



# Natural organic matter removal by adsorption onto magnetic permanently confined micelle arrays

Hongtao Wang<sup>a,b</sup>, Arturo A. Keller<sup>b,\*</sup>, Kristin K. Clark<sup>b</sup>

<sup>a</sup> State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

<sup>b</sup> Bren School of Environmental Science and Management, University of California, Santa Barbara, CA 93106, USA

## ARTICLE INFO

### Article history:

Received 3 May 2011

Received in revised form 19 July 2011

Accepted 22 July 2011

Available online 5 August 2011

### Keywords:

Natural organic matter

Adsorption

Magnetic adsorbent

Surfactant

Water treatment

## ABSTRACT

To remove natural organic matter (NOM) from water, magnetic permanently confined micelle arrays (Mag-PCMAS) were synthesized by coating the surface of  $\text{Fe}_3\text{O}_4$  particles with a silica/surfactant mesostructured hybrid layer. An environmental scanning electron microscope (ESEM) was used to characterize the particle size and surface morphology of the Mag-PCMAS. The zeta potential was used to assess the surface charge. Batch experiments were performed to investigate the adsorption of NOM by Mag-PCMAS. It was determined that NOM removal efficiency by Mag-PCMAS could be as high as 80% at a wide range of initial pH values ( $\sim 6.0$ – $10.0$ ). The adsorption isotherm was fitted well by a Langmuir model. Although  $\text{Fe}_3\text{O}_4$  had a high positive charge and Mag-PCMAS a small negative charge, Mag-PCMAS had a higher removal efficiency of NOM than uncoated  $\text{Fe}_3\text{O}_4$  particles (which are also magnetic), which indicated that the adsorption of NOM onto Mag-PCMAS was not dominated by electrostatic interactions. Possible mechanisms of the adsorption of NOM onto Mag-PCMAS were hydrophobic interactions and hydrogen bonding. It was feasible to reuse Mag-PCMAS after regeneration. These results indicate that Mag-PCMAS can be very attractive for the removal of NOM from aqueous matrices.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The presence of natural organic matter (NOM) in water sources is an important issue [1,2]. NOM affects water quality, such as color, taste and odor. NOM not only reacts with disinfectants to produce disinfection by-products (DBPs) harmful to human health [3–7], but also leads to the fouling of filters and membranes, reducing the efficacy of some advanced water treatment process [8–15]; the presence of NOM in solution also has a stabilizing effect on the dispersion of some potentially hazardous nanoparticles in water, which enhances the mobility of those nanoparticles and poses potential threat to the environment [16,17]. In addition, NOM could enhance the transport of some persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) to aquatic organisms [18]. Adding to this concern, a recent study found that NOM concentrations have increased over the past decade in many streams, including some sources for drinking water [19]. Therefore, the development of technologies to remove NOM from water is of great importance.

The removal of NOM from aqueous media has been widely investigated [20–33]. Current options for NOM removal include

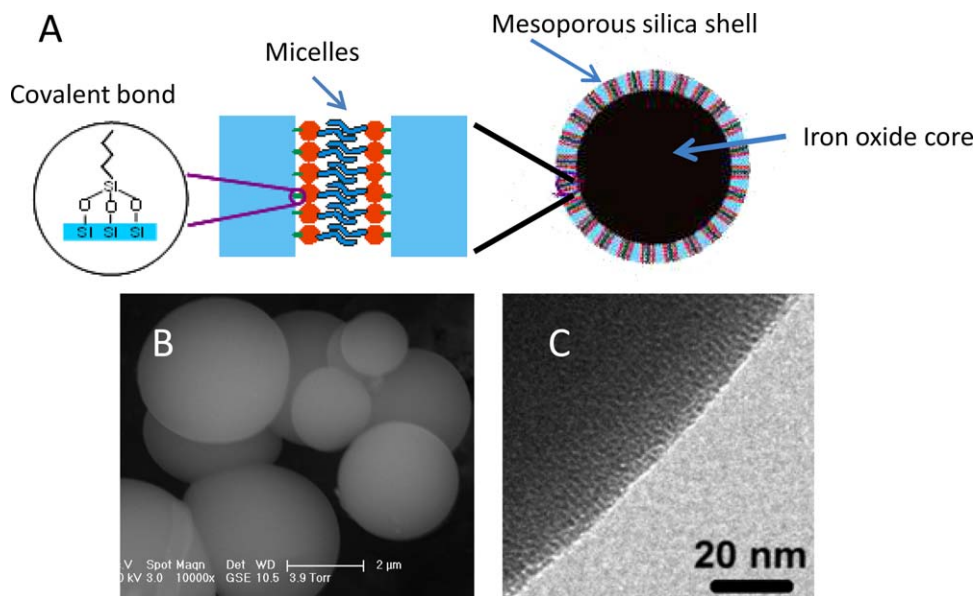
ozonation and other advanced oxidation [20–24], coagulation [25,26], ion exchange [27], biodegradation [23], membranes [20,21,24], and adsorption [28]. A great variety of adsorbents have been investigated to remove NOM from water, including activated carbon [28], granular ferric hydroxide [30], iron oxide [31], and some novel nanoparticles such as carbon nanotubes [32,33] and  $\text{TiO}_2$  [34]. Among these adsorbents, activated carbon has been widely used. However, the major drawback of activated carbon is the high operating cost.

In recent years, magnetic particles have received a lot of attention as powerful adsorbents because their inherent superparamagnetic properties make them desirable for magnetic field assisted separations [35–38]. For instance, magnetic iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) have been reported as effective adsorbents for the removal of pollutants from the aqueous media [12,39–41].

In consideration of the fact that the surface characteristics of adsorbents are very important to the adsorption process of NOM, it is possible to modify the surface of adsorbents to enhance the adsorption process. For example, coated  $\text{Fe}_3\text{O}_4$  magnetic particles were found to be highly efficient in the removal of NOM, heavy metals and microcystins from water [42–44]. These functionalized adsorbents, which possess a modified surface and a magnetic core, have provided a good option to remove pollutants such as NOM from aqueous environment. Since sorption of organics can be enhanced by the coating of surfactants onto the sorbent [45,46], in a previous study [47], we synthesized Mag-PCMAS, with a magnetite

\* Corresponding author. Tel.: +1 805 893 7548; fax: +1 805 893 7612.

E-mail addresses: [hwang@bren.ucsb.edu](mailto:hwang@bren.ucsb.edu) (H. Wang), [keller@bren.ucsb.edu](mailto:keller@bren.ucsb.edu) (A.A. Keller).



**Fig. 1.** (A) Conceptual structure of the Mag-PCMA particles (adapted from [47]), not to scale; (B) environmental scanning electron micrograph of synthesized Mag-PCMA particles indicating their shape, size and surface smoothness; and (C) transmission electron micrograph of synthesized Mag-PCMA particles showing the silica mesoporous structure, which is around 15–20 nm thick.

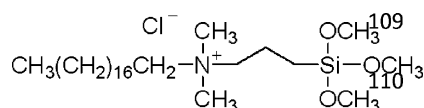
core and a silica porous layer that permanently confines surfactant micelles within the mesopores. The sorption of four representative hydrophobic organic compounds (HOCs) showed that Mag-PCMA particles were effective sorbents and they could be regenerated.

The objective of this study was to determine the effectiveness of Mag-PCMA particles to remove NOM from water. Given that the structure of NOM is quite different from the HOCs used in the previous study, this work can widen the application of Mag-PCMA particles for the removal of organic pollutants from water. The microenvironment of the interactions between the mesoporous layers of the Mag-PCMA particles and the multiple binding sites on NOM make it a significant study for sorbents in complex chemical environments, such as water treatment.

## 2. Materials and methods

### 2.1. Chemicals

Standard Suwannee River NOM was obtained from the International Humic Substances Society (IHSS, St. Paul, MN, USA). The composition and molecular weight of this NOM were reported by Hyung et al. [17]. All aqueous solutions were prepared using deionized (DI) water (Barnstead). NOM stock solution (400 mg/L) was prepared by mixing a known amount of NOM with DI water for 24 h. The pH of the stock solutions was then adjusted to 8 with NaOH. The solution pH was adjusted using 0.1 M and 0.01 M NaOH and HCl to attain the desired pH value and was measured using an Oakton pH meter (Ion 510 series). Tetramethylammonium hydroxide (TMAOH) (25 wt.% in water), tetraethyl orthosilicate (TEOS), and [3-(trimethoxysilyl)propyl]-octadecyldimethylammonium chloride (TPODAC) (72 wt.% in methanol), a cationic surfactant, were purchased from Sigma–Aldrich (San Louis, MO). The molecular structure of TPODAC is:



The preparation of other chemicals and solutions can be found in [47].

### 2.2. Synthesis of Mag-PCMA particles

The synthesis process of Mag-PCMA particles is presented in [47]. Briefly, by means of cooperative assembly of silica oligomers and TPODAC on the  $\text{Fe}_3\text{O}_4$  particles, the Mag-PCMA particles were prepared with a core–shell structure. The structure of Mag-PCMA particles is illustrated in Fig. 1a. In the synthesis process, the reaction (stirring) time was 3 h instead of 6 h, because our optimization experiments indicated that this time was sufficient for the coating process, and other researchers also indicate that too much coating with silica reduces the magnetic strength, and increases the particle size [49].

### 2.3. ESEM observation

Electron microscopic images were analyzed by an environmental scanning electron microscope (ESEM) (Philips Electron Optics, Eindhoven, The Netherlands) using an accelerating voltage of 3.00 kV.

### 2.4. Zeta potential measurements

The zeta potential was measured by a Malvern Zetasizer (Nano-ZS; Malvern Instruments, Southborough, MA). The concentration of NOM was 20 mg/L, and the Mag-PCMA concentration was 200 mg/L for the zeta potential measurement. The pH range was from 5 to 10. At each pH, the zeta potential was measured three times and averaged. All of the other data in this study are also the average of triplicate samples.

### 2.5. Batch experiment for NOM adsorption

The NOM adsorption kinetics was determined by batch experiments. Aliquots (2 mg) of Mag-PCMA particles were mixed with 10 mL of NOM solution in 20 mL glass tubes. The initial NOM concentration was 20.0 mg/L in all cases (mass concentration). All NOM concentrations in this study are mg/L as NOM (not mg/L as C). The tubes were shaken in an end-over-end shaker on a Dayton-6Z412A Parallel Shaft roller mixer with a speed of 70 rpm at  $22 \pm 2^\circ\text{C}$  continuously. One tube was taken out to measure the NOM concentration

at the end of each 10 min, 30 min, 1 h, 3 h, 4 h, 5 h, 6 h, 12 h, 18 h, 21 h, 23 h, 25 h, 27 h, 30 h, 48 h, 50 h, 52 h, 54 h, 72 h, 76 h, 90 h, and 93 h. Then the Mag-PCMA and uncoated  $\text{Fe}_3\text{O}_4$  particles with adsorbed NOM were separated from the mixture with a permanent hand-held magnet. The NOM concentration was monitored by measuring the absorbance of UV at 254 nm (Shimadzu BIOSPEC-1601 UV/Vis spectrophotometer, Kyoto, Japan) using a 1 cm quartz cell.  $\text{UV}_{254}$  is widely used as a surrogate for NOM concentration [17], although it does not reflect all DOC, since  $\text{UV}_{254}$  only measures UV-absorbing (i.e., aromatic-rich) NOM. Our preliminary results also showed a good correlation of NOM mass concentration with  $\text{UV}_{254}$  ( $R^2 = 99.97$ ). Calibration was also performed after some adsorption tests under different water quality and mixing conditions, which confirmed that TOC and  $\text{UV}_{254}$  exhibited the same trend after treatment. The supernatant (3.5 ml) was taken for NOM concentration analysis. The amount of NOM adsorbed onto Mag-PCMA was calculated as the difference between the initial and final NOM mass in the aqueous phase.

To prepare the NOM adsorption isotherms, solutions with varying initial NOM concentrations were treated with the same procedure as above at room temperature ( $22 \pm 2^\circ\text{C}$ ). The equilibration time was 48 h uniformly, which was determined to be sufficient for NOM adsorption equilibrium to be reached. The NOM concentrations ranged from 2 mg/L to 80 mg/L, and the Mag-PCMA concentrations were 200 mg/L, 400 mg/L and 600 mg/L, respectively.

The solid-phase concentrations were determined by mass balance, according to Eq. (1):

$$q_e = V * \frac{(C_0 - C_e)}{M} \quad (1)$$

where  $C_0$  and  $C_e$  is the initial and equilibrium concentration of NOM in the liquid phase (mg/L), respectively,  $q_e$  is the equilibrium concentration of NOM adsorbed on the unit mass of Mag-PCMA (mg/g),  $V$  is the volume of solution, and  $M$  is the mass of dry Mag-PCMA (g).

## 2.6. Regeneration and reuse of Mag-PCMA

To investigate the ability of regeneration and reuse of Mag-PCMA, 20 mg/L NOM was used with the same adsorption process, followed by separation of the Mag-PCMA from solution by magnet. The residual NOM adsorbed on the Mag-PCMA was extracted with methanol. The concentration of NOM in the presence of methanol was determined by measuring the absorbance of UV at 301 nm, where the absorbance of methanol was zero. Our preliminary results also indicated a good correlation of NOM mass concentration with  $\text{UV}_{301}$ . After regeneration, the Mag-PCMA was reused for the removal of NOM. When the particles were reused after regeneration, there was no methanol carryover and absorbance at 254 nm. The processes of regeneration and reuse were repeated for 5 cycles.

## 3. Results and discussion

### 3.1. Characterization of $\text{Fe}_3\text{O}_4$ and Mag-PCMA

The ESEM images of Mag-PCMA are presented in Fig. 1b. The shapes of uncoated particles (raw  $\text{Fe}_3\text{O}_4$ ) were diverse, including round-shape, rod-shape and irregular-shape, and the sizes of agglomerates for those uncoated particles varied. However, the sizes and shapes of Mag-PCMA were comparatively more homogeneous than  $\text{Fe}_3\text{O}_4$ . The average size of Mag-PCMA particles was 1–3  $\mu\text{m}$  for round shaped particles (Fig. 1b).

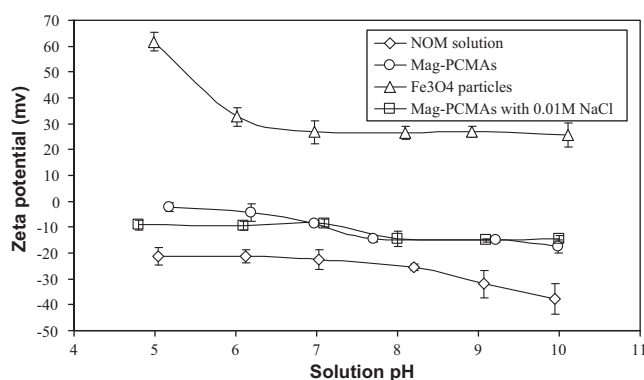


Fig. 2. Zeta potential as a function of pH.

### 3.2. Zeta potential

The zeta potential in the initial pH range of 5 to 10 is presented in Fig. 2 for a NOM solution, uncoated  $\text{Fe}_3\text{O}_4$ , Mag-PCMA in DI water, and Mag-PCMA in the presence of 0.01 M NaCl. In this pH range, the zeta potential of the NOM solution was negative (–21 to –38 mV), and the zeta potential of uncoated  $\text{Fe}_3\text{O}_4$  particles was positive (25–62 mV over the measured pH range). The Mag-PCMA possessed a much lower zeta potential than the uncoated particles (–17–3 mV). The decrease of zeta potential indicates the formation of anionic negatively charged surface complexes on the Mag-PCMA. The point of zero charge (PZC) for Mag-PCMA was determined to be less than 5.18, with a net negative charge in solution above this pH. To investigate the influence of ionic strength on the zeta potential of Mag-PCMA, 0.01 M NaCl was added to the Mag-PCMA solution. The increase in ionic strength had a small effect on the zeta potential of Mag-PCMA, slightly increasing the negative charge on these particles at lower pH.

### 3.3. Adsorption kinetics of NOM onto Mag-PCMA

Mag-PCMA are much more effective in removing NOM than the uncoated  $\text{Fe}_3\text{O}_4$  particles (Fig. 3). NOM removal by Mag-PCMA exceeds 80%, although the adsorption time is long. In contrast with the removal efficiency of NOM by some other technologies, this removal rate is comparatively high. For example, one study showed that the NOM removal rate by coagulation is typically 35% and could be increased to about 45% with an optimum pH of 5.2 [50]. Another study indicated that when the integration of coagulation with ultrafiltration was used, NOM removal was less than 67% [51].

The higher removal by Mag-PCMA compared to uncoated  $\text{Fe}_3\text{O}_4$  indicates that the adsorption of NOM onto the surface of Mag-PCMA is not dominated by electrostatic interactions, because the

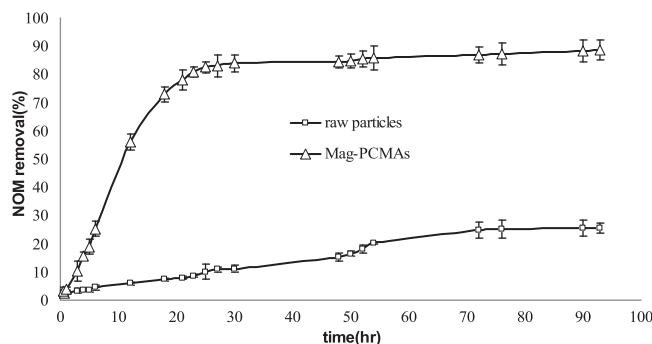


Fig. 3. NOM adsorption kinetics: comparison of Mag-PCMA and  $\text{Fe}_3\text{O}_4$  in NOM removal.

zeta potential of Mag-PCMA was much lower and negative than for the uncoated positively charged  $\text{Fe}_3\text{O}_4$  particles (Fig. 2). One likely adsorption mechanism is hydrophobic interaction between the confined micelles and NOM. As is well known, NOM consists of both hydrophobic and hydrophilic regions [52]. This heterogeneity makes it possible for the hydrophobic fraction of NOM to attach onto the Mag-PCMA through hydrophobic interactions. Another possible mechanism is hydrogen bonding, which results from the combination of hydrophilic functional groups in NOM and the hydrophilic head of the surfactant. For example, there is possibility that the carboxylic groups on NOM can interact with oxygen on 3-(trimethoxysilyl)propyl via hydrogen bond:

It should be noted that each TPODAC molecule can provide 3 positions (oxygen) to combine with NOM to form hydrogen bond, while here we only illustrate one. Still another mechanism might be the entanglement of NOM in the mesopores which makes it difficult to come out. The entanglement of NOM is due to its abundant functional groups and complex molecular structure, which has been reported elsewhere [48,52,53]. The surface coating of  $\text{Fe}_3\text{O}_4$  facilitated these interactions, thus improved the adsorption ability of Mag-PCMA.

Although Mag-PCMA resulted in high removal of NOM, the time for equilibrium was long. The proposed explanation for this phenomenon is the high molecular weight of NOM which results in a lower diffusion rate into the confined micelle and a longer attachment process. In addition, if hydrophobic interactions are the main process, these are weaker forces than electrostatic interactions such as the case with anion exchange. In our previous study, it was determined that the mesostructured layer was approximately 100 nm [47]. On the other hand, the NOM used in this study has a molecular mass (weight-average,  $M_w$ ) of about 18,700–33,200 g/mol, or a hydraulic radius of about 20–90 nm [54]. These large macromolecules may take a long time to attach to the outer surface of the mesostructured layer of Mag-PCMA, and then interact with the surfactant within the layer. In addition, due to the size and composition of mesostructured layer, the entanglement of NOM within the layer also needs sufficient time.

Besides diffusion through the micelles and attachment, NOM has to diffuse from the liquid phase through a boundary layer to the exterior of Mag-PCMA. As the first step in the adsorption process, the diffusion through the boundary layer may be accelerated by agitation which reduces the thickness of boundary layer. To investigate the effect of agitation (via mixing) on adsorption, a vortex (Vortex Genie 2, Scientific Industries Inc., Bohemia, NY, USA) was used instead of a roller. When the vortex was set at intensity “2”, NOM removal was almost 70% within 1 h (Fig. 4). A method blank sample with [NOM] = 20 mg/L in the absence of Mag-PCMA was vortexed for 16 h, but there was no removal at all (data not shown

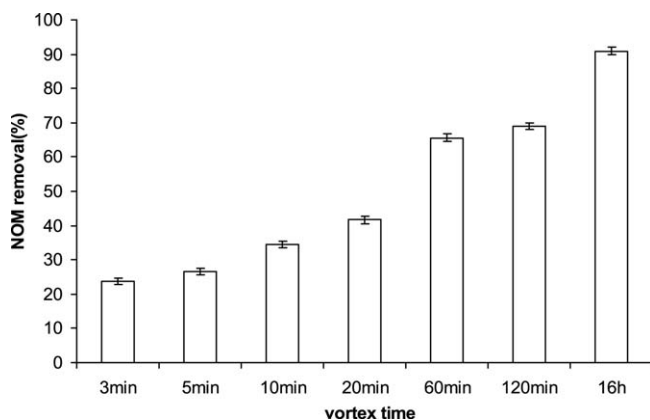


Fig. 4. NOM removal as a function of vortex time.

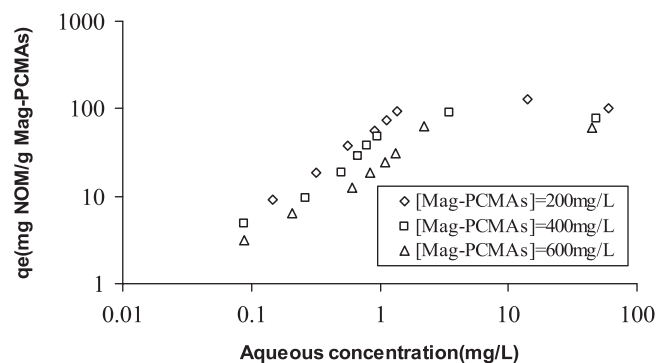


Fig. 5. NOM adsorption isotherm.

in this figure). This result indicates that mixing power can accelerate the adsorption of NOM by Mag-PCMA, probably by reducing the thickness of the boundary layer.

### 3.4. Adsorption isotherms of NOM onto Mag-PCMA

The adsorption behavior of NOM onto Mag-PCMA at three different sorbent dosages is presented in Fig. 5. The Langmuir and Freundlich isotherm models have been used to describe NOM adsorption onto iron oxides surfaces [31]. In this study, both Freundlich and Langmuir models were considered for the evaluation of the experimental results. It was found that Freundlich model could only be used for low NOM concentrations, while the Langmuir isotherm model was adequate for the entire range of NOM concentrations considered.

The Langmuir model is described by the following equation:

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad (2)$$

where  $q_e$  and  $C_e$  are the same with those in Eq. (1),  $q_m$  (mg/g) and  $b$  (L/mg) are the Langmuir coefficients.

The Langmuir isotherm fitting had a high regression coefficient (0.97–0.99). The corresponding Langmuir coefficients are presented in Table 1. As seen in Fig. 5 and Table 1, the adsorption indicates a dependence on Mag-PCMA dose. The maximum adsorption capacity corresponding to complete monolayer coverage ( $q_m$ ) decreased with increasing adsorbent dose. From Fig. 5 the adsorption includes two stages: at lower Mag-PCMA concentrations, the adsorption is linear, while at higher Mag-PCMA concentrations, the adsorption becomes asymptotic. This has been observed by other studies which investigated the adsorption of NOM by carbon nanotubes. The dose-dependent adsorption may result from preferential adsorption due to the heterogeneity of NOM [32].

### 3.5. Influence of pH on NOM adsorption

To investigate the influence of pH on NOM adsorption, a pH range of 5–10 was studied (Fig. 6). It was shown that NOM removal via Mag-PCMA was almost independent of pH for the range from 6 to 9, although there was a noticeable decrease in NOM removal at a pH of 5. As indicated in Section 3.3 carboxylic and phenolic

Table 1  
Langmuir model adsorption isotherm coefficients.

Mag-PCMAa (mg/L)	$q_m$ (mg/g)	$b$ (1/mg)	$R^2$
200	286	0.229	0.98
400	87.7	0.626	0.97
600	53.8	0.67	0.99



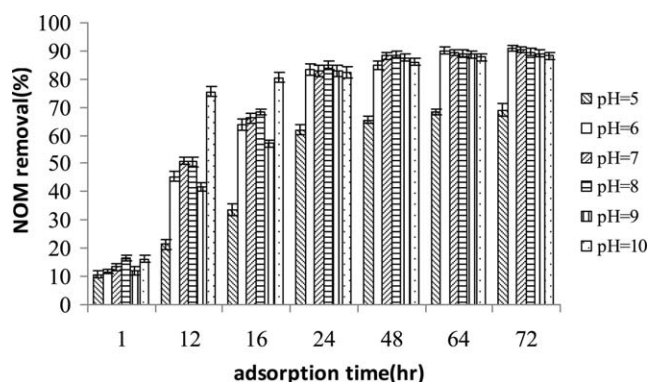


Fig. 6. pH influence on NOM removal by Mag-PCMA.

groups may significantly contribute to the adsorption of NOM [55]. At pH > 6, both mechanisms (hydrophobic interactions and hydrogen bonding) are likely to be occurring, while at pH < 6 the carboxylic groups are neutralized and thus this mechanism does not play an important role. The results in Fig. 6 demonstrated that Mag-PCMA performed well in a wide range of pH that is relevant for water treatment.

### 3.6. Regeneration and reuse of Mag-PCMA

To investigate the possibility of regenerate and reuse of Mag-PCMA, methanol was used to extract the adsorbed NOM on Mag-PCMA. Methanol is extremely polar and tends to interact with NOM via hydrogen bonding. It was found that the recovery of adsorbed NOM onto Mag-PCMA with methanol was high in 5 cycles of regeneration and reuse. In the first two cycles of regeneration, the removal efficiency of NOM by Mag-PCMA was decreased from 85% to 83%, although this efficiency was reduced to around 70% after that. No carryover was observed during 5 cycles of regeneration, demonstrating that it was feasible to regenerate and reuse the Mag-PCMA for the removal of NOM.

## 4. Conclusions

Mag-PCMA with a core-shell structure were used to effectively remove a large percentage of NOM from water. Compared to Fe<sub>3</sub>O<sub>4</sub> particles, Mag-PCMA exhibited remarkable enhancement of NOM removal efficiency because of the coated silica-surfactant hybrid layer on the surface of Fe<sub>3</sub>O<sub>4</sub> particles. The most likely mechanisms of adsorption of NOM onto Mag-PCMA are (1) hydrophobic interactions; (2) hydrogen bonding; and (3) entanglement of the NOM in the surfactant micelles. Electrostatic interactions are less likely to play a role for the removal of NOM by Mag-PCMA. If electrostatic interactions were at play, faster sorption would be observed, such as in anion exchange. Also, the removal of 80–85% of the adsorbed NOM with a simple methanol wash indicates that hydrophobic interactions are most significant. The pH dependence of a certain fraction of the sorption indicates that hydrogen bonding is also important, but only at higher pH when the carboxylic groups in the NOM are deprotonated.

Mag-PCMA achieve higher NOM removal than many other approaches, including coagulation and membrane filtration, without some of the undesirable side effects such as membrane clogging. They also avoid some of the issues associated with activated carbon. The synthesis procedure is simple and the Mag-PCMA with adsorbed NOM can be easily removed from water via magnetic separation. Increasing the input energy can shorten the time needed for equilibrium. The Mag-PCMA perform well in a wide range of pH and can be regenerated and reused, although

the NOM removal process would need shorter contact times than used here, and the regeneration needs to be optimized further. It is expected that the Mag-PCMA will have potentially wide application in the removal of NOM from water. In the future, it is important to investigate possible competitive adsorption of NOM and other pollutants such as minerals into the mesopores, or the coating of NOM on the surface of minerals and their synergetic effect on the adsorption process.

## Acknowledgements

This work was partially supported by the University of California Lead Campus for Nanotoxicology Training and Research, funded by the University of California Toxic Substances Research & Training Program, and by the National Science Foundation (NSF) and the U.S. Environmental Protection Agency (USEPA) under Cooperative Agreement Number EF 0830117. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the NSF or the USEPA. This work has not been subjected to USEPA review and no official endorsement should be inferred.

## References

- [1] A.B.M. Giasuddin, S.R. Kanel, H. Choi, Adsorption of humic acid onto nanoscale zerovalent iron and its effect on arsenic removal, *Environ. Sci. Technol.* 41 (2007) 2022–2027.
- [2] E.L. Sharp, S.A. Parsons, B. Jefferson, Seasonal variations in natural organic matter and its impact on coagulation in water treatment, *Sci. Total Environ.* 363 (2006) 183–194.
- [3] T.H. Boyer, P.C. Singer, Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors, *Water Res.* 39 (2005) 1265–1276.
- [4] X. Yang, C. Shang, P. Westerhoff, Factors affecting formation of haloacetonitriles, halo ketones, chloropicrin and cyanogen halides during chloramination, *Water Res.* 41 (2007) 1193–1200.
- [5] Y.R. Tan, J.E. Kilduff, M. Kitis, T. Karanfil, Dissolved organic matter removal and disinfection byproduct formation control using ion exchange, *Desalination* 176 (2005) 189–200.
- [6] B. Bolto, D. Dixon, R. Eldridge, Ion exchange for the removal of natural organic matter, *React. Funct. Polym.* 60 (2004) 171–182.
- [7] N. Ates, M. Kitis, U. Yetis, Formation of chlorination by-products, in waters with low SUVA-correlations with SUVA and differential UV spectroscopy, *Water Res.* 41 (2007) 4139–4148.
- [8] A.R. Costa, M.N. de Pinho, M. Elimelech, Mechanisms of colloidal natural organic matter fouling in ultrafiltration, *J. Membr. Sci.* 281 (2006) 716–725.
- [9] S.R. Gray, C.B. Ritchie, T. Tran, B.A. Bolto, P. Greenwood, F. Buseti, B. Allpike, Effect of membrane character and solution chemistry on microfiltration performance, *Water Res.* 42 (2008) 743–753.
- [10] N. Her, G. Amy, A. Plottu-Pecheux, Y. Yoon, Identification of nanofiltration membrane foulants, *Water Res.* 41 (2007) 3936–3947.
- [11] Q.L. Li, M. Elimelech, Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter, *J. Membr. Sci.* 278 (2006) 72–82.
- [12] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (2008) 301–310.
- [13] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, H. Ozaki, The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes, *Desalination* 212 (2007) 191–208.
- [14] S. Lee, J.W. Cho, M. Elimelech, Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling, *J. Membr. Sci.* 262 (2005) 27–41.
- [15] X.H. Huang, M. Leal, Q.L. Li, Degradation of natural organic matter by TiO<sub>2</sub> photocatalytic oxidation and its effect on fouling of low-pressure membranes, *Water Res.* 42 (2008) 1142–1150.
- [16] P. Wang, A.A. Keller, Enhanced environmental mobility of carbon nanotubes in the presence of humic acid and their removal from aqueous solution, *Small* 4 (2008) 2166–2170.
- [17] H. Hyung, J.D. Fortner, J.B. Hughes, J.H. Kim, Natural organic matter stabilizes carbon nanotubes in the aqueous phase, *Environ. Sci. Technol.* 41 (2007) 179–184.
- [18] T.L.T. Laak, M.A.T. Bekke, J.L.M. Hermens, Dissolved organic matter enhances transport of PAHs to aquatic organisms, *Environ. Sci. Technol.* 43 (19) (2009) 7212–7217.
- [19] J. Hruska, P. KrAm, W.H. McDowell, F. Oulehle, Increased dissolved organic carbon (DOC) in Central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity, *Environ. Sci. Technol.* 43 (12) (2009) 4320–4326.

- [20] K.H. Choo, R. Tao, M.J. Kim, Use of a photocatalytic membrane reactor for the removal of natural organic matter in water: effect of photoinduced desorption and ferrihydrite adsorption, *J. Membr. Sci.* 322 (2008) 368–374.
- [21] D. Sun, T.T. Meng, T.H. Loong, T.J. Hwa, Removal of natural organic matter from water using a nano-structured photocatalyst coupled with filtration membrane, *Water Sci. Technol.* 49 (2004) 103–110.
- [22] H. Selcuk, L. Rizzo, A.N. Nikolaou, S. Meric, V. Belgiorno, M. Bekbolet, DBPs formation and toxicity monitoring in different origin water treated by ozone and alum/PAC coagulation, *Desalination* 210 (2007) 31–43.
- [23] A. Matilainen, M. Sillanpää, Removal of natural organic matter from drinking water by advanced oxidation processes, *Chemosphere* 80 (2010) 351–365.
- [24] T. Leiknes, M. Lazarova, H. Odegaard, Development of a hybrid ozonation biofilm-membrane filtration process for the production of drinking water, *Water Sci. Technol.* 51 (2005) 241–248.
- [25] M. Edwards, Predicting DOC removal during enhanced coagulation, *J. Am. Water Works Assoc.* 89 (1997) 78–89.
- [26] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, *Adv. Colloid Interface Sci.* 159 (2) (2010) 189–197.
- [27] B. Bolto, D. Dixon, R. Eldridge, S. King, K. Linge, Removal of natural organic matter by ion exchange, *Water Res.* 36 (2002) 5057–5065.
- [28] M. Bjelopavlic, G. Newcombe, R. Hayes, Adsorption of NOM onto activated carbon: effect of surface charge, ionic strength, and pore volume distribution, *J. Colloid Interface Sci.* 210 (1999) 271–280.
- [29] W. Cheng, S.A. Dastgheib, T. Karanfil, Adsorption of dissolved natural organic matter by modified activated carbons, *Water Res.* 39 (2005) 2281–2290.
- [30] A. Genz, B. Baumgarten, M. Goernitz, M. Jekel, NOM removal by adsorption onto granular ferric hydroxide: equilibrium, kinetics, filter and regeneration studies, *Water Res.* 42 (2008) 238–248.
- [31] B.H. Gu, J. Schmitt, Z.H. Chen, L.Y. Liang, J.F. McCarthy, Adsorption and desorption of natural organic-matter on iron-oxide – mechanisms and models, *Environ. Sci. Technol.* 28 (1994) 38–46.
- [32] C.Y. Lu, F.S. Su, Adsorption of natural organic matter by carbon nanotubes, *Sep. Purif. Technol.* 58 (2007) 113–121.
- [33] H. Hyung, J.H. Kim, Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters, *Environ. Sci. Technol.* 42 (2008) 4416–4421.
- [34] P.F. Lee, D.D. Sun, J.O. Leckie, Adsorption and photodegradation of humic acids by nano-structured TiO<sub>2</sub> for water treatment, *J. Adv. Oxid. Technol.* 10 (2007) 72–78.
- [35] A.H. Latham, M.E. Williams, Controlling transport and chemical functionality of magnetic nanoparticles, *Acc. Chem. Res.* 41 (2008) 411–420.
- [36] M.S. Toprak, B.J. McKenna, M. Mikhaylova, J.H. Waite, G.D. Stucky, Spontaneous assembly of magnetic microspheres, *Adv. Mater.* 19 (2007) 1362–1368.
- [37] R.D. Ambashta, M. Sillanpää, Water purification using magnetic assistance, a review, *J. Hazard. Mater.* 180 (2010) 38–49.
- [38] C.T. Yavuz, J.T. Mayo, W.W. Yu, A. Prakash, J.C. Falkner, S. Yean, L.L. Cong, H.J. Shipley, A. Kan, M. Tomson, D. Natelson, V.L. Colvin, Low-field magnetic separation of monodisperse Fe<sub>3</sub>O<sub>4</sub> nanocrystals, *Science* 314 (2006) 964–967.
- [39] Z.H. Ai, Y. Cheng, L.Z. Zhang, J.R. Qiu, Efficient removal of Cr(VI) from aqueous solution with Fe@Fe<sub>2</sub>O<sub>3</sub> core-shell nanowires, *Environ. Sci. Technol.* 42 (2008) 6955–6960.
- [40] T. Tuutijärvi, J. Lu, M. Sillanpää, G. Chen, As (V) adsorption on maghemite nanoparticles, *J. Hazard. Mater.* 166 (2009) 1415–1420.
- [41] W. Yantasee, C.L. Warner, T. Sangvanich, R.S. Addleman, T.G. Carter, R.J. Wiacek, G.E. Fryxell, C. Timchalk, M.G. Warner, Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles, *Environ. Sci. Technol.* 41 (2007) 5114–5119.
- [42] B. Bolto, D. Dixon, R. Eldridge, S. King, Cationic polymer and clay or metal oxide combinations for natural organic matter removal, *Water Res.* 35 (2001) 2669–2676.
- [43] J.F. Liu, Z.S. Zhao, G.B. Jiang, Coating Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water, *Environ. Sci. Technol.* 42 (2008) 6949–6954.
- [44] Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, Superparamagnetic high-magnetization microspheres with an Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core and perpendicularly aligned mesoporous SiO<sub>2</sub> shell for removal of microcystins, *J. Am. Chem. Soc.* 130 (2008) 28.
- [45] H.K. Karapanagioti, D.A. Sabatini, R.S. Bowman, Partitioning of hydrophobic organic chemicals (HOC) into anionic and cationic surfactant-modified sorbents, *Water Res.* 39 (2005) 699–709.
- [46] Z.H. Li, T. Burt, R.S. Bowman, Sorption of ionizable organic solutes by surfactant modified zeolite, *Environ. Sci. Technol.* 34 (2000) 3756–3760.
- [47] P. Wang, Q.H. Shi, Y.F. Shi, K.K. Clark, G.D. Stucky, A.A. Keller, Magnetic permanently confined micelle arrays for treating hydrophobic organic compound contamination, *J. Am. Chem. Soc.* 131 (2009) 182–188.
- [48] A. Matilainen, E.T. Gjessing, T. Lahtinen, L. Hed, A. Bhatnagar, M. Sillanpää, An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment, *Chemosphere* 83 (11) (2011) 1431–1442.
- [49] P.S. Haddad, E.L. Duarte, M.S. Baptista, G.F. Goya, C.A.P. Leite, R. Itri, Synthesis and characterization of silica-coated magnetic nanoparticles, *Prog. Colloid Polym. Sci.* 128 (2004) 232–238.
- [50] J.J. Qin, M.H. Oo, K.A. Kekre, F. Knops, P. Miller, Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water, *Sep. Purif. Technol.* 49 (2006) 295–298.
- [51] M. Kabsch-Korbutowicz, Effect of Al coagulant type on natural organic matter removal efficiency in coagulation/ultrafiltration process, *Desalination* 185 (2005) 327–333.
- [52] S. Wong, J.V. Hanna, S. King, T.J. Carroll, R.J. Eldridge, D.R. Dixon, B.A. Bolto, S. Hesse, G. Abbt-Braun, F.H. Frimmel, Fractionation of natural organic matter in drinking water and characterization by C-13 cross-polarization magic-angle spinning NMR spectroscopy and size exclusion chromatography, *Environ. Sci. Technol.* 36 (2002) 3497–3503.
- [53] S. Ghosh, H. Mashayekhi, B. Pan, P. Bhowmik, B.S. Xing, Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter, *Langmuir* 24 (2008) 12385–12391.
- [54] D.B. Wagoner, R.F. Christman, G. Cauchon, R. Paulson, Molar mass and size of Suwannee River natural organic matter using multi-angle laser light scattering, *Environ. Sci. Technol.* 31 (1997) 937–941.
- [55] J.D. Filius, J.C.L. Meeussen, D.G. Lumsdon, T. Hiemstra, W.H. Van Riemsdijk, Modeling the binding of fulvic acid by goethite: the speciation of adsorbed FA molecules, *Geochim. Cosmochim. Acta* 67 (2003) 1463–1474.