH$_0$ of 11, flow rate of 3 L min^{-1}, ozone dose of 21 mg min^{-1}; Fenton oxidation: pH$_0$ of 3, H$_2$O$_2$ of 8×10^{-4} M, H$_2$O$_2$/Fe^{2+} of 10:1; Fe^0/air treatment: Fe^0 of 20 g L^{-1}, pH$_0$ of 3, t = 9 min.

effectively destroyed chromophore groups (A_{400}) and benzene components (A_{254}). Only a small amount of UV absorption spectrum (A_{254} = 0.406) remained after treatment. The spectrum changes of HA solution by Fenton and UV/Fenton were evaluated. Fig. 6c indicates that UV–vis spectrum still remained after Fenton oxidation (A_{400} = 0.229 and A_{254} = 1.018). In contrast, UV/Fenton effectively diminished HA UV–vis absorption bands at 235–600 nm. Fig. 6d illustrates the HA spectrum changes during Fe^0/air treatment. Fig. 6d shows that the absorption bands were reduced rapidly and uniformly during Fe^0/air treatment. Both A_{400} and A_{254} were smaller than 0.01 after 9 min. The changes of HA spectrum by UV/Fe^0/air treatment were similar to those treated by the Fe^0/air process.

In this study, high benzene components (A_{254}) and organic matter (COD) remained in the treated solution (Fig. 6a). This is because ozone only partially oxidized unsaturated carbon bonds and broke the benzene ring, resulting in the generation of HA intermediates like formic acid and oxalic acid [5,6,9]. Ozone could not effectively degrade the intermediates. In contrast, UV/ozone effectively decreased the spectrum area and COD. This might be because UV/ozone can produce free radicals (Eqs. (2), (3) and (8)) and effectively destroy HA (chromophore and benzene components) and oxidize intermediates [11,13]. Similarly, UV irradiation can enhance Fenton reaction to produce free radicals (Eqs. (7)–(8)) [11,13]. Therefore, photo-Fenton decreased the absorption spectrum and COD more effectively than Fenton oxidation (Figs. 5 and 6c).

In this study, the HA spectrum bands diminished uniformly during Fe^0/air and UV/Fe^0/air treatments (Fig. 6e). This implies that HA removal by iron corrosion coagulants might be the major mechanism responsible for HA removal by the Fe^0/air and UV/Fe^0/air processes [16,18–20,36]. The small UV absorbance in the Fe^0/air-treated solution also suggests that the concentrations of residual benzene intermediates were low in the treated solution.

3.5. Trihalomethane formation potentials of treated HA solution

Table 1 indicates the trihalomethane formation potentials (THMFPs) of different treated HA solutions. Because NaOCl was used for chlorination, chloroform (CHCl$_3$) was the major THM detected. Results indicate that without UV irradiation, the THMFP was the highest in the ozonation-treated HA solution (499 μg L^{-1}), followed by Fenton-treated solution (226 μg L^{-1}). The THMFP of Fe^0/air-treated HA solution was the lowest (114 μg L^{-1}). When UV

irradiation was used during treatment, the THMFP of the UV/ozone-treated solution (650 μg L^{-1}) was higher than that of ozone-treated solution. The THMFP of UV/Fenton-treated solution (211 μg L^{-1}) was close to that of Fenton-treated solution. However, THMFP of UV/Fe^0/air-treated solution (502 μg L^{-1}) was much higher than that of Fe^0/air-treated solution.

In this study, even though the decrease of COD and A_{254} by ozonation and that by Fenton oxidation was close (Table 1), the THMFP of ozone-treated solution (499 μg L^{-1}) was much higher than that of Fenton-treated solution (226 μg L^{-1}). This suggests that besides organic content (COD) and benzene components (A_{254}), there should be other factors influencing the THMFPs of treated solution, such as different properties of intermediates in these two treated solutions (Eqs. (4)–(6)). Several studies have reported that after ozonation, HA forms more active sites, which react easily with free chlorine and generate THMs [37]. In contrast, Fenton reaction degrades HA through free radical oxidation [11,13]. In this study, the THMFP of the Fe^0/air-treated solution was low (114 μg L^{-1}). This is possibly because the major mechanism responsible for HA removal by Fe^0/air process was chemical coagulation (which in fact removed most HA) instead of oxidation.

The above results indicate that although UV/ozone removed much more COD and A_{254} than ozonation, the THMFP of solution treated by UV/ozone was higher than that treated by ozonation. This phenomenon also suggests that besides organic matter and A_{254}, there should be other factors responsible for the THMFP of treated solution. This is possibly because of the lower molecular weight of intermediates produced by UV/ozone than that produced by ozonation [11,13]. Zhao et al. [8] indicated that organic matter with a low molecular weight is a major precursor for THM production during disinfection. Similar results were also observed in both Fenton and UV/Fenton-treated solutions. Liu et al. [38] used UVA/TiO$_2$ and UVA/TiO$_2$/H$_2$O$_2$ to degrade HA and found that, although A_{254} was very low in both treated solutions, the treated solutions were still very reactive to chlorine and that high THMs were formed during chlorination. Table 1 also shows that although COD and A_{254} were low in both Fe^0/air- and UV/Fe^0/air-treated solutions, the THMFP in UV/Fe^0/air-treated solution was much higher than that in the Fe^0/air-treated solution. This might be because UV photolysis and Fenton-like reaction occur in the UV/Fe^0/air process (Eqs. (16)–(18)) [24], which change the properties of intermediates or increase low molecular weight intermediates in the treated solution. However, the molecular weight distribution of intermediates was not analyzed in this study. Further studies on molecular weight distribution are suggested in order to investigate their relations with THMFPs. Besides, Results of this study indicated that Fe^0/air rapidly removed HA color (>99%) and COD (90%) within 9 min. This implies that most of the organics in the HA solution have been removed. Total organic carbon can help to understand the importance of intermediates generated during treatment. Further studies on TOC removal by different processes are suggested to explain the results obtained by COD and THMFP.

3.6. Biotoxicity evaluation

The toxicity of treated solutions before and after chlorination was investigated by *V. fischeri* light inhibition test. Na$_2$S$_2$O$_3$ was used to reduce the residual H$_2$O$_2$ and chlorine. Fig. 7a indicates that the biotoxicity of Fe^0/air-treated solution (light inhibition of 6.7%) was much lower than those of ozonation-treated (light inhibition of 32%) and Fenton treated (light inhibition of 44%) solutions. After addition of Na$_2$S$_2$O$_3$, the biotoxicity of Fenton-treated solution decreased to light inhibition 31%.

The UV irradiation enhanced ozonation, Fenton, and Fe^0/air to the point of reducing the biotoxicity of their treated solutions.
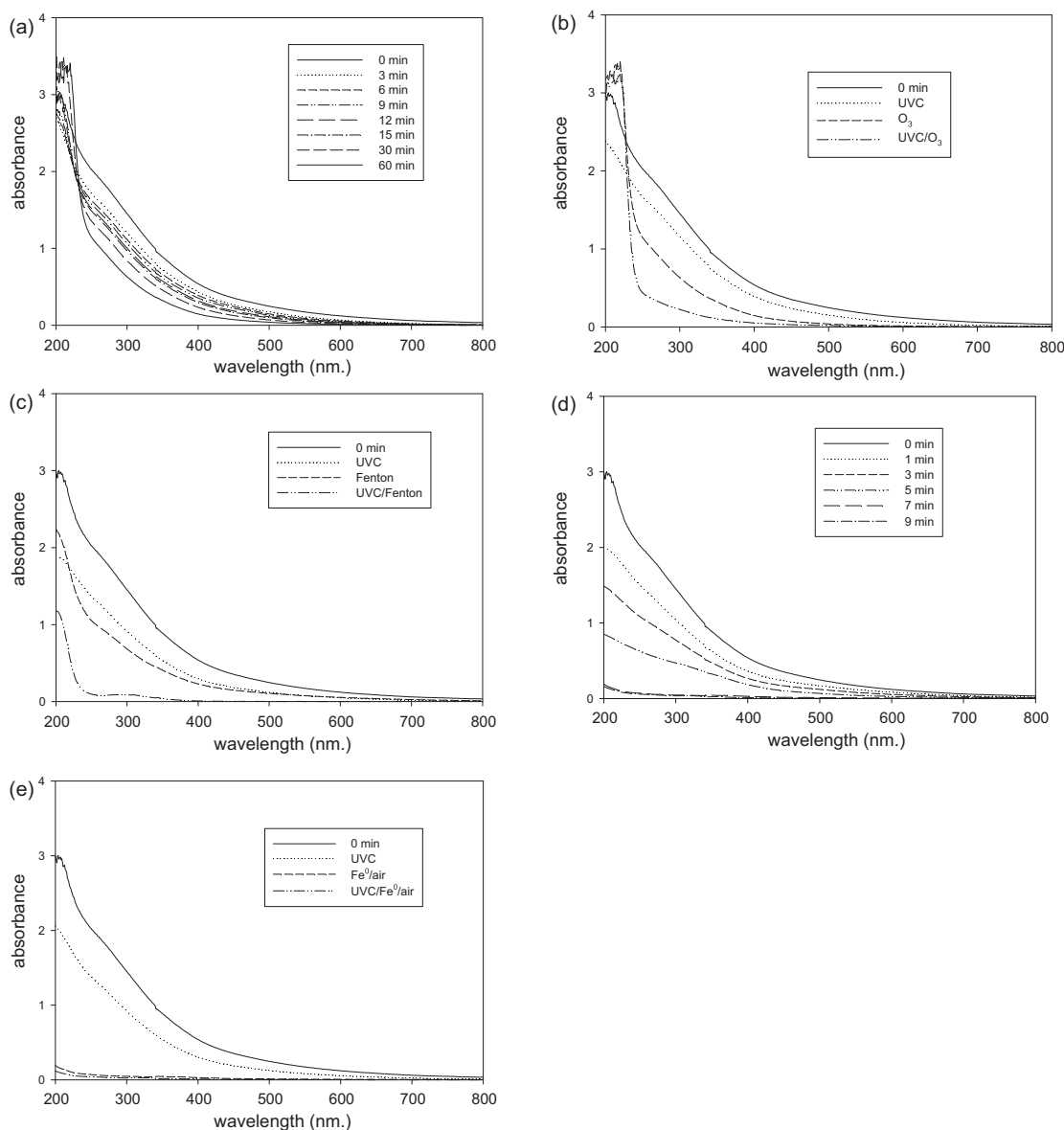
Fig. 6. UV–vis spectrum change of humic acid solution by ozonation, Fenton, and Fe^0/air treatments. If not mentioned otherwise, conditions are humic acid of $50\,mg\,L^{-1}$, flow rate of $5\,L\,min^{-1}$, UVC of $9\,W$. (a) ozonation, pH_0 of 11, flow rate of $3\,L\,min^{-1}$, O_3 dose of $21\,mg\,min^{-1}$; (b) UVC, O_3 and UV/O_3, $t = 60\,min$; (c) Fenton and UVC/Fenton, pH_0 of 3, H_2O_2 of $8 \times 10^{-4}\,M$, H_2O_2/Fe^{2+} of 10:1; $t = 60\,min$; (d) Fe^0/air method, Fe^0 of $20\,g\,L^{-1}$, pH_0 of 3, $t = 9\,min$; (e) UVC, Fe^0/air and UV/Fe^0/air.
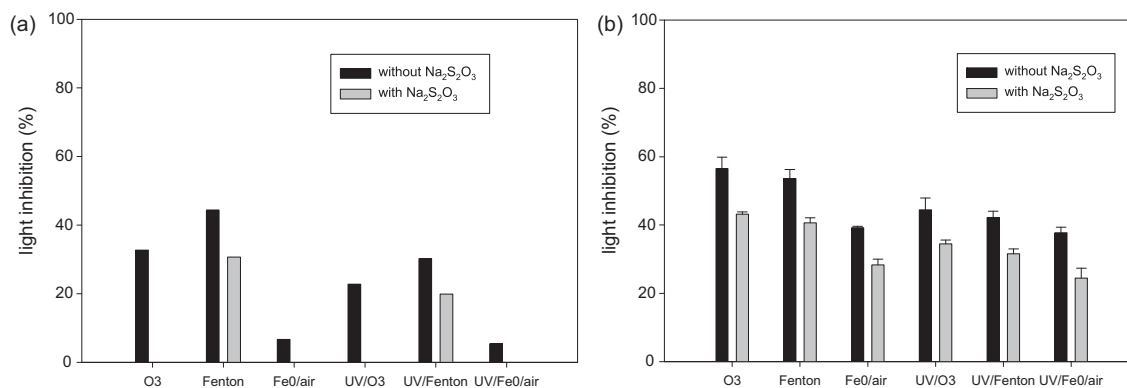
This might be because UV enhancement of ozonation, Fenton, and Fe^0/air generate free radicals, which would lead to more complete intermediate removal. Effects of chlorination on biotoxicity of the treated solutions were also assessed. Fig. 7b shows that the

biotoxicity of treated solutions (38–57%) after chlorination was higher than those without chlorination. After addition of $Na_2S_2O_3$ to dechlorinate the residual chlorine, the toxicity of chlorinated solutions (24–43%) was still higher than those without chlorination.

Table 1
The THMFPs of HA solutions treated by different methods.

	Color removal (%)	COD removal (%)	A_{400}	A_{254}	$CHCl_3$ ($\mu g\,L^{-1}$)	$CHBrCl_2$ ($\mu g\,L^{-1}$)	$CHBr_2Cl$ ($\mu g\,L^{-1}$)	$CHBr_3$ ($\mu g\,L^{-1}$)
Without UV								
O_3	81	43	0.146	1.096	499	ND	ND	ND
Fenton	51	50	0.229	1.018	226	ND	ND	ND
Fe^0/air	99	90	0.029	0.067	114	ND	ND	ND
With UV								
UV/O_3	88	83	0.052	0.406	650	ND	ND	ND
UV/Fenton	93	87	0.008	0.088	211	ND	ND	ND
UV/Fe^0/air	99	91	0.01	0.039	502	ND	ND	ND

If not mentioned otherwise, conditions are humic acid of $50\,mg\,L^{-1}$, flow rate of $5\,L\,min^{-1}$, UVC of $9\,W$, $t = 60\,min$. Ozonation: pH_0 of 11, flow rate of $3\,L\,min^{-1}$, ozone dose of $21\,mg\,min^{-1}$; Fenton oxidation: pH_0 of 3, H_2O_2 of $8 \times 10^{-4}\,M$, H_2O_2/Fe^{2+} of 10:1; Fe^0/air treatment: Fe^0 of $20\,g\,L^{-1}$, pH_0 of 3, $t = 9\,min$.

Fig. 7. Biotoxicity of ozonation-, Fenton-, and Fe^0/air-treated humic acid solution. (a) Before chlorination and (b) after chlorination. Experimental conditions for different treatments, if not mentioned otherwise: humic acid of $50\,mg\,L^{-1}$, flow rate of $5\,L\,min^{-1}$, UVC of $9\,W$, and $t = 60\,min$. Ozonation: pH_0 of 11, flow rate of $3\,L\,min^{-1}$, O_3 of $21\,mg\,min^{-1}$; Fenton oxidation: pH_0 of 3, H_2O_2 of $8 \times 10^{-4}\,M$, and H_2O_2/Fe^{2+} of 10:1; Fe^0/air treatment: Fe^0 of $20\,g\,L^{-1}$, pH_0 of 3, and $t = 9\,min$.

The relationship between biotoxicity and $CHCl_3$ concentrations of the dechlorinated solutions was also evaluated. The correlations between biotoxicity and $CHCl_3$ were insignificant ($r = 0.128$, $p > 0.05$). This implies that besides $CHCl_3$, there were other intermediates that contributed to the acute toxicity of the dechlorinated solution. Further study on intermediate identification is suggested to investigate the relationship between intermediates and biotoxicity in dechlorinated solutions.

As shown in Fig. 6d, the spectrum of Fe^0/air treatment shows that prolonged Fe^0/air treatment from 7 min to 9 min only slightly reduced the spectrum of HA solution. In this study, the *V. fischeri* light inhibition test was used to evaluate the biotoxicity evolution of Fe^0/air-treated solution before and after chlorination. The biotoxicity of the Fe^0/air-treated solution after chlorination was higher than those without chlorination (Fig. 7b). This implies that the residual organic matter in the Fe^0/air-treated solution reacted with free chlorine and generated toxic byproducts like THMs. Since ZVI is a strong reducing agent that is capable of abiotically dehalogenating chlorinated solvents (e.g., trichloroethene), further study on dechlorination of trihalomethane byproducts by ZVI is suggested.

4. Conclusions

The effects of UV irradiation on HA removal by different processes were investigated. In addition, the THMFP and biotoxicity of treated solutions were evaluated. The experimental conditions were ozone dose of $7\,mg\,L^{-1}$, UVC of $9\,W$, H_2O_2 of $8 \times 10^{-4}\,M$, Fe^0 of $20\,g\,L^{-1}$, and air flow of $5\,L\,min^{-1}$. Fe^0/air rapidly and effectively removed HA color (>99%) and COD (91%) within 9 min. In contrast, 51–81% of decolorization and 43–50% of COD removal were obtained by ozonation and Fenton oxidation after 60 min. UV radiation enhanced HA removal by ozonation and Fenton oxidation. The effect of UV on HA removal by Fe^0/air process was slight. Spectrum results indicated that all methods effectively diminished UV–vis spectra, except for ozonation. The THMFP of solution treated by Fe^0/air was much lower than those treated by Fenton and ozonation. Fe^0/air process with UV obviously increased the THMFP of its treated solution. Chlorination increased the toxicity of treated solutions. The relationship between toxicity and chloroform in the chlorinated solution after $Na_2S_2O_3$ addition was insignificant.

Acknowledgement

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