Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Study on the Removal of Humic Acid Using Advanced Oxidation Processes

Sanly[a]; M. Lim[a]; K. Chiang[a]; R. Amal[a]; R. Fabris[b]; C. Chow[b]; M. Drikas[b]
[a] ARC Centre for Functional Nanomaterials, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, Australia [b] CRC for Water Quality and Treatment, Australian Water Quality Centre, Salisbury, Australia

To cite this Article Sanly, Lim, M. , Chiang, K. , Amal, R. , Fabris, R. , Chow, C. and Drikas, M.(2007) 'A Study on the Removal of Humic Acid Using Advanced Oxidation Processes', Separation Science and Technology, 42: 7, 1391 — 1404
To link to this Article: DOI: 10.1080/01496390701289799
URL: http://dx.doi.org/10.1080/01496390701289799

Separation Science and Technology, 42: 1391–1404, 2007

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701289799

A Study on the Removal of Humic Acid Using Advanced Oxidation Processes

Sanly, M., Lim, K. Chiang, and R. Amal
ARC Centre for Functional Nanomaterials, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, Australia

R. Fabris, C. Chow, and M. Drikas
CRC for Water Quality and Treatment, Australian Water Quality Centre, Salisbury, Australia

Abstract: Humic acid (HA) removal using advanced oxidation processes (AOPs) was investigated, particularly UVA/H_2O_2 and photo Fenton-like process (UVA/Fe(III)/H_2O_2). Changes in the UV_{254} absorbance, dissolved organic carbon (DOC), apparent molecular weight (AMW) distribution, and the Trihalomethane formation potential (THMFP) of the organics were monitored. UVA/Fe(III)/H_2O_2 based process was found to be effective in removing more than 80% DOC and 90% UV_{254} absorbance. Differences in the reduction profiles of AMW distributions for UVA/Fe(III)/H_2O_2 based process and UVA/H_2O_2 process were observed, with the latter showing preferential removal of a certain molecular weight range. Selected samples were then fractionated into four components: very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA), and hydrophilic neutral (NEU). The HA used is found to consist mostly of VHA fraction that is very susceptible to AOP treatments. The results illustrate that the degradation process occurred via the fragmentation of VHA fraction to form SHA, CHA, and NEU fractions.

Keywords: Natural organic matter, disinfection by-product, size exclusion chromatography, Fenton, resin fractionation

Received 3 November 2006, Accepted 16 January 2007

Address correspondence to R. Amal, ARC Centre for Functional Nanomaterials, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney NSW 2052, Australia. E-mail: r.amal@unsw.edu.au

INTRODUCTION

Humic acids (HAs) are derived from the decomposition of organic matter originating from plant and animal materials. They are ubiquitous in surface and ground water sources (1). The removal of HAs is widely investigated due to their adverse interference with many water treatment processes. HAs impart an undesirable taste, colour, and odour to drinking water. Due to their high complexation ability, HAs may also act as a vehicle for transport of many heavy metal ions and organo-pollutants such as pesticides and herbicides (2). Most importantly, the reaction of humic substances with chlorine causes the formation of a variety of harmful disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (3). Both human epidemiology and animal toxicology studies have found that there is an association between chlorinated drinking water and an increased risk of cancer, reproductive, and developmental problems (4). As a result, several water regulatory bodies have lowered the maximum allowable levels of THMs and HAAs in drinking water. The U.S. Environmental Protection Agency has currently set maximum contamination levels of total THMs and HAA5 at 80 ppb and 60 ppb, respectively (5) whilst the standard for THMs in the UK is 100 ppb (6).

Increasingly stringent DBPs legislation has driven the research growth on advanced treatment methods to remove HA, including a category of processes known as advanced oxidation processes (AOPs). The term AOPs apply to processes where highly oxidative hydroxyl radicals ($OH^{\bullet}$) are produced in situ from the combination of chemical oxidants and a source of radiation. These hydroxyl radicals have the potential to mineralize most of the organic pollutants to non-toxic products, i.e. carbon dioxide and water via the formation of lower molecular weight intermediates. Photo Fenton based AOP technologies have been widely investigated due to their effectiveness in pilot scale studies (7). Up to 90% removal of HA within 30 minutes in a bench scale reactor using photo Fenton process has been reported (8). In the $UVA/Fe(III)/H_2O_2$ process, hydroxyl radicals are produced from the irradiation of iron(III) solution with light of a suitable wavelength (180 nm–400 nm), and the subsequent reaction between iron(II) formed and hydrogen peroxide (H_2O_2) (9).

Humic acids are generally a heterogeneous mixture of polymeric organic compounds. The physical and chemical characteristics of HAs can vary depending on the source, age, interactions with the environment, and the extraction process. Characterization of the changes in the physicochemical properties of HA is an integral part of assessing the efficiency and outcome of an AOP treatment process. One technique that has been found to provide useful information in the characterization of HAs is high performance size exclusion chromatography (HPSEC), which determines the molecular weight distribution of the dissolved organic matter (10). Using this technique, investigators were able to demonstrate the effectiveness of a certain treatment process for removing HAs from a particular molecular weight range (11, 12). More recently, Chow et al. (2004) have developed the rapid resin fractionation technique which separates dissolved organic matter in water into its four key components designated here as very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), hydrophilic charged (CHA), and hydrophilic neutral (NEU) (11).

Whilst these fractions are more operationally than structurally defined, organic compounds can be judiciously assigned to a particular fraction according to their chain length and functional groups as shown in Table 1. The functional groups and chain lengths observed in each fraction will determine the chemical and physical behaviors of the fraction, including its interactions with the chemical reagents used in the AOPs. This will in turn determine the fraction's susceptibility to AOP treatment, and its reactivity with chlorine to form DBPs. In this work, the changes in the characteristics of HAs after various AOP treatments were studied by monitoring the changes in DOC levels, UV_{254} absorbance, molecular size distributions, and trihalomethane formation potentials (THMFPs) of the water samples under different process conditions. Selected samples were also fractionated to their VHA, SHA, CHA, and NEU components in order to further establish the link between HA characteristics and AOP treatment efficiencies.

Table 1. Proposed composition of HA fractions separated using rapid fractionation technique (adapted from Buchanan et al. (2005) (12))

Fraction	Organic compounds
Hydrophobic (VHA and SHA)	
Acid	Soil fulvic acids, C_5-C_9 aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, 1- and 2-ring phenols.
Base	1- and 2-ring aromatics (except pyridine), proteinaceous substances.
Neutral	Mixture of hydrocarbons, $>C_5$ aliphatic alcohols, amides, aldehydes, ketones, esters, $>C_9$ aliphatic carboxylic acids and amines, >3 ring aromatic carboxylic acids and amines.
Hydrophilic (CHA and NEU)	
Acid	Mixtures of hydroxy acids, $<C_5$ aliphatic carboxylic acids, Polyfunctional carboxylic acids.
Base	Pyridine, amphoteric proteinaceous material (i.e. aliphatic amino acids, amino sugars, $<C_9$ aliphatic amines, peptides, and proteins).
Neutral	$<C_5$ aliphatic alcohols, polyfunctional alcohols, short-chain aliphatic amines, amides, aldehydes, ketones, esters; cyclic amides, polysaccharides and carbohydrates.

MATERIALS AND METHODS

The AOP reactions were carried out in a laboratory scale annular photoreactor (Fig. 1). The photoreactor (1) is fabricated from borosilicate glass for transmission of UV and visible wavelengths >320 nm. The reactor is mounted vertically on a support and a NEC 20 W blacklight fluorescent lamp (2) with maximum emission at 365 nm is fitted through the centre of the reactor. The photoreactor is connected to a 250 mL flask which serves as both a loading and sampling port (3) by means of Masterflex® flexible tubings. A Masterflex® Quick Load peristaltic pump (4) is used to circulate the solution in the loop. Compressed air at a flow rate of $50\,\mathrm{mL}\cdot\mathrm{min}^{-1}$ was used to aerate the solution during irradiation.

UVA/Fe(III) Degradation of Humic Acid

Humic acid stock solution was prepared by mixing 5 g of humic acid (Fluka) in 1 L of 0.1 M sodium hydroxide (Univar) over a period of 3 days. The stock solution was filtered through a Whatman® No. 1 filter paper to remove all suspended solid and stored at 4°C. A stock solution containing 100 mM Fe(III) was prepared by dissolving Fe(III) perchlorate (Sigma Aldrich) in Milli-Q™ water. The 30% H_2O_2 solution (Univar) was used as received. Known aliquots of iron(III) were added to the diluted humic acid solution to yield a final solution containing 10 ppm of total organic carbon and 0.1 mM iron(III). The suspension pH was adjusted to 4 ± 0.05 by using a perchloric acid solution. An 800 mL volume of the thus prepared solution was loaded into the photoreactor through the loading port and circulated within the reactor by the pump. The degradation process was initiated by turning on the UV

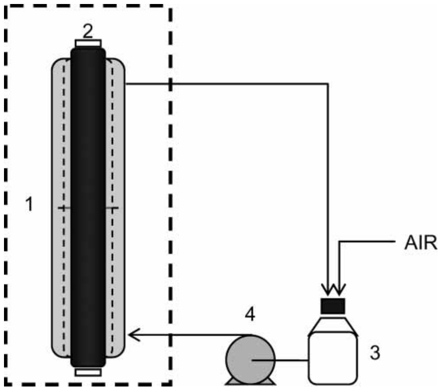


Figure 1. Schematic diagram of the photo reactor showing the annular reactor (1), UVA lamp (2), loading/sampling port (3) and Masterflex® Quick Load peristaltic pump (4).

lamp and if needed, adding aliquots of H_2O_2. Over a period of 2.5 hours, 30 mL samples of the humic acid solution were collected at 30 minutes interval and filtered through pre-washed 0.45 μm cellulose acetate membrane. Dissolved organic carbon (DOC) of the samples was measured using a Shimadzu total organic carbon analyzer. The absorbance of the humic acid solution at 254 nm was determined using a Cary 300 UV–visible spectrophotometer.

High Performance Size Exclusion Chromatography

The HPSEC analysis was carried out using a Waters 2690 Alliance system with a temperature-controlled oven (30°C) and a Shodex KW802.5 glycol functionalized silica gel column. A Waters 996 photodiode array detector was used to measure the absorbance of samples at 260 nm. After passing through a 0.22 μm membrane filter, a sample volume of 100 μl was injected into a carrier solvent which consisted of a 0.02 M phosphate buffer at pH 6.8 adjusted to an ionic strength of 0.1 M with sodium chloride. An isocratic conditions with an eluent flow rate of $1.0\,\mathrm{mL \cdot min^{-1}}$ was used. The retention time was converted to the apparent molecular weight by calibrating against polystyrene sulfonate standards (Polysciences, USA). The findings of the current study must be interpreted cautiously; recognizing that the polystyrene sulfonate standards are more flexible polyelectrolytes than HA, and therefore the AMW reported may not be truly representative.

Rapid Resin Fractionation

The fractionation setup as designed by Chow et al. (2004) (11) was used to determine concentrations of the four HA fractions prior to and at the end of the treatment process. After the initial 0.22 μm membrane filtration and pH adjustment to 2, the water sample was then passed through a series of 4 columns. The VHA fraction was adsorbed by DAX-8 resin and the SHA in the resultant effluent were adsorbed by the XAD-4 resin. The effluent from the XAD-4 resin was then adjusted to pH 8 to enable the selective adsorption of CHA onto the third column packed with IRA-958 resin. The final effluent from the series of resins constituted the NEU fraction. The concentrations of VHA, SHA, and CHA fractions in the sample were determined by subtracting the DOC concentrations of the water sample in the effluent from the influent. The uncertainty in replicate experiments was smaller than the error in the DOC analysis, and therefore, the total uncertainty was determined using the error of the DOC analysis. The accuracy of DOC analysis is generally reported as $0.1\,\mathrm{mg \cdot l^{-1}}$ (11); however, since the fractions are determined by difference (with the exception of the NEU), the uncertainty of the concentration was taken as $0.2\,\mathrm{mg \cdot l^{-1}}$.

Trihalomethane Formation Potential Measurements

THMFPs of the treated humic acid samples after certain irradiation times were determined and compared with that of the initial humic acid sample. The THMFP measurement was carried out according to Standard Method 5710 (13), which involved buffering samples at neutral pH using phosphate solution, chlorinating the samples with excess free chlorine and storing the sample at 25°C for 7 days. The THMs (chloroform, dichlorobromomethane, dibromochloromethane, and bromoform) were extracted using Solid phase micro extraction (SPME) and their concentrations determined by a Hewlett Packard 6890 series GC system with a HP5973 Mass selective detector. Analyte separation was carried out with a HP-5MS capillary column (30.0 m × 250 μm × 0.25 μm nominal thickness).

RESULTS AND DISCUSSION

UVA/Fe(III) Degradation of Humic Acid

Figure 2 shows that up to 80% DOC removal and 90% UV_{254} removal were achieved in the UVA/Fe(III)/H_2O_2 degradation of humic acid at the end of 2.5 hours irradiation, under our optimum studied condition. Both the reaction rate and removal efficiency were found to increase with increase in the molar ratio of H_2O_2 to Fe(III) when the molar ratio was less than 10. At a molar ratio greater than 10, removal efficiency no longer increased. The dependency of the degradation rate on the H_2O_2 concentration has been observed by other investigators (8) and can be explained by the significant $OH^\bullet$ scavenging effect of H_2O_2 at higher H_2O_2 concentrations. There is also some evidence that the decomposition rate of H_2O_2 decreases at higher H_2O_2 concentrations, leading to a drop in the amount of $OH^\bullet$ radicals available for the degradation process (14).

Figure 2 also shows that in the absence of Fe(III) (UVA/H_2O_2 only), and in the absence of H_2O_2 (UVA/Fe(III) only), the processes were less effective in reducing the DOC level and the UV_{254} absorbance of the HA solution. Whilst in principle H_2O_2 can decompose to form $OH^\bullet$ under ultraviolet irradiation, the reaction requires a large dissociation energy (213 $kJ \cdot mol^{-1}$) in order to cleave the O-O bond, and this can only be accomplished fully with short wave UVC irradiation (<290 nm) (15). Possible reaction mechanisms for the degradation of HA in UVA/Fe(III) only treatment involve the direct photolysis of the dominant aqueous ferric complexes at pH 4 forming hydroxyl radicals which further oxidize the organics or the direct photoreduction of Fe(III)-humic complexes creating organic radicals which then participate in subsequent oxidation reaction. Slow degradation in UVA/Fe(III) treatment implies that the photolysis of ferric complexes does not produce enough hydroxyl radicals for oxidising the organics. With the addition of

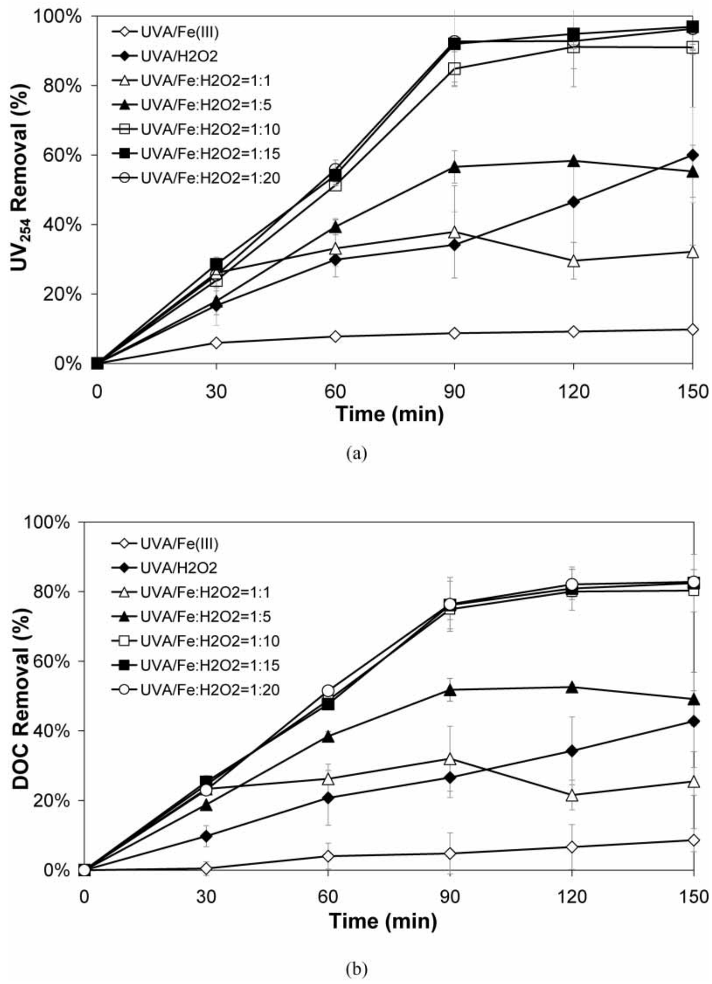


Figure 2. The removal of DOC (a) and UV_{254} (b) at different H_2O_2 to Fe(III) molar ratio.

hydrogen peroxide, Fe(II) ions produced from the photolysis of Fe(III) complexes are oxidized back to Fe(III), creating a redox cycle between Fe(III)-Fe(II) state and a continuous production of $OH^{\bullet}$ radicals.

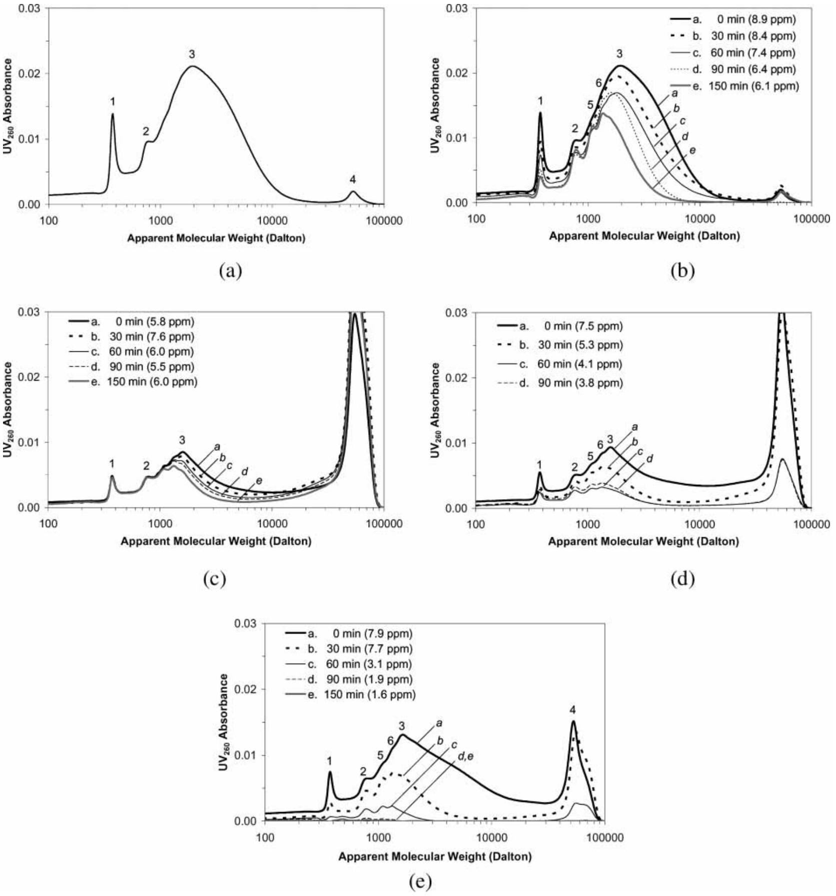
In general, the UV_{254} removal at the end of treatment period is on average 10% higher than that of DOC when the H_2O_2 to Fe(III) molar ratio is greater than 5. The higher drop in UV_{254} value suggests chromophores in the HA macro-molecules, which consist mostly of large molecular weight aromatic rings and are rapidly broken down into lower molecular weight by-products. The higher DOC value throughout the experiments implies that these by-products and/or recalcitrant molecules in the original HA are less susceptible to attacks by $OH^{\bullet}$ radicals and therefore are not mineralized completely. The intermediate fragments usually undergo a series of complicated reactions prior to mineralization. This observation is consistent with degradation pathway observed in large, specifically aromatic, organic molecules (16, 17).

The degradation profile is characterized by two stages: an initial sharp increase in removal efficiency, followed by a stabilization phase. The rapid initial rate may be due to the break down of large UV-absorbing molecules. It could be deduced that the decrease in the degradation rate towards the end of the treatment is ascribed to the changes in the chemical structure of HA as a result of treatment. Approximately 20% (~2 ppm) of DOC remained in the solution even after 2.5 hours of irradiation under the optimum condition suggesting the presence of highly refractory molecules, either pre-existing in the HA solution or produced as by-products in the treatment process, which are not removed by the UVA/Fe(III)/H_2O_2 process. While the degradation by-products were not investigated in this study, it has been reported that small carboxylic acids, such as maleic, oxalic, acetic, and formic acids are typical oxidation products of larger molecules after fragmentation. Oxalic acid is readily degraded with UV irradiation of Fe(III) species (18). The remaining carboxylic acids, in particular, acetic acid are weakly reactive toward hydroxyl radicals, which might explain the slow mineralization of DOC after 150 minutes of irradiation time. Kavitha and Palanivelu (2004) (18) reported that acetic acid was responsible for the low residual DOC after the photo Fenton treatment of phenol.

HPSEC Characterisation of Humic Acid Degradation

The HPSEC chromatograms of untreated humic acid sample at pH 4 prior to treatment are shown in Fig. 3a. As expected, the molecular weight distribution of untreated humic acid sample is notably broad and shows a vast abundance of highly UV absorbing large molecules (1 to 10 kDa). These are typical characteristics of hydrophobic aromatic and long chain aliphatic molecules. The HPSEC chromatograms exhibit three key peaks (1, 3, and 4) at approximately 380, 1090, and 52200 Da respectively, and a shoulder (2) at 770 Da.

The peak denoted as fraction 4 represents the exclusion limit of the HPSEC column, that is, any molecules larger than this size will have the same retention time. While the high apparent molecular weight and UV absorbance of this peak may imply the presence of highly aromatic components, it is more likely that peak denoted as fraction 4 is caused by colloidal materials in the water samples. Very fine colloidal materials have been known to permeate membrane filters that are used to remove solid materials from the samples prior to the HPSEC analysis (19). Other investigators have also observed similar characteristics in the HPSEC analysis of their water sample (20–22), which they attributed to interaction between humic acid



(a) (b) (c) (d) (e)

Figure 3. HPSEC chromatograms of (a) untreated samples at pH 4, and of water samples treated using (b) UVA/H_2O_2 pH 4; (c) UVA/Fe(III) pH 4; (d) UVA/Fe(III)/H_2O_2 pH 4 $[H_2O_2]$:[Fe] = 1; (e) UVA/Fe(III)/H_2O_2 pH 4 $[H_2O_2]$:[Fe] = 10 after various periods of irradiation. Peaks are numbered as referred to in the text. It should be noted that although peaks have been numbered similarly in different HPSEC chromatograms, they do not necessarily refer to the same chemical groups or species. Numbers in parentheses represent the corresponding DOC values.

and inorganic components such as sulfide, silicates, iron, and aluminium cations. The fact that peak 4 is most prominent in the chromatograms of initial samples of the UVA/Fe(III) treatment (Fig. 3c, 3d and 3e), in which agglomeration could be formed due to interaction between Fe(III) and the abundant humic acid molecules, further supports this hypothesis (23). The decrease in peak 4 value for UVA/Fe(III)/H_2O_2 treatments (Figs. 3d and 3e) with time indicates the presence of H_2O_2 is essential to remove the humic acid molecules that interact with Fe ions forming this fraction.

Figures 3b to 3e show the decrease in the apparent molecular weights (AMW) of humic acid with increased irradiation time after treatment using different AOP processes. Variation in the reductions of AMW profile could be seen as a result of studied AOP treatments, which suggest that the added chemical reagents interact differently with humic acid components.

The UVA/H_2O_2 treatment (Fig. 3b) exhibits preferential degradation of organic compounds with apparent molecular weight between 1500 and 10 000 Da compared to compounds with lower apparent molecular weight (less than 1000 Da). As a consequence, there is a significant shift of the apparent molecular weight distributions to the lower range. The change in the DOC level after 1 hour of treatment is less than 33%. This suggests that although large humic acid molecules were broken into smaller fragments in UVA/H_2O_2 treatment, the level of mineralisation was actually low.

In UVA/Fe(III) treatment (Fig. 3c), agglomeration of the organic molecules by Fe to form larger molecular weight compounds with an absorbance peak at around 55 000 Da was observed. A significant level of lower molecular weight compounds remained after a long period of irradiation, suggesting that the UVA/Fe(III) process condition is ineffective for the complete removal of humic acid. This is also confirmed by the insignificant change in UV_{254} and DOC level after 150 min of irradiation.

In contrast, when H_2O_2 was added to UVA/Fe(III) system at H_2O_2 to Fe(III) ratios of 1:1 (Fig. 3d) and 10:1 (Fig. 3e), a more effective removal was observed across the whole range of molecular weights. UVA/Fe(III) system with a H_2O_2 to Fe(III) ratio of 10:1 was found to produce a more effective degradation of the organic compounds and reduction in DOC level compared to the system with the ratio of 1:1. This shows that at the optimum conditions, UVA/Fe(III)/H_2O_2 system has the potential to remove organics with a broad range of molecular weight. This is consistent to the results from Murray and Parsons (2004) (8) who reported that photo Fenton is excellent at removing both the low and high molecular weight fractions and therefore is superior to conventional coagulation.

Rapid Resin Fractionation Analysis

Figure 4 shows the DOC concentrations of the VHA, SHA, CHA, and NEU fractions in humic acid samples prior to and after 150 min of treatments using (a) UVA/H_2O_2 at pH 4 and (b) UVA/Fe(III)/H_2O_2 with H_2O_2 to Fe(III) ratio of 10 at pH 4.

From the fractionation analysis, the VHA fraction comprises about 85% of the DOC of untreated humic acid at pH 4. Each of the other three fractions (SHA, CHA, and NEU) represents less than 6% of the DOC. As listed in Table 1, the VHA fraction potentially consists of soil fulvic acids, C5-C9 aliphatic carboxylic acids, 1- and 2-ring aromatic carboxylic acids, and 1- and 2-ring phenols (12).

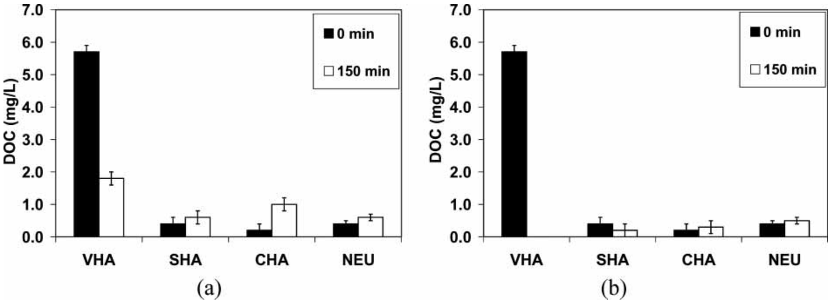


Figure 4. DOC concentrations of the VHA, SHA, CHA, and NEU fractions of humic acid sample prior to and after 150 min irradiations for (a) UVA/H_2O_2 at pH 4; (b) UVA/Fe(III)/H_2O_2 at pH 4 with H_2O_2 to Fe(III) ratio of 10.

UVA/H_2O_2 treatment at pH 4 was found to significantly reduce the DOC concentration of the VHA fraction (Fig. 4a). A corresponding increase in the concentration of the CHA and NEU fractions, in particular the former, was also observed at the end of the treatment. This indicates that compounds belonging to the CHA fraction, which includes low molecular weights ($<C_5$) carboxylic acids and amphoteric proteinaceous materials, were produced as a result of the breakdown of the VHA fraction. Buchanan et al (2005) (12) also reported that hydrophobic fractions (VHA and SHA) are preferentially removed by UV and VUV irradiation. They postulated that this is due to the structure of hydrophobic fractions (i.e larger UV-absorbing aromatic compounds) which is more easily degraded.

In UVA/Fe(III)/H_2O_2 treatment at pH 4 with H_2O_2 to Fe(III) ratio of 10, the VHA fraction was completely removed and only very low levels of the SHA, CHA, and NEU fractions remained in the treated water sample (Fig. 4b). Those three fractions could be responsible for the approximately 2 ppm DOC remaining in the solution even after 2.5 hours of irradiation.

Trihalomethane Formation Potential (THMFP)

Table 2 shows the total trihalomethanes (TTHMs) levels in untreated and treated water samples. Chloroform was found to be the main contributor to the total THMFP since the Fluka HA sample has a low level of bromine. Untreated 10 ppm HA sample is shown to have THMFP of 590 ppb.

It could be seen that there is a significant reduction in THMFP as a result of AOP treatments. Interestingly, the THMFP after UVA/Fe(III)/H_2O_2 treatment (438 ± 129 ppb) was higher than that of UVA/H_2O_2 (222 ± 12 ppb), considering the fact that all of the fractionation, HPSEC, and DOC results showed more organics were removed by the UVA/Fe(III)/H_2O_2 process. The results indicate that although the UVA/Fe(III)/H_2O_2 system

Table 2. TTHM concentrations in the HA samples before and after treatment

Treatment process	TTHM (ppb)
HA	590 ± 125
UVA/H_2O_2	222 ± 12
UVA/Fe(III)	397 ± 35
UVA/Fe(III)/H_2O_2 pH 4 with H_2O_2 to Fe(III) ratio of 1	357 ± 12
UVA/Fe(III)/H_2O_2 pH 4 with H_2O_2 to Fe(III) ratio of 10	438 ± 129

could remove a substantial amount of DOC, the organic compounds that remained in the sample at the end of treatment were fairly reactive to chlorine. It is also possible that the presence of iron under the studied conditions breaks down the organic matters into more reactive structures and therefore plays a role in the observed high THMFP in UVA/Fe(III)/H_2O_2 system. To confirm this, the sample after UV/H_2O_2 treatment was spiked with iron and the THMFP was found to be 348 ppb, a significant increase from 222 ppb. The results presented here suggest that caution should be exercised when estimating the reactivity of the organic matter with chlorine using DOC, UV absorbance, HPSEC, and rapid fractionation analysis.

CONCLUSIONS

In this study, more than 80% of the DOC and 90% of the UV_{254} absorbance removal can be achieved over 2.5 hours of illumination under studied conditions. For UVA/Fe(III) process, addition of H_2O_2 enhanced the removal kinetics and the degradation of HA was found to depend on the molar ratio of H_2O_2 to Fe. HPSEC and Rapid Fractionation analysis show that the untreated HA sample consists of hydrophobic, mainly large molecular weight (1 to 10 kDa) and high UV absorbing organic molecules. In general, AOPs degraded the large aromatic or long aliphatic chain molecules into lower molecular weight organics. HPSEC chromatograms of humic acid treated with different AOPs were varied, suggesting that the chemical reagents in AOPs interacted differently with humic acid components. From Rapid Fractionation analysis, the VHA fraction of the Fluka humic acid sample has been identified as the most susceptible to AOPs treatment. The breakdown of the hydrophobic VHA fraction resulted in corresponding increase of the hydrophilic fraction. Under this investigation, the presence of iron may have lead to an increased THM formation. While the results from DOC, UV absorbance, HPSEC, and rapid fractionation analysis do provide useful information regarding the change in the organic characteristics after treatment, these analytical techniques alone could not predict the trihalomethane formation potential (THMFP) of the treated water.

REFERENCES

1. Stevenson, F.J. (1994) *Humus Chemistry: Genesis, Composition, Reactions*; Wiley: New York.
2. McCarthy, J.F. (1989) Bioavailability and toxicity of metals and hydrophobic organic contaminants. In *Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants*; Suffet, I.H. and MacCarthy, P. (eds.); American Chemical Society: Washington, D.C.
3. Richardson, S.D. (1998) Drinking water disinfection by-products. In *Encyclopedia of Environmental Analysis and Remediation*; Wiley: New York.
4. United States Environmental Protection Agency. (2005) *Economic Analysis for the Stage 2 Disinfectants and Disinfection Byproducts Rule*, EPA 815-R-05-010, December 2005.
5. United States Environmental Protection Agency. (1998) *National Primary Drinking Water Regulations: Disinfections and Disinfection Byproducts: Final Rule*, Federal Register 63(241):69390–476, United States of America.
6. Drinking Water Inspectorate. (1998) In *New Drinking Water Regulations in the United Kingdom*; United Kingdom.
7. Gernjak, W. et al. (2003) Photo-Fenton treatment of water containing natural phenolic pollutants. *Chemosphere*, 50 (1): 71.
8. Murray, C.A. and Parsons, S.A. (2004) Removal of NOM from drinking water: Fenton's and photo-Fenton's processes. *Chemosphere*, 54: 1017.
9. Parson, S. (2004) *Advanced Oxidation Processes for Water and Wastewater Treatment*; IWA Publishing: London.
10. Zhou, Q., Cabaniss, S.E., and Maurice, P.A. (2004) Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Res*, 34: 3505.
11. Chow, C.W.K., Fabris, R., and Drikas, M. (2004) A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes. *J Water SRT-Aqua.*, 53: 85.
12. Buchanan, W., Roddick, F., Porter, N., and Drikas, M. (2005) Fractionation of UV and VUV pretreated natural organic matter from drinking water. *Environ. Sci. Technol.*, 39: 4647.
13. American Water Works Association. (1998) Standard Methods for the Examination of Water and Wastewater, American Public Health Association; American Water Works Association and Water Environment Federation, Washington D.C.
14. Wang, G.S., Liao, C.H., and Wu, F.J. (2001) Photodegradation of humic acids in the presence of hydrogen peroxide. *Chemosphere*, 42: 379.
15. Wang, G.S., Hsieh, S.T., and Hong, C.S. (2000) Destruction of humic acid in water by UV light-catalysed oxidation with hydrogen peroxide. *Water Res.*, 34: 3882.
16. Perez-Estrada, L.A. et al. (2005) Photo-fenton degradation of diclofenac: Identification of main intermediates and degradation pathway. *Environ. Sci. Technol.*, 39: 8300.
17. Konstantinou, I.K. and Albanis, T.A. (2004) TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. *Appl. Catal. B-Environ.*, 49: 1.
18. Kavitha, V. and Palanivelu, K. (2004) The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere*, 55: 1235.
19. Buesseler, K.O. et al. (1996) An intercomparison of cross-flow filtration techniques used for sampling marine colloids: Overview and organic carbon results. *Mar. Chem.*, 55: 1–31.

20. Allpike, B.P. et al. (2005) Size exclusion chromatography to characterize DOC removal in drinking Water treatment. *Environ. Sci. Technol.*, 39: 2334–2342.
21. Huber, S.A. and Frimmel, F.H. (1996) Gelchromatographie mit Kohlenstoffdetektion (LC-OCD): Ein rasches und aussagekräftiges Verfahren zur Charakterisierrung hydrophiler organischer Wasserinhaltsstoffe. *Vom Wasser*, 86: 277–290.
22. Schmitt, D. et al. (2003) NOM facilitated transport of metal ions in aquifers: Importance of complex-dissociation kinetics and colloid formation. *Water Res*, 37: 3541.
23. Schmitt, P. et al. (1996) Flocculation of humic substances with metal ions as followed by capillary zone electrophoresis. *Fresenius J. Anal. Chem.*, 354: 915.