Removal of natural organic matter using surfactant-modified iron oxide-coated sand

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ARTICLE INFO

ABSTRACT

Iron oxide-coated sand (IOCS) was modified with hexadecyltrimethyl ammonium (HDTMA) and tested as an adsorbent for the removal of natural organic matter (NOM) from water. The modification did not change the physical properties of the IOCS but coated HDTMA onto its surface. The HDTMA-modified IOCS displayed a faster initial NOM adsorption and substantially higher capacity than the unmodified IOCS over a wide pH range in both batch and column adsorption. The enhancement was more pronounced at higher pH. Compared to unmodified IOCS, the HDTMA-modified IOCS removed more hydrophobic and larger NOM molecules and its NOM adsorption was less sensitive to the changes in ionic strength. The adsorption capacity of the modified IOCS was regenerated in-situ with NaOH solution and ex-situ with HDTMA solution. HDTMA-modified IOCS adsorption may be a promising alternative technology for NOM removal.

1. Introduction

Natural organic matter (NOM) is present in all natural water sources. It is a complex mixture of organic compounds containing both hydrophilic (phenolic and carboxylic) functional groups and hydrophobic (aromatic, aliphatic) moieties [1]. NOM itself is not harmful, but it can react with disinfectants to form disinfection by-products [2]. In addition, NOM reduces the effectiveness of water treatment by interfering with flocculation processes, fouling membranes and adsorbents, and interfering with oxidation and precipitation of dissolved iron and manganese. As a result, NOM often increases the dose requirements for coagulants, oxidants, adsorbents and the frequency of membrane cleaning.

To remove NOM during water treatment, a great variety of processes have been designed or modified, such as enhanced coagulation, membrane filtration, ozonation/biofiltration, and adsorption. Among these processes, adsorption on low-cost media is particularly an attractive option in many situations. Iron oxide-coated sand (IOCS) with a layer of iron oxides coated on the sand surface has been demonstrated as an effective NOM adsorbent [3–5]. IOCS has several advantages for NOM removal over other adsorbents. It is easy to prepare, convenient to apply in filtration setup, easy to separate from treated water, and easily regenerated

[3]. Additionally, IOCS can be developed in groundwater treatment plants where sand filters are used for removing iron from groundwater [6]. This is especially important in developing countries where high-cost absorbents are not generally accessible or affordable. For all of these reasons, IOCS is an adsorbent worth-developing for NOM removal from water.

One disadvantage of IOCS is that its NOM adsorption is strongly pH dependent and often works best at a rather acidic pH (usually around 4–5) but less well in neutral and basic conditions [3,5]. Adjusting pH to the acidic range may not be cost-effective with water that requires the addition of large amounts of acid. Modifying IOCS to function well over a wider pH range would make it more competitive with other adsorbents for NOM removal.

Surface modification with cationic surfactants or polymers can enhance adsorbents' capacity for organic solutes by creating an organic surface layer. Quaternary ammonium compounds (QACs) are frequently used. QAC-modified clays and zeolites have been investigated extensively and proven to be effective for removal of organic contaminants from water [7–10]. IOCS coating with QACs has not been evaluated before, but it should be promising. The hypothesis is that coating the IOCS surface with QACs containing hydrophobic tails and pH-independent cationic head groups may improve the hydrophobicity and/or positive charge density of the IOCS surface. This should strengthen surface interactions between NOM and the IOCS. Such tailored IOCS shall then have better NOM adsorption performance, stability and durability, and it possibly adsorb NOM over a larger pH range.

A previous study in our laboratory [11] determined the optimum conditions for coating QACs onto IOCS by simple adsorption. The preliminary results showed that modification with long-chain QAC, hexadecyltrimethyl ammonium (HDTMA), enhanced NOM adsorption at low to high pH significantly better than modification with short-chain QAC, tetrapropylammonium chloride.

This study was therefore designed to extensively evaluate the NOM removal performance of the HDTMA-modified IOCS in lab-scale batch and column reactors under different conditions, and to investigate regeneration of the modified IOCS for repeated use.

2. Materials and methods

2.1. Adsorbents preparation and characterization

Iron oxide-coated sand (IOCS) was prepared through a process developed by Chang et al. [3] with slight modification, which has been demonstrated in our previous work [12] to have good stability and NOM adsorption capability. The IOCS produced was hereafter referred to as "unmodified IOCS".

HDTMA–Br (Sigma–Aldrich) was used to modify IOCS through the procedure described in Ref. [11]. A portion of IOCS and HDTMA–Br solution (with 0.2% H_2O_2 addition) were mixed at 140 rpm for 2.5 h (pH was controlled at 10.0 ± 0.2 with NaOH addition), resulting in an equilibrium concentration of 4.0 mM, which is above its CMC (0.9 mM). Then, the supernatant was discarded and the IOCS was washed with DI water several times to remove the loosely attached HDTMA until no detectable HDTMA was measured in the washing water. The material was dried at 110 °C for 4 h at last and stored until use. The obtained HDTMA-modified IOCS was hereafter referred to as "modified IOCS".

The BET specific surface areas of the media were determined using a surface area analyzer (Coulter, Model SA3100, USA). The mineralogy of IOCS was characterized by an X-ray diffraction (XRD) meter (Philips, Model PW1830, The Netherlands). The surfaces of IOCS were analyzed by X-ray photoelectron spectroscopy (XPS) on a surface analysis PHI 5600 system (Physical Electronics, Inc., Chanhassen, MN), with a monochromatized Al Kα X-ray source ($h\nu$ = 1486.6 eV). The Fourier transform infrared (FTIR) spectra of samples were recorded in the transmission mode at room temperature on a 1725X PerkinElmer infrared (FTIR & IR) spectrometer (Waltham, Massachusetts, USA) using the KBr disk technique. Due to the size and density of the prepared IOCS, a pH drift technique [13] was used to estimate the pH of the point of zero charge (pH_{PZC}) of the IOCS grains.

2.2. Batch experiments

A stock solution of NOM was prepared by dissolving an appropriate amount of Suwannee river NOM (RO isolate, IHSS) in ultra-pure water. The NOM concentration in the stock solution was determined using a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). All batch adsorption tests were conducted in glass vessels agitated on an orbital shaker at 140 rpm at ambient temperature (23 ± 2 °C). An appropriate amount of IOCS was weighed into a 250 mL flask and 100 mL of the NOM solution at a given concentration was added. NaNO$_3$ was added to adjust the background ionic strength to 0.01 or 0.1N. The solution pH was adjusted to a desired value with dilute NaOH or HCl. During the adsorption process, the pH was periodically checked and adjusted using dilute NaOH or HCl. Water samples were taken at different time intervals and after 24 h for kinetic and equilibrium tests. The samples were filtered through 0.45 μm filters and analyzed for NOM using their UV$_{254}$ absorbance (Spectromic 3000, Milton Roy, USA). The effects of pH and nitrate (as a result of adjusting the ionic strength) on the UV absorbance were accounted for in the analysis. Interference

with the UV absorbance at 254 nm from dissolved ferric ions in the filtered samples was tested for and found to be negligible.

NOM samples before and after adsorption were fractionated using XAD-8 (Supelite, Sigma–Aldrich) and XAD-4 (Amberlite, Sigma–Aldrich) resins to isolate their hydrophilic (HPIA), transphilic (TPIA) and hydrophobic (HPOA) acid fractions, following the procedures suggested by Aiken et al. [14] and Kennedy et al. [15]. The NOM samples' molecular weight distributions were measured through size exclusion spectroscopy (Shimdzu, Japan) using the method described by Chin et al. [16] and Zhou et al. [17] with a macrosphere gel permeation chromatography column (7.5 mm × 300 mm, Grace, USA).

2.3. Column experiments

Bench-scale filtration columns with short empty bed contact times (EBCTs) of 2–5 min were used to simulate NOM removal by filters packed with the tailored IOCS. Each glass column of 2.5 cm in diameter and 40 cm long was packed with 75 g of the unmodified or HDTMA-modified IOCS, giving a bulk bed volume of around 50 mL. During the column tests, following an equilibration step with a 0.01N NaNO$_3$ solution at the desired pH, the tested NOM solution (ionic strength adjusted to 0.01N with NaNO$_3$) was pumped up through the column with a peristaltic pump. The NOM breakthrough capacity of the columns was investigated as a function of influent solution pH, flow rate and DOC. The effluent was sampled at regular intervals and its NOM concentration was measured.

Desorption of adsorbed NOM and regeneration of the HDTMA-modified IOCS were investigated and the detailed procedures are described in Text 1 in Supplementary Materials.

3. Results and discussion

3.1. Characterization of IOCS

The specific BET surface area of the HDTMA-modified IOCS was 2.9 m^2/g, slightly lower than that of the unmodified IOCS, 3.2 m^2/g, probably due to some iron detachment during the modification. The XPS results show that after modification with HDTMA, the percentages of the C and N atoms on the IOCS surface increased from 6.70% to 22.9% and from 0.17% to 0.98%, respectively, confirming that HDTMA was retained on the IOCS surface after the modification. The pH_{PZC} values of the unmodified and HDTMA-modified IOCS were approximately 6.8 and 9.7 (raw data shown in Figure S1), respectively. The former agrees with values reported in the literature [3,18–20]. The significantly increased PZC value of the modified IOCS indicates that the modification added positive charges to the surface. The modification of IOCS with HDTMA did not change the mineralogy of the IOCS, which remained crystalline goethite (Figure S2), according to the data published by the Joint Committee on Powder Diffraction Standards (JCPDS pattern number: 29-0713).

Fig. 1 shows the FTIR spectra of the unmodified IOCS, the HDTMA-modified IOCS and HDTMA alone. The strongest bands of HDTMA alone near 2919 and 2849 cm^{-1} are associated with the asymmetric and symmetric C–H stretching vibrations of CH$_2$ groups, respectively; the second strongest band clusters between 1383 and 1487 cm^{-1} arise from the C–H bending vibration of CH$_2$ groups or CH$_3$ groups [21]. The spectrum of the unmodified IOCS is rather featureless. The spectrum of the modified IOCS displays a mixture of the unmodified IOCS and HDTMA spectra, with the general band characteristics of the unmodified IOCS and additional peaks at 2924, 2851 and 1476 cm^{-1} attributable to HDTMA. This clearly establishes the presence of HDTMA on the modified IOCS surface.
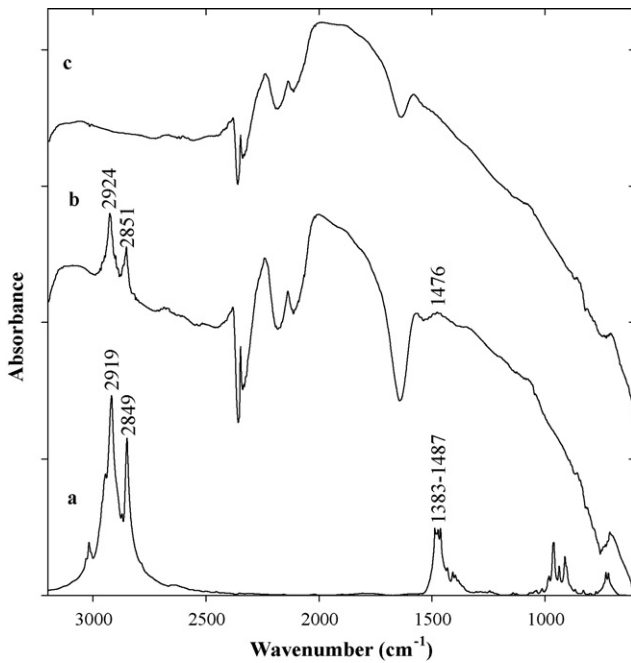
Fig. 1. FTIR spectra of (a) HDTMA, (b) HDTMA-modified and (c) unmodified IOCS.

3.2. NOM removal in batch tests

3.2.1. Adsorption kinetics

Fig. 2 shows the kinetics of NOM adsorption on the unmodified and modified IOCS at pH 4.5 ± 0.2 and 9.0 ± 0.1, along with curves predicted from a pseudo-second-order kinetic model. Under both acidic and basic conditions, NOM adsorption on the unmodified or modified IOCS was fast at the very beginning, but slowed down soon after the initial uptake, and the amount of NOM adsorbed then increased slowly to reach a plateau in approximately 20 h. Such rapid initial NOM adsorption followed by slow adsorption later has previously been reported for iron oxides [22,23]. The rapid initial adsorption has been attributed to physical adsorption mechanisms such as electrostatic interactions, which determine the attachment of NOM to the solid surface at the beginning stage. The decreased adsorption rate thereafter has been assigned to ligand exchange.

The pseudo-second-order rate model has been widely applied to adsorption of pollutants from aqueous solutions [24]. The advantage of using this model is that the model calculates the rate constant and the equilibrium capacity so that there is no need
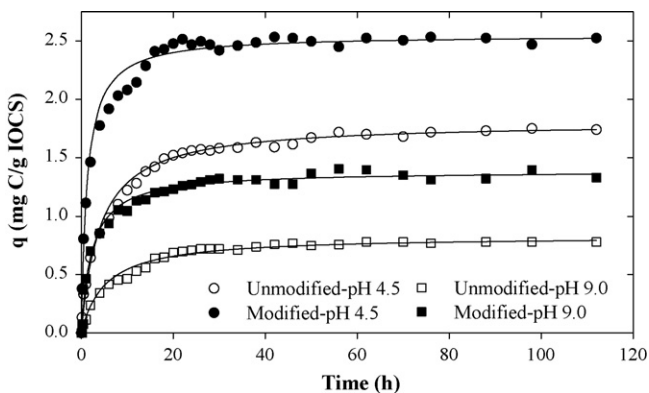

Fig. 2. Adsorption of NOM onto the unmodified and HDTMA-modified IOCS at pH 4.5 ± 0.2 and pH 9.0 ± 0.1. Initial concentration of 10 mg/L NOM, 0.1N NaNO$_3$ ionic strength, 2.5 g IOCS/L.
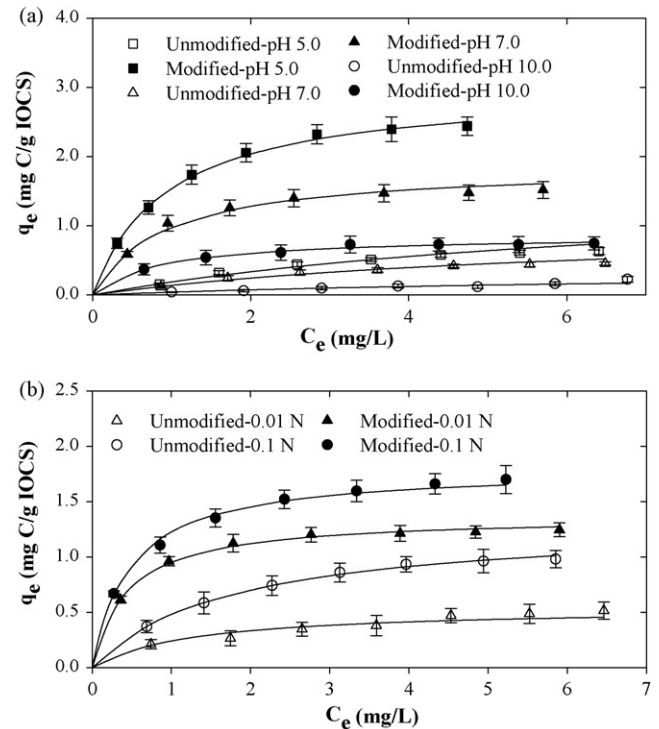

Fig. 3. Adsorption isotherms of NOM (a) at pH 5.0 ± 0.1, 7.0 ± 0.1 and 10.0 ± 0.1, with an ionic strength of 0.01N and (b) with an ionic strength of 0.01 and 0.1N, at pH 7.5 ± 0.1 onto the unmodified and HDTMA-modified IOCS, with an equilibration time of 24 h.

to obtain the latter from isotherm experiments [25]. The pseudo-second-order rate model is expressed as [24]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

or

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{2}$$

where q_e and q_t are the amount (mg/g) of the adsorbate adsorbed at equilibrium and time t, respectively, and k is the adsorption rate constant (g/mg/min). Fig. 2 shows that the experimental data agreed well with such model. Table S1 presents the kinetic parameters of NOM adsorption derived for both the unmodified and modified IOCS. The rate constants of NOM adsorption on the modified IOCS were higher than those on the unmodified IOCS at both acidic and basic pH, suggesting a stronger driving force for NOM adsorption on the HDTMA-modified IOCS.

3.2.2. Adsorption isotherms

NOM adsorption isotherms were developed at pH 5.0 ± 0.1, 7.0 ± 0.1 and 10.0 ± 0.1. The pH 10 was above the PZC of the modified IOCS. The ionic strengths tested were 0.01 or 0.1N NaNO$_3$. The experimental data plotted with curves predicted from a Langmuir model are shown in Fig. 3a and b. The Langmuir adsorption model is expressed as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

where C_e is the equilibrium concentration in mg/L, q_e is the amount adsorbed at equilibrium in mg/g, q_m is the maximum amount of adsorbate that can be adsorbed up to monolayer coverage, and b is the Langmuir constant, which is related to the binding strength. As shown, the experimental data fitted with the Langmuir model well, indicating that the two IOCS surfaces were relatively homogeneous

and NOM was interacting with certain limited specific binding sites on the IOCS. The model's fit parameters are summarized in Table S2.

As shown in Fig. 3a and Table S2, the HDTMA-modified IOCS showed much greater NOM adsorption capacity than the unmodified IOCS at all pH conditions studied. Modification increased the maximum quantity (q_m) of NOM adsorption, from 1.62 to 3.00 mg C/g IOCS at pH 5, from 0.98 to 1.87 mg C/g IOCS at pH 7, and from 0.38 to 0.87 mg C/g IOCS at pH 10. The percentage enhancement was 85%, 91% and 129% at pH 5, 7 and 10, respectively, showing that enhancement is more marked at higher pH. As the pH was increased from 5 to 7 and then to 10, the q_m of NOM adsorbed on the unmodified IOCS dropped by 40% and 77%, respectively; on the modified IOCS it dropped by 38% and 71%, respectively. So modification may have slightly decreased the pH sensitivity of NOM adsorption. One plausible explanation would be that after modification, the IOCS surface became more hydrophobic, and adsorption could partly have resulted from enhanced hydrophobic interaction, the strength of which is not appreciably affected by pH [26]. It should be noted that, in this paper, the "hydrophobic interaction" is defined specifically as the specific attraction between the hydrophobic groups on the adsorbent's surface and those of the adsorbate molecules. Although high pH can reduce the hydrophobicity of NOM molecules due to the increased lateral electrostatic repulsion, this influence at basic pH is negligible.

Fig. 3b shows that the modified IOCS had better NOM adsorption performance at both ionic strengths, and that NOM adsorption on both the unmodified and modified IOCS increased with increasing ionic strength. According to Hayes et al. [27], negative ionic strength dependency suggests the adsorption occurs primarily through the formation of outer-sphere complexes, while inner-sphere complex formation shows little or even positive ionic strength dependency. Our results suggest that outer-sphere complexes (e.g., electrostatic attractions) do not play a major role in the NOM adsorption process, while mostly inner-sphere complexes should form between NOM and the unmodified or modified IOCS.

Positive or neutral salt dependency of NOM adsorption on iron oxides has also been reported in the literature, and the adsorption of NOM on iron oxide surfaces has usually been attributed to ligand exchange [28–30]. The increased NOM adsorption at higher ionic strength was mainly because lateral electrostatic repulsion among the segments of NOM molecules was better screened, and thus resulted in denser NOM macromolecular structures and decreased molecular size, which helped NOM better contact the surface and thus more easily adsorb through ligand exchange or other mechanisms. Fig. 3b also shows that ionic strength had a stronger influence on NOM adsorption onto the unmodified IOCS than onto the modified IOCS. When ionic strength increased from 0.01 to 0.1N, the maximum NOM adsorption capacity (q_m) of the unmodified IOCS increased 142%, from 0.54 to 1.31 mg C/g IOCS, while that of the modified IOCS increased 32%, from 1.37 to 1.80 mg C/g IOCS. The diminished effect of ionic strength on NOM adsorption with modified IOCS might result from the increased importance of hydrophobic interaction, the strength of which is rather independent of solution ionic strength [26]. The fitted affinity coefficients (b) of the Langmuir model (Table S2) for NOM adsorption were higher for the modified than for the unmodified IOCS, meaning that the modification improved the affinity between NOM and active sites on the IOCS surface.

3.2.3. Preferential adsorption of NOM

To investigate competition among UV-absorbing NOM components during the adsorption on the modified IOCS, fractions of NOM remaining in solution before and after adsorption were measured using XAD fractionation and HPSEC. Fig. 4 presents the mass of each XAD-separated fraction before and after adsorption. The dominant fraction of the original NOM solution, the HPOA fraction, was pref-

Fig. 4. Mass of each NOM fraction by hydrophobicity.

erentially removed by the modified IOCS, although the mass of the other two fractions was also reduced after adsorption. Compared to the unmodified IOCS, the modified IOCS adsorbed less TPIA. The better removal of the hydrophobic fraction of NOM suggests that the enhanced NOM adsorption of the modified IOCS may be due to stronger hydrophobic interactions.
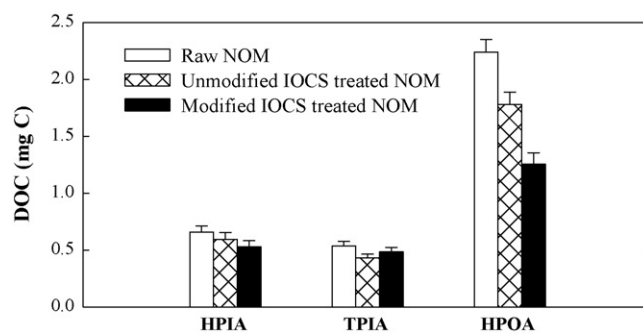
Figure S3 shows HPSEC-UV profiles before and after treatment. Two large peaks can be seen in the HPSEC-UV curves of the raw and treated NOM solutions. It should be noted, however, that the HPSEC-UV curve of the pure NaNO₃ solution also shows a broad, large peak at the retention time of the second peak (the lower molecular weight fraction), around 18 min, suggesting its large contribution to the second peak of the NOM solution curves. It is therefore inappropriate to attempt to interpret the small differences among the second peaks. As for the first peak (the higher molecular weight fraction), the modified IOCS further decreased the UV absorbance of the peak, which is closely proportional to the NOM concentration, and further shifted the peak towards longer retention time, i.e., towards relatively smaller molecules. Therefore, compared to the unmodified IOCS, the HDTMA-modified IOCS showed better binding of larger NOM molecules. Since hydrophobic NOM is relatively larger than its hydrophilic counterpart [31], the selective removal of larger NOM molecules implies that hydrophobic NOM content was preferentially removed. This agrees well with the XAD separation results, supporting the improved hydrophobic interactions between NOM and IOCS after modification with HDTMA.

3.3. NOM removal in column tests

3.3.1. Adsorptive filtration of NOM

Fig. 5a presents NOM removal by filtration columns packed with the unmodified and HDTMA-modified IOCS at different influent pH. Consistent with the results of the batch tests, NOM adsorption capacity of both the unmodified and modified IOCS decreased with increasing pH, i.e., breakthrough occurred earlier at higher pH. But the pH dependent breakthrough trend was less significant with the modified IOCS (the 0% breakthroughs at the three pH were quite similar with the modified IOCS, while those with the unmodified IOCS differed). Fig. 5a shows that the HDTMA-modified IOCS performed better than the unmodified IOCS at three pH studied. Assuming 30% NOM breakthrough is permitted, treatable bed volumes with the modified IOCS increased over the unmodified volumes from 81 to 139, from 36 to 70, and from 18 to 52 at pH of 4.5, 6.5 and 9.5 respectively (Table S3). The corresponding percentages of enhancement were 72%, 94% and 189%, indicating that the enhancement was more pronounced at higher pH. Together with the less pH dependent breakthrough of the modified IOCS reported above, the results promise better real-world performance of the modified IOCS in dealing with water of high alkalinity.
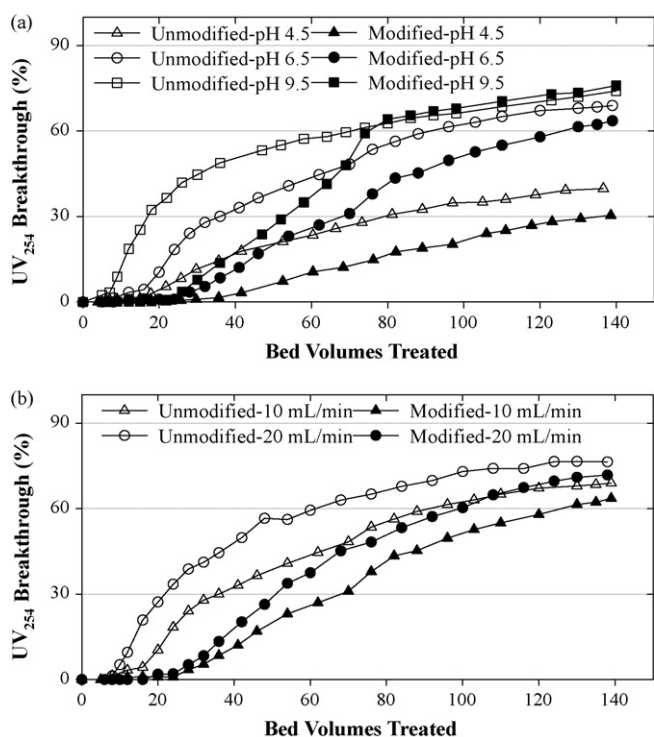
Fig. 5. Breakthrough curves for NOM adsorption onto the unmodified and HDTMA-modified IOCS at various (a) influent pH values (influent conc. = 5 mg/L, flow rate = 10 mL/min) and (b) influent flow rates (influent conc. = 5 mg/L, pH 6.5).

Fig. 6. (a) Desorption of NOM by NaOH at various flow rates; (b) Adsorption of NOM by the unmodified IOCS, virgin and regenerated modified IOCS, as well as the re-modified IOCS (influent initial pH 6.5, flow rate = 10 mL/min, conc. = 5 mg/L).

These results again support the idea that modification introduces additional adsorption driving forces such as the pH-independent hydrophobic interactions previously discussed. The enhanced hydrophobic interactions seem to provide for NOM adsorption in two stages. Initially, NOM may adsorb onto the surface-attached HDTMA through hydrophobic interactions, rendering the adsorption less pH dependent. At the second stage, when all the HDTMA sites have been occupied, NOM may be adsorbed largely onto the uncovered iron oxide on the IOCS surface. This is known to be governed by ligand exchange and is highly pH dependent [28,29]. As some of the surface sites for ligand exchange on the modified IOCS surface have been occupied by HDTMA, the fewer available ligand exchange sites on the modified IOCS could lead to the steep increase in the breakthrough curves of the HDTMA-modified IOCS.

The breakthrough curves at different feed flow rates were determined and are presented in Fig. 5b. The treated bed volumes of the NOM solution before reaching any given percentage of breakthrough decreased when the flow rate was increased from 10 to 20 mL/min. Because the empty bed contact time used to mimic real-world filtration was much less than the time for reaching equilibrium (20 h), this flow rate-dependency can be explained by the different contact times at the different flow rates. The lower flow rate allowed the NOM solution to better approach equilibrium with the IOCS surface. At both feed rates, the HDTMA-modified IOCS outperformed the unmodified IOCS in removing NOM. Table S3 shows the treatable bed volumes to reach 30% breakthrough.

The effect of influent DOC concentration on breakthrough was also investigated (Figure S4). Initially, the different NOM concentrations, on the basis of cumulative mass of DOC treated, showed similar breakthrough curves, but as each run progressed, more NOM was adsorbed at higher feed concentrations due to the higher equilibrium concentrations. The modified IOCS had higher NOM removal capacity than the unmodified IOCS at the both influent concentrations (Table S3).
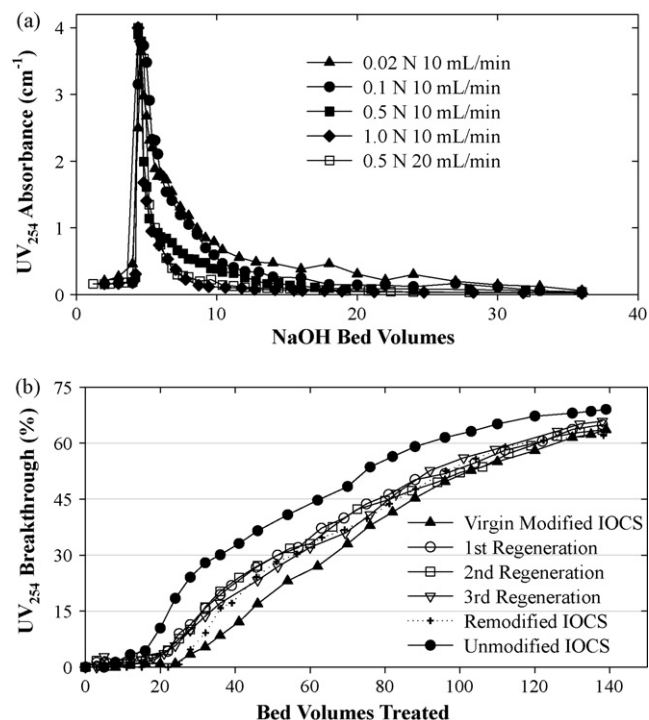
3.3.2. Regeneration and reuse

Fig. 6a shows the effect of NaOH concentrations and flow rates on desorption of NOM. In all cases, the adsorbed NOM was released rapidly when the first six bed volumes of NaOH were passed through the column. Afterwards, the desorption kinetics depended on the OH⁻ concentration and the flow rate of the regenerant, with a higher concentration or flow rate resulting in a higher desorption rate. The higher flow rate presumably improved diffusion of NOM across the stagnant layer.

The success of regeneration, however, is not judged by the extraction efficiency but by the adsorption capacity regained after regeneration [32]. The NOM removal efficiency of the regenerated HDTMA-modified IOCS was evaluated by applying the protocols described in Text 1. Three adsorption–desorption–resorption cycles were performed. The breakthrough curves of the virgin and the regenerated HDTMA-modified IOCS are displayed in Fig. 6b. For comparison, the breakthrough curve of the unmodified IOCS obtained under the same adsorption conditions is also shown. The results show that the first regeneration led to some reduction in adsorption capacity, presumably due to the detachment of some loosely attached HDTMA. The second and the third regenerations, however, did not further reduce the adsorption capacity, and regenerated modified IOCS always outperformed the unmodified IOCS. So it appears that HDTMA-modified IOCS can be repeatedly regenerated and continue to yield similar performance.

Another operational issue is the potential for re-modifying IOCS if its adsorption capacity has to be restored after long-term operation. Re-modification was examined using the protocol described in Text 1. The breakthrough curve of the re-modified IOCS is presented in Fig. 6b. As shown, the re-modified IOCS performed slightly better than the regenerated modified IOCS initially, and similarly in the later stages of the run. So it appears that re-modification can largely restore NOM adsorption capacity of the modified IOCS.

4. Conclusions

HDTMA-modified IOCS showed better NOM adsorption performance than unmodified IOCS in both batch and column operations over a wide pH range. The modified IOCS had a faster initial adsorption rate, higher adsorption capacity and weaker pH and ionic strength dependence. The HDTMA-modified IOCS preferentially removed more hydrophobic and larger NOM molecules.

HDTMA-modified IOCS was readily regenerated by short-duration exposure to NaOH solutions. The adsorption capacity after first regeneration was reduced slightly, but it remained approximately constant through three adsorption–desorption–resorption cycles. Re-modification largely restored its adsorption capacity.

Adsorptive filtration with the HDTMA-modified IOCS has the potential to lower NOM concentrations to target levels over a wide pH range. It is envisioned that this approach could be used after common coagulation, flocculation and sedimentation to fine tune the concentration of NOM, or it could be applied as an alternative to enhanced coagulation in water treatment. The beauty of this approach is that there is no chemical addition and no sludge generated, saving on coagulant and the costs of sludge treatment and disposal. Although the cationic surfactant used in the modification costs eight times more than metal coagulants [33], the amount of the surfactant needed for monolayers coating is quite small and the surfactant solution can be repeatedly utilized for modification. As a result, the overall chemical cost is expected to be less than that of the enhanced coagulation. Nonetheless, it should be noted that this has been the first attempt to evaluate this modified adsorbent, using rather simple solutions in controlled, bench-scale experiments. Full-scale and long-term repeated field testing with natural surface water and backwashing are recommended. Future evaluation should also demonstrate the long-term chemical and biological stability of the modified IOCS.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.09.089.

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