Aqueous natural organic matter removal by quaternary-ammonium-compound-modified iron-oxide-coated sand

Chunli Ding, Chii Shang and Yujung Chang

ABSTRACT

In this study, modification of iron-oxide-coated sand (IOCS) with three quaternary ammonium compounds (QACs) was tested as a means to improve the removal of aqueous natural organic matter (NOM) by IOCS. The assessment was conducted in batch, isotherm setup with changes in types and concentrations of QACs, modification pH, additions of H$_2$O$_2$ during modification, and adsorption pH. IOCS modification with long chain QACs, including hexadecyltrimethylammonium bromide (HDTMA) and hexadecylbenzyldimethylammonium chloride (HDBDMA) significantly increased the adsorption of NOM, while coating IOCS with short chain QAC, tetrapropylammonium chloride (TPA) had no positive effect. The enhancement increased with increasing pH and increasing QAC concentration used during modification. Co-additions of long chain QACs with H$_2$O$_2$ during modification could further improve NOM adsorption. Modification of IOCS with 10.0 mM HDTMA at pH 9.9 with the 0.2% H$_2$O$_2$ addition doubled NOM adsorption capacity on IOCS at pH 9.1. The results presented here suggest that the modification of IOCS using long chain QACs can enhance NOM removal by IOCS during drinking water treatment.

Key words | adsorption, iron-oxide-coated sand, natural organic matter, quaternary ammonium compounds

INTRODUCTION

In recent years, water quality and treatment issues related to NOM have gained a lot of focus around the world. NOM is removed from drinking water for a number of reasons. The primary concern for the drinking water community is that NOM can serve as a precursor in the formation of potentially harmful disinfection by-products (DBPs). During purification and disinfection of drinking water, humic substances in natural water react with chlorine to produce trihalomethanes (THMs), haloacetic acids (HAAs), and other halogenated DBPs, a number of which have been linked to cancers (Singer 1999). Although other disinfectants such as ozone, UV, monochloramine and chlorine dioxide are also being considered for DBP control, removing DBPs and/or their precursors (e.g. NOM) is commonly needed to meet more stringent water quality standards. Improving the removal of NOM is also of importance to minimize membrane fouling and growth of pathogens in distribution systems.

Considerable emphasis has been placed on better removal of aqueous NOM both by optimizing conventional processes and by developing new processes over the last few years. Commonly used technologies for aqueous NOM removal include enhanced coagulation, membrane filtration, ozonation/biofiltration and adsorption. Adsorption on low-cost media is an attractive means for NOM removal from water. Activated carbon, anion exchange resins, and metal oxides are reported effective adsorbents for NOM removal. Iron-oxide-coated media operated in adsorptive filtration processes (Chang et al. 1997; Korshin et al. 1997; McMeen & Benjamin 1997; Lai & Chen 2001)

demonstrate an easier mode of operation to overcome the difficulties in collection and regeneration of powder iron oxide (Edwards & Benjamin 1989; Bailey et al. 1992; Benjamin et al. 1996). IOCS is also found to be much less expensive and easier to prepare, regenerate, and apply, compared to granular activated carbon (GAC) and other commercially available adsorbents. However, NOM adsorption by IOCS is strongly pH dependent and often yields a maximum at slightly acidic pH (usually around 4–5) but is less favored at neutral and basic pH (Chang et al. 1997; Lai & Chen 2001). As a result, controlling pH in the acidic range is needed but might not be cost-effective for water with high alkalinity that requires large amounts of acid additions. Therefore, modification of IOCS to function well at wider pH will benefit NOM adsorption by IOCS and make IOCS more competitive to other adsorbents for the purpose of NOM removal.

Surfactant (QAC) adsorption is a common way to modify adsorbent surfaces to achieve better removal of organic contaminants (Smith & Galan 1995; Lo et al. 1996; Zhu & Chen 2000). Co-additions of a small quantity of a cationic surfactant, benzyltrimethylammonium bromide (BTMA) and bentonite form organobentonite flocs that bind dissolved organic matter (DOM) (Shen 2002). Bolto et al. (2001) applied quaternary-ammonium-containing cationic polymers in combination with suspended metal oxides to enhance coagulation of NOM by both adsorption of NOM and precipitation of the NOM-polymer complex. Kim & Walker (1994) adsorbed iron oxide particles with cationic polymers at high pH to reverse the negative surface charge of the bare iron oxides at pH 9.5, resulting in doubling the capacity of humic acid adsorption at low ionic strength. These past studies motivated us to use QACs to modify the surface of IOCS. We hypothesized that creating a more positive surface and/or providing more organophilic sites with cationic surfactants is a possible and good solution to improve aqueous NOM adsorption by IOCS at neutral and basic pH. We examine the hypothesis by batch, isotherm studies with changes of parameters including the types and concentrations of QACs, modification pH, additions of H2O2 during modification, and pH in NOM adsorption.

### METHODS

#### Solution preparation

All chemicals used were reagent grade, unless otherwise noted. Suwannee NOM (RO isolate) obtained from International Humic Substance Society (IHSS) was diluted and used to represent aqueous NOM. Tetrapropylammonium chloride (TPA ≥ 98% pure), hexadecyltrimethylammonium bromide (HDTMA ≥ 98% pure) and hexadecylbenzyldimethylammonium chloride (HDBDMA ≥ 98% pure) tested were obtained from Sigma-Aldrich. The alkylammonium cations of these salts provide wide ranges of molecular sizes and configurations of QACs as shown in Table 1. Ultrapure water produced by a Barnstead NANOpure Diamond system was used in all cases.

#### Preparation and modification of IOCS

Iron-oxide-coated sand (IOCS) was synthesized through the procedure described in Chang et al. (1997). In brief, sands of 0.60–0.85 mm in diameter (20–30 mesh) were first cleaned and soaked in a 50 percent sulfuric acid solution for at least 24 h and rinsed with de-ionized water until the pH of the rinse water exceeded 5.0. The washed sands were then dried at 105°C for 24 h and rinsed with de-ionized water until the pH of the rinse water exceeded 5.0. The washed sands were then dried at 105°C for 24 h before storing in containers for future use. To coat the cleaned sands, iron oxide sludge was prepared with hydrated ferric chloride (200 g) and 200 mL of ultra pure water, with gradual additions of sodium hydroxide (10 M, 185 mL) followed by oven heating at 110°C for 20–21 h. The iron oxide sludge (water content of

<table>
<thead>
<tr>
<th>QACs</th>
<th>Abbreviations</th>
<th>Molecular Weight (g)</th>
<th>Formula</th>
</tr>
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<tbody>
<tr>
<td>Tetrapropylammonium chloride</td>
<td>TPA</td>
<td>221.82</td>
<td>C12H28N·Cl</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium bromide</td>
<td>HDTMA</td>
<td>364.46</td>
<td>C19H42N·Br</td>
</tr>
<tr>
<td>Hexadecylbenzyldimethylammonium chloride</td>
<td>HDBDMA</td>
<td>396.09</td>
<td>C24H46N·Cl</td>
</tr>
</tbody>
</table>
the sludge was about 45 percent) was mixed with sand grains at a sludge-to-sand weight ratio of 0.1 and the mixture was solidified by heating at 110°C for 20 h. Three coating cycles were applied to increase the amount of iron attached to the surface.

The surface modification of IOCS with QACs was achieved by adsorption. A portion of the IOCS was mixed with an aliquot volume of one QAC solution and the mixture was agitated on a horizontal shaker at 140 rpm for 2 h at room temperature. The 2-h time was selected based on our preliminary kinetic data showing that adsorption of QACs onto IOCS is fast and can reach equilibrium within 2 h. At the end of mixing, the solution was decanted and the solids were washed with ultra pure water for 4 times (50 mL each) to remove the loosely attached QACs and then dried at 110°C for 2 h. The dried QAC-modified IOCS was stored in capped bottles until use. The quantities of QAC adsorbed on IOCS with different operational variables (QAC types and concentrations, pH, and H₂O₂ additions) during modification were studied by establishing and comparing the adsorption isotherms obtained under different conditions. A few modified IOCS were then selected for further NOM adsorption assessments. No buffer is added during the modification and the solution pH was adjusted and maintained with diluted NaOH or HCl.

**NOM adsorption**

In NOM adsorption tests, an aliquot amount of modified or unmodified IOCS was added to a 100 mL NOM solution in a 250 mL flask where both the amount of IOCS and the concentration of NOM varied to obtain the adsorption isotherm. The ionic strength of the NOM solution was adjusted to 0.1 N with NaNO₃. The solution pH was maintained at 4.2 and 9.1 (buffered with 0.005 N carbonate). The mixture was mixed on a horizontal shaker at 140 rpm and at 23 ± 2°C. Adsorption isotherm was obtained after 20-h equilibrium, which was verified by kinetic studies.

**Analytical method**

Concentrations of QACs in solutions (filtered through 0.22 μm filters) were determined by an ion chromatograph equipped with a Surfactant/R column (Alltech), an Alltech 335 suppressor module, and a conductivity detector according to Alltech Application Note #A0019 (1997). Concentrations of NOM in solutions (filtered through 0.45 μm filters) were determined by standardized UV₂₅₄ absorbance. The UV absorbance was corrected in data analysis to remove the effects from pH and residual iron concentrations. The absorbance of UV₂₅₄ attributable to residual TPA, HDTMA, and HDBDMA in all solutions was negligible, compared to that attributable to NOM.

**RESULTS AND DISCUSSION**

**QAC adsorption on IOCS**

The affinity between QACs and IOCS was first examined. The adsorption of TPA, HDTMA and HDBDMA on IOCS at pH 10.0 ± 0.2 is shown in Figure 1. The adsorption of TPA on IOCS was very limited at pH 4 to pH 12. The adsorption of HDTMA and HDBDMA on IOCS was much better than that of TPA (Figure 1) and increasing pH increased the adsorption of HDTMA (Figure 2) and HDBDMA (not shown). Previous studies have demonstrated that the electrostatic interaction is an important mechanism in controlling the adsorption of QACs on clay minerals (Smith & Galan 1995). QACs are also known to be hydrogen bonded to anionic surfaces by interactions with absorbed water on the surfaces (Ohlhausen & Ludwiq 2006). However, if the QAC adsorption on IOCS was solely electrostatic in nature, TPA would be more effectively...
adsorbed to IOCS. Thus, the findings discussed above suggest that both electrostatic and non-electrostatic interactions are important in this QAC-IOCS system.

Figure 1 also shows that at low concentrations, there is a marked increase in HDTMA and HDBDMA adsorption. With increasing QAC concentration, the adsorption gradually reaches a plateau. This characteristic is in agreement with the findings of Ghosh et al. (1995) in investigation of the adsorption of some quaternary ammonium salts on silica gel. At low bulk concentrations, there exists an electrostatic attraction between the charged surface and the ionic surfactant. After the first surface layer is built up, a hydrophobic attraction between the adsorbed surfactant and the incoming surfactant is possible. The adsorption is complete when the surface coverage is fully saturated, which has been reported to occur around or above the bulk critical micelle concentration (CMC) (Ghosh et al. 1995). Based on these results, three concentrations, corresponding to low and medium bulk concentrations and a high concentration far above CMC in equilibrium were chosen in later evaluation of the effect of QAC concentrations on NOM adsorption by modified IOCS.

Ohlhausen & Ludwiq (2006) also reported that organic cations can be better bonded to the anionic surface that is associated with hydroperoxide ions than that is associated with hydroxide ions. Thus, we hypothesize that hydrogen peroxide additions during QAC adsorption may provide improved bonding between QACs and IOCS at pH higher than the point of zero charge of IOCS (around pH 7.5) where the IOCS surface is negatively charged. The verification test results are shown in Figure 2. However, H₂O₂ additions did not seem to increase the quantities of HDTMA and HDBDMA adsorbed on IOCS.

**NOM adsorption on QAC-modified IOCS**

The adsorption of NOM on QAC-modified IOCS was carried out to evaluate the effects of the QAC modification on NOM removal. Figure 3 displays the adsorption isotherms of NOM at pH 9.1 obtained with unmodified IOCS and IOCS modified with TPA, HDTMA and HDBDMA. The initial concentrations of QACs used during modification were 10.0 mM, which gave an equilibrium concentration far above CMC, and the pH was 10.0 ± 0.2. As shown, NOM adsorption on unmodified IOCS (filled circles) increased with increasing equilibrium concentrations and reached a plateau, which indicates monolayer coverage of NOM on IOCS and is well fitted by the Langmuir isotherm. Coating IOCS with short-chain QAC (TPA) provided little or no enhancement on the adsorption of NOM (open squares). On the other hand, when IOCS was coated with long-chain QACs, HDTMA (open triangles) and HDBDMA (open circles), the maximum amounts of NOM adsorbed, expressed as mg TOC/g IOCS, significantly increased, from 0.9 mg/g on unmodified IOCS to 1.2 mg/g on HDTMA-modified IOCS and 1.7 mg/g
on HDBDMA-modified IOCS. The shape of the NOM adsorption isotherms on TPA- and HDTMA-modified IOCS is also of Langmuir type. However, the NOM adsorption isotherm on HDBDMA-modified IOCS is linear, which indicates that NOM adsorption on this adsorbent is mostly due to partition. However, it should be noted that iron oxide detachment was observed when HDBDMA-modified IOCS was used for NOM adsorption. The reason attributable to this observation is unknown and needs further investigation. The effect of initial HDTMA concentrations used during modification on NOM adsorption on HDTMA-modified IOCS was also studied. As expected, the adsorption capacity increased with increasing initial concentration (from 0 to 10.0 mM) of HDTMA used during modification (data not shown). Modification with 10.0 mM HDTMA gave the largest increase in NOM adsorption (1.4 times), compared to the data obtained with unmodified IOCS.

Adsorption of NOM at pH 9.1 on IOCS modified at pH 3.3, 10.0 ± 0.2 and 11.5 ± 0.1 with 6.0 mM HDTMA is shown in Figure 4. The maximum amount of NOM adsorbed on IOCS modified at pH 3.3 was almost the same as that adsorbed on unmodified IOCS, roughly 0.9 mg/g. The quantities of NOM adsorbed on IOCS increased to around 1.2 and 1.1 mg/g on IOCS modified at pH 10.0 and 11.5, respectively. This is consistent with the pH-dependent QAC adsorption results, which show that HDTMA adsorption on IOCS is higher at alkaline pH than at acid pH. The higher quantities of QACs available on the modified IOCS surface yield the better NOM adsorption.

Figure 5 shows the effect of H$_2$O$_2$ additions during modification on NOM adsorption. It should be recalled that a 0.2% H$_2$O$_2$ addition didn’t notably increase the quantity of QAC adsorbed on IOCS. Nevertheless, H$_2$O$_2$ additions unexpectedly further enhanced the NOM adsorption and almost doubled the NOM adsorption capacity at pH 9.1, compared to the NOM adsorption achieved with unmodified IOCS. However, further increases of concentrations of H$_2$O$_2$ from 0.2 to 1.0% did not further enhance NOM adsorption much, especially at higher NOM concentrations.

To examine the performance of the QAC-modified IOCS on NOM removal at different pH, NOM adsorption isotherms were studied and obtained at pH 4.2 and 9.1 to present the two extreme cases possible encountered in water production (Figure 6). At pH 4.2, the modification increased the maximum quantity of NOM adsorption from 1.9 mg/g to 3.1 mg/g. At pH 9.1, the modification increased the maximum quantity of NOM adsorption from 0.9 mg/g to 1.6 mg/g. The percentage of enhancement remains relatively similar at different pH. The results indicate that the pH dependency of NOM adsorption on modified IOCS remains the same, although the quantities of that increase.

A number of mechanisms may influence the adsorption of NOM on the QAC-modified IOCS. Coating IOCS with cationic QACs will influence both chemical and electrostatic interactions between NOM and the IOCS surface.
To gain better insight into the role of electrostatic interactions in controlling NOM adsorption on QAC-modified IOCS, tests of chromate adsorption on QAC-modified IOCS were conducted. Our rationale is that chromate adsorption on IOCS relies primarily on electrostatic interaction but not partitioning (hydrophobic interaction). If the enhancement of NOM adsorption on QAC-modified IOCS was primarily achieved/controlled by the electrostatic interaction, we would expect that the modification of IOCS with QACs also facilitates better chromate adsorption as a result of the higher positive charge densities brought from QACs to the IOCS surface. However, results (data not shown) showed that the modified-IOCS could not provide better chromate adsorption at the pH domain where chromate predominates (pH > 6), indicating that electrostatic interactions were not likely to be important. We therefore postulate that the enhancement of NOM adsorption on QAC-modified IOCS is attributable to mechanisms such as partitioning. The IOCS modified with long-chain QACs has higher adsorption capacities than that modified with a short-chain QAC does. This characteristic is in agreement with the findings of Boyd (1988) where the uptake mechanism of organics by montmorillonite treated with long-chain organics is attributable to a partitioning process between the organic phase on the montmorillonite and the hydrophobic organic compounds. The interactions between QACs and NOM in solution may also contribute to the NOM removal. We observed some QAC-NOM-complex-like structures in the aqueous solution, although the modified IOCS was washed four times and dried after modification and there was no detectable QACs found in the last rinse water. We believe some QACs may desorb to the solution phase during NOM adsorption, especially at low pH. Further investigation to explain the mechanisms is needed.

CONCLUSIONS

The results of this study showed that modification of the IOCS surface with QACs is a possible way to improve the removal of NOM by IOCS. Analysis of NOM adsorption isotherms on unmodified and QAC-modified IOCS indicates that coating IOCS with long-chain QACs, HDTMA and HDBDMA significantly increased adsorption of NOM at low to high pH to reduce the concentration of the DBP precursor. The amount of NOM adsorbed on IOCS increased with increasing QACs concentration and pH used during modification. H₂O₂ additions during the modification process further facilitated NOM removal by IOCS. The enhancement in NOM removal by the modified IOCS is most likely attributable to partitioning (hydrophobic interaction) but not electrostatic interactions. Coating IOCS with long-chain QACs may provide an effective approach for enhancing NOM removal during drinking water production if adsorptive filtration processes with IOCS are selected as the primary means to control NOM and DBPs.

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