Characterization and predicting DOM treatability by enhanced coagulation

Dongsheng Wang, Jiankun Xie, Chris W. K. Chow, Linan Xing and John van Leeuwen

ABSTRACT

The dissolved organic matter (DOM) plays significant role in water safety due to not only the natural occurrence but also man-induced pollution. To characterize and predict DOM treatability becomes therefore a very important and hot topic. In this paper, enhanced coagulation by four typical coagulants ($FeCl_3$, $Al_2(SO_4)_3$, polyaluminum chloride (PAC) and high performance polyaluminum chloride (HPAC)) without pH control was characterized using the chemical fractionation (resin adsorption, RA) and physical fractionation (high performance size exclusion chromatography (HPSEC) combined with peak fitting technique). The results show that the DOM removal can be separated into two stages, rapid removal and continual slow removal. The PAC exhibits efficient removal in the rapid part while the traditional salts are more efficient in the latter part. It is also very important for pH control to improve DOM removal by the traditional coagulants. DOM treatability per unit dosage (1×10^{-4} mol/l) for the four coagulants was then calculated in the order of HPAC (26.0%) > PAC (17.3%) > $FeCl_3$ (14.3%) > $Al_2(SO_4)_3$ (12.0%). Two sets of DOM treatability models, i.e. removal efficiency, for enhanced coagulation of the four coagulants were developed by combining the chemical and physical DOM fractions based on the quantitative analysis of the removal state of raw water. The two sets of models could be transformed to each other. The composition of the removable DOM by enhanced coagulation of the four coagulants was revealed and validated using 29 raw waters (in 13 source waters in three seasons), and as a result the low deviation indicated that the predicted data matched well with the actual data. It provided the possibility for the application in practical operation of water plant.

Key words | chemical fractionation, DOM, enhanced coagulation, modeling, physical fractionation, treatability

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INTRODUCTION

The presence of dissolved organic matter (DOM) in drinking water treatment could cause a series of significant problems, such as reacting with chlorine disinfectant to reduce its concentration, reacting with chlorine to form disinfection by-products such as trihalomethanes (THMs), haloacetic acids (HAAs) and other organochlorines, supporting bacterial regrowth in the distribution system, contributing color, taste and odor of drinking water (Edwards 1997; van Leeuwen *et al.* 2003; Kastl *et al.* 2004; Chow *et al.* 2008;

Wei *et al.* 2008; Wei *et al.* 2011). Due to water pollution, a number of toxic organics are also presented in source water associated with natural organic matter (NOM) (MartinMousset *et al.* 1997; Kitis *et al.* 2002; Leenheer & Croue 2003; Wei *et al.* 2008; Wei *et al.* 2011). Therefore, maximizing the removal of DOM in water has become a significant topic in drinking water treatment. Enhanced coagulation, i.e. coagulation with higher dosage of coagulant for maximum removal of DOM than that required for color and turbidity

removal, is proposed by the US Environmental Protection Agency (EPA) in the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR) as a best available technology to remove NOM (Edwards 1997; van Leeuwen *et al.* 2003; Kastl *et al.* 2004; Chow *et al.* 2008).

The removal of DOM by enhanced coagulation is greatly impacted by the chemical and physical characteristics of DOM in raw water. Resin adsorption (RA) as an effective method for chemical fractionation has been widely employed in characterization of the chemical property of DOM in past years (MartinMousset *et al.* 1997; Kitis *et al.* 2002; Leenheer & Croue 2003; Wei *et al.* 2008; Wei *et al.* 2011). The use of XAD-8 (or DAX-8) and XAD-4 resin to determine the humic/nonhumic distribution has provided the most useful information in water researches.

High performance size exclusion chromatography (HPSEC) as a popular technique for characterization of the physical property of DOM and evaluation of water treatment processes has been developed and employed in recent years (Chin *et al.* 1994; Gjessing *et al.* 1998; Vuorio *et al.* 1998; Chow *et al.* 1999; Bolto *et al.* 2001; van Leeuwen *et al.* 2002; Allpike *et al.* 2005; Her *et al.* 2008). However, the apparent molecular weight (AMW) distribution profile of DOM with overlapped peaks can only provide qualitative information by comparing the profiles of different raw waters or waters before and after certain treatment processes. To obtain more quantitative information, Chow *et al.* (2008) developed a peak fitting technique to resolve the overlapped peaks into several individual peaks, representing the removable or non-removable DOM.

The quantitative description of the DOM removal process by enhanced coagulation is always a significant objective in coagulation research. Recently, a great deal of work aimed at modeling the DOM removal by enhanced coagulation has been reported, including Edwards (1997); Baxter *et al.* (1999); Urfer *et al.* (1999); Stanley *et al.* (2000); van Leeuwen *et al.* (2003); Kastl *et al.* (2004); van Leeuwen *et al.* (2005); Chow *et al.* (2008). Some of them were of empirical nature and developed based on the regression analysis (Urfer *et al.* 1999; van Leeuwen *et al.* 2003; van Leeuwen *et al.* 2005) and artificial neural network (ANN) (Baxter *et al.* 1999; Stanley *et al.* 2000). Several semi-empirical models (Edwards

1997; Kastl *et al.* 2004; Chow *et al.* 2008) were developed based on some theoretical basis such as the Langmuir adsorption isotherm. However, to address the difference of DOM components and their treatability, to relate the disinfection byproduct formation potential (DBPFP) accordingly, to yield the optimum removal conditions in relation to coagulant speciation, are still considerable challenges and targets.

Speciation of coagulants exhibits significant control in DOM treatability. Polyaluminum chloride (PAC) has been shown to be effective in DOM removal for many years. However, the difference between traditional and polymer species remains unclear. Recently, high performance polyaluminum chloride (HPAC) has been developed for the treatment of micro-polluted water (Yan *et al.* 2006; Dixon *et al.* 2011). In this paper, two kinds of traditional coagulants, i.e. ferric chloride ($FeCl_3 \cdot 6H_2O$) and alum ($Al_2(SO_4)_3 \cdot 18H_2O$), and two kinds of polymer coagulants, i.e. PAC and HPAC, were then selected for a comparison for DOM removal to address the different role of species. On the basis of the previous work (van Leeuwen *et al.* 2003; Chow *et al.* 2008), this paper attempted to characterize and predict the DOM treatability by enhanced coagulation following the direction of DOM characterization. This work extended into the use of chemical fractionation in conjunction with physical fractionation for characterization and prediction. In addition, the coagulation processes were carried out without pH adjusting in order to agree with the practical operation in most drinking water treatment plants.

MATERIALS AND METHODS

Materials

Four typical coagulants were selected, including $FeCl_3 \cdot 6H_2O$ (analytical grade), $Al_2(SO_4)_3 \cdot 18H_2O$ (analytical grade), PAC (OH/Al = 2.4, prepared in the laboratory) and HPAC. The HPAC, an innovative composite coagulant, was produced by a local factory using the patent technique developed in this laboratory. It was prepared from mixing or co-polymerization of PAC and other organic and

inorganic additives, such as active silicates and polyacrylamide (PAM) (Yan *et al.* 2006).

Water samples were obtained from 13 typical locations throughout eastern China (Xie 2011; Xie *et al.* 2012). Water samples were collected not only from all 13 locations in October 2008 (autumn), but also from HS, HM, BS, DY, NC, XQ, GX and GB in February 2009 (winter) and May 2009 (spring), respectively. These waters were all source waters for local drinking water treatment plants and well represented the feature of source water quality in China. The general water quality parameters of the 29 raw water samples were analyzed in previous papers (Xie 2011; Xie *et al.* 2012).

Jar tests

Jar tests were performed using 500 ml raw waters and a programmable jar testing apparatus with a standard procedure: 30 s of rapid mixing at 250 rpm, followed by coagulant addition, 2 min of rapid mixing at 250 rpm, 15 min of slow mixing at 40 rpm and 30 min of settling. After settling was completed, water samples were collected at 1 cm below the water surface, and were measured for turbidity and pH, and filtered through 0.45 μm cellulose acetate membranes for analysis of dissolved organic carbon (DOC), UV_{254}, residual metal content, chemical fractionation and AMW fractionation. In order to simulate the practical operation conditions in most water treatment plants, the coagulation processes were performed without pH adjusting, and the jar tests in autumn and spring were performed at the water temperature around 25 °C, whereas those in winter were performed at the water temperature around 8 °C. The enhanced coagulation jar tests without pH adjusting for all 29 raw waters using four kinds of coagulants were conducted, and the response curves of DOC, UV_{254}, pH and turbidity versus dosage were obtained.

Analytical methods

Turbidity was measured using a turbidity meter (2100P, Hach, USA). DOC was determined using a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). UV_{254} was determined using a UV/vis spectrophotometer (UV-VIS 8500, Tianmei, China) with a 1 cm quartz cell. The specific UV absorbance (SUVA) was calculated by (UV_{254}/DOC) × 100. pH was measured using a pH meter (MP220, Mettler-Toledo, Switzerland). Alkalinity was measured using an automatic titration pH meter (716 DMS Titrino, Metrohm, Switzerland). The residual metal content was determined using an inductively coupled plasma optical emission spectrometer (OPTIMA 2000, PerkinElmer, USA).

Chemical fractionation of DOM

The chemical fractionation of DOM was performed by RA method described by Wei *et al.* (2008). Amberlite XAD-8 and Amberlite XAD-4 resins were used to divide the DOM into five fractions: hydrophobic base (HoB), hydrophobic neutral (HoN), hydrophobic acid (HoA), weakly hydrophobic acid (WHoA) and hydrophilic matter (HiM). The HoB, HoN, HoA and WHoA could be combined to hydrophobic matter (HoM, HoM = HoB + HoN + HoA + WHoA). The HoB, HoN and HoA could be combined to strong hydrophobic matter (STHoM, STHoM = HoB + HoN + HoA).

Physical fractionation of DOM

The physical fractionation of DOM was performed by HPSEC and peak fitting technology. First, the AMW distribution profile was determined by HPSEC using a high performance liquid chromatography system (Waters 1525, Waters, USA) and a size exclusion chromatography column (Shodex PROTEIN KW-802.5, Shoko, Japan) at 30 °C. The mobile phase with a flow rate of 0.8 ml/min consisted of 0.005 mol/l phosphate buffer solution at pH 6.8. NaCl was added to obtain an ionic strength of 0.01 mol/l. The polystyrene sulfonate (PSS) standards were used to calibrate the retention time for AMW. The UV absorbance of the sample was monitored at 254 nm.

Then, the AMW distribution profile with overlapped peaks was resolved into five individual peaks, i.e. Peak 1, Peak 2, Peak 3, Peak 4 and Peak 5 (representing five physical fractions) using a peak fitting software, PeakFit (Version 4, AISN Software Inc.) according to Chow *et al.* (2008). 'Chromatography Log Normal-4 Area' was selected as the peak type to represent the resolved component peaks. The AMW of the five physical fractions (peaks)

distributed around 250 Da (Peak 1), 450 Da (Peak 2), 1,000 Da (Peak 3), 1,700 Da (Peak 4) and 2,400 Da (Peak 5) respectively.

RESULTS AND DISCUSSION

Characterization of the DOM treatability by enhanced coagulation

First of all, in order to characterize the DOM treatability by enhanced coagulation (i.e. the DOM removal efficiency at the enhanced coagulation point), the enhanced coagulation point for nearly maximum DOM removal should be determined based on a certain rule. In this study, from the DOC reduction curves the enhanced coagulation point of four coagulants were determined when DOC reduction was less than 0.1 mg/l with dosage increment increased by 1×10^{-4} mol/l (as Al or Fe), i.e. where a gradient (Δ DOC/Δ dosage) of 0.0018, 0.0037, 0.0037 and 0.0037 for FeCl$_3$ (as Fe), Al$_2$(SO$_4$)$_3$ (as Al), PAC (as Al) and HPAC (as Al) was obtained, respectively. At these points with the above arbitrarily selected gradients, it was considered that further coagulant dosing would provide only minor DOC removal. At these enhanced coagulation points of four coagulants, the residual turbidities were all below 1.5 NTU, and the contents of residual Al and Fe were all below 7.41×10^{-6} and 5.37×10^{-6} mol/l respectively.

The BS water in autumn was selected as a representative case study. The DOC and pH reduction curves versus dosage for the four coagulants are shown in Figure 1. The enhanced coagulation points of the four coagulants were selected at the dose of 3.5×10^{-4} mol/l (as Fe) for FeCl$_3$, 3×10^{-4} mol/l (as Al) for Al$_2$(SO$_4$)$_3$, 1.5×10^{-4} mol/l (as Al) for PAC and 1.0×10^{-4} mol/l (as Al) for HPAC, respectively.

As seen from Figure 1, the DOM treatability by enhanced coagulation for the four coagulants was in the order of FeCl$_3$ (50%) > Al$_2$(SO$_4$)$_3$ (36%) > PAC (26%) $\approx$ HPAC (26%). It can be seen that PAC and HPAC exhibit obvious advantage at low dosage and higher pH region than the traditional salts. The traditional salts keep a continual removal of DOM with higher dose with significant lower pH. It indicates that the DOM removal can be separated
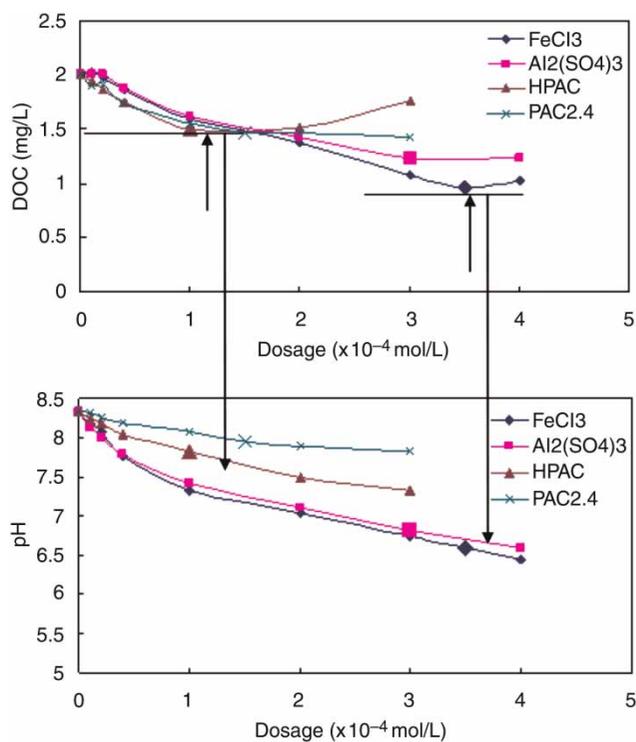

Figure 1 | The DOC and pH reduction curves versus dosage of the four coagulants.

into two stages, rapid removal and continual slow removal. The PAC exhibits efficient removal in the previous part while the traditional salts are more efficient in the latter part. It is also very important for pH control to improve DOM removal by the traditional coagulants. The DOM treatability per unit dosage (1×10^{-4} mol/l) for the four coagulants was then calculated in the order of HPAC (26.0%) > PAC (17.3%) > FeCl$_3$ (14.3%) > Al$_2$(SO$_4$)$_3$ (12.0%). It indicated that, HPAC and PAC possessed higher DOM treatability per unit dosage, whereas FeCl$_3$ and Al$_2$(SO$_4$)$_3$ possessed higher total DOM treatability.

DOM is a complex matrix composed of various organics. Representing the total DOM, the parameter DOC could not reveal the difference in coagulation characteristics between the different chemical fractions or physical fractions inside DOM (Chow *et al.* 2005). Characterizing not only the raw water but also the treated waters after enhanced coagulation of the four coagulants by chemical and physical fractionation and comparing the raw water with the treated waters could provide a further understanding of the DOM treatability and the difference between the four coagulants by revealing the removal of every chemical

and physical fractions inside the DOM of raw water in detail.

Figure 2 shows the result of chemical fractionation of the DOM in BS raw water and treated waters at the dosages needed by enhanced coagulation of the four coagulants. It could be seen that, for all coagulants, the treatability of five chemical fractions was in the order of STHoM (including HoB, HoN and HoA) > WHoA > HiM, decreasing with the shift from hydrophobic property to hydrophilic property of the chemical fraction. Like the treatability of total DOM, the treatability of every chemical fraction by enhanced coagulation of the four coagulants was also in the order of $FeCl_3$ > $Al_2(SO_4)_3$ > PAC ≈ HPAC. The treatability of STHoM by all the four coagulants was high. The treatability of WHoA by PAC and HPAC was low, whereas the treatability of WHoA by $FeCl_3$ and $Al_2(SO_4)_3$ was relatively high. The treatability of HiM by PAC and HPAC was slight, whereas, the treatability of HiM by $FeCl_3$ and $Al_2(SO_4)_3$ was relatively noticeable.

Figure 3 shows the result of physical fractionation of the DOM in BS raw water and treated waters at the dosages needed by enhanced coagulation of the four coagulants. The AMW distribution profiles are displayed in Figure 3(a), and the peaks (fractions) after peak fitting are displayed in Figure 3(b) for detailed comparison. It could be seen that, for all coagulants, the treatability of five physical fractions was in the order of Peak 5 > Peak 4 > Peak 3 > Peak 2 > Peak 1, decreasing with the decrease in AMW of the physical fraction. Like the treatability of total DOM, the treatability of every physical fraction by enhanced coagulation of the four coagulants was also in the order of $FeCl_3$ > $Al_2(SO_4)_3$ > PAC ≈ HPAC. The treatability of Peak 5 by all the four
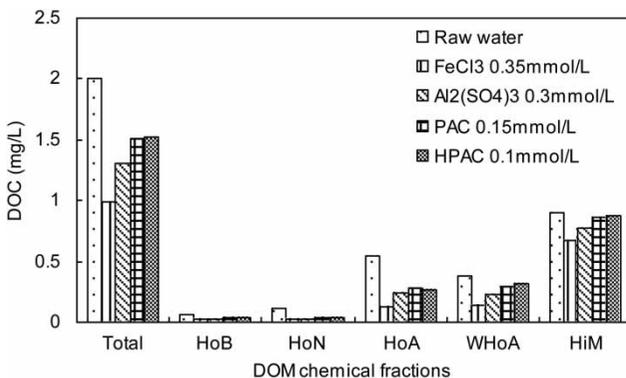

Figure 2 │ The chemical fractionation of DOM in BS raw water and treated waters.
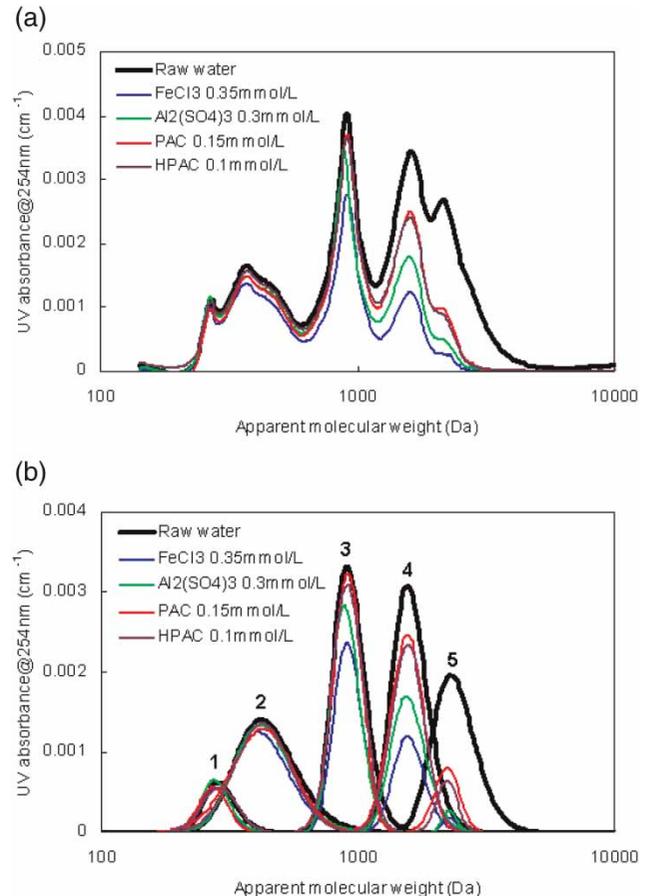

Figure 3 │ The physical fractionation of DOM in BS raw water and treated waters. (a) AMW distribution profiles. (b) Resolved peaks after peak fitting.

coagulants was high. The treatability of Peak 4 by PAC and HPAC was low, whereas, the treatability of Peak 4 by $FeCl_3$ and $Al_2(SO_4)_3$ was relatively high. The treatability of Peak 3 by PAC, HPAC and $Al_2(SO_4)_3$ was slight, whereas the treatability of Peak 3 by $FeCl_3$ was relatively noticeable. The treatability of Peak 1 and Peak 2 by all the four coagulants was slight.

The difference in treatability by enhanced coagulation of total DOM and every chemical and physical fraction between the four coagulants could be explained by the difference in coagulation mechanism between the four coagulants. For the PAC and HPAC which was pre-hydrolyzed by adding alkali during the preparation process, the pH of raw water decreased slightly after dosing (Figure 1) due to the weak hydrolysis of PAC and HPAC, and the DOM was removed mainly by the mechanism of charge neutralization (between organics and the preformed effective

hydrolyzed species) and adsorption bridging. For the traditional coagulant $FeCl_3$ and $Al_2(SO_4)_3$, the pH of raw water decreased sharply after dosing (Figure 1) due to the strong hydrolysis of $FeCl_3$ and $Al_2(SO_4)_3$, and DOM was removed mainly by mechanism of protonation, complexation and adsorption bridging when pH was depressed to acidic range (Wang 2009).

DOM treatability by enhanced coagulation of $FeCl_3$ and $Al_2(SO_4)_3$ was higher than that of PAC and HPAC because of the presence of H^+ and more effective hydrolyzed species formed *in situ* for adsorption-neutralization which resulted from the sharp decrease in pH. The DOM treatability by $FeCl_3$ was higher than $Al_2(SO_4)_3$ due to the sharper decrease in pH and higher degree of hydrolysis of $FeCl_3$, i.e. more H^+ for protonation and more effective hydrolyzed species for complexation. Although the DOM treatability by enhanced coagulation of HPAC and PAC were approximate, the dose needed by HPAC was lower than that of PAC due to that HPAC was prepared to enhance the charge neutralization and adsorption ability of PAC.

Predicting the DOM treatability by enhanced coagulation

Quantitative analysis by chemical fractions

It can be assumed that DOM removal by $FeCl_3$ (Removed DOM_{FeCl_3}) comprises portions of HoM and HiM of the raw water in Figure 2. The percentage of the removed HoM is calculated to be 72%, which is approximate to the percentage of Peak 3, Peak 4 and Peak 5 (74%) in total DOM of the BS raw water. The percentage of the removed HiM was calculated to be 25%, which is approximate to the percentage of Peak 5 in total DOM of the BS raw water (21%), i.e.

$$Removed\ DOM_{FeCl_3} = 72\% \times HoM + 25\% \times HiM$$
$$\approx (Peak\ 3\% + Peak\ 4\% + Peak\ 5\%) \times HoM$$
$$+ Peak\ 5\% \times HiM \qquad (1)$$

In the case of $Al_2(SO_4)_3$, it can also be assumed that DOM removal by $Al_2(SO_4)_3$ (Removed $DOM_{Al_2(SO_4)_3}$) comprises portions of HoM and HiM of the raw water. The

percentage of the removed HoM is calculated to be 52%, which is approximate to the percentage of Peak 4 and Peak 5 (48%) in total DOM of the BS raw water. The percentage of the removed HiM is calculated to be 15%, which is approximate to Peak5% in total DOM of the BS raw water (21%), i.e.

$$Removed\ DOM_{Al_2(SO_4)_3} = 52\% \times HoM + 15\% \times HiM$$
$$\approx (Peak\ 4\% + Peak\ 5\%) \times HoM + Peak\ 5\% \times HiM \qquad (2)$$

In the case of PAC, because HiM is only slightly removed, it can be assumed that DOM removal by PAC (Removed DOM_{PAC}) is a portion in HoM of the raw water. The percentage of the removed HoM is calculated to be 42%, which is also approximate to the Peak 4% + Peak 5% in total DOM of the BS raw water (48%), i.e.

$$Removed\ DOM_{PAC} \approx 42\% \times HoM$$
$$\approx (Peak\ 4\% + Peak\ 5\%) \times HoM \qquad (3)$$

In the case of HPAC, because HiM is only slightly removed, it can be assumed that DOM removal by HPAC (Removed DOM_{HPAC}) is a portion in HoM of the raw water. The percentage of the removed HoM is calculated to be 41%, which is also approximate to the Peak 4% + Peak 5% in total DOM of the BS raw water (48%), i.e.

$$Removed\ DOM_{HPAC} \approx 41\% \times HoM$$
$$\approx (Peak\ 4\% + Peak\ 5\%) \times HoM \qquad (4)$$

Based on the quantitative analysis of the removal of chemical fractions, the Equations (1), (2), (3) and (4) made it possible to develop models to predict the treatability, i.e. removal efficiency of total DOM in raw water by enhanced coagulation for the four coagulants.

Chemical and physical fractionations were simply to divide DOM according to two different means. Actually, each chemical fraction in raw water could be further fractionated into five physical fractions, and each physical fraction in raw water also could be further fractionated into five chemical fractions.

It was assumed that the percentages of five physical fractions (peaks) of each chemical fraction of raw water was quantitatively equal to those in total DOM of raw water. It

can be considered that, for $FeCl_3$, the removable DOM by enhanced coagulation comprises Peak 3, Peak 4 and Peak 5 of HoM and Peak 5 of HiM of the raw water. For $Al_2(SO_4)_3$, the removable DOM by enhanced coagulation comprises Peak 4 and Peak 5 of HoM and Peak 5 of HiM of the raw water. For PAC and HPAC, the removable DOM by enhanced coagulation comprises Peak 4 and Peak 5 of HoM of the raw water.

Based on the above assumptions, the removal efficiency of DOM in raw water by enhanced coagulation using the four coagulants (DOM Removal $\%_{coagulant}$) can be predicted by a set of models as follows:

$$\begin{aligned} \text{DOM Removal } \%_{FeCl_3} &= (\text{Peak 3\%} + \text{Peak 4\%} + \text{Peak 5\%}) \\ &\times \text{HoM\%} + \text{Peak 5\%} \times \text{HiM\%} \end{aligned}$$

$$(5)$$

$$\begin{aligned} \text{DOM Removal } \%_{Al_2(SO_4)_3} &= (\text{Peak 4\%} + \text{Peak 5\%}) \\ &\times \text{HoM\%} + \text{Peak 5\%} \times \text{HiM\%} \end{aligned} \tag{6}$$

$$\text{DOM Removal } \%_{PAC} = (\text{Peak 4\%} + \text{Peak 5\%}) \times \text{HoM\%} \tag{7}$$

$$\text{DOM Removal } \%_{HPAC} = (\text{Peak 4\%} + \text{Peak5 \%}) \times \text{HoM\%} \tag{8}$$

where HiM% is the percentage of hydrophilic matter in total DOM of raw water.

Quantitative analysis by physical fractions

In Figure 3(b), in the case of $FeCl_3$, because the Peak 1 and Peak 2 were only slightly removed and the Peak 5 was almost completely removed, it can be assumed that DOM removal by $FeCl_3$ (Removed DOM_{FeCl_3}) comprises Peak 5 and portions of Peak 3 and Peak 4 of raw water. The percentage of the removed Peak 3 and Peak 4 is calculated to be 51%, which is approximate to the percentage of HoM (HoM %) in total DOM of the BS raw water (55%), i.e.

$$\begin{aligned} \text{Removed DOM}_{FeCl_3} &\approx \text{Peak 5} + 51\% \times (\text{Peak 3} + \text{Peak 4}) \\ &\approx \text{Peak 5} + \text{HoM\%} \times (\text{Peak 3} + \text{Peak 4}) \end{aligned} \tag{9}$$

In the case of $Al_2(SO_4)_3$, because the Peak 1, Peak 2 and Peak 3 is only slightly removed and the Peak 5 is almost completely removed, it can be assumed that DOM removal by $Al_2(SO_4)_3$ (Removed $DOM_{Al_2(SO_4)_3}$) comprises Peak 5 and portions of Peak 4 of raw water. The percentage of the removed Peak 4 is calculated to be 48%, which is also approximate to the HoM% of the BS raw water (55%), i.e.

$$\begin{aligned} \text{Removed DOM}_{Al_2(SO_4)_3} &\approx \text{Peak 5} + 48\% \times \text{Peak 4} \\ &\approx \text{Peak 5} + \text{HoM\%} \times \text{Peak 4} \end{aligned} \tag{10}$$

In the case of PAC, because the Peak 1, Peak 2 and Peak 3 is only slightly removed, it can be assumed that DOM removal by PAC (Removed DOM_{PAC}) comprises portions of Peak 4 and Peak 5 of raw water. The percentage of the removed Peak 4 and Peak 5 is calculated to be 49%, which is also approximate to the HoM% of the BS raw water (55%), i.e.

$$\begin{aligned} \text{Removed DOM}_{PAC} &\approx 49\% \times (\text{Peak 4} + \text{Peak 5}) \\ &\approx \text{HoM\%} \times (\text{Peak 4} + \text{Peak 5}) \end{aligned} \tag{11}$$

In the case of HPAC, because the Peak 1, Peak 2 and Peak 3 is only slightly removed, it can be assumed that DOM removal by HPAC (Removed DOM_{HPAC}) comprises portions of Peak 4 and Peak 5 of raw water. The percentage of the removed Peak 4 and Peak 5 is calculated to be 52%, which is also approximate to the HoM% of the BS raw water (55%), i.e.

$$\begin{aligned} \text{Removed DOM}_{HPAC} &\approx 52\% \times (\text{Peak 4} + \text{Peak 5}) \\ &\approx \text{HoM\%} \times (\text{Peak 4} + \text{Peak 5}) \end{aligned} \tag{12}$$

Based on the quantitative analysis of the removal of physical fractions, Equations (9), (10), (11) and (12) also made it possible to develop models to predict the treatability of total DOM in raw water by enhanced coagulation for the four coagulants.

It is assumed that the percentage of five chemical fractions in each physical fraction (Peak) of raw water is quantitatively equal to those of the total DOM of raw water. It can be considered that, for $FeCl_3$, the removable

DOM by enhanced coagulation comprises the DOM of Peak 5 and the HoM of Peak 3 and Peak 4 of the raw water. For $Al_2(SO_4)_3$, the removable DOM by enhanced coagulation comprises of the DOM of Peak 5 and the HoM of Peak 4 of the raw water. For PAC and HPAC, the removable DOM by enhanced coagulation comprises the HoM of Peak 4 and Peak 5 of the raw water.

Based on the above assumptions, the removal efficiency of DOM in raw water by enhanced coagulation using the four coagulants (DOM Removal $\%_{coagulant}$) can also be predicted by a further set of models as follows:

$$\text{DOM Removal } \%_{FeCl_3} = \text{Peak 5\%} + \text{HoM\%}$$
$$\times (\text{Peak 3\%} + \text{Peak 4\%}) \qquad (13)$$

$$\text{DOM Removal } \%_{Al_2(SO_4)_3} = \text{Peak 5\%} + \text{HoM\%} \times \text{Peak 4\%} \qquad (14)$$

$$\text{DOM Removal } \%_{PAC} = \text{HoM\%} \times (\text{Peak 4\%} + \text{Peak 5\%}) \qquad (15)$$

$$\text{DOM Removal } \%_{HPAC} = \text{HoM\%} \times (\text{Peak 4\%} + \text{Peak 5\%}) \qquad (16)$$

Models (5), (6), (7) and (8) were developed on the basis of chemical fractionation, whereas models (13), (14), (15) and (16) were developed based on physical fractionation. The two sets of models provide two different ways of understanding the composition of removable DOM by enhanced coagulation. It was found that the two sets of models could be integrated indicating that two DOM characterization methods were actually consistent.

The differences in the DOM treatabilities by enhanced coagulation between the four coagulants can be found from the two sets of models. PAC is able to remove approximately the same DOM by enhanced coagulation as HPAC. $Al_2(SO_4)_3$ is able to remove more hydrophilic DOM (i.e. the HiM of Peak 5) by enhanced coagulation than PAC and HPAC. $FeCl_3$ is able to remove lower AMW DOM (i.e. the HoM of Peak 3) by enhanced coagulation than $Al_2(SO_4)_3$.

As the basis of the two sets of models, the assumption in this study is different from the actual DOM inside characteristics of raw water. The percentages of the five chemical fractions in each physical fraction of raw water and the percentages of the five physical fractions in each chemical fraction of raw water are not quantitatively equal to those in total DOM of raw water. The percentage of high AMW fractions such as Peak 5 and Peak 4 of STHoM is actually higher than that in WHoA, followed by that of HiM. Also, the percentage of more hydrophobic fraction such as STHoM of Peak 5 is actually higher than that of Peak 4, followed by that of Peak 3, Peak 2 and Peak 1 (Xie 2011; Xie et al. 2012).

Although HPSEC has been widely used for DOM characterization and is particularly well accepted by water treatment operators, the system commonly used is a UV detector. Strictly speaking, this type of detector is limited to the detection of UV absorbing compounds, and therefore it cannot detect all components of DOM. However, the chemical fractionation is based on the detection of DOC that represents all components of DOM. In this study the difference in detection of DOM between the chemical and the physical fractionation method should be a main reason for the deviation of the DOM removal efficiency prediction.

Model validation

Data for all the 29 raw water samples in 13 locations collected in three seasons were selected to validate the two sets of models. The 29 raw waters were characterized by chemical and physical fractionations, and the results are provided in previous papers (Xie 2011; Xie et al. 2012). The DOC removal efficiencies by enhanced coagulation of the four coagulants for the 29 raw waters were predicted using the models and were compared to the actual DOC removal efficiencies by enhanced coagulation determined by the jar tests shown in Figure 4.

It was found that the deviation was lower than 5% for all four coagulants, indicating that the predicted data matched well with the actual data. The predicted residual DOC values of the 29 raw waters after enhanced coagulation were also calculated, and were compared to the actual residual DOC determined by the jar tests. It was
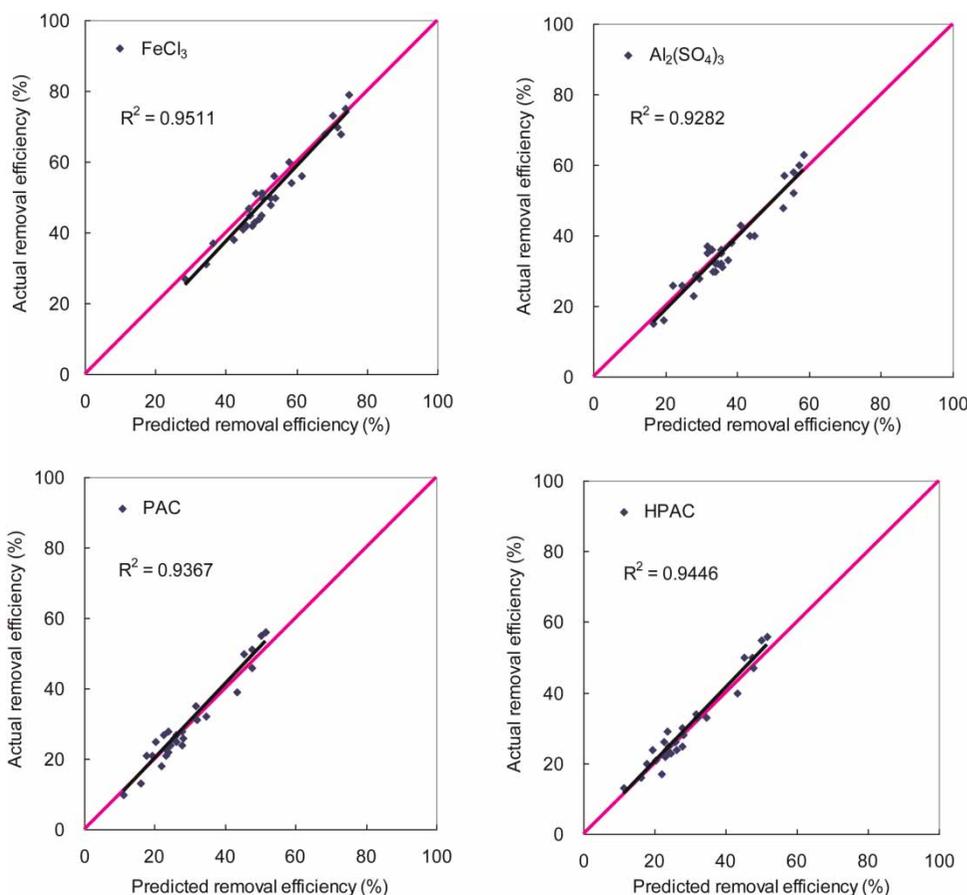
Figure 4 │ Comparison of the actual DOC removal efficiency with the predicted DOC removal efficiency by models based on quantitative analysis.

found that the deviation was lower than 0.2 mg/l for all four coagulants. The validation results of the two sets of models in this study indicate potential for the application of the models in practical operation of the drinking water treatment plant to predict the DOM treatability by enhanced coagulation without pH control. However, further validation by pilot plant tests is needed before this can be applied in a full-scale practice. The application of the models should also be validated in the site specific testing. This feed-forward prediction may also be used with the feed-back parameters of treated water quality to determine DOM treatability by enhanced coagulation.

CONCLUSIONS

The treatability of total DOM and chemical and physical fractions by enhanced coagulation using four coagulants

was found to be in the order of $FeCl_3 > Al_2(SO_4)_3 >$ $PAC \approx HPAC$. For the four coagulants, the treatability of the five chemical fractions decreased with the shift from hydrophobic to hydrophilic property, and the treatability of the five physical fractions reduced with decrease of AMW.

Two sets of DOM treatability models that describe removal efficiency by enhanced coagulation for four typical coagulants ($FeCl_3$, $Al_2(SO_4)_3$, PAC and HPAC) without pH control were developed by combining the chemical and physical DOM fractions based on the quantitative analysis.

The proposed models were validated using the data of 29 raw water samples, and the predicted data correlated well with the actual data. This indicated the potential application of the models in full-scale operation of drinking water treatment plants. However, further testing using a pilot plant is still required prior to full-scale application. In practice, the prediction of DOM treatability by enhanced coagulation

using these models should take into account site specific validation and include feed-back parameters of treated water quality.

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