



The adsorptive removal of disinfection by-product precursors in a high-SUVA water using iron oxide-coated pumice and volcanic slag particles

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ABSTRACT

The main objective of this work was to study the effectiveness of iron oxide-coated pumice and volcanic slag particles in removing disinfection by-product (DBP) precursors from a raw drinking water source with high specific UV absorbance (SUVA₂₅₄) value. Iron oxide coating of particles significantly increased dissolved organic carbon (DOC) uptakes and decreased DBP formation after chlorination compared to uncoated particles. pH values close to neutral levels during adsorption and chlorination provided DOC, trihalomethane and haloacetic acid reductions around 60–75% employing 6 g/L coated particle dosage. Higher degree of DOC and DBP reductions (>85%) were obtained with increasing particle dose. The uptake of bromide by iron oxide surfaces was negligible and increasing bromide concentrations (up to 550 µg/L) did not negatively impact the DOC uptake. However, due to competition between natural organic matter (NOM) and bicarbonate for the iron oxide surfaces, increasing bicarbonate alkalinity levels reduced DOC uptakes. Overall, the results indicated that the iron oxide-coated pumice/slag particles are effective adsorbents to remove NOM and control DBP formation in waters with relatively high DOC and SUVA₂₅₄ levels. However, they may not be effective for waters with alkalinity levels above 250 mg CaCO₃/L.

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1. Introduction

Disinfection by-products (DBPs) are regulated in several countries due to their various negative impacts on public health [1]. To date, several studies have been conducted using cheap and locally available natural adsorbents to evaluate their effectiveness in removing natural organic matter (NOM), the main precursors of DBPs. While some of these natural materials were directly used as adsorbents, others were surface-modified to enhance their NOM uptake. One of these modifications is the coating of natural particles (e.g., sand, olivine, pumice) with iron oxides (e.g., goethite, hematite, ferrihydrite, or other iron oxides) [2–9]. The major mechanisms of NOM adsorption on iron oxide or aluminum oxide surfaces are shown to be surface complexation and/or ligand exchange reactions [7,10–13]. An increase in pH, observed as a result of adsorption is an indication of NOM replacing hydroxyls on iron oxide surfaces.

In our previous work, as an alternative to sand, natural pumice particles, abundantly present in Turkey, were used as granular support media and coated with iron oxides to investigate their adsorptive NOM removal from waters [7]. The results showed that for all the pumice particle size fractions, iron oxide coating of nat-

ural pumices significantly increased their NOM uptakes both on an adsorbent mass- and surface area-basis. Strong correlations were found among the iron contents of coated pumices and adsorption capacities, which proved that the enhanced NOM uptake was due to iron oxides bound on pumice surfaces. However, in that study, the adsorptive effectiveness of the coated pumice particles was evaluated in a natural water with relatively low specific UV absorbance (SUVA) value (SUVA_{280nm}: 1.4; SUVA_{254nm}: 1.9 L/mg-m). Natural waters with SUVA₂₅₄ values less than 2.0 generally contain mainly hydrophilic and low molecular weight NOM moieties [14–17]. On the other hand, waters with higher SUVA₂₅₄ values (i.e., >4 L/mg-m) mainly contain humic materials of higher molecular weight and hydrophobic character. Such waters after chlorination may exert higher concentrations of disinfection by-products [16,18,19]. Iron oxides have been shown to exhibit higher adsorption capacity for larger molecular size hydrophobic NOM fractions and acidic NOM fractions rich in carboxyl/hydroxyl functional groups such as aromatic moieties in humic materials [3,5,11,20]. Thus, it was hypothesized that iron oxide-coated pumice and slag particles will be more effective for NOM removal and DBP control in high-SUVA waters.

The main objective of this study was to investigate the effectiveness of iron oxide-coated pumice and volcanic slag particles in removing DBP precursors from a high-SUVA₂₅₄ water. Batch adsorption experiments were conducted using iron oxide-coated pumice and slag particles from different sources and with different

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particle size fractions. After adsorption experiments, the samples were chlorinated, and trihalomethanes (THMs) and haloacetic acids (HAAs) were measured. Speciation within the measured DBP groups was also evaluated, especially in terms of brominated DBP species. Another objective of this study was to determine the impacts of bromide, alkalinity and pH on the adsorption of NOM and subsequent DBP formation and speciation after chlorination.

2. Experimental procedures

Raw water sample was obtained from the influent of drinking water treatment plant in Myrtle Beach (MB), South Carolina (SC) USA. NOM in MB water was concentrated using a pilot-scale reverse osmosis (RO) membrane system, which allowed conducting all adsorption experiments at a constant initial dissolved organic carbon (DOC) concentration (4.1–4.2 mg/L) from one single batch of raw water. The RO concentrate was diluted to the target DOC using distilled and deionized water (DDW). Table 1 shows the selected physicochemical characteristics of the diluted MB water used in the experiments. Pumice and volcanic slag particles were obtained from the Pumice Research and Application Center at Suleyman Demirel University, Isparta, Turkey. The following pumice samples from different sources in Turkey were used in this work: Isparta (Isp), Kayseri (Kay) and Nevsehir (Nev). A volcanic slag (Cur) with basic character from Kula, Turkey was also tested. The raw pumice/slag stones were ground by a hammer-type crusher and then sieved to four different particle size fractions (<63, 63–125, 125–250, and 250–1000 μm). These fractions were coated with iron oxides using reagent grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and employing the method reported by Lai et al. [21] and Lai and Chen [6] with some modifications. The detailed coating methodology and the characteristics of uncoated and coated particles were presented in [7].

Bottle-point adsorption isotherms were conducted in 60-mL glass amber completely mixed batch reactors (CMBRs) sealed with PTFE screw-caps. After dosing pumice or slag particles, CMBRs were kept well-mixed (100rpm) in oxic conditions in a temperature-controlled orbital shaker until equilibrium was reached. Preliminary kinetic adsorption tests indicated that equilibrium was attained at around 18–24 h depending on various pumice/slag particles. Thus, 24 h contact time was used for all isotherms. The pumice/slag dosages ranged between 0.03 and 10 g/L. At the end of the isotherms, water in each bottle was filtered using a 0.45- μm membrane filter paper (polyethersulfone) to remove particles, and the supernatant was analyzed for UV_{254} absorbance and DOC to quantify NOM removal. The filter papers were pre-washed with 1000 mL of DDW prior to sample filtration, which was found to be adequate degree of washing to prevent leak of any organic material from the filter matrix. Control experiments indicated that leaks from the pre-washed filters were below the minimum quantification limit of the TOC analyzer (50 $\mu\text{g/L}$). In addition, control experiments also showed that DOC adsorption

Table 1
Physicochemical characteristics of the tested water (diluted RO concentrate of MB water).

Parameter (unit)	Value ^a
DOC (mg/L)	4.2
UV_{254} absorbance (cm^{-1})	0.201
SUVA_{254} ($\text{L}/\text{mg}\cdot\text{m}$)	4.8
Bromide ($\mu\text{g/L}$)	47
pH	7.3
Conductivity ($\mu\text{S}/\text{cm}$)	48
Total hardness (mg CaCO_3/L)	60
Alkalinity (mg CaCO_3/L)	35
Total iron (mg/L)	0.4

^a Values are the average of triplicate measurements.

onto pre-washed polyethersulfone filter papers were negligible, i.e., within standard errors of DOC measurements.

In order to investigate the impacts of bromide, alkalinity and pH on the NOM adsorption by the uncoated and coated particles and subsequent DBP formation and speciation after chlorination, isotherms were conducted with MB water at the following levels by changing the value of one parameter at a time: bromide: 47 (original water), 140, 300, and 550 $\mu\text{g/L}$; pH: 4, 6, 8, and 10; bicarbonate alkalinity: 35 (original water), 70, 150, and 280 mg CaCO_3/L . Analytical grade (>99.9% purity, EMD) sodium bromide was used to prepare stock solutions for bromide spikes to water samples. Alkalinity adjustments were performed using stock solutions of sodium bicarbonate and sodium carbonate buffers (99.9% purity, Sigma–Aldrich). Hydrochloric acid and/or sodium hydroxide solutions with various concentrations were used to adjust pH values of water samples, when necessary. All adsorption and chlorination experiments were conducted at 20 ± 1 °C. Initial DOC concentration was constant (4.1–4.2 mg/L) in all water samples before adsorption.

Chlorination of the water samples after adsorption experiments was performed according to the uniform formation condition (UFC) protocol [22]. No further buffering was employed after isotherms prior to chlorination. UFC protocol requires free chlorine residuals of 1.0 ± 0.4 mg/L after 24 h contact time. Preliminary chlorination experiments for the raw water and water samples after adsorption were conducted to determine Cl_2/DOC ratios required to provide such free chlorine residuals after 24 h contact time. The determined Cl_2/DOC ratios at constant initial DOC concentration prior to chlorination were similar, ranging from 1.5 to 2.0 mg/mg. Chlorination was performed using stock solutions prepared from sodium hypochlorite solution (5%, J.T. Baker). Residual free chlorine was measured after 24 h of incubation employing the Standard Method 4500-Cl F [23] and was quenched using stoichiometric amount of sodium sulfite prior to analysis for UV absorbance and DBPs. THMs were measured employing liquid–liquid extraction and gas chromatography (GC) equipped with an electron-capture detector, as described in USEPA method 551.1 [24]. HAAs (9 HAA species) were measured employing USEPA method 552.3 [25]. The minimum reporting limits for THM and HAA species ranged between 1 and 2.5 $\mu\text{g/L}$.

DOC concentrations were measured using a high-sensitivity TOC analyzer (TOC-VCPH, Shimadzu) employing high-temperature combustion. A UV-visible spectrophotometer (UV-1601, Shimadzu) was used to measure the UV absorbances in water samples. Bromide concentration was determined using ion chromatography according to USEPA method 300 [26]. The minimum reporting limit of bromide measurements was 25 $\mu\text{g/L}$.

3. Results and discussion

3.1. NOM removal and DBP control

Uncoated original pumice or slag particles were not effective in adsorbing NOM from MB water. Reductions in UV_{254} absorbance and DOC by the uncoated particles were only about 15 and 10%, respectively, even at high pumice/slag dosages (6–10 g/L) after 24 h contact time. Similar result (i.e., <10% removals) was obtained with the low-SUVA water in our previous study [7]. For all pumice/slag sources and their size fractions, iron oxide coating significantly increased NOM uptakes in MB water, and the NOM uptake increased with decreasing particle size (Fig. 1). The small size fraction (<63 μm) of Isp pumice exhibited the highest NOM uptake among all coated or uncoated pumices/slugs tested. The maximum decreases in UV_{254} absorbance and DOC by this coated size fraction were 96 and 83%, respectively. The best performance of the coated Isp pumice (<63 μm) was due to its highest

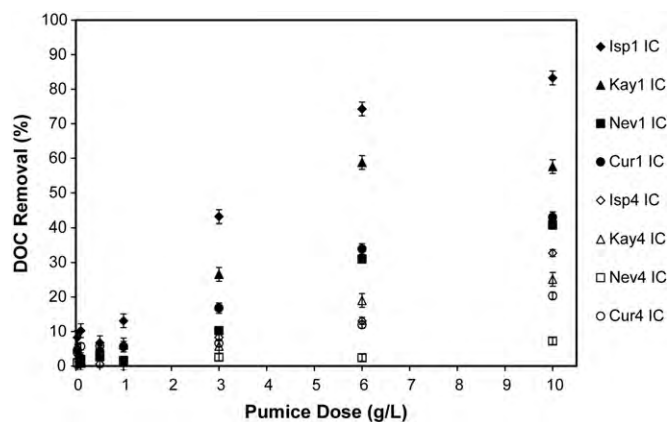


Fig. 1. DOC removals in MB water by the iron oxide-coated pumice and slag particles. (Codes of 1 and 4 in the legend represent pumice particle size fractions of <63 and 250–1000 μm , respectively. IC: iron oxide-coated. pH: 7.3. Error bars indicate 95% confidence intervals.)

specific surface area ($9.2\text{ m}^2/\text{g}$) and iron content (16.2 mg Fe/g) among all pumices/slags tested. The main factors in the adsorption were specific surface area accessible to NOM adsorption and the amount of iron oxides coated on surfaces. Various physico-chemical characteristics of all pumice particles were presented in our previous publication [7]. Mainly surface complexation–ligand exchange reactions are favored by many researchers as the mechanism of NOM adsorption on iron oxide or aluminum oxide surfaces [3,7,11–13]. It was also found that as the dosages of coated pumice particles increased SUVA₂₅₄ values of the remaining MB waters after adsorption decreased. This finding indicated that iron oxide surfaces preferentially adsorbed UV₂₅₄-absorbing fractions of NOM such as aromatic moieties and confirmed the hypothesis of this study. The preferential adsorption of UV₂₅₄-absorbing NOM fractions by iron oxide surfaces was also observed in our previous study with low-SUVA waters [7].

After adsorption experiments, filtered water samples were chlorinated according to the UFC protocol and THMs were measured (Fig. 2). Total concentration of THMs (chloroform, dichlorobromo methane (DCBM), dibromochloro methane (DBCM), bromoform) in MB raw water was $197\text{ }\mu\text{g/L}$. Consistent with the NOM removals, for all the tested pumice/slag sources and size fractions, iron oxide coating of particles significantly reduced the THM formation. For example with a dosage of 3 g/L , about 30–50% reductions in THM concentrations were achieved by the coated Isp and Kay pumice particles. THM concentrations generally decreased with increas-

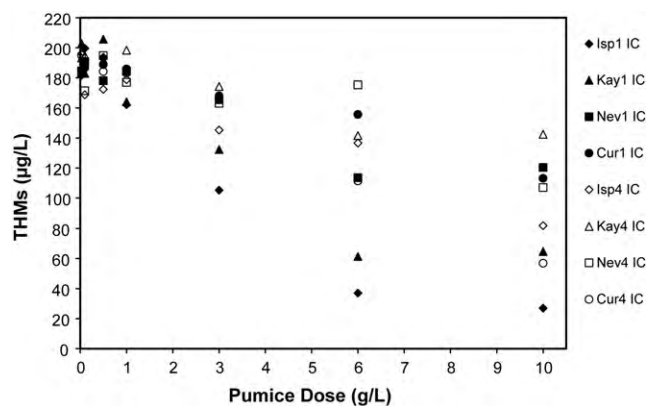


Fig. 2. THM reductions in MB water by the iron oxide-coated pumice and slag particles. (Codes of 1 and 4 in the legend represent pumice particle size fractions of <63 and 250–1000 μm , respectively. IC: iron oxide-coated. pH: 7.3. Bromide: $47\text{ }\mu\text{g/L}$.)

ing coated particle dosages. Among all tested coated pumice/slag particles, the lowest THM concentration was achieved by the small size fraction (<63 μm) of Isp pumice (THMs: $27\text{ }\mu\text{g/L}$, 10 g/L pumice dosage), corresponding to 86% reduction in THMs compared with the raw water. For each pumice/slag source, the small particle size fraction generally provided higher degree of THM reduction than the large size fraction. A linear correlation among DOC removals and THM reductions was found using the data of all particle types ($R^2 = 0.78$). Similar linear correlation was also found among UV₂₅₄ absorbance and THM reductions ($R^2 = 0.83$). Overall, the adsorptive removals of NOM by the coated particles agreed well with THM reductions. This is also consistent with the fact that higher SUVA₂₅₄ NOM components, preferentially removed by iron oxide-coated particles, play an important role in THM formations, as documented in previous studies [16,27].

Chloroform was the dominant THM specie, followed by DCBM, DBCM and bromoform, which was in agreement with chloroform being generally the dominant THM specie in many drinking waters having low bromide concentrations (i.e., <50 $\mu\text{g/L}$). The concentration ranges of chloroform, DCBM, DBCM, and bromoform found for all particle types and dosages were 190–13, 13–4, 6–2, and 4–1 $\mu\text{g/L}$, respectively. Concentrations of chloroform, DCBM, DBCM, and bromoform achieved by the coated <63 μm size fraction of Isp pumice were 13, 4, 6, and 4 $\mu\text{g/L}$, respectively (10 g/L dosage). Similar to NOM removals, this fraction provided lowest concentrations of total THMs and chloroform.

In order to investigate the role of bromide on DBP speciation, the bromine incorporation factor (BIF), which expresses the extent of brominated DBP formation, was calculated for all of the chlorinated samples. The BIF is the total moles of bromine incorporated divided by total moles of species formed in a given DBP class. Thus, for example, it defines “average” THM specie with the formula $\text{CHBr}_n\text{Cl}_{3-n}$, where n represents the BIF for THMs (THM-BIF). The value of n for THM species may vary between 0 (e.g., for chloroform) and 3 (e.g., for bromoform) [28]. The calculated THM-BIF value for the raw MB water was 0.15, indicating the dominance of chlorinated THM species (especially chloroform) in the raw water. This result was expected since raw MB water contained low bromide level ($47\text{ }\mu\text{g/L}$). It was generally found that THM-BIF values increased with increasing iron oxide-coated pumice/slag dosages. For example, increasing coated Isp pumice (<63 μm) dosage from 0.03 to 10 g/L increased THM-BIF value from 0.12 to 0.73, indicating a shift from chlorinated to brominated THM species. This was mainly due to adsorption of NOM by coated particles without the removal of bromide with increasing coated pumice/slag dosages. Even at the highest particle dosages, bromide uptakes by the iron oxide surfaces were generally less than 5%. Similarly, uncoated original pumice/slag particles with mainly silica surfaces also did not adsorb bromide ion. Therefore, Br^-/DOC and Br^-/Cl_2 ratios increased with pumice dose resulting in a shift towards brominated THM species. While Br^-/DOC ratio was $11.3\text{ }\mu\text{g/mg}$ in the raw water, it was about 6 times larger ($67.7\text{ }\mu\text{g/mg}$) in the water contacted with 10 g/L dosage of coated Isp pumice (<63 μm). Using the data of all coated particle types and size fractions, a strong positive linear correlation between THM-BIF values and Br^-/DOC ratios was found ($R^2 = 0.97$, data not shown). Furthermore, a positive non-linear correlation was found between THM-BIF values and Br^-/Cl_2 ratios (data not shown). As expected, as Br^-/DOC or Br^-/Cl_2 ratios increased, bromine became more competitive than chlorine, resulting in a shift towards brominated THM species.

3.1.1. The effect of pH

In order to determine the effect of pH on NOM adsorption and subsequent DBP formation after chlorination, batch adsorption isotherm experiments were conducted at four different pH values (4, 6, 8, and 10) using coated particles. After adsorption,

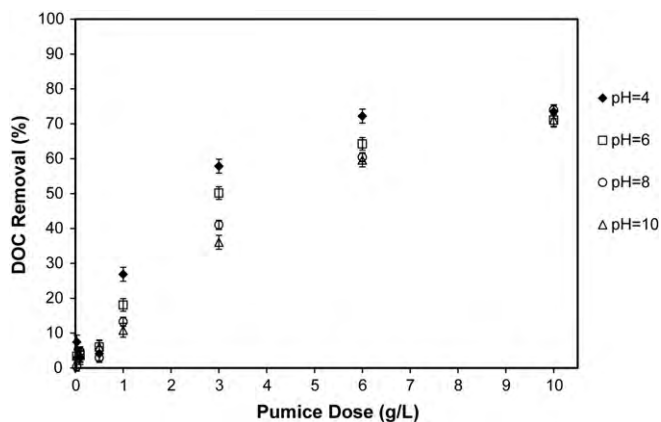


Fig. 3. The effect of pH on DOC removals by the iron oxide-coated pumice particles in MB water. (<63 μm coated Isp pumice, bromide: 47 $\mu\text{g/L}$. Error bars indicate 95% confidence intervals.)

water samples were chlorinated at the same pH values. The results showed that at constant pumice dose NOM removals increased with decreasing pH (Fig. 3). DOC removals were 58, 50, 41, and 36% at pH 4, 6, 8, and 10, respectively (3 g/L coated pumice dose). Highest DOC removals were obtained at pH 4, except for the highest pumice dosage (10 g/L), which provided similar DOC removals independent of pH. This may be due to the excessive presence of adsorption sites for NOM which may diminish the pH effect. DOC reductions around 60–65% were obtained at pH levels 6–8 in MB water employing 6 g/L coated pumice dosage.

The pH_{PZC} value (the pH at which the total net surface charge is zero) of the coated Isp pumice (<63 μm) was 6.2. At solution $\text{pH} < \text{pH}_{\text{PZC}}$, iron oxide-coated particles become dominantly positively charged. The pK_a values of acidic sites on various humic materials are generally in the range of 3–4.5 [29]. At solution pH larger than these pK_a values, functional groups (i.e., carboxylic) on humic materials start to ionize and humic materials become dominantly negatively charged. Therefore, at pH 4, it is expected that iron oxide surfaces are dominantly positively charged and humic materials are slightly negatively charged. Thus, highest extents of NOM uptakes were obtained at pH 4 as a result of electrostatic attractions. At pH 6 ($\text{pH} \approx \text{pH}_{\text{PZC}}$), the net charge of iron oxide surfaces becomes neutral while net charge of NOM becomes increasingly negative, reducing NOM uptakes compared to those at pH 4. At pH 8 and 10 ($\text{pH} > \text{pH}_{\text{PZC}}$), both iron oxide surfaces and humic materials are expected to be dominantly negatively charged. Thus, NOM uptakes further decreased at these pH values due to electrostatic repulsions. These results indicate the importance of electro-chemical properties of iron oxide surfaces and humic materials, which are strongly dependent on pH. Similar to our results, NOM adsorption onto iron oxide surfaces was higher at lower pH values (around 4–5) [3–5].

Fig. 4 shows the impacts of different pH values on DBP formations after chlorination of MB water treated with iron oxide-coated pumice particles. The results showed that pH impacted the formations of both THMs and HAAs. At constant initial DOC level and pumice dosage, increasing pH from 4 to 10 increased THM concentrations. On the other hand, reverse trend was observed for HAAs, generally consistent with the literature [30,31]. It is widely accepted in the literature that the precursors of THMs and HAAs may be different in various natural waters. The extent and kinetics of THM and HAA formations may also be affected by background water chemistry, chlorination conditions, pH, and temperature. For all pH values, increasing coated pumice dosage decreased both THM and HAA concentrations. The impacts of pH on THM and HAA formations were generally diminished by higher pumice dosages since excessive sorption sites were available to remove a great portion

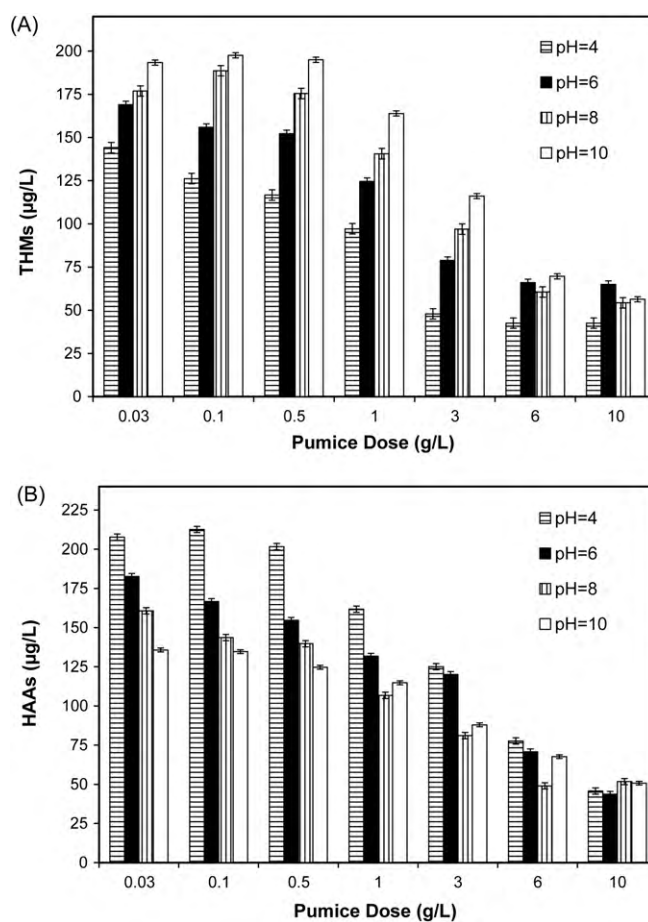


Fig. 4. The effect of pH on THM (A) and HAA (B) formations after chlorination of MB water treated with iron oxide-coated pumice particles (<63 μm coated Isp pumice, bromide: 47 $\mu\text{g/L}$. Error bars indicate 95% confidence intervals.)

of DBP precursors during adsorption at dosages higher than 3 g/L. For example, at a dosage of 10 g/L, the ranges of THM and HAA concentrations were relatively narrow for all pH values tested (43–65 and 44–52 $\mu\text{g/L}$, respectively). The ranges of THM-BIF and HAA-BIF values were 0.14–0.44 and 0.10–0.35, respectively, for all samples at different pH values. Such values are relatively low indicating the dominance of chlorinated THM or HAA species in all tested pH values. For many samples, chloroform in THMs and trichloro acetic acid (TCAA) and dichloro acetic acid (DCAA) in HAAs were generally the most dominant species. These results are consistent with previous studies in which chloroform, DCAA and especially TCAA were generally found to be dominant in waters with high-SUVA₂₅₄ values and low bromide concentrations [16,27]. Due to the fact that bromide was not adsorbed by coated pumices, both THM-BIF and HAA-BIF values increased with increasing coated pumice dosages at all pH values, indicating a shift towards brominated THM or HAA species although chlorinated species were still dominant. At constant pumice dosage, THM-BIF values decreased with increasing pH from 4 to 10. On the other hand, reverse trend was found for HAA-BIF values.

3.1.2. The effect of bromide

Adsorption experiments were conducted with raw MB water samples having four different initial bromide concentrations but at the same DOC concentration. Similar DOC removals were found at each bromide level. Maximum DOC removals obtained at 47 (original MB water), 140, 300, and 550 $\mu\text{g/L}$ bromide concentrations were 83, 76, 78, and 78%, respectively. Furthermore, bromide measure-

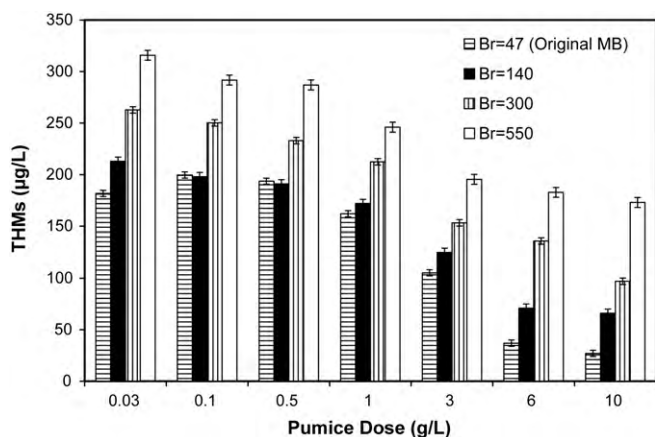


Fig. 5. The effect of bromide concentration on THM formations after chlorination of MB water treated with iron oxide-coated pumice particles ($63 \mu\text{m}$ coated lsp pumice, pH: 7.3, bromide: $\mu\text{g/L}$. Error bars indicate 95% confidence intervals.)

ments in MB water also indicated that bromide uptake by the iron oxide-coated particles was negligible after 24 h of contact time; the concentration differences among initial value and after adsorption were always less than $7 \mu\text{g/L}$. Overall, the results indicated that iron oxide surfaces do not have adsorption affinity for bromide and that bromide cannot compete with NOM for sorption sites, even at concentrations ($550 \mu\text{g/L}$) much higher than those at typical natural surface waters. It should also be noted that while DOC concentrations were in mg/L levels, bromide concentrations were in $\mu\text{g/L}$ levels.

Fig. 5 shows the impacts of initial bromide concentrations on THM formation. At constant coated pumice dose, total THM concentrations increased with increasing initial bromide concentration while all other factors were constant. Same trend was also observed for HAAs. Maximum total THM and HAA concentrations were found at $550 \mu\text{g/L}$ bromide concentration for all pumice dosages. These results indicated that waters with very high bromide concentrations may be problematic in meeting THM or HAA standards, especially if they are also high-SUVA₂₅₄ waters. As discussed previously, both THM and HAA concentrations decreased with increasing coated pumice dosages for each bromide level. As the initial bromide concentration was increased from 47 to $550 \mu\text{g/L}$, the concentrations of brominated THM and HAA species increased. Furthermore, the spectrum of HAA species also changed. For example, at initial bromide concentrations of 47 and $140 \mu\text{g/L}$, only 7 HAA species were detected. On the other hand, the other two HAA species, tribromo- and dibromo acetic acid, were also detected at 300 and $550 \mu\text{g/L}$ bromide concentrations. While the maximum THM-BIF value was 0.73 in the original MB water, values as high as 1.80 was found with $550 \mu\text{g/L}$ bromide level. Maximum HAA-BIF values were 0.23 and 0.80 for 47 (original water) and $550 \mu\text{g/L}$ bromide levels, respectively. It was found that THM-BIF values were generally higher than HAA-BIF values at constant conditions. Furthermore, as the initial bromide levels were increased the relative increases of THM-BIF values were higher than those of HAA-BIF, suggesting that bromide had more impacts on THMs formation. Therefore, the extent of shifts towards brominated species was larger for THMs than those of HAAs.

3.1.3. The effect of alkalinity

Fig. 6 shows the impact of bicarbonate alkalinity levels on NOM adsorption in MB water while all other variables were kept constant. NOM uptakes decreased with increasing alkalinity levels from 35 to $280 \text{ mg CaCO}_3/\text{L}$ at each pumice dosage. However, the negative impacts of bicarbonate on NOM uptakes were more pro-

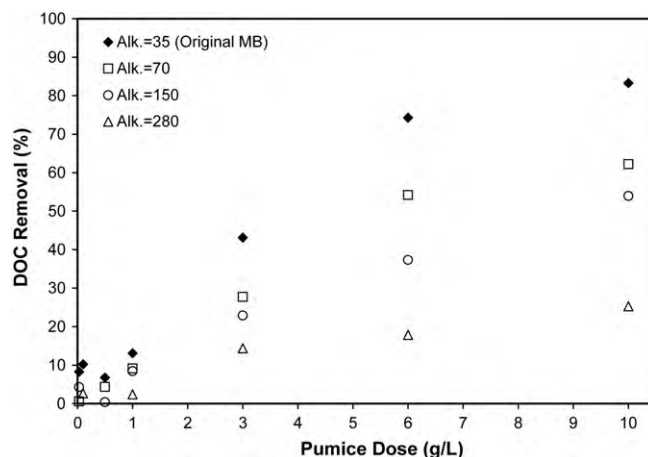


Fig. 6. The effect of alkalinity (bicarbonate) concentration on DOC removals by the iron oxide-coated pumice particles in MB water ($63 \mu\text{m}$ coated lsp pumice, pH: 8.0–8.2, bromide: $47 \mu\text{g/L}$, alkalinity: $\text{mg CaCO}_3/\text{L}$.)

nounced at higher pumice dosages (i.e., $>3 \text{ g/L}$). Maximum DOC removals achieved by the highest coated pumice dosages were 83, 62, 54, and 25% for 35 (original water), 70, 150, and $280 \text{ mg CaCO}_3/\text{L}$ bicarbonate alkalinity concentrations, respectively. These data clearly indicate that bicarbonate competes with NOM for iron oxide surfaces. In addition, bicarbonate concentrations are much higher than DOC concentration. Alkalinity experiments were conducted at pH 8.0–8.2. NOM fractions, especially humic materials, are expected to have dominantly negative surface charge due to ionization of acidic functional groups at this pH. Similarly, bicarbonate being the dominant carbonate specie at pH 8.0–8.2, is also an anion. Thus, NOM moieties and bicarbonate having both anionic properties may have similar electrostatic relations with iron oxide surfaces. Furthermore, bicarbonate may form surface complexes with iron oxides, similar to complexes formed by phosphate. Such complexes may also change the surface properties of iron oxides. Since increasing bicarbonate concentrations reduced DOC removals, it also resulted in more DBP formations after chlorination. For example, at constant pumice dosage, increasing bicarbonate alkalinity concentration from 35 to $280 \text{ mg CaCO}_3/\text{L}$ resulted in about 20–30% more THM and HAA concentrations. Overall, the results suggested that bicarbonate negatively impacts NOM removal and subsequent DBP control by the iron oxide-coated pumice process.

4. Conclusions

Due to their highly porous structures, availability, abundance, and low cost, the use of natural or modified pumice/volcanic slag particles may be considered in various treatment processes including filtration, adsorption, catalytic oxidation, etc. In this study, different natural pumice and volcanic slag particles obtained from various parts of Turkey were coated with iron oxides. Iron oxide coating of particles significantly increased NOM uptakes compared to uncoated particles. Iron oxide surfaces preferentially adsorbed UV₂₅₄-absorbing fractions of NOM, and they were effective in removing both THM and HAA precursors from waters. As the specific surface area and iron contents of the particles increased both NOM uptake and further DBP reductions also increased. pH affected NOM uptake and further DBP control performance of iron oxide-coated particles, mainly due to pH dependence of electro-chemical properties of iron oxides surfaces and humic materials. Although pH 4 was found to provide highest DOC removal by the iron oxide-coated pumice/slag particles, such pH level may not be appropriate for practical treatment applications due to chemical demands and

associated costs to decrease pH, potential release of iron from coated surfaces, and other infrastructure corrosion issues. Therefore, when evaluated overall in terms of DOC removal and further DBP control, neutral pH values around 6–8 are suggested for the iron oxide-coated pumice/slag process. These pH levels provided DOC and THM/HAA reductions around 60–75% employing 6 g/L coated particle dosage in the tested MB water. The results indicated that iron oxide surfaces do not have adsorption affinity for bromide and that bromide cannot compete with NOM for sorption sites, even at concentrations (550 µg/L) much higher than those at typical natural surface waters. At constant coated particle dosage, total THM and HAA concentrations increased with increasing initial bromide concentration while all other factors were constant. A shift towards the formation of brominated DBP species was also found with increasing bromide concentrations. It was found that bicarbonate alkalinity negatively impacts NOM uptake and further DBP control by the iron oxide-coated particles, due to competition among NOM and bicarbonate for the iron oxide surfaces. Control experiments showed that the coated iron oxides on particle surfaces were stable and iron leak to waters was negligible at pH values 5.5–8.5 even with the highest coated particle dosages. On the other hand, at pH 4, about 3–5 mg/L of total iron was released to the solution after 10 g/L of coated pumice dosage.

Overall, the results suggested that the iron oxide-coated pumice/slag particles are effective adsorbents to remove NOM and control DBP formation in waters with relatively high DOC and SUVA₂₅₄ levels. However, the iron oxide-coated pumice/slag process may not be effective for waters with alkalinity levels above 250 mg CaCO₃/L. Further studies will be conducted in the next phase of the project to evaluate the regeneration efficiency of the coated particles after use both in completely mixed suspended and fixed-bed reactor configurations.

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