Dissolved organic matter removal and disinfection byproduct formation control using ion exchange

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Abstract

Three different ion exchange resins were evaluated for their ability to remove dissolved organic matter (DOM) and reduce formation of disinfection byproducts (DBPs) formed during chlorination of surface waters sampled from the Intercoastal Waterway, Myrtle Beach, SC, USA (MB water), and the Tomhannock Reservoir, Troy, NY, USA (TMK water). At resin doses up to 600 mg/L, DOC levels were reduced from 30 to 70%, while total trihalomethane and haloacetic acid formation reactivity (i.e., TTHM/DOC and HAA9/DOC) was reduced from 40 to 70% and 50%, respectively. This suggests that ion exchange, alone or in combination with other processes, holds promise for removing a broad spectrum of DBP precursors. Chloride release was measured to confirm an ion exchange mechanism, but the possibility of physisorption and hydrogen bonding mechanisms was not ruled out. Ion exchange appeared to selectively remove high-specific UV-absorbing (i.e., $SUVA_{254}$) DOM components from the TMK water; these components also had the highest molecular weights. However, this was not the case for the MB water. The "$SUVA_{254}$ profile", the relationship between $SUVA_{254}$ and DBP formation reactivity (TTHM/DOC and HAA9/DOC), showed significant differences from the patterns observed previously for separation processes (e.g., coagulation and activated carbon adsorption) that rely primarily on hydrophobic interactions as a separation mechanism.

Keywords: NOM; DOM; DBP formation; Ion exchange; THM; HAA; SUVA

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1. Introduction

The removal of natural dissolved organic matter (DOM) has been identified as one strategy to reduce the risk of disinfection byproducts (DBPs) formed during the chlorination of natural water. This strategy is likely to increase in importance as the allowable concentrations of such DBPs as trihalomethanes (TTHMs) and haloacetic acids (HAAs) in drinking water are lowered. For example, the United State Environmental Protection Agency (USEPA) lowered the maximum contamination level (MCL) for the four THMs from 100 to 80 μg/L and has set the MCL for five HAAs (mono-, di-, and trichloroacetic acids and mono- and dibromo acetic acids, HAA5), at 60 μg/L.

DOM is a complex and heterogeneous mixture of organic compounds with various physical and chemical properties (e.g. structure, functionality, molecular weight, UV absorbance, fluorescence, etc.) [1]. Although its complex nature has hindered complete understanding of its detailed structure, it is known that aquatic DOM consists of aromatic and aliphatic moieties with carboxyl, phenolic, carbonyl, alcoholic hydroxyl, and methoxyl functional groups [2,3]. DOM components can be classified as hydrophobic and hydrophilic, defined operationally based on adsorption by XAD resin [4]. Previous research showed that hydrophobic components consist of compounds having high aromaticity [5].

Extensive work has focused on enhanced coagulation, activated carbon adsorption and membrane processes as strategies to remove DOM and thus reduce DBP formation. Pressure-driven membrane processes separate dissolved solutes according to their molecular size and charge. Although processes such as ultrafiltration have been shown to be effective in removing DOM components based on their molecular size, previous studies revealed no clear relationship between molecular size and DBP formation during chlorination [6–8]. Alum coagulation and clarification have been shown to be effective in removing large molecular components of DOM [9–11]. In contrast, smaller size components (those that can access surface area in nanometer-sized pores) were removed preferentially by activated carbon [11–13]. Both alum coagulation and activated carbon adsorption were shown to be effective in reducing DBP formation potentials by removing more hydrophobic and aromatic DOM components [7,14–16].

Many properties of DOM have been evaluated for their correlation with DBP formation potentials. Previous research has shown that UV absorbance and specific ultraviolet absorbance at 245 nm (i.e., $SUVA_{254}$ — UV absorbance normalized by dissolved organic carbon concentration) are two of the most successful parameters for this purpose [17–21]. Such success has been explained by the theory that the DOM molecules with activated aromatic structures account for most of the chlorine consumption [18]. Correlations between DBP formation and SUVA appear particularly significant for DOM fractions from the same water source, while they tend to be weaker for DOM derived from different types of sources [14,22,23].

Most correlations developed in previous studies were established by employing fractionation and/or removal techniques (e.g. coagulation, activated carbon, XAD resin adsorption) that were based on hydrophobicity, i.e. targeting more hydrophobic and aromatic DOM components. These processes generally remove high $SUVA_{254}$ components preferentially. While high $SUVA_{254}$ components have been shown to be strong precursors of THMs and HAAs, hydrophilic components with low $SUVA_{254}$ values were also shown to yield significant DBP formation during chlorination [8,15,16,21,24,25]. More importantly, some research indicated that hydrophilic fractions were more reactive with bromine than their corresponding hydrophobic fractions from the same water source [14,16]. This is important because DBP species containing bromine are thought to be more toxic than species having high chlorine substitution [26].

Anion exchange processes have received increased attention in recent years as an efficient alternative technique for removing DOM [25,27–29]. Anion exchange removes DOM components by ionic group attachment (e.g. carboxyl group) [30], with hydrophobicity playing a secondary role. Therefore, it has the potential to target more hydrophilic, charged DOM components that are not readily removed by conventional techniques [25]. Used in combination with conventional processes, it can provide the drinking water industry with another strategy to reduce DBP formation by removing a broader spectrum of precursors. Another advantage of employing anion exchange in water treatment is the ability to regenerate resins after the treatment without using a thermal process, saving energy and prolonging resin life. Heijman et al. [31] estimated the treatment costs of iron oxide, activated carbon and ion exchange in bench-scale experiments. Ion exchange was found to have the lowest cost (0.05 €/m³), compared to activated carbon (0.11 €/m³) and iron oxide (0.28 €/m³).

Despite the potential advantages, relatively little work has been done to investigate the ability of ion exchange treatment of DOM to reduce subsequent DBP formation. Although it was not their main purpose, the data presented by van Leeuwen et al. [15] showed that anion exchange was effective in reducing TTHMs (total THMs) formation. Kim and Symons [32] used an ion exchange column to study the TOC removal and THM reduction. They found that ion exchange was able to remove relatively large organic fractions, which accounted for the majority of THM production. They observed significant competition from sulfate, which displaced DOM in fixed bed adsorbers. Bolto et al. [25] concluded that ion exchange resins preferentially removed smaller, highly charged hydrophilic molecules, which also exhibited significant THM formation potentials. Singer and Bilyk [28] studied the treatment of nine waters using a combination of enhanced coagulation and a magnetic ion exchange resin

(MIEX®). The combination of treatments was very effective in removing THM and HAA precursors, and it was better than coagulation alone.

The objectives of our study were to: (1) evaluate DOM removal by ion exchange, with emphasis on the role played by the heterogeneous nature of DOM; (2) evaluate the effectiveness of ion exchange in reducing DBP formation; and, (3) examine the correlation between the $SUVA_{254}$ and the DBP formation of DOM solutions remaining after ion exchange sorption (i.e. the reactivity profile). In addition, the molecular size distribution (MSD) of DOM components was measured to provide insight into the relationships between the molecular size of DOM, its uptake by ion exchange resins, and DBP formation. The behavior of ion exchange was compared with other removal strategies in terms of DOM components targeted, ability to remove UV absorbing components, and reduction in DBP formation.

2. Materials and methods

2.1. Water samples

The water samples were collected from the Tomhannock Reservoir, Troy, NY (TMK), and the Intercoastal Waterway, Myrtle Beach, SC (MB). Natural water was filtered, softened, and concentrated in the field using a reverse osmosis unit as described elsewhere [14,33]. After transport to the lab, concentrates were adjusted to pH 4, and refrigerated at 4°C in the dark. The characteristics of water samples (after Kitis et al. [8]) are listed in Table 1.

2.2. DOM adsorption and fractionation by ion exchange resins

Three different types of anion exchange resin were used to examine the adsorption of DOM solutions. Their important characteristics are listed in Table 2. Resin selection was based on functional group type (strong and weak base) and matrix (gel and macroporous) to cover a spectrum for

Table 1
Source water properties

Parameter	Troy TMK	Myrtle Beach
DOC, mg/L	3.3	20.2
UV_{254}, cm^{-1}	0.069	0.939
$SUVA_{254}$, L/mg DOC·m	2.1	4.7
Alkalinity, mg $CaCO_3$/L	39	44
Hardness, mg $CaCO_3$/L	54	26
pH	7.0	7.2

comparison. Resins were pre-conditioned using following procedures [30]. First, the resins were extensively backwashed using DI water (tap water treated with mixed bed ion exchange, activated carbon, and microfiltration) to remove fines and low-density beads. Then they were soxhlet-extracted with methanol to remove any residual organics attached to beads during manufacturing. This was followed by two cyclic exhaustions carried out using 2-N sodium hydroxide and 2-N hydrochloric acid with intermediate and final DI water rinses. The resins were then converted into chloride form by treating with 1-N sodium chloride followed by a slow rinse (over 12 h) with 0.005-N sodium chloride. Finally, following the protocol of Husson and King [34], resins were dried at 60°C under vacuum (30 mm Hg) to constant weight and stored in a vacuum desiccator before use.

Isotherms and rate studies were conducted using the bottle-point method employing well-mixed batch reactors (amber bottles with Teflon-

lined rubber caps). The initial pH of DOM solutions was adjusted to pH 7.5 using a dilute reagent grade sodium hydroxide solution; no buffer was employed. Carboxylic groups, which comprise a large proportion of the acidic functional groups in humic and fulvic acids, are expected to be ionized at this pH. Rate studies indicated that statistically significant changes in solution DOC concentration did not occur after 10 days; therefore, this period of time was used for all isotherm experiments. Based on the results from control bottles, it was concluded that there was no measurable loss of DOM from reactors, and all changes of solution concentration were attributed to adsorption by resins. After equilibration, aliquots of the solution phase were withdrawn from the reactors, microfiltered (using pre-cleaned 0.45 micron Gelman Supor membrane filters), and analyzed for total organic carbon (Model 1010, Oceanographics International, College Station, Texas, USA) and UV absorbance (λ = 254 nm, UV_{254}) (HP 8452A, Hewlett-Packard). The supernatants obtained from the isotherms constituted DOM fractions that were used in subsequent chlorination experiments to be described below. Equilibrium pH values between 4.9 and 6.5 were measured.

2.3. Molecular weight distribution

The molecular weight distribution (MWD) of DOM solutions was measured using the HPSEC technique [12]. Polystyrene sulfonate (PSS) was used as an external standard to calibrate a Waters

Table 2
Anion exchange resin properties[a]

Name	Type	Functional group	Matrix	Exchange capacity (eq/L)	Water content (%)
Marathon A	Strong base Type I	Trimethylamine	Gel	1.30	50–60
Dowex 22	Strong base Type II	Dimethylethanolamine	Macroporous	1.20	48–56
Dowex M-43	Weak base	Polyamine	Macroporous	1.55	40–50

[a]All data was obtained from the resin manufacturer, Dow Inc. All resins are made with a styrene-divinylbenzene polymer backbone.

Protein Pak 125 column with silica based gel stationary phase operated on a HP 1100 HPLC system. Because DOM size, structure, and possible interactions with the stationary phase depend on solution pH and ionic strength, a consistent ionic strength of 0.1 M and pH 6.8 was maintained in all standard and sample solutions. The high ionic strength acts to compress or coil analyte molecules (both standards and DOM) and mitigate electrostatic interactions with the stationary phase.

2.4. Chlorination and DBP formation

Fractions obtained from DOM isotherms were chlorinated per the Uniform Formation Conditions (UFC) protocol, as proposed by Summers et al. [35]. Preliminary experiments were conducted to determine appropriate chlorine to DOC ratios to yield a residual chlorine concentration of 1.0 ± 0.4 mg/L after an incubation period of 24 ± 1 h. Duplicate samples were chlorinated under the identical conditions, one for chlorine residual and the other for DBP formation measurements. After incubation, the residual chlorine concentrations were determined using the amperometric titration method (Standard Method 4500-Cl D) with an auto-titrator (Mettler-Toledo DL55). The formed THMs were extracted with hexane and analyzed according to Standard Method 6232 B. The HAAs were reacted with acidic methanol to yield esters, extracted with methyl-tert-butyl-ether (MTBE) and analyzed according to EPA Method 552.2. Individual THM and HAA species were identified and quantified using a gas chromatography system (Agilent 6890) equipped with micro-ECD detector. Standard Method 6232 B and EPA Method 552.2 were capable of quantifying four THM (TTHM) and nine HAA (HAA9) species, respectively. TTHM and HAA9 standards were purchased (Supelco) and spiked into reagent-grade I water (DI water treated further with a Milli-Q system, Millipore Corp., Billerica, MA, USA) to prepare external standards that were then extracted and analyzed in the same manner as samples.

3. Results and discussion

Uptake of TMK DOM by the three types of resin was evaluated with two different initial DOM concentrations for each type of resin. Each isotherm was measured using 12–14 batch reactors, containing a range of resin dosages (0–600 mg/L), and the supernatant from each reactor was subsequently chlorinated and assessed for TTHM and HAA9 formation. Uptake of MB DOM was measured using only the Dowex M-43 resin; this resin was also used in further studies to investigate the MWD in DOM fractions, and the mechanism of ion exchange sorption.

3.1. Sorption of DOM

DOM is a heterogeneous mixture of components having different adsorption properties, which may result in competition among components when adsorption sites are limited [12]. The competition is higher when the absorbent dose is small relative to the initial DOM concentration (C_o), because the adsorption sites are limited compared to adsorbate amount. Under such conditions, only the most adsorbable components are removed from the solution. Only when more adsorption sites are available, i.e. more adsorbent is added, can the less preferred components be removed from solution. When different variable absorbent dose isotherms are measured with several constant initial DOM concentrations, the extent of adsorption is higher with lower initial DOM concentration (i.e., adsorption capacity increases upon dilution).

In this study, each resin was equilibrated with two different initial DOM concentrations, and the ion exchange isotherms were measured. Uptake of TMK DOM by Dowex M-43 resin is illustrated in Fig. 1a. Clearly, ion exchange removal capacity depends on both the equilibrium concentration and the initial DOM concentration. For a given C_e, the adsorption capacity, q_e increases with a decreasing initial DOM concentration, providing evidence for competition among multiple com-
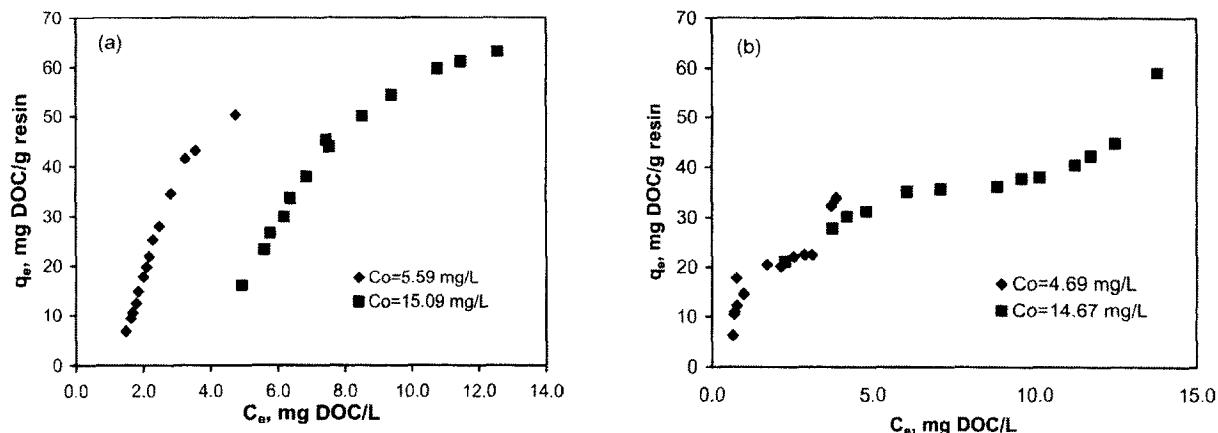
Fig. 1. Uptake of DOM by Dowex M-43 resin at two initial DOM concentrations. (a): TMK DOM; (b): MB DOM.

ponents comprising the heterogeneous DOM. Uptake of MB DOM by Dowex M-43 resin is illustrated in Fig. 1b. Here, the effect of C_o is less significant than for the TMK water, suggesting less heterogeneity among species with an affinity for the resin. It is clear from the data in Figs. 1a and 1b that the TMK water exhibits greater uptake than the MB water, over a wide range of equilibrium concentrations, and for both initial DOM concentrations. For ion exchange resins, the exchange capacity is limited by the number of functional groups. Therefore, affinity is expected to be related to the properties and number of ionic functional groups of each DOM component. Therefore, a possible explanation is the higher acidity of the TMK as compared to MB water, 11.2 vs. 8.6 meq/g DOC, as measured by acid-base titration from pH 3 to pH 7 [33].

Uptake of TMK DOM by three different resins is compared in Fig. 2. The highest extent of removal was demonstrated by the Dowex Marathon A resin, followed by Dowex M-43 resin, while Dowex 22 resin had the lowest uptake. Dowex Marathon A is a gel type, strong base anion resin. Although gel-type resins have no true pore structure, the gel matrix can swell in water, increasing its accessibility to even large organic molecules. In contrast, the macroporous structure of the Dowex M-43 and Dowex 22 resins is more rigid.
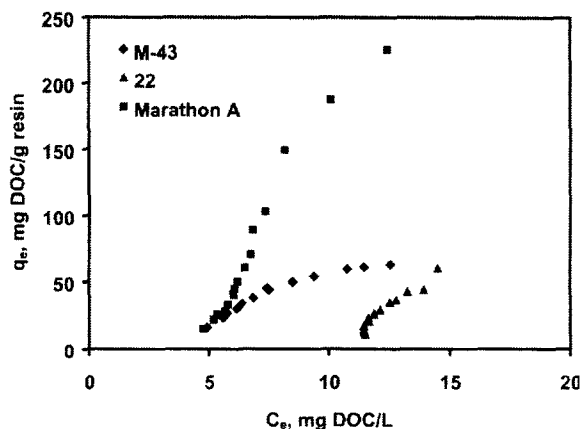

Fig. 2. Uptake of TMK DOM by Dowex M-43 (C_o = 15.12 mg DOC/L), Dowex 22 (C_o = 15.8 mg DOC/L), and Dowex Marathon A (C_o = 14.3 mg DOC/L) resins.

Although Dowex M-43 is a weak base anion resin, it has higher removal capacity than Dowex 22, which is a strong base anion resin. While the Dowex 22 resin has the lowest exchange capacity (according to manufacturer data), it is only about 8% and 23% lower than the Dowex Marathon A and M-43 resins, respectively, and does not explain the difference in observed uptake. This demonstrates that functional group basicity does not alone govern uptake; one explanation is that pore structure is also important for DOM removal.

The significance of pore structure (e.g., cross-linking, water content) has been previously demonstrated by Fu et al. [30] in six strong base anion resins.

The competition between DOM components and their removal by anion exchange resins was studied by examining the change in $SUVA_{254}$ after treatment, as shown in Fig. 3. For the TMK water shown in Fig. 3a, $SUVA_{254}$ values decrease with increasing resin dose, indicating a preferential removal of high $SUVA_{254}$ components from solution. The components that have highest affinity for the resin also appear to have the highest $SUVA_{254}$ values, although the whole water $SUVA_{254}$ value is rather low. The results for the other two types of resin are similar (data not shown). In contrast, the MB water exhibits significantly different behavior (Fig. 3b). The $SUVA_{254}$ values initially increase for the fractions with initial DOM concentration of 4.69 mg DOC/L, before decreasing with further increases in resin dose. This is similar to the changes in SUVA observed by Kitis et al. [22] as a function of granular activated carbon dosage. With a higher initial DOM concentration of 14.67 mg DOC/L, the $SUVA_{254}$ values always increase for the range of resin doses investigated here (although it seems likely that with still higher resin doses, the

$SUVA_{254}$ would decrease). The results with MB water suggest that DOM components having the highest aromaticity are not those that contain the greatest acidic functional group density and/or affinity for the resin. Alternatively, the MB water may contain a high concentration of non-UV absorbing acidic species that compete with aromatic components for sorption sites. It is also possible that background anions such as sulfate compete more strongly with UV absorbing species than with species having lower SUVA values. It is not likely that competition was from bicarbonate ion; Fu et al. [30] found that bicarbonate concentration was not changed after the ion exchange treatment, suggesting negligible competitive effects from that anion. Comparing the $SUVA_{254}$ change for TMK and MB waters, it is clear that ion exchange sorption behavior depends not only on the type of resin, but also on the DOM structure and mixture composition. For the same water source, the results are quite consistent for different ion exchange resins (although the extent of removal may be different depending on resin exchange capacity). This is consistent with the observations made by Kitis et al. [14,22] who found a similar pattern of $SUVA_{254}$ change for several different activated carbons having a wide range of surface and structural properties.
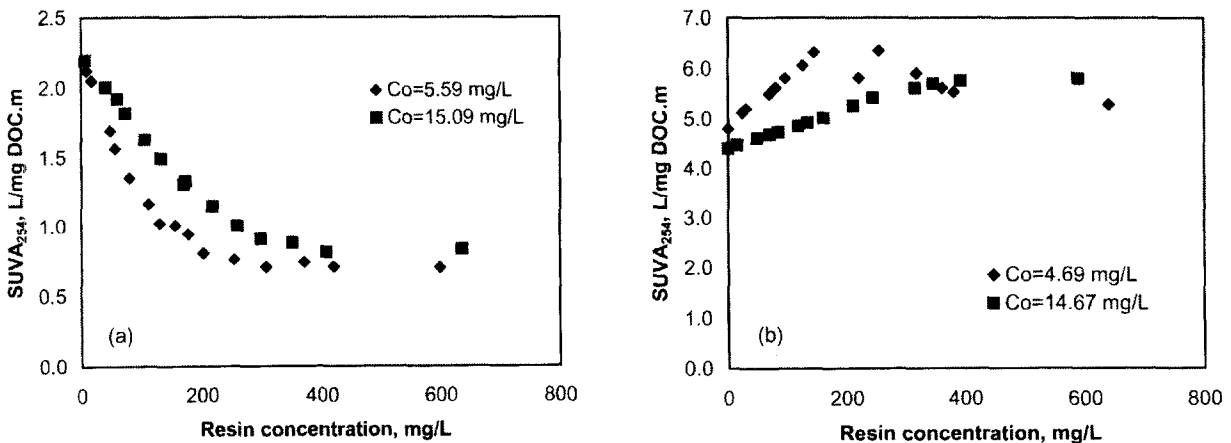

Fig. 3. Effect of resin dose on $SUVA_{254}$ of DOM components remaining in solution after sorption by Dowex M-43 resin. (a): TMK DOM; (b): MB DOM.

Kitis et al. [22] studied DOM removal from TMK and MB water using alum coagulation, XAD-8 resin adsorption, and activated carbon adsorption. The separation mechanism of these techniques is based primarily on hydrophobicity, not ionic group attachment. For the TMK water, the patterns of $SUVA_{254}$ change using alum coagulation, XAD-8 resin adsorption, and activated carbon adsorption were similar to those observed in this study using ion exchange. For the MB water, the patterns of $SUVA_{254}$ change using activated carbon adsorption and alum coagulation were most similar to those observed in this study using ion exchange. Therefore, to confirm the removal mechanism of anion exchange resin, we measured the chloride ion concentration in solution after ion exchange treatment (recall the anion exchange resins used in this research were all in chloride form). If ion exchange is the dominant mechanism, organic molecules removed by ion exchange will result in the release of an equivalent amount of chloride ion. The significant chloride ion release shown in Fig. 4 confirms the ion exchange mechanism. Therefore, as expected, ion exchange is the significant mechanism in the removal process, although some extent of pure physical adsorption may also occur. This is in
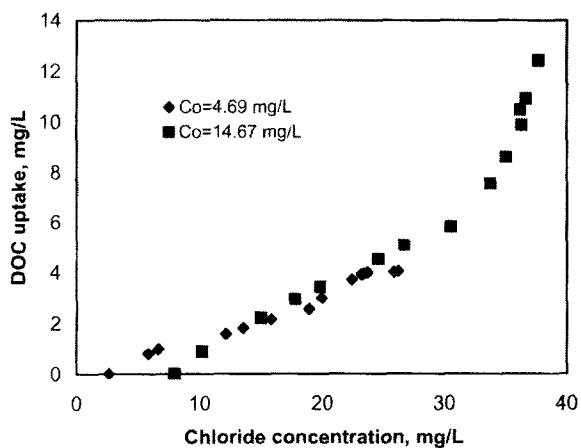
agreement with the findings of Fu et al. [30]. The non-linear pattern of chloride release corresponds to high sorbent dosages. When the sorbent dosage is large, uptake of species with lower affinity is increased; in addition, the surface coverage is low and thus it is possible that uptake by non-specific physisorption also increases. Bolto et al. [29] and Husson and King [34] propose a mechanism by which undissociated acids are removed by a hydrogen bonding mechanism; it seems likely that if such a mechanism was operative here, it would be most important when the resin dosage is large and the surface coverage is low.

Although research has been done to study the role of DOM molecular weight and MWD on the efficacy of various DOM removal techniques [9–13], and some research has found that the MWD is correlated with DBP formation [36], very few measurements have been made to examine the role of DOM molecular weight on ion exchange sorption. In this study, TMK DOM fractionated by Dowex M-43 resin was studied. The molecular weight distribution of several representative HPSEC chromatograms of DOM solution remaining after ion exchange sorption is shown in Fig 5. With an increase in resin dose, the total mass of DOM in solution is greatly reduced. In addition,

Fig. 4. Effect of DOM uptake on release of chloride by Dowex M-43 resin.
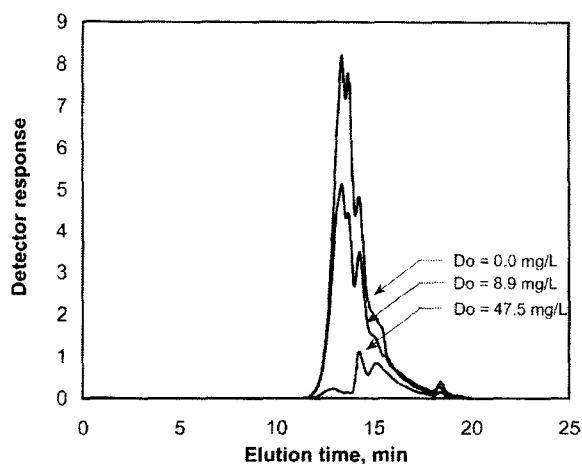

Fig. 5. Size exclusion chromatograms of DOM remaining in solution after sorption by Dowex M-43 resin. Initial DOM concentration 5.58 mg DOC/L.

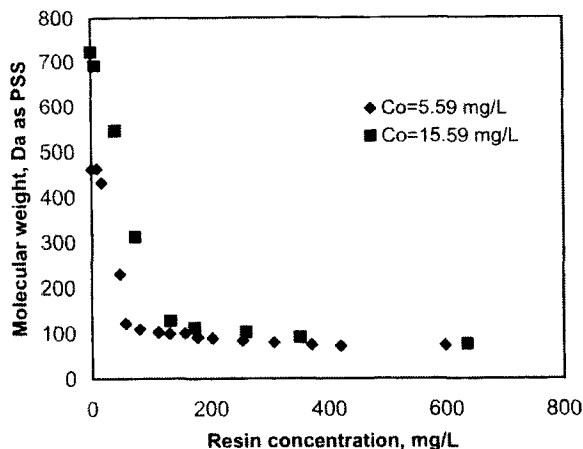Fig. 6. Effect of Dowex M-43 resin dose on the weight-averaged molecular weight of DOM [Da as PSS] remaining in remaining in solution after sorption by Dowex M-43 resin.
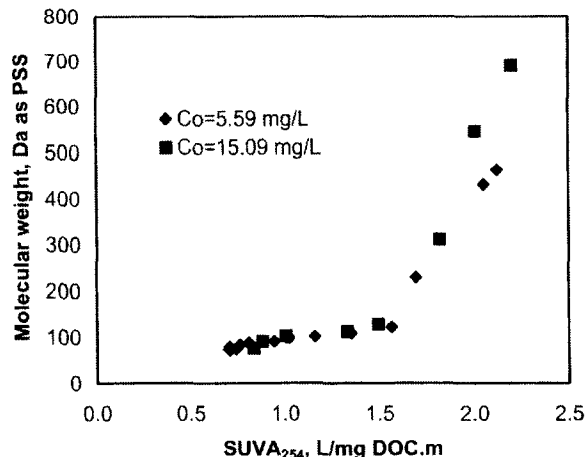

Fig. 7. Correlation of the weight-averaged molecular weight of DOM [Da as PSS] with $SUVA_{254}$ values in TMK DOM remaining in solution after sorption by Dowex M-43 resin.

response corresponding to short elution time and high MW is reduced to a greater extent than response corresponding to low MW. This indicates that DOM with large molecular weight is removed preferentially from solution, which is consistent with the result reported by van Leeuwen et al. [15]. This result is clearly illustrated in Fig. 6; with an increase in resin dose, the weight-averaged molecular weight decreases. The reduction in molecular weight with dose is greatest when the resin dose is small, indicating that larger MW species compete favorably for ion exchange sites. The DOM molecular weights are also correlated with $SUVA_{254}$ values, resulting a positive correlation, as shown in Fig. 7. Generally, molecular weight increases with increasing $SUVA_{254}$ value, i.e. molecules with the highest aromaticity are the largest molecules. This finding is consistent with the data of Chin et al. [37], although our correlation is non-linear with a significant change in slope at $SUVA_{254}$ values of about 1.5.

3.2. DBP formation

Alum coagulation, activated carbon adsorption, and XAD resin adsorption have been shown

to be effective techniques to remove DBP precursors and reduce DBP formation in water treatment by removing more hydrophobic, more aromatic components [8,14–16,22]. Although anion exchange is also capable of removing DOM, as shown in this research, we hypothesized that its effect on DBP formation could be different from the above techniques, because it employs a different separation mechanism. In our research, the DOM fractions generated from anion exchange fractionation were chlorinated, and the DBP formation was quantified.

The DBP formation normalized by equilibrium DOM concentration decreases in fractions from both water sources with an increase in resin dose. Fig. 8 shows the results for DOM solutions treated with the Dowex M-43 resin. The results for the other two resins are similar (not shown). The formation of TTHMs (formed during chlorination of TMK water) and HAA9 (formed during chlorination of MB water) was significantly lowered with increasing resin dosage; reduction in reactivity after ion exchange sorption was similar to that observed by Kitis et al. [14,22] using other physicochemical processes. The
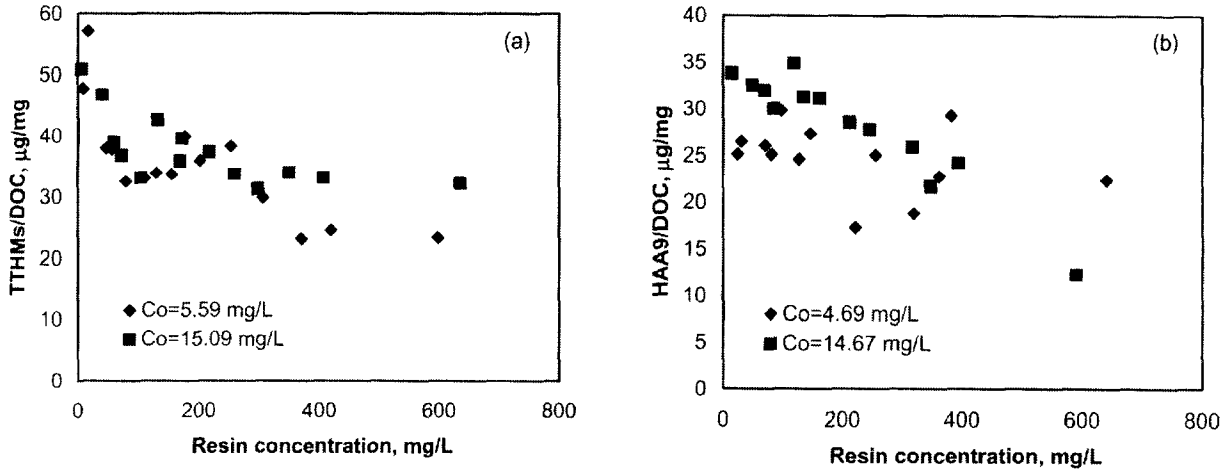
Fig. 8. The effect of resin dose on DBP formation by chlorinated DOM remaining in solution after sorption by Dowex M-43 resin. (a): TTHM formation by chlorinated TMK DOM; (b): HAA9 formation by chlorinated MB DOM.

observed trends appear somewhat weaker, and there is more scatter, in the data corresponding to low (C_o about 5 mg DOC/L) initial DOM concentrations; this is due, in part, to the low DOC after ion exchange sorption and the correspondingly low concentrations of DBPs formed during chlorination.

$SUVA_{254}$ values in DOM fractions resulting from physicochemical treatment of a single water

sample have been successfully correlated with DBP formation in conventional treatment processes, and are believed to be a robust surrogate parameter [14,22]. This correlation was evaluated for anion exchange; the results are plotted in Fig. 9. As shown in Fig. 9a for TMK water, the TTHM formation generally increases with increasing $SUVA_{254}$ values — DOM components with high aromaticity tend to form more TTHMs
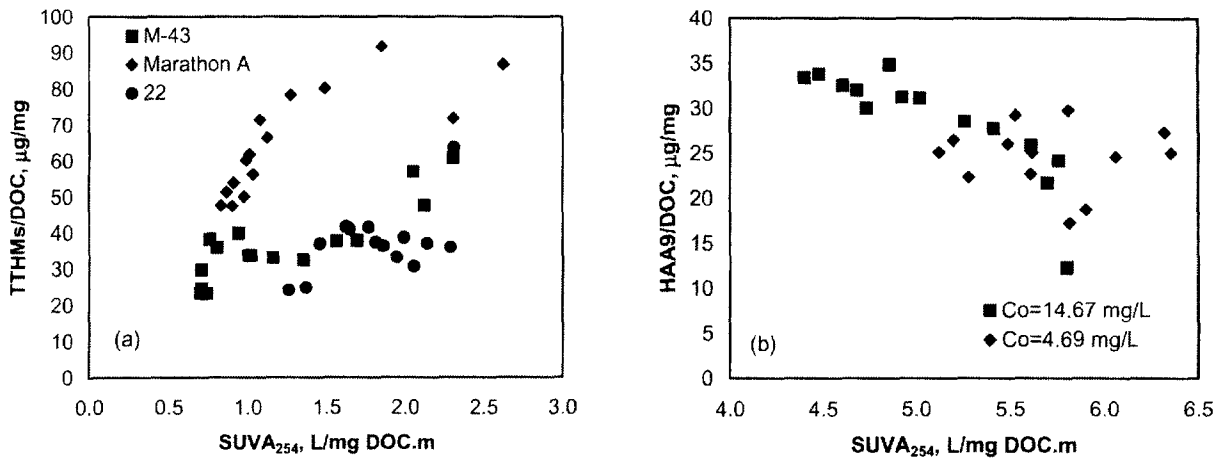

Fig. 9. Correlation of $SUVA_{254}$ with DBP formation by chlorination of DOM fractions by chlorinated DOM remaining in solution after sorption. (a): TTHM formation by TMK DOM after sorption by Dowex M-43, Dowex 22, and Dowex Marathon A resins. (b) HAA9 formation by MB DOM after sorption by Dowex M-43 resin.

during chlorination. This is in agreement with the observation by other researchers [17–21]. This positive correlation is consistent with the findings of Kitis et al. [14,22]. However, in that work a single correlation was found regardless of whether DOM solutions were treated with activated carbon, alum coagulation, or XAD resin adsorption. In contrast, the correlation found in this work is different depending on the type of resin. This is consistent with the fact that the ion exchange separation mechanism is different from other physicochemical processes that separate DOM based on hydrophobicity.

In contrast to TTHM formation by TMK water, HAA9 formation by MB water decreases somewhat with increasing $SUVA_{254}$, as shown in Fig. 9b. As discussed above, anion exchange resins preferentially remove DOM with low $SUVA_{254}$ values from MB water; however, these components are reactive in forming HAAs. Therefore, with increasing resin dosage, $SUVA_{254}$ increases and HAA reactivity decreases. This is in contrast to the findings of Kitis et al. for other physicochemical processes that separate DOM primarily by a hydrophobic mechanism, which yielded positive correlations between $SUVA_{254}$ and both THM and HAA formation. The results obtained for ion exchange suggest that the relationship between $SUVA_{254}$ and DBP reactivity may depend to some extent on the separation mechanism of the treatment process — the reactivity profile obtained may depend on the specificity of interactions with the sorbent surface. Ion exchange involves specific interactions while those of activated carbon, coagulation and XAD resin adsorption are relatively non-specific.

While different ion exchange resins may exhibit different affinity for DOM and hence different reactivity profiles, two of the three anion exchange resins reduced TTHM formation to about the same extent, with the same maximum resin dose (about 600 mg/L). As shown in Fig. 9a, the Dowex M-43 and Dowex 22 reduce TTHM/DOC level to 23.4 and 24.2 μg/mg, respectively, representing a 70% reduction in TTHM reactivity.

4. Summary

Anion exchange effectively removes DOM from solution and reduces DBP formation during chlorination. It employs a different separation mechanism from other physicochemical techniques that rely on hydrophobic interactions, such as carbon adsorption, hydrophobic resin adsorption, and coagulation. However, for the TMK water, changes in $SUVA_{254}$ and the correlation between $SUVA_{254}$ and DBP reactivity are consistent with other physicochemical processes. Still, the specificity of surface interactions that are characteristic of ion exchange processes result in some significant differences as compared to these other processes. First, the correlation between $SUVA_{254}$ and DBP reactivity may depend on resin type, presumably as a result of specific interactions with surface functional groups and/or resin structure. Second, as observed for the MB water, the correlation between $SUVA_{254}$ and DBP reactivity may be quite different as compared to other physicochemical processes. This likely results from the heterogeneous structure of DOM and/or competition among species in solution.

Acknowledgements

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