Journal of Hazardous Materials 195 (2011) 324–331

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

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ARTICLE INFO

Article history:
Received 26 April 2011
Received in revised form 7 August 2011
Accepted 15 August 2011
Available online 22 August 2011

Keywords:
Fenton
Ozone
Fe^0/air
Vibrio fischeri

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_2O_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 disinfection 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_2O 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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doi:10.1016/j.jhazmat.2011.08.044

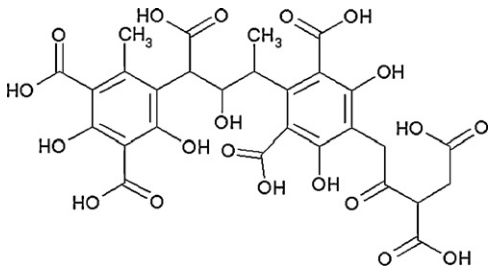

Fig. 1. Molecular structure of humic acid.

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]:

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

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