Environmental Science Nano

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Evaluation of Polymer-Coated Magnetic Nanoparticles for Oil Separation under Environmentally Relevant Conditions: Effect of ionic strength and natural organic macromolecules

*Seyyedali Mirshahghassemi[1], Bo Cai[2] and Jamie R. Lead[3]**

AUTHOR INFORMATION

Corresponding Author

*Phone: (803) 777-0091. Fax: (803) 777-3391

E-mail: jlead@mailbox.sc.edu.

[1, 3] Center for Environmental Nanoscience and Risk (CENR), Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, South Carolina 29208, United States

[2] Department of Epidemiology and Biostatistics, Arnold School of Public Health, University of South Carolina, Columbia, South Carolina 29208, United States

NANO IMPACT

The limitations of current oil remediation techniques has inspired research into the application of nanotechnology in this area. Here, we report excellent oil removal efficiencies using polyvinylpyrrolidone-coated magnetic iron oxide nanoparticles under various environmentally relevant conditions. Results showed excellent removal capacity, which increased in the presence of major ions and decreased in high concentrations of natural organic macromolecules. Under all conditions, efficient separation could be performed by altering the experimental conditions. This study highlights the application of nanoparticles for oil remediation in marine and non-marine systems.

ABSTRACT

Oil spills in marine and non-marine environments can have dramatic effects on the environment. Previously, we reported near 100% removal of a reference MC252 oil using polyvinylpyrrolidone (PVP)-coated magnetic nanoparticles (NPs) from an oil-water mixture in ultra-pure water and synthetic seawater with low concentration of Suwannee River fulvic acid (SRFA). In this study, the same type of NPs were used to remove oil from oil-water mixtures (oil concentration used was 0.15 ± 0.05 g L^{-1}) in synthetic freshwaters and seawater in the presence and absence of low (1 ppm) and high (10 ppm) concentration of SRFA or alginic acid. For the optimum NP concentration (17.6 ppm) and separation time (1 h), data showed essentially 100% oil removal from synthetic freshwaters and seawater in the absence of natural organic macromolecules (NOM). Nearly 100% of C9-C20 alkanes were removed as measured by gas chromatography-mass spectrometry (GC-MS), although removal of the longer chain alkanes was slightly lower. The presence of NOM led to a statistically significant decrease in oil removal by acting as a competitive phase for either PVP or oil and reducing NP-oil interactions driven by hydrophobic effect of PVP coating. Ionic strength facilitated oil sorption presumably by enhancing magnetic separation of the oil-NP complex or altering PVP hydrophobicity. Alteration of the separation conditions allowed optimal oil removal, with essentially 100% oil removal under most, but not all conditions. Results show that these NPs are a cheap, facile and reliable technique for removing oil under a wide range of environmentally relevant conditions.

INTRODUCTION

Oil can be released into the aquatic environment from different sources such as natural seeps or during extraction, transportation and consumption of petroleum. The estimated amount of released oil in the environment from production to consumption of oil is approximately 670,000 tons per year worldwide.[1] In 2010, there were two well-known oil spills (Deepwater Horizon and Enbridge oil spill) in the Unites States. In the Deepwater Horizon oil spill (April 2010), 4.9 million barrels of oil released in the Gulf of Mexico and had catastrophic impact on marine species, terrestrial wildlife and nearshore habitats.[2, 3] Three months later, in an inland oil spill incident, a pipeline ruptured in Michigan, releasing approximately 20,000 barrels of crude oil into the Talmadge Creek and then to the Kalamazoo River.[4] While the marine spills are highly publicized, freshwater oil spills are more common and have a greater potential to contaminate water supplies and impact population centers; clearly oil remediation is required not only from the marine environment but also from fresh water resources.[5]

Skimming, *in-situ* burning, dispersants and sorbents are current clean-up techniques for removing spilled oil in water systems.[6] Mechanical techniques have a low removal efficiency and are only effective on thick oil slicks[7], while *in-situ* burning is only effective on a thick surface layer of oil and may cause public health and air pollution issues.[8] Dispersants remove oil from water surface and re-disperse them in the water column, however, the dispersed oil-dispersant mixture can adversely impact plankton or other water column organisms such as coral reefs.[9] In the case of oil spills in freshwaters, major commercially available dispersants (e.g. Corexit 9500 and 9527) have low efficacy and have been formulated for use in marine systems.[9] Dispersant application in freshwater systems is unlikely because they can increase the hydrocarbon concentration in the drinking water resources.[9] Consequently, using dispersants not only has environmental concerns but also can have human health concerns.

Recently, nanotechnology has attracted considerable interest in the field of oil remediation and many researchers have reported producing hydrophobic materials for oil removal from aqueous solutions.[10-15] For instance, Yuan et al.[16] used a vapour deposition technique to produce a superhydrophobic nanowire membrane which can absorb up to 20 times its own mass of oil. Lei et al.[17] produced a porous boron nitride nanosheet with an oil absorption capacity up to 33 times its own weight which can be easily cleaned for reuse by burning or heating in air. Despite the excellent performance of these types of materials, they are often expensive, use and produce toxic materials and are most effective on surface oil slicks due to their hydrophobicity. To overcome these limitations, Pavia-Sanders et al.[18] synthesized a magnetic shell cross-linked knedel-like (MSCK) nanoparticles (NPs) which amphiphilic nature of the MSCK system allows its application for removal of submerged oil. Similarly, Palchoudhury et al.[19] produced a water soluble polyvinylpyrrolidone (PVP)-coated iron oxide NPs capable of sorbing over 150 times its own volume of oil. Despite their excellent oil absorption capacity, their performance under realistic conditions is unclear. For example, the interaction of NPs and naturally occurring organic macromolecules, including both humic and non-humic substances, can reduce oil absorption capacity of NPs by forming a coating on the surface of NPs and/or replacing of their existing surface coating.[20-23] Moreover, the presence of monovalent and divalent cations can enhance NP aggregation and reduce efficiency of the NPs by reducing their specific surface area.[24]

Previously, we developed a cheap and facile synthesis technique to produce PVP-coated iron oxide NPs which showed approximately 100% oil removal from ultra-pure water and synthetic sea water in the presence of low concentrations of fulvic acid.[25] In the current study, the oil removal capability of these NPs was tested in different environmentally relevant and more challenging conditions, including a wide range of natural organic macromolecules (NOM) concentrations and ionic strengths.

METHODOLOGY

The hydrothermal synthesis method used to produce PVP-coated iron oxide NPs as well as the NP characterization have been published previously and a short summary of NP characterization is given below.[25] PVP-coated magnetic NPs were synthesized using a facile and low cost hydrothermal technique which requires low temperatures and ambient pressure and does not use any inert gases. Figure S1 shows an example of atomic force microscopy (AFM) scans (10 × 10 μm) of PVP-coated magnetic NPs. Based on AFM results, the median particle size is 11.2 nm (interquartile range: 6.3-18.3 nm). The hydrodynamic size is 127.4±4.2 nm as measured by dynamic light scattering (DLS). The Fourier transform infrared spectrometer (FTIR) result suggests that NPs are coated by PVP through the PVP carbonyl group. Details of the FTIR result and assigned chemical groups for each wavenumbers are provided in Table S1. According to X-ray diffraction (XRD) pattern, the dominant phase of NPs is magnetite (Fe_3O_4), although the presence of maghemite cannot be discounted. Moreover, 8.5% of mass of NPs belong to their PVP coating and 91.5% to the iron oxide NPs as obtained from the thermogravimetric analysis (TGA).

Oil concentration was measured by fluorescence spectroscopy and gas chromatography-mass spectrometry (GC-MS). Emission spectra of oil samples were recorded over the range of 350 to 650 nm at the excitation wavelength of 337 nm on a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. This excitation wavelength has been widely used in the literature for detecting polycyclic aromatic hydrocarbons of crude oil.[26, 27] A calibration curve was obtained based on known oil concentration samples using the fluorescence spectroscopy. Using this calibration curve and the integration of the fluorescence spectrum for oil samples before and after magnetic separation, oil removal was quantified. GC-MS analysis was performed on an

Agilent 6890N gas chromatography system and an Agilent 5975 mass spectrometer to quantify the removal efficiency for individual alkanes. Details for GC-MS analysis are described in the supporting information. To measure NP removal efficiency, NPs in the suspension before and after magnetic separation were digested using aqua regia and the total iron concentration was measured using inductively coupled plasma-optical emission spectrometer (ICP-OES; Varian 710-ES).

Crude oil from the Deepwater Horizon spill (sample ID number: A0068H, Aecom Environment) was mixed well with ultra-pure water (Millipore) in a vial via sonication (Branson 2800, 40 kHz, ambient conditions) for 30 min to prepare the oil samples for the oil removal experiment.[19] The oil concentration used was 0.15 ± 0.05 g L^{-1} which is based on literature data[28] and similar to our previous works.[19, 25] To study the effect of ionic strength on oil sorption capacity of NPs, experiments were performed in synthetic soft, hard and sea waters in the absence of NOM. The effect of NOM on oil removal efficiency was investigated by performing experiments with two environmentally relevant NOM types of Suwannee River fulvic acid (SRFA, International Humic Substances Society) and alginic acid (AA, Alfa Aesar) separately in synthetic waters. The synthetic waters were prepared following the U.S. Environmental Protection Agency protocol (EPA-821-R-02-012).[29] The composition of the various synthetic waters is tabulated in Table S2 and S3. In a typical oil removal experiment, accurately known masses of NPs were added to the oil-water mixtures and mixed for 5 minutes via sonication prior to magnetic separation. NPs were then magnetically separated using a 1 1/2" cubic neodymium magnet (Grade N 52, K&J Magnetics Inc.) for specific periods of time. The remaining oil-water solution in each vial was collected for further measurement. NP concentrations in the range 17.6-52.8 ppm were tested, with higher concentrations used for the more challenging conditions.

The correlations between the monovalent and divalent cations, NOM and oil removal efficiency were analyzed by calculating Pearson correlation coefficients obtained by a code in R Project software (version 3.2.1). For the statistical analysis, the GC-MS data using initial NP concentration of 17.6 ppm and 1 h separation time as well as GC-MS results from our previous work[25] were analyzed.

RESULT AND DISCUSSION

Oil removal in synthetic environmental waters without NOM. Previously, we have reported that PVP-coated magnetic NPs can remove near 100% of oil from synthetic seawaters in the presence and absence of low concentration of SRFA.[25] However oil spills occur in different aquatic systems with different properties. The oil removal potential in soft, hard and sea waters in the absence of NOM was examined using the optimum conditions established by our previous work[25] (initial NP concentration = 17.6 ppm and magnetic separation time = 1 h). A large and significant reduction in fluorescence spectra for all solutions after NP treatment compared to the original oil-water mixture was observed, clearly showing the removal of aromatic compounds (Figure 1a). Based on these results, the percentage of oil removal was 95.7%, 99.7% and 99.3% in soft, hard and sea waters without NOM, respectively, suggesting excellent oil removal efficiency in a short reaction time. Based on our calculations, each NP sorbed 8.5 times its own mass of oil. Previously, we have shown that PVP-coated magnetic NPs can sorb up to 180 times its own volume of oil.[19] In addition, chromatography peaks for all final solutions after NP treatment are significantly reduced compared to the original oil-water mixture showing the removal of alkanes (Figure 2a). Essentially 100% of the lower molecular mass alkanes (C9-C20) were removed from different solutions (soft, hard and sea waters) (Figure 2b). For longer chain alkanes, NP showed higher removal efficiency from the sea water compared to the fresh waters indicating an improved removal efficiency at high ionic strengths (Figure 2b).

Oil removal experiments in synthetic environmental waters with NOM. To further challenge the NPs and to mimic natural fresh and sea waters, oil removal in soft, hard and sea waters in the presence of 1 and 10 ppm SRFA and AA was performed. The initial NP concentration in this set of experiments was 17.6 ppm and separation time was 1 h. Based on the fluorescence results, for the oil removal experiment in the presence of 1 ppm SRFA the percentage of oil removal was 54.7%, 93.6% and 98.7% in soft, hard and sea waters, respectively (Figure 1b), again showing that there is a positive effect of ionic strength on oil removal and suggesting that NOM reduces efficacy of the oil remediation. In the presence of 1 ppm SRFA, using this separation condition the GC-MS results showed 100% removal of lower molecular mass alkanes (C9-C16) and lower removal efficiency for longer chain alkanes (Figure 3a). At 1 ppm AA, the oil removal percentage was 39.3%, 87.1% and 99.3% in soft, hard and sea waters, respectively (Figure 1d). Moreover, in the presence of 1 ppm AA, 100% of C9-C19 were removed in hard and sea waters while these removal percentages in soft water were 40 - 70% (Figure 3c). No significant difference between the effects of SRFA and AA on the oil removal capability of NPs was observed.

To obtain the optimum separation conditions for oil removal in the presence of NOM, higher NP concentration (35.2 ppm) and longer separation time (18 h) were used. Fluorescence and GC-MS results showed a significant increase in oil removal efficiency from all the solutions (Figure S2 and S3). For example in the presence of 1 ppm SRFA and the presence of 1 and 10 ppm AA, GC-MS results showed 100% removal of most of lower chain alkanes (C9-C21) from the oil-water mixture in hard waters and marine waters (Figure S3).

For the highest NOM concentrations used (10 ppm), which is typical of high-organic freshwater systems, oil removal was less than 100% under these conditions. As a result, NP concentrations of up to 52.8 ppm and separation time of 18 h were used. At 10 ppm SRFA, oil removal percentages increased from 47.9% to 71.6% in soft water, and from 53.2% to 71.3% in hard water by increasing NP concentration from 35.2 to 52.8 ppm (Figure S2b and 4a). Using a higher NP concentration (52.8 ppm), the removal percentages of C9-C21 were greater than 70% in both soft and hard waters and were 100% for the experiment in sea water (Figure 5a). Better removal is expected using higher NP concentrations and longer times. For longer chain alkanes (C22-C26), the removal percentages were greater than 30%, 35% and 70% in soft, hard and sea waters, respectively (Figure 5a). In the presence of 10 ppm AA, oil removal percentage was 83.4%, 92.1% and 95.8% in soft, hard and sea waters, respectively (Figure 4b). At 10 ppm AA, 100% of C9-C21 were removed from all three solutions (Figure 5b). The removal percentages of C22-C26 were greater than 25%, 50% and 50% in soft, hard and sea waters, respectively (Figure 5b).

To study correlations between NOM, monovalent and divalent cations and oil removal efficiency, a Pearson correlation test was performed on the hydrocarbon removal data (Table 1). The correlation coefficients between the alkanes removal efficiency and monovalent and divalent cations were positive and statistically significant ($p\text{-value} < 0.05$). This positive correlation can be seen by comparing the fluorescence and GC-MS results for the oil removal experiment in the presence of NOM in Figure 1 and 2. Results also show a statistically significant negative correlation between NOM (both SRFA and AA) and oil removal ($p\text{-value} < 0.05$). Nevertheless, our results showed that this negative effect can be compensated by altering the experimental remediation conditions.

Finally, the removal efficiency of the iron oxide NPs themselves (rather than the oil) was also measured under different conditions by measurement of total iron after a magnetic separation. Greater than 96% removal of the NPs from all synthetic waters without NOM was observed, and increased NOM concentration (both SRFA and AA) led to a decrease in the NP removal (Table 2). For example, the oil removal in hard water decreased from 99.1% to 65.2% when the SRFA concentration increased from 0 to 10 ppm. However, the lower removal efficiency was offset by increased magnetic separation time and NP concentration (Table S4). In sea water solutions, greater than 95% removal of the iron oxide NPs was observed under all conditions (Table 2). Using higher NP concentrations and longer magnetic separation times, nearly 100% removal was observed in most of conditions.

The mechanism of oil removal and effect of ionic strength and NOM on oil removal efficiency can be explained as follows. Oil sorption is likely driven by the hydrophobic effect, with hydrophobic moieties of the NP coating allowing preferential sorption of hydrocarbons from the oil-water mixture onto the NPs and from the aqueous phase.[30] These nonpolar interactions between the hydrophobic fractions of the PVP and hydrocarbons cause the oil sorption. By increasing the ionic strength of the solution, higher oil and NP separation efficiencies were observed. Increasing the ionic strength can potentially explain this phenomena in two ways: (1) increased agglomeration, possibly through reduced electrostatic (electrosteric in this case) repulsion forces and/or enhancement of bridging flocculation.[24, 31-33] As the magnetic NPs are single-domain and magnetic force upon a magnetic particle is linearly proportional to volume, magnetic separation would be more effective on the agglomerated NPs resulting in higher NP, and therefore oil, removal efficiency.[34] (2) Increased oil sorption by altering PVP hydrophobicity. In addition, the added NOM reduces oil removal from the aqueous phase. NOM likely acts as a competitive phase for either PVP or the oil.[35, 36] If the NOM binds to PVP it will competitively block the potential for oil sorption. However, if NOM binds to the oil, it increases the solubility of the oil, decreasing the hydrophobic driver. Previous work has shown that NOM interactions with PVP are minimal[37], so increased solubility of oil from the formation of oil-NOM complexes is likely. However, we have little direct evidence for these mechanisms and further works need to be performed. The reduction in effectiveness of the separation in the presence of the NOM can be corrected by alteration of the experimental conditions (NP:oil ratio and separation time).

CONCLUSION

In summary, our results showed that the PVP-coated magnetic NPs are a cheap, facile and reliable technique for removing oil under various environmentally relevant conditions in the presence of a wide range of NOM concentrations. Under optimized conditions, results showed complete or near-complete oil removal. This study shows that the application of nanomaterials for oil remediation depends on the aqueous properties such as NOM and ionic strengths and optimization according to those conditions is required. Statistical analysis indicated that NOM decreases oil removal effectiveness, while major cations improve removal.

ASSOCIATED CONTENT

ACKNOWLEDGMENTS

The authors thank the SmartState Center for Environmental Nanoscience and Risk (CENR) for financial support. We also thank Dr. Mike Walla for use of GC-MS. We are grateful to the BP (Aecom) for providing reference MC252 surrogate oil (sample ID number: A0068H).

Supporting Information

Additional information on the NP characterization, GC-MS analysis, composition of synthetic waters and results for oil removal experiment are provided in supporting information.

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Table 1. Correlation coefficients of NOM and cations with oil removal, all based on GC-MS results.

	Correlation coefficient	P-value
SRFA	-0.472	<0.001
AA	-0.141	0.018
Monovalent cations (Na and K)	0.165	<0.001
Divalent cations (Mg and Ca)	0.214	<0.001

Table 2. NP magnetic separation efficiency (initial NP concentration = 17.6 ppm and separation time = 1 h). *The lower removal at 10 ppm NOM in soft water was improved by increasing the separation time and the concentration of NPs.

Solution condition	Oil removal experiment in the presence of SRFA		Oil removal experiment in the presence of AA	
	SRFA concentration (ppm)	NP removal efficiency (%)	AA concentration (ppm)	NP removal efficiency (%)
Soft water	0	96.6		
	1	93.5	1	92.0
	10	43.6*	10	45.5*
Hard water	0	99.1		
	1	98.7	1	97.9
	10	65.2	10	96.8
Sea water	0	99.8		
	1	99.4	1	98.3
	10	98.0	10	95.8

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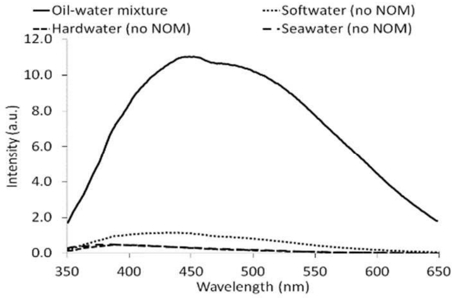

Fluorescence spectra for the oil-water mixtures before and after oil removal using PVP-coated magnetic nanoparticles under different environmentally relevant conditions.

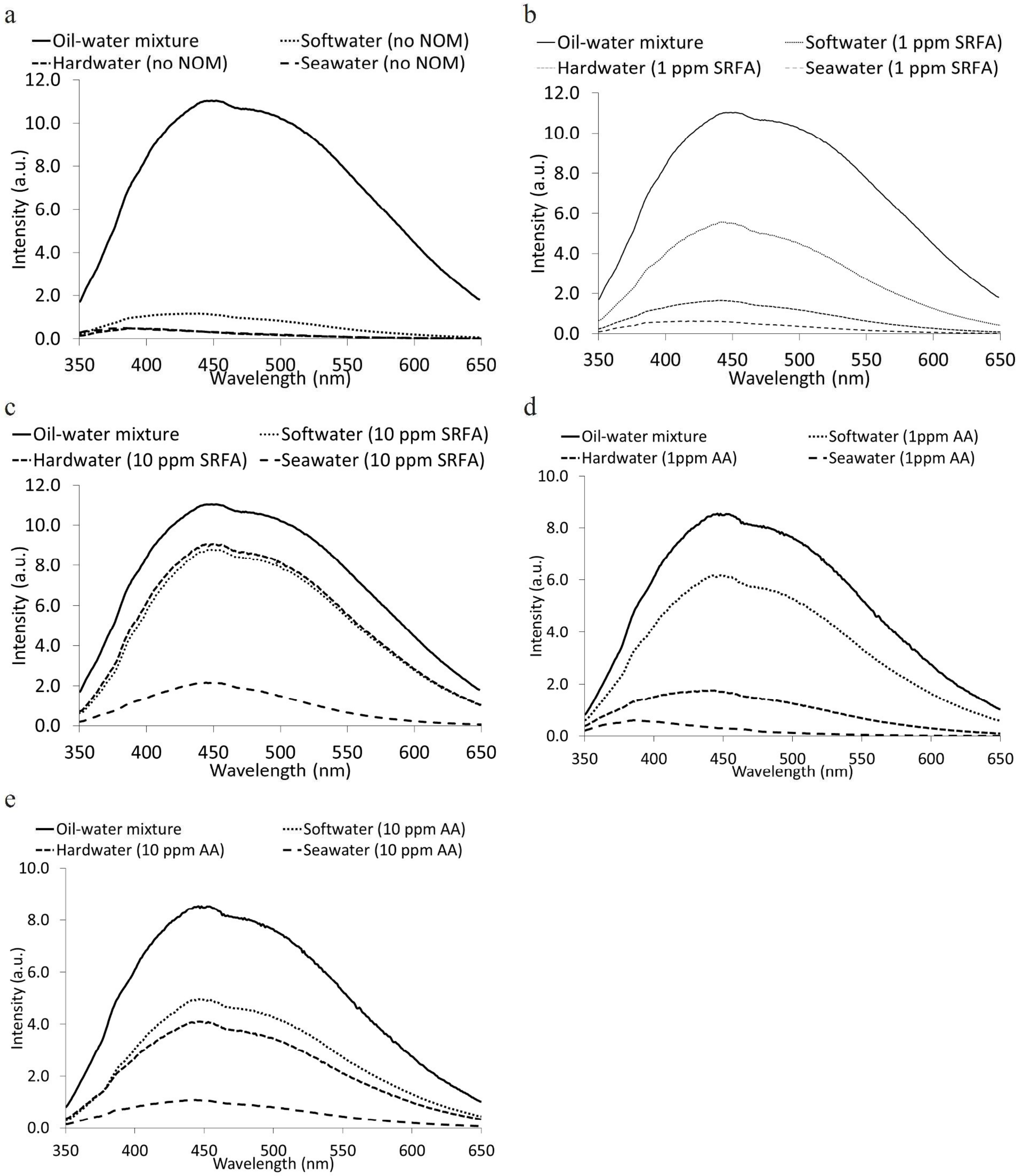

Figure 1. Fluorescence spectra before and after oil removal. Oil removal in the (a) absence of NOM, presence of (b) 1 ppm SRFA, (c) 10 ppm SRFA, (d) 1 ppm AA and (e) 10 ppm AA (Solution conditions: soft, hard and sea waters, NP concentration = 17.6 ppm and separation time = 1 h).

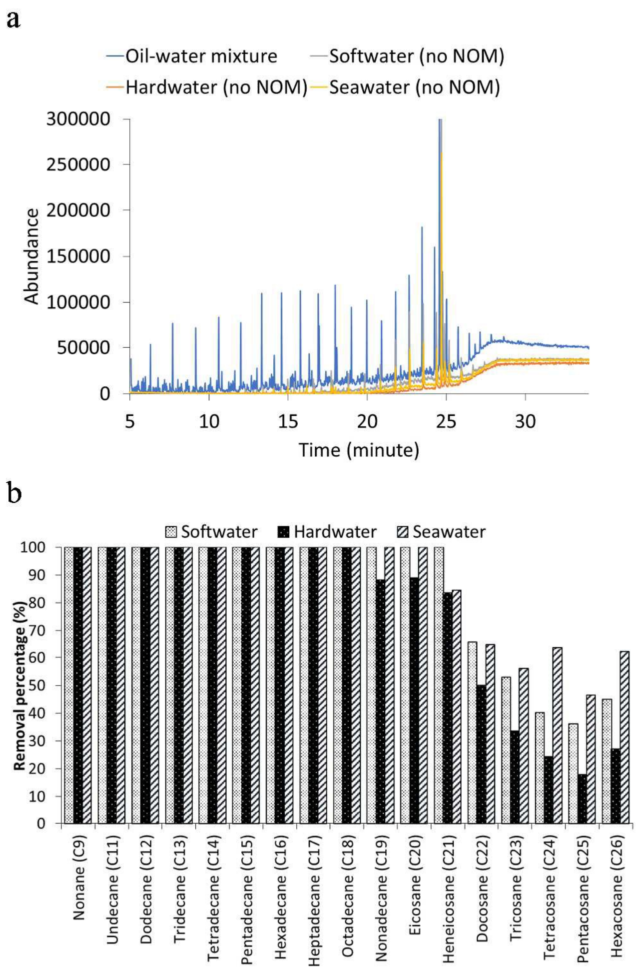

Figure 2. GC-MS results for oil removal in the absence of NOM (a) chromatograms and (b) results shown as removal percentages. (Solution condition: soft, hard and sea waters, NPs concentration= 17.6 ppm and separation time= 1 h).

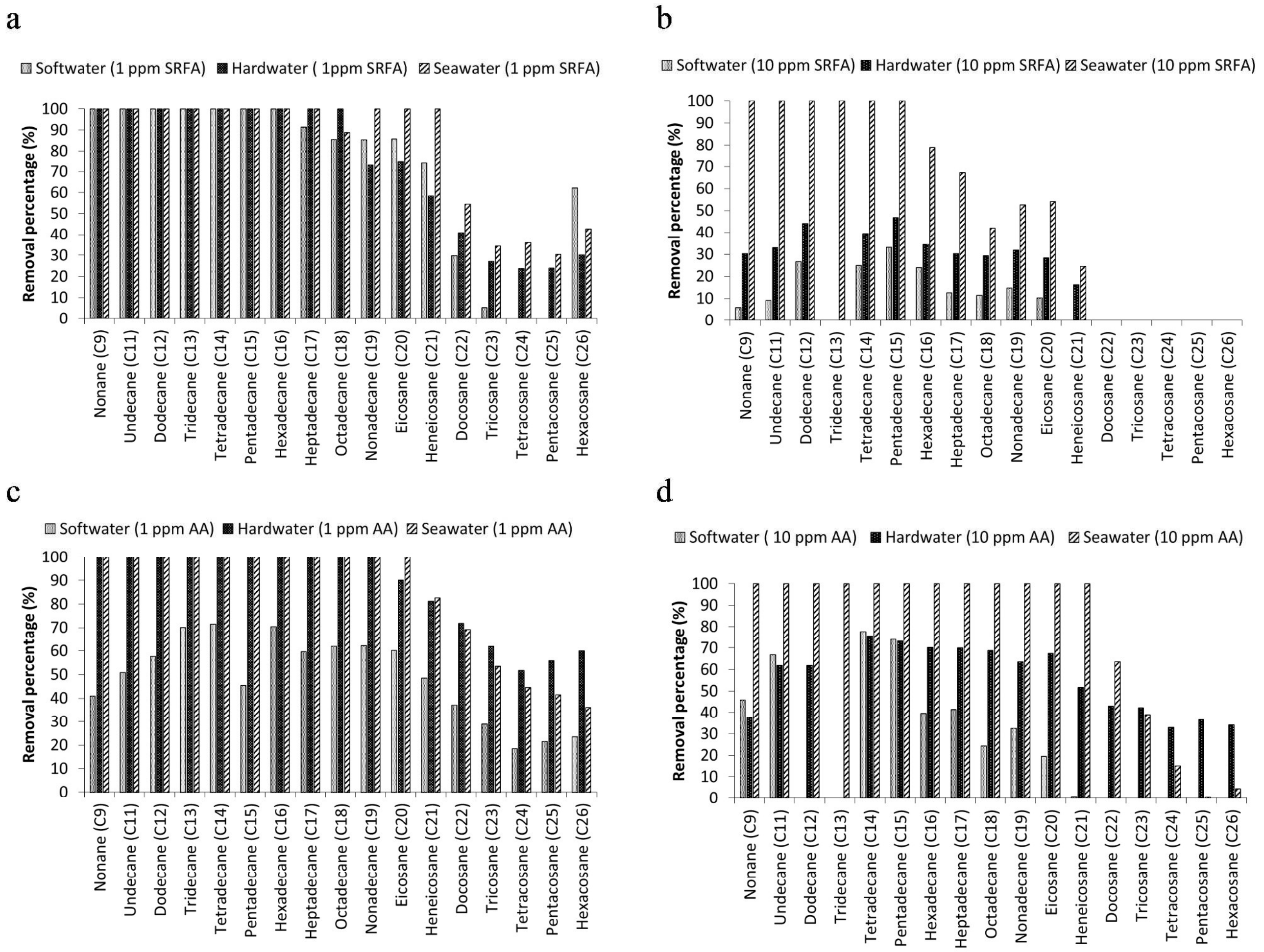

Figure 3. GC-MS removal percentages for oil removal in the presence of (a) 1 ppm SRFA, (b) 10 ppm SRFA, (c) 1 ppm AA and (d) 10 ppm AA. (Solution condition: soft, hard and sea waters, NPs concentration= 17.6 ppm and separation time= 1 h).

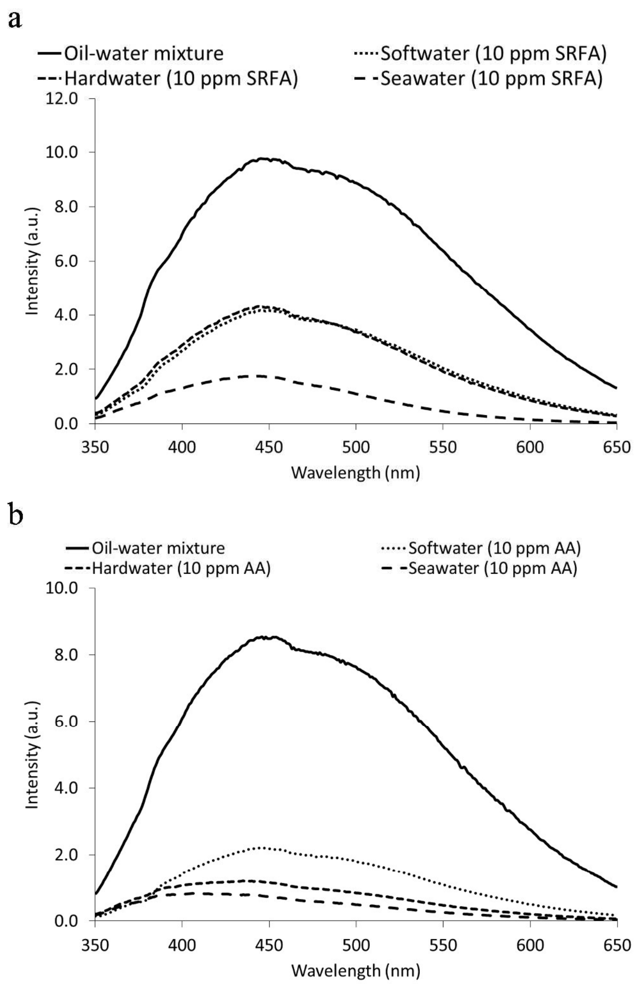

Figure 4. Fluorescence spectra before and after oil removal. Oil removal in the presence of (a) SRFA and (b) AA (Solution conditions: soft, hard and sea waters, NP concentration = 52.8 ppm and separation time = 18 h).

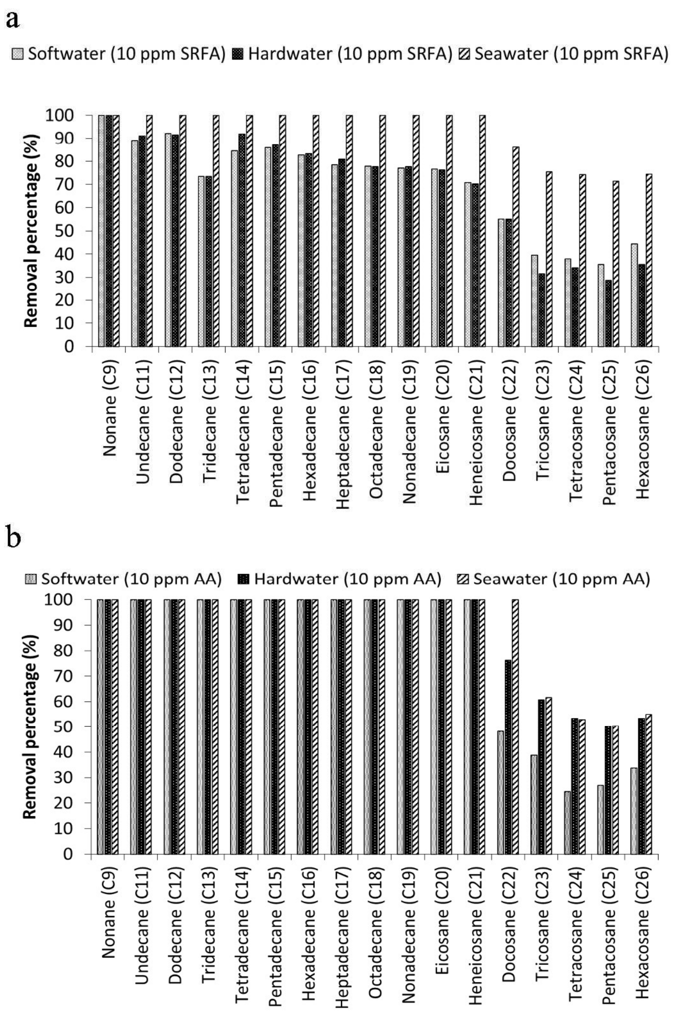

Figure 5. GC-MS results for oil removal in the presence of (a) 10 ppm SRFA and (b) 10 ppm AA. (Solution condition: soft, hard and sea waters, NPs concentration= 52.8 ppm and separation time= 18 h).