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Removal and transformation of dissolved organic matter in secondary effluent during granular activated carbon treatment*

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Abstract: This paper focused on the removal and transformation of the dissolved organic matter (DOM) in secondary effluent during the granular activated carbon (GAC) treatment. Using XAD-8/XAD-4 resins, DOM was fractionated into five classes: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N) and hydrophilic fraction (HPI). Subsequently, the water quality parameters of dissolved organic carbon (DOC), absorbance of ultraviolet light at 254 nm (UV-254), specific ultraviolet light absorbance (SUVA) and trihalomethane formation potential (THMFP) were analyzed for the unfractionated and fractionated water samples. The results showed that the order of the DOC removal with respect to DOM fractions was observed to be HPI>HPO-A>HPO-N>TPI-A>TPI-N. During the GAC treatment, the THMFP of the unfractionated water samples decreased from 397.4 μg/L to 176.5 μg/L, resulting in a removal efficiency of 55.6%. The removal order of the trihalomethanes (THMs) precursor was as follows: HPO-A>TPI-A>TPI-N>HPO-N>HPI. By the GAC treatment, the specific THMFP of HPO-A, TPI-A, TPI-N and the original unfractionated water samples had a noticeable decrease, while that of HPO-N and HPI showed a converse trend. The Fourier transform infrared (FTIR) results showed that the hydroxide groups, carboxylic acids, aliphatic C–H were significantly reduced by GAC treatment.

Key words: Dissolved organic matter (DOM), Fractionation, Trihalomethane formation potential (THMFP), Specific THMFP, Fourier-transform infrared (FTIR)

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INTRODUCTION

Reuse of domestic effluents for potable and non-potable purposes is rapidly becoming a necessity practice for many countries throughout the world, especially for the arid and semi-arid regions. The growing water demand in those regions has resulted in an increased use of effluents from wastewater treatment plants for irrigation, industrial reuse and groundwater recharge (Rebhun *et al.*, 1987; Quanrud *et al.*, 1996; Chen *et al.*, 2005; Zhao *et al.*, 2007). As compared with freshwater, secondary effluents contain higher concentrations of harmful organic and inorganic components. The dissolved organic matter (DOM) in the secondary effluent has been of great concern because it not only may affect the behavior of other pollutants by redox reaction and hydrophobic/hydrophilic sorption (Kim and Osako, 2004), but also could potentially be converted to carcinogenic disinfection by-products, such as trihalomethanes (THMs), haloacetonitriles (HANs), haloacetic acids (HAAs) and haloketons (HKs) (McGeehin *et al.*, 1993; Villanueva *et al.*, 2003). Thus, understanding the chemical characteristics of DOM in secondary effluent is essential for further reuse of wastewater effluent.

DOM is a heterogeneous mixture of complex organic materials including hydrophilic acids, humic substances, proteins, lipids, carboxylic acids, poly-

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saccharides, amino acids and hydrocarbons (Leenheer and Croué, 2003; Cheng *et al.*, 2005). Because of its complex polymeric properties, DOM is still among the least characterized and understood components. To better understand the characters of DOM, it is often necessary to isolate and fractionate sufficient amounts of DOM into characteristic compound classes. The DOM fractionation method was developed by Leenheer (1981), and modified in different forms to fractionate DOM in natural water (Ma *et al.*, 2001), eutrophic lakes (Imai *et al.*, 2001), peat soils (Chow *et al.*, 2003) and some other wastewater samples.

Trihalomethane formation potential (THMFP) is influenced by the amount and chemical characteristics of the DOM presented in the water samples (Lin *et al.*, 2001; Chow *et al.*, 2005). Considerable work had been done to study the chlorine reactivity of different DOM fractions in the past decades. White *et al.*(2003) obtained good relationships between the formation of THMs and the variation in ultraviolet light at 254 nm (UV-254) of DOM fractions. Also, they concluded that both aromatic and phenolic components correlated well with THMs formation. The work conducted by Croue *et al.*(2000) showed that more hydrophobic and acidic fractions provided more active precursor sites. In addition, some recent studies also reported that the chlorination reactivity of hydrophilic fraction was comparable to that of hydrophobic fraction when the THMFP was normalized on a dissolved organic carbon (DOC) basis (Imai *et al.*, 2003; Xue *et al.*, 2007). These findings pointed out a possibility that hydrophilic fraction can be a significant THMs precursor as well. All of these results showed the effects of structural characteristics of DOM on THMFP.

Granular activated carbon (GAC) adsorption is one of the best available technologies recommended by the US Environmental Protection Agency (EPA) for the control of THMs. Due to its high adsorption capacity (especially for hydrophobic organic compounds) and fast adsorption kinetics, the GAC adsorption is generally regarded as a "best available technology" for DOM removal (Karanfil *et al.*, 1999). The ability of GAC to remove a broad spectrum of organic compounds from water is well-documented (Newcombe *et al.*, 1997; Schreiber *et al.*, 2005; Cheng *et al.*, 2005). However, most of the studies mainly focused on natural waters, seldom on the secondary effluents (Vahala *et al.*, 1999; Imai *et al.*, 2003; Kim, M.H. and Yu, 2005b). Moreover, the impacts of the GAC treatment on the DOM structure remain unclear. The main objectives of the study were to: (1) investigate the reductions of different DOM fractions by the GAC, in terms of DOC, absorbance of UV-254, specific ultraviolet light absorbance (SUVA) and THMFP; (2) determine the effects of the GAC on the chlorine reactivity of different DOM fractions; (3) examine the impacts of the GAC on the structure of different DOM fractions using Fourier Transform Infrared (FTIR) spectroscopy.

MATERIALS AND METHODS

Chemicals

Chloroform (TCM) (>99% purity), dibromochloromethane (DBCM) (>98% purity), dichlorobromomethane (BDCM) (>98.6% purity) and bromoform (TBM) (>99.5% purity) were obtained from China National Analytical Center, Guangzhou. Primary standard solutions of THMs were made in methanol from Aldrich Chemical Company (St. Louis, Missouri, USA).

The 0.45 μm cellulose nitrate membrane filter was purchased from Haining Shenghua Medical Chemistry Equipment Plant (Haining, China). Sodium hypochlorite (analytical purity) was obtained from Wenzhou Tiansheng Electrochemical Company (Wenzhou, China). Sodium sulfite (Na_2SO_3) (analytical purity) was purchased from Shanghai Runjie Chemical Plant (Shanghai, China). Ultra-pure water (Milli-Q) obtained from a Millipore Milli-Q system was used for the preparation of solutions. All the other reagents were above analytical grade.

Water sampling and characterization

The secondary effluent analyzed in this study was collected from Wenchang Wastewater Treatment Plant (WWTP) (Harbin, China), which employed the anaerobic-aerobic activated sludge treatment. The original raw water of WWTP was mainly municipal wastewater and a small portion of industrial wastewater. The collection of raw water sample was only performed once, with 100 L of sample being collected on 5 July, 2006. This water sample was used for all experiments in this work and stored in a cold room

with a temperature controlled at 4 °C before and after fractionation. Table 1 summarizes the water quality of the secondary effluent which were collected from June 2006 to June 2007 of WWTP.

Table 1 Water quality of secondary effluent of WWTP (n=20)

Parameter	Mean±*SD*	Parameter	Mean±*SD*
pH	7.8±0.1	Nitrate (mg N/L)	3.2±1.7
COD (mg/L)	50±4.6	Ammonia (mg N/L)	7.3±1.7
TOC (mg/L)	9.68±1.3	TP (mg/L)	3.3±1.2
DOC (mg/L)	8.25±0.9	Chloride (mg/L)	40.9±10.4
UV-254 (m^{-1})	16.3±0.7	Sulfate (mg/L)	29.9±11.1

COD: chemical oxygen demand; TOC: total organic carbon; TP: total phosphorus

Fractionation procedure

DOM was fractionated using Amberlite XAD-8/XAD-4 resins into five fractions: hydrophobic acid (HPO-A), hydrophobic neutral (HPO-N), transphilic acid (TPI-A), transphilic neutral (TPI-N) and hydrophilic fraction (HPI).

The cleaning method of the resin followed the modified sequential Soxhlet extraction method (Thurman and Malcolm, 1981). Prior to use, resin was intensively refined with 0.1 mol/L NaOH for 24 h and sequentially extracted with acetonitrile (8 h) and methanol (16 h) for another 24 h in a set of Soxhlet extraction apparatus. The clean resin was transferred into columns (50 ml) in slurry of methanol. The packed resin was rinsed with three cycles of 6 bed volumes of 0.1 mol/L NaOH, 500 ml Milli-Q water, and 6 bed volumes of 0.1 mol/L HCl, and finished with Milli-Q water until the conductivity and DOC concentration of the effluents were below 10 μs/cm and 0.2 mg/L, respectively.

The procedure for DOM fractionation is outlined in Fig.1. DOM fractionation was performed in triple for each sample. The steps were as follows: (1) 5 L water samples (filtered through 0.45 μm cellulose nitrate membrane filter) were acidified to pH 2 and passed through XAD-8 and XAD-4 resins columns using a peristaltic pump with Tygon tubing at a flow rate of 10 bed volumes per hour. HPI is the organic carbon in the XAD-4 effluent; (2) each of the resin columns was eluted backward with 0.1 mol/L NaOH at a flow rate of 2 bed volumes per hour, separately, followed by 2 bed volumes of Milli-Q water. The eluate from XAD-8 is defined as HPO-A and that from XAD-4 is defined as TPI-A; (3) HPO-N and TPI-N are those compounds which adsorb onto XAD-8 and XAD-4 resins, respectively, but not dissolved during the back elution with NaOH. HPO-N and TPI-N were desorbed from the XAD resins using a 75% acetonitrile/25% Milli-Q water solution (v/v). Acetonitrile was subsequently removed using rotary evaporation and the resin isolates were lyophilized. HPI was not isolated because of the large volume of water to be evaporated, which was stored at 4 °C. DOM fractions were desalted using cation exchange resin and freeze-dried using a vacuum freeze dry system.

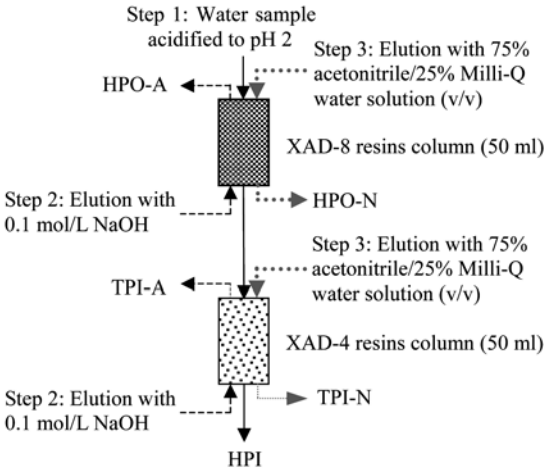

Fig.1 Schematic diagram of the procedure for DOM fractionation

THMFP measurement

The unfractionated and fractionated samples before and after GAC treatment were diluted with Milli-Q water to produce a DOC concentration of 1 mg/L before chlorination. Because each of the samples had the same DOC concentration, differences in reactivity with chlorine could be attributed to differences in the structural character of the samples. Freeze-dried HPO-N and TPI-N samples were reconstructed in Milli-Q water.

THMFP measurements were performed using Standard Method 5710B (APHA, 1987). All samples were adjusted to a pH of 7±0.2, buffered with a phosphate solution, and chlorinated with an adequate excess amount of concentrated sodium hypochlorite, assuring a residue concentration of free chlorine of about 3~5 mg/L at the end of the reaction period (requiring 7 d at (25±2) °C). At the end of this reac-

tion period, the residual chlorine was immediately quenched with sodium sulfite (Na_2SO_3) and the analysis of THMs was conduct without delay.

GAC adsorption

The GAC used in this study was commercial products purchased from Shanghai Mebao Company (Shanghai, China). It was made with the precursor of coconut. The GAC has a specific surface area of about 1000 m^2/g, micropore surface area of 76% and micropore volume of about 94.4%.

As a pretreatment, the GAC was boiled in distilled water, which was changed once an hour, for 5 h, subsequently rinsed with Milli-Q water and dried in an electric oven at 120 °C overnight. Based on a GAC dosage study, 1.0 g/L GAC dosage was chosen in this study because there exhibited a plateau in DOC sorption isotherms when the dosage exceeded 1.0 g/L. The GAC adsorption method was referenced from Cloirec *et al.*(1997). In this study, 1.0 g GAC was weighed into a 1 L tube and mixed with 1000 ml of secondary effluent. The mixture was stirred using a magnetic stirrer for 1 h at room temperature ((20±2) °C). The speed was around 100 r/min to avoid the break down of carbon particles at higher speed.

Analytical methods

All water samples were filtered using 0.45 μm cellulose nitrate membrane filter and stored at 4 °C prior to analysis. Each filter was rinsed with 1000 ml Milli-Q water to remove any residual organic contaminants before use (Karanfil *et al.*, 2003). An initial 25 ml of the filtrate on a filter must be discarded before samples for analysis were collected to minimize the impact of DOM losses to filters.

DOC was analyzed using a combustion technique with a Shimadzu TOC-5000 Total Organic Carbon Analyzer (Shimadzu, Japan). UV absorbance was measured with a Shimadzu UV-2550 UV/VIS spectrophotometer (Shimadzu, Japan) at 254 nm using a quartz cell with a 1 cm path length. The instrument was zeroed using Milli-Q water as a blank. SUVA was calculated as UV-254/DOC. SUVA is a measure of the contribution of aromatic structures to DOC (Leenheer and Croué, 2003).

The concentrations of TCM, BDCM, DBCM and TBM were measured using a Hewlett Packard 5890 II gas chromatograph fitted with an auto injector, a capillary split-splitless inlet, and a Nickle63 electron capture detector (Hewlett Packard, USA). THMFP was calculated as the sum of the four THM species. All THMs samples were analyzed in duplicate to compensate for the inherent variability of the analytical procedures. Samples with relative percent differences of the duplicates that exceeded 30% were reanalyzed.

The infrared spectra of HPO-A, HPO-N, TPI-A and TPI-N were obtained using 2~5 mg of powder lyophilized in potassium bromide pellets. The Perkin-Elmer Spectrum One B FTIR spectrometer (Perkin-Elmer, USA) was set to scan from 4000 cm^{-1} to 400 cm^{-1}. Spectra were baseline corrected and normalized to 1.0 for purpose of comparison.

RESULTS

DOC removal by GAC treatment

Fig.2a presents the DOC concentrations for the original unfractionated water samples and DOM fractions before and after GAC treatment. The fractionation results of the secondary effluent showed that HPI was the major component (49.8%) whilst HPO-A was the second (30.0%). These two fractions alone constituted as much as 75% of the total organic content. The remaining of the organic fractions were HPO-N (12.8%) and TPI-A (6.8%) whereas TPI-N existed the lowest (5.0%). During the GAC treatment, the bulk DOC of the secondary effluent decreased from 8.6 mg/L to 5.3 mg/L, resulting in a removal efficiency of 38.7%. In particular, the DOC concentration of HPO-A gradually decreased from 3.2 mg/L to 1.3 mg/L during the GAC treatment, whilst that of HPI decreased from 4.8 mg/L to 2.8 mg/L. As shown in Fig.2a, the order of the DOC removal with respect to DOM fractions was observed to be HPI>HPO-A>HPO-N>TPI-A>TPI-N. These observations suggested that the bulk DOC reduction of the secondary effluent was dominated by the removal of HPO-A and HPI, particularly of HPI for its relatively large content.

Compared to the unfractionated water samples, higher DOC removal efficiency was observed for HPO-A, HPO-N and TPI-A, with a removal efficiency of 52.0%, 46.2% and 47.3%, respectively. However, lower DOC removal efficiency was ob-

served for HPI and TPI-N, with a removal efficiency of 28.1% and 32.7%, respectively. As a result, the post-GAC effluent had higher HPI, TPI-A and TPI-N percents and lower HPO-A and HPO-N percents relative to the secondary effluent. Moreover, Aiken *et al.*(1992) and Maurice *et al.*(2002) stated that HPO-A and HPO-N contained higher molecular than TPI-A, TPI-N and HPI, which implied that the GAC treatment was accessible to adsorb macromolecules preferentially.

UV-254 removal by GAC treatment

UV-254 was always used to define the aromaticity of DOM, which was usually measured as an indicator of THMs precursors in the DOM fractions (Leenheer and Croué, 2003; Her *et al*., 2003). The UV-254 of the original unfractionated water samples and DOM fractions before and after GAC is plotted in Fig.2b.

As shown in Fig.2b, the UV-254 of the secondary effluent decreased from 17.5 m^{-1} to 11.4 m^{-1} during the GAC treatment, yielding a removal efficiency of 34.9%. The order of the UV-254 removal efficiency was as follows: HPO-A>TPI-N>HPO-N> TPI-A>HPI. Compared with the original unfractionated water samples, HPO-A had a relatively high UV-254 (from 9.5 m^{-1} to 5.4 m^{-1}) removal efficiency of 43.2%. The UV-254 removal efficiencies of HPO-N, TPI-A, TPI-N and HPI were 27.3%, 22.2%, 33.3% and 17.9%, respectively. Each of them is lower than that of the original unfractioned water sample. As shown in Fig.2b, HPO-A showed both higher UV-254 value and higher removal efficiency than the other fractions. It was indicated that the dominated fraction of aromatic components in HPO-A was preferentially adsorbed by GAC. Similarly, the GAC inclined to adsorb more nonaromatic components of HPI.

Influences of GAC treatment on SUVA

Fig.2c presents the SUVA of the original unfractionated water samples and DOM fractions before and after GAC treatment. SUVA always represents the enrichment of THMs precursors in DOC (White *et al*., 2003). Amy and Cho (1999) reported that there exists a positive correlation between Disinfection by-product (DBP) precursors and SUVA.

As shown in Fig.2c, the SUVA of the secondary effluent increased from 2.1 L/(m·mg) to 2.2 L/(m·mg), exhibiting an increase rate of 5.9% during the GAC treatment. Moreover, the SUVA of HPO-A, HPO-N, TPI-A and HPI fractions increased by 18.4%, 35.2%, 26.6% and 22.1%, respectively. It was indicated that HPO-A, HPO-N, TPI-A and HPI might have increased in the relative content of aromatic components during the GAC treatment, while TPI-N showed a converse trend, with a decrease of 7.3% in SUVA during the GAC treatment.

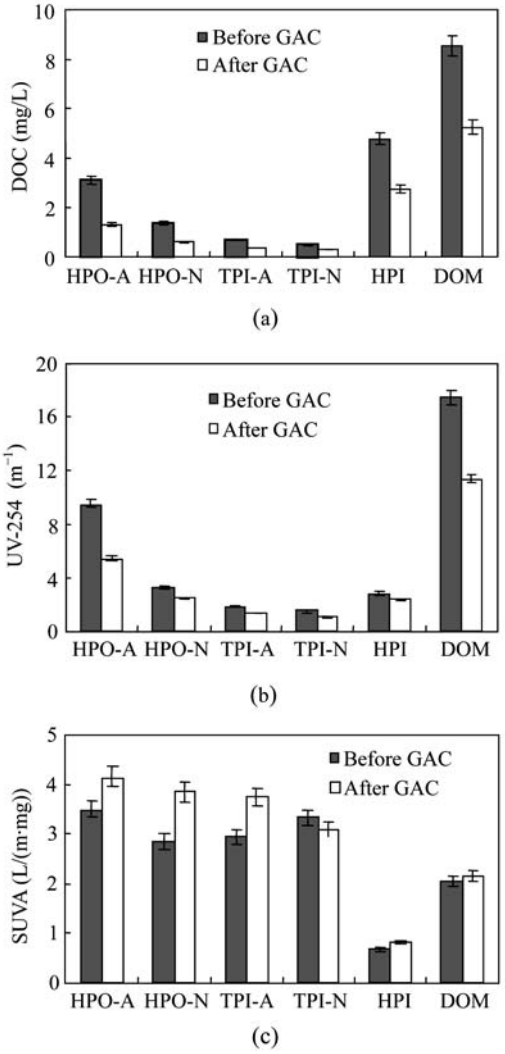

Fig.2 DOC (a), UV-254 (b) and SUVA (c) of the original unfractionated water samples and DOM fractions before and after GAC treatment (DOM presents the bulk DOC in the original unfractionated water samples). Error bars indicate standard deviations determined by triple measurement

THMFP removal by GAC treatment

The reactivity of DOM with chlorine was always assessed in terms of THMFP. In our study, TCM, BDCM, DBCM and TBM were measured in duplicate for the original unfractionated water samples and DOM fractions which had been chlorinated. Of the four THM species, TCM was the most abundant fraction, followed by BDCM and DBCM; TBM was low enough to be ignored, for all samples. The results of THMFP experiments are presented in Fig.3a.

The first two main precursors of THMFP in the secondary effluent were found to be HPO-A and HPI with 45% and 34% by weight of THMFP, respectively. HPO-N, TPI-A produced the same level of THMFP at around 6%~10% by weight, whereas TPI-N was found to give the smallest quantity of THMFP. This result was quite consistent with the study conducted by Kim, H.C. and Yu (2005a). They reported that HPO-A was the main THMFP precursor of the DOM fractions for the secondary effluent. The THMFP of the secondary effluent decreased from 397.4 μg/L to 176.5 μg/L, yielding a removal efficiency of 55.6%. It was noted that up to a 70.7% reduction of THMFP (from 171.0 μg/L to 50.0 μg/L) was found for HPO-A, whereas only a 37.8% reduction of THMFP (from 128.6 μg/L to 79.9 μg/L) occurred for HPI. The two fractions were also the main THMs precursors for the post-GAC effluent, accounting for about 80% of the bulk THMFP collectively. However, HPI became the major THMs precursors in the post-GAC effluent (48%) whilst HPO-A was the second (30%) as a result of the GAC treatment. The removal efficiency of THMFP from HPO-N, TPI-A and TPI-N was 39.6%, 69.8% and 63.5%, respectively. When the removed THMFP of the DOM fractions was expressed as percentage of the bulk removed THMFP, HPO-A, HPO-N, TPI-A, TPI-N and HPI accounted for 57.5%, 5.8%, 8.4%, 5.2% and 23.1%, respectively. It was obvious that the bulk THMFP reduction of the secondary effluent was dominated by the removal of THMFP from HPO-A. Therefore, preferential removal of HPO-A during the GAC treatment would significantly reduce the THMFP of the secondary effluent. On the other hand, the THMs precursors which site in HPI were not effectively reduced by the GAC treatment. Thus, additional advanced processes are needed to further remove HPI following the GAC treatment.

In addition, the sum of THMFP from all DOM fractions isolated from both the original unfractionated secondary effluent and post-GAC effluents were compared with the THMFP values of the corresponding bulk samples to check the possible influences of the fractionation procedures on the THMFP. It was noticed that the bulk THMFP in the original unfractionated secondary effluent was 9% larger than the sum of the corresponding five DOM fractions, which implied that the THMs precursors were not desorbed from the XAD resins absolutely. On the other hand, the mass balance of THMFP for the post-GAC effluent indicated a percent surplus of 10% which meant that the THMFP weight from the five fractions exceeded the total amount of bulk THMFP. This weight surplus may have come from resin bleeding during the elution process, and these organic contaminants might be THMs precursors.

Influences of GAC treatment on specific THMFP

THMFP of water samples was always dependent on DOC concentration, so the reactivity of forming THMFP was also reported in terms of specific THMFP (μg THMFP/mg DOC) (Galapate *et al.*, 2001). The objective of defining specific THMFP was to facilitate the evaluation of the potential of each organic fraction in the formation of THMs. Fig.3b presents the specific THMFP of the original unfractionated water samples and DOM fractions before and after GAC treatment.

The specific THMFP of the secondary effluent decreased from 46.4 μg/mg to 33.5 μg/mg during the GAC treatment, resulting in a removal efficiency of 27.8%. The specific THMFP of the DOM fractions varied widely during the GAC treatment. The specific THMFP of HPO-A, TPI-A and TPI-N decreased by 29.1%, 42.7% and 40.9%, respectively, whilst that of HPO-N and HPI increased by 39.3% and 7.5%, respectively. The most likely explanation to the significant decrease in specific THMFP of HPO-A, TPI-A and TPI-N, was that the removal of THMs precursors resulted in a sharp drop in THMFP while a corresponding removal of DOC was not significantly observed. On the other hand, it was contrary for HPI and HPO-N.

HPI in the post-GAC effluent was found to give a relatively low specific THMFP at 28.9 μg/mg, indicating that HPI was relatively inactive in forming

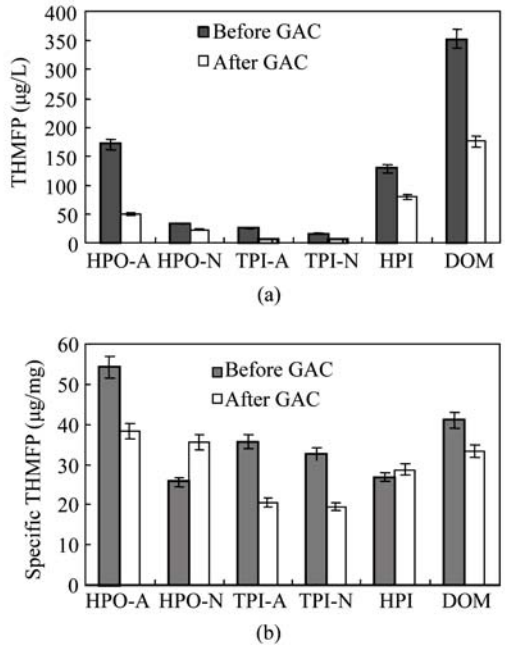

Fig.3 THMFP (a) and Specific THMFP (b) for DOM and its fractions before and after GAC treatment (DOM presents the bulk DOC in the original unfractionated water samples). Error bars indicate standard deviations determined by duplicate measurement

THMs among these DOM fractions. However, the THMFP from HPI was the highest among the five fractions isolated from the post-GAC effluent. The main reason was that the organic substances in the post-GAC effluent were predominantly HPI as indicated by the significantly higher DOC concentration of HPI compared to that of the other fractions (Fig.2a). Thus, the highest THMFP was obtained from HPI in spite of its lower specific THMFP. Hence, with its high quantity presented in the post-GAC effluent, HPI could then be considered as a problematic THM precursor. In addition, we further found that HPO-A and TPI-A had a significantly increased SUVA but decreased specific THMFP during the GAC treatment. The result was contrary to the conventional conclusion that SUVA was positively correlated with specific THMFP, possibly due to the presence of the unreactive aromatic components in the two fractions (Goi *et al*., 2005; Chow *et al*., 2005).

FTIR spectra of the DOM fractions

Fig.4 illustrates the FTIR spectra of the DOM fractions isolated from the pre- and post-GAC effluents. Because the mass of powdered sample for each FTIR analysis sample was not exactly the same to each other, the absorbance values in the *y*-axis were not provided. The analyzing method of FTIR spectra was referenced from Kim, H.C. and Yu (2005a).

According to the relevant investigations by Kim, H.C. and Yu (2005a) and Lin *et al.*(2001), the band at around 3400 cm^{-1} is generally attributed to OH groups and bands at 2950 cm^{-1}~2850 cm^{-1} are assigned to aliphatic C–H, C–H_2 and C–H_3 stretching. The bands at 1725 cm^{-1}~1640 cm^{-1} are assigned to C=O stretching of carboxylic acids. The bands at 1640 cm^{-1}~1550 cm^{-1} are attributed to C=C stretching vibration of aromatic compounds. Because of the presence of aromatic rings and unsaturated functions groups, the components corresponding to the bands at 1640 cm^{-1}~1550 cm^{-1} were always considered to be the major THMs precursors (Reckhow *et al.*, 1990; Westerhoff *et al.*, 2004). The bands at 1470 cm^{-1}~1420 cm^{-1} and 1400 cm^{-1}~1380 cm^{-1} are attributed to C–H deformation of aliphatic and CH_3 groups, respectively. Also, bands in the 1280 cm^{-1}~1137 cm^{-1} region are attributed to C–O stretching of esters, ethers and phenols, and bands at 880 cm^{-1}~750 cm^{-1} can be assigned to OH stretching vibration of carboxylic groups.

As shown in Fig.4, the FTIR spectra of HPO-A, HPO-N, TPI-A and TPI-N in the original unfractionated secondary effluent and post-GAC effluents were characterized by the aliphatic C–H (3300 cm^{-1}~3670 cm^{-1}, 1725 cm^{-1}~1640 cm^{-1}, 1470 cm^{-1}~1390 cm^{-1}) and aromatic C=C peaks (1640 cm^{-1}~1550 cm^{-1}). The aromatic C=C peak in the spectra of HPO-A was more pronounced than that in HPO-N, TPI-A and TPI-N, which agreed with its significantly higher specific THMFP as compared to that of the other fractions. Moreover, HPO-A and HPO-N in the secondary effluent were enriched in C=O functional groups (1725 cm^{-1}~1640 cm^{-1}).

Further inspection of the FTIR spectra indicates appreciable differences in strength of assigned peaks among the DOM fractions during the GAC treatment. For example, the post-GAC HPO-A decreased in the absorption intensity for the peaks at 1640 cm^{-1}~1550 cm^{-1}, 1390 cm^{-1} and 1720 cm^{-1} relative to the corresponding pre-GAC samples, suggesting that the aromatic C=C, aliphatic C–H and C=O in HPO-A were efficiently removed by GAC. HPO-N in the

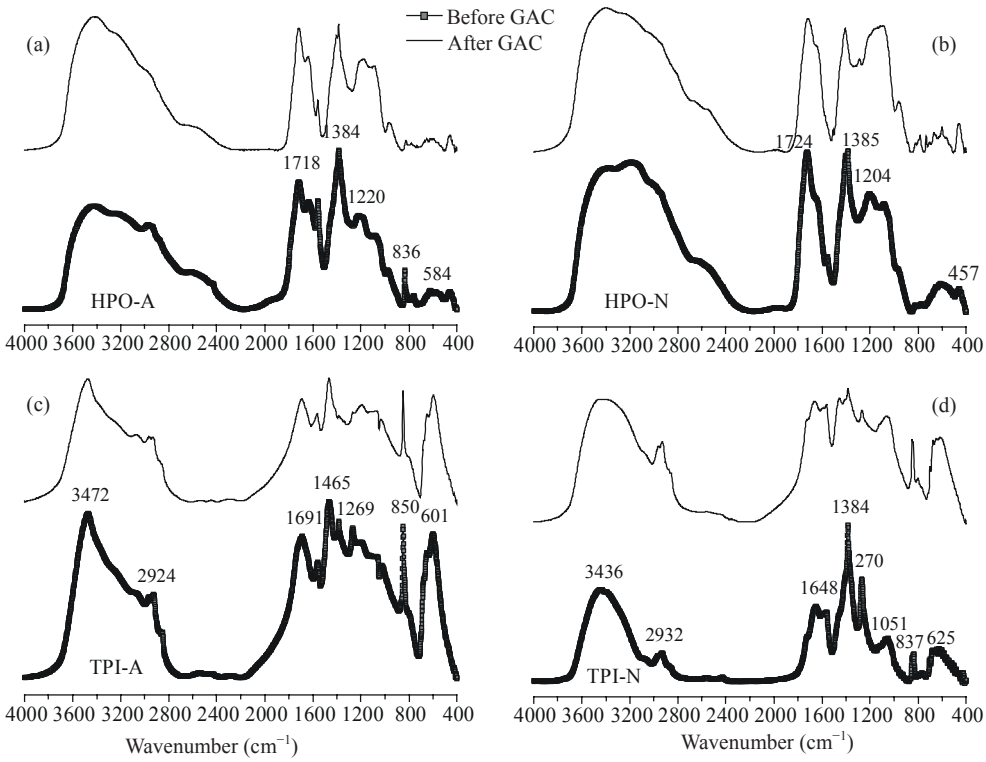

Fig.4 FTIR spectra of HPO-A (a), HPO-N (b), TPI-A (c), TPI-N (d) isolated from the pre- and post-GAC effluents

post-GAC effluent showed relatively lower absorption intensity for the aliphatic C–H peak, indicating the decreased aliphatic C–H content in HPO-N during the GAC treatment. TPI-A had decreased content of C–O of esters, ethers and phenols during the GAC treatment, as illustrated by the narrower and less intense peak near 1270 cm^{-1} in the spectra of post-GAC TPI-A as compared to that of pre-GAC TPI-A. The peak near 1390 cm^{-1} in TPI-N showed a sharp decrease in absorption intensity, implying that the aliphatic C–H in TPI-N was sufficiently adsorbed by GAC.

CONCLUSION

The bulk DOC and UV-254 of the secondary effluent were efficiently removed during the GAC treatment, with a removal efficiency of 38.5% and 33.7%, respectively. However, an increase rate of 5.9% in SUVA was observed.

HPI and HPO-A predominated in both original unfractionated secondary effluent and post-GAC effluents, accounting for about 75% of the DOM collectively. The bulk DOC reduction was dominated by the removal of HPO-A and HPI. The order of the DOC removal efficiency was observed to be HPO-A> HPO-N>TPI-A>TPI-N>HPI. The removal efficiency of UV-254 was as follows: HPO-A>TPI-N >HPO-N> TPI-A>HPI. The comparison between the DOC and UV-254 removals indicated that the GAC inclined to adsorb aromatic molecules in HPO-A and more non-aromatic components in HPI.

The first two main precursors of THMFP in the secondary effluent were found to be HPO-A and HPI, accounting for about 80% of THMFP collectively. The bulk THMFP reduction was dominated by the removal of THMFP from HPO-A. Thus, preferential removal of HPO-A during the GAC treatment will significantly reduce the THMFP of the secondary effluent. In addition, additional advanced processes are needed to further remove HPI following the GAC treatment. HPO-A, TPI-A, TPI-N and the original unfractionated secondary effluent had a noticeable decrease in specific THMFP during the GAC treatment, indicating the decreased chlorine reactivity of forming THMs, while HPO-N and HPI showed a converse trend.

References

Aiken, G.R., McKnight, D.M., Thorn, K.A., Thurman, E.M., 1992. Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Organic Geochemistry*, **18**(4):567-573. [doi:10.1016/0146-6380(92)90119-I]

Amy, G., Cho, J., 1999. Interactions between natural organic matter (NOM) and membranes: rejection and fouling. *Water Science and Technology*, **40**(9):131-139. [doi:10.1016/S0273-1223(99)00649-6]

APHA (American Public Health Association), 1987. Standard Methods for the Examination of Water and Wastewater. Washington, DC.

Chen, H.H., Yeh, H.H., Shiau, S., 2005. The membrane application on the wastewater reclamation and reuse from the effluent of industrial WWTP in northern Taiwan. *Desalination*, **185**(1-3):227-239. [doi:10.1016/j.desal.2005.03.079]

Cheng, W., Dastgheib, S.A., Karanfil, T., 2005. Adsorption of dissolved natural organic matter by modified activated carbons. *Water Research*, **39**(11):2281-2290. [doi:10.1016/j.watres.2005.01.031]

Chow, A.T., Tanji, K.K., Gao, S.D., 2003. Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. *Water Research*, **37**(18):4475-4485. [doi:10.1016/S0043-1354(03)00437-8]

Chow, A.T., Guo, F.M., Gao, S.D., Breuer, R., Dahlgren, R.A., 2005. Filter pore size selection for characterizing dissolved organic carbon and trihalomethane precursors from soils. *Water Research*, **39**(7):1255-1264. [doi:10.1016/j.watres.2005.01.004]

Cloirec, P.L., Brasquet, C., Subrenat, E., 1997. Adsorption onto fibrous activated carbon: applications to water treatment. *Energy Fuels*, **11**(2):331-336. [doi:10.1021/ef9601430]

Croue, J.P., Violleau, D., Labouyrie, L., 2000. Disinfection Byproduct Formation Potentials of Hydrophobic and Hydrophilic Natural Organic Matter Fractions: a Comparison Between a Low- and a High-humic Water. *In*: Barrett, S.E., Krasner, S.W., Amy, G.L. (Eds.), Natural Organic Matter and Disinfection By-Products—Characterization and Control in Drinking Water. ACS Symposium Series 761, American Chemical Society, Washington, DC.

Galapate, R.P., Baes, A.U., Okada, M., 2001. Transformation of dissolved organic matter during ozonation effects on trihalomethane formation potential. *Water Research*, **35**(9):2201-2206. [doi:10.1016/S0043-1354(00)00489-9]

Goi, D., Tubaro, F., Barbone, F., Dolcetti, G., Bontempelli, G., 2005. Evaluation of chlorinated by-products in drinking waters of central Friuli (Italy). *Annali di Chimica*, **95**(9-10):617-627. [doi:10.1002/adic.200590073]

Her, N., Amy, G., McKnight, D., Sohn, J.S., Yoon, Y.M., 2003. Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water Research*, **37**(17):4295-4303. [doi:10.1016/S0043-1354(03)00317-8]

Imai, A., Takehiko, F., Kazuo, M., Kim, Y.H., 2001. Fractionation and characterization of dissolved organic matter in a shallow eutrophic lake, its inflowing rivers, and other organic matter sources. *Water Research*, **35**(17):4019-4028. [doi:10.1016/S0043-1354(01)00139-7]

Imai, A., Kazuo, M., Takashi, N., 2003. Trihalomethane formation potential of dissolved organic matter in a shallow eutrophic lake. *Water Research*, **37**(17):4284-4294. [doi:10.1016/S0043-1354(03)00310-5]

Karanfil, T., Kitis, M., Kilduff, J.E., Wigton, A., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 2. Natural organic matter. *Environmental Science and Technology*, **33**(18):3225-3233. [doi:10.1021/es9810179]

Karanfil, T., Erdogan, I., Schlautman, M.A., 2003. Selecting filter membranes for measuring DOC and UV 254. *American Water Works Association*, **95**(3):86-100.

Kim, H.C., Yu, M.J., 2005a. Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. *Water Research*, **39**(19):4779-4789. [doi:10.1016/j.watres. 2005.09.021]

Kim, M.H., Yu, M.J., 2005b. Characterization of NOM in the Han River and evaluation of treatability using UF-NF membrane. *Environmental Research*, **97**(1):116-123. [doi:10.1016/j.envres.2004.07.012]

Kim, Y.J., Osako, M., 2004. Investigation on the humification of municipal solid waste incineration residue and its effect on the leaching behavior of dioxins. *Waste Management*, **24**(8):815-823. [doi:10.1016/j.wasman.2004.04.004]

Leenheer, J.A., 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science and Technology*, **15**(5):578-587. [doi:10.1021/es00087a010]

Leenheer, J.A., Croué, J.P., 2003. Characterizing dissolved aquatic organic matter. *Environmental Science and Technology*, **37**(1):18A-26A.

Lin, C.F., Liu, S.H., Hao, O.J., 2001. Effect of functional groups of humic substances on UF performance. *Water Research*, **35**(10):2395-2402. [doi:10.1016/S0043-1354(00)00525-X]

Ma, H.Z., Herbert, E.A, Yin, Y.J., 2001. Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. *Water Research*, **35**(4):985-996. [doi:10.1016/S0043-1354(00)00350-X]

Maurice, P.A., Pullin, M.J., Cabaniss, S.E., 2002. A comparison of surface water natural organic matter in raw filtered water samples, XAD, and reverse osmosis isolates. *Water Research*, **36**(9):2357-2371. [doi:10.1016/S0043-1354(01)00442-0]

McGeehin, M.A., Reif, J.S., Becher, J.C., Mangione, E.J., 1993. Case-control study of bladder cancer and water disinfection methods in Colorado. *Epidemiology*, **138**(7):492-501.

Newcombe, G., Drikas, M., Hayes, R., 1997. Influence of characterized natural organic material on activated carbon

adsorption: II effect on pore volume distribution and adsorption of 2-methylisoborneol. *Water Research*, **31**(5): 1065-1073. [doi:10.1016/S0043-1354(96)00325-9]

Quanrud, D.M., Arnold, R.G., Wilson, L.G., Martha, H.C., Conklin, M.H., 1996. Effect of soil type on water quality improvement during soil aquifer treatment. *Water Science and Technology*, **33**(10-11):419-431. [doi:10.1016/0273-1223(96)00445-3]

Rebhun, M., Goodman, N.L., Barker, F.B., 1987. Monitoring and study program of an interregional wastewater reclamation system for agriculture. *Journal Water Pollution Control Federation*, **59**(5):242-248.

Reckhow, D.A., Singer, P.C., Malcolm, R.L., 1990. Chlorination of humic materials: byproduct formation and chemical interpretations. *Environmental Science and Technology*, **24**(11):1655-1664. [doi:10.1021/es00081a-005]

Schreiber, B., Brinkmann, T., Schmalz, V., Worch, E., 2005. Adsorption of dissolved organic matter onto activated carbon—the influence of temperature, absorption wave-length, and molecular size. *Water Research*, **39**(15):3449-3456. [doi:10.1016/j.watres.2005.05.050]

Thurman, E.M., Malcolm, R.L., 1981. Preparative isolation of aquatic humic substances. *Environmental Science and Technology*, **15**(4):463-466. [doi:10.1021/es00086a 012]

Vahala, R., Langvik, V.A., Laukkanen, R., 1999. Controlling adsorbable organic halogens (AOX) and trihalomethanes (THM) formation by ozonation and two-step granule activated carbon (GAC) filtration. *Water Science and Technology*, **40**(9):249-256. [doi:10.1016/S0273-1223(99)00663-0]

Villanueva, C.M., Kogevinasa, M., Grimaltb, J.O., 2003. Haloacetic acids and trihalomethanes in finished drinking waters from heterogeneous sources. *Water Research*, **37**(4):953-958. [doi:10.1016/S0043-1354(02)00411-6]

Westerhoff, P., Chao, P., Mash, H., 2004. Reactivity of natural organic matter with aqueous chlorine and bromine. *Water Research*, **38**(6):1502-1513. [doi:10.1016/j.watres.2003.12.014]

White, D.M., Garland, D.S., Narr, J., Woolard, C.R., 2003. Natural organic matter and DBP formation potential in Alaskan water supplies. *Water Research*, **37**(4):939-947. [doi:10.1016/S0043-1354(02)00425-6]

Xue, S., Zhao, Q.L., Wei, L.L., Wang, L.N., Liu, Z.G., 2007. Fate of secondary effluent dissolved organic matter during soil-aquifer treatment. *Chinese Science Bulletin*, **52**(18):2496-2505. [doi:10.1007/s11434-007-0339-1]

Zhao, Q.L., Xue, S., You, S.J., Wang, L.N., 2007. Removal and transformation of organic matter during soil-aquifer treatment. *Journal of Zhejiang University SCIENCE A*, **8**(5):712-718. [doi:10.1631/jzus.2007.A0712]