Supporting Information

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

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Methodology

GC-MS analysis

The analytical GC column was an Agilent TG-5MS (30 m × 0.25mm I.D., 0.25 µm film thickness) coated with 5% phenylmethylsiloxane stationary phase. The initial oil-water mixture and the final sample after NP treatment were extracted by methyl tert-butyl ether (MTBE, Alfa Aesar) for GC-MS analysis. 1µl of extracted sample was injected by the injection port in the splitless mode. High-purity helium gas (99.9%) with a constant flow rate of 1.5 mL min^{-1} was used as the carrier gas. Spectra were obtained in the electron impact mode (70 eV) scanning from 40 to 400 m/z for the quantitative analysis of the oil samples. The oven temperature was operated from 40 to 300 °C rising at 10 °C min^{-1}. A full scan mode was used and saturated hydrocarbons were monitored. The detected hydrocarbons were approximately 8% of total components in the reference oil sample, although saturated hydrocarbons of sample were 56% of total components.[1]

Composition of synthetic waters

The composition of the synthetic fresh and sea waters are provided in Table S2 and S3, respectively. After adding each salt, the solution was stirred well and the final solution was aerated for 24 h following the U.S. EPA protocol (EPA-821-R-02-012).[2] Based on our calculation, the ionic strength for synthetic soft, hard and sea waters is 1.146, 4.584 and 829.853 mmol L^{-1}, respectively.

Result and discussion

Figure S2 and S3 show the fluorescence and GC-MS results for the oil removal experiment using higher NP concentration (35.2 ppm) and longer separation time (18 h), respectively. Results indicate that by increasing NP concentration and magnetic separation time the oil removal efficiency increased. At 10 ppm SRFA, the percentage of oil removal was 47.9%, 53.2% and 93.1% in soft, hard and sea waters as measured by fluorescence spectroscopy, respectively (Figure S2a). For the same separation condition, at 1 ppm AA the oil removal percentage was 53.8%, 90.6% and 100% in soft, hard and sea waters, respectively (Figure S2b).

Comparison between synthesis techniques

We modified our previous calculation[3] on the chemical cost and required materials for producing 100 g of PVP-coated iron oxide NPs. These calculations are based on stoichiometric reactions and the Sigma-Aldrich website was used for material cost (for non-bulk ordering; bulk ordering will clearly lower the cost for all systems). This comparison is reported as a representative of the material cost for producing magnetic nanoparticles and shows that the material cost for the hydrothermal synthesis technique is substantially lower compared to our previous solvothermal synthesis technique[4].

Solvothermal synthesis technique[4]: 654 mL Triethylene glycol, 458 g $Fe(acac)_3$ and 196 g PVP. (Total material cost: $216)

Hydrothermal synthesis technique[3] (used in the current study): 51.5 g $FeCl_2.4H_2O$, 280 g $FeCl_3.6H_2O$, 1.6 L ammonium hydroxide and 780 g PVP. (Total material cost: $157)

Table S1. Summary of FTIR wavenumber and assigned chemical group[3].

Chemical group	Wavenumber (cm^{-1})
CH_2	1425, 2952 and 2887
C-N	1291
C=O	1656
O-H	3371

Table S2. Composition of synthetic soft and hard waters

	$NaHCO_3$ (mg L^{-1})	$CaSO_4.2H_2O$ (mg L^{-1})	$MgSO_4$ (mg L^{-1})	KCl (mg L^{-1})
Soft water	48.0	30.0	30.0	2.0
Hard water	192.0	120.0	120.0	8.0

Table S3. Composition of synthetic seawater

Compound	Concentration (g L^{-1})
NaCl	21.03
Na_2SO_4	3.52
KCl	0.61
KBr	0.088
$Na_2B_4O_7.10H_2O$	0.034
$MgCl_2.6H_2O$	9.50
$CaCl_2.2H_2O$	1.32
$SrCl_2.6H_2O$	0.02
$NaHCO_3$	0.17

Table S4. NP removal efficiency. (Initial NP concentration = 35.2 ppm, separation time = 18 h).

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	1	99.4	1	99.1
	10	83.3	10	78.3
Hard water	1	99.4	1	99.9
	10	88.9	10	87.1
Sea water	1	99.5	1	99.2
	10	99.9	10	99.9

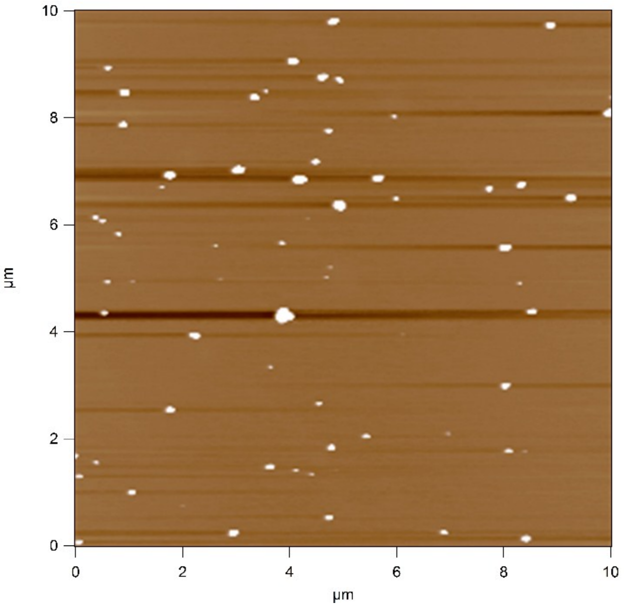

Figure S1. Topographical AFM image of PVP-coated iron oxide NPs.

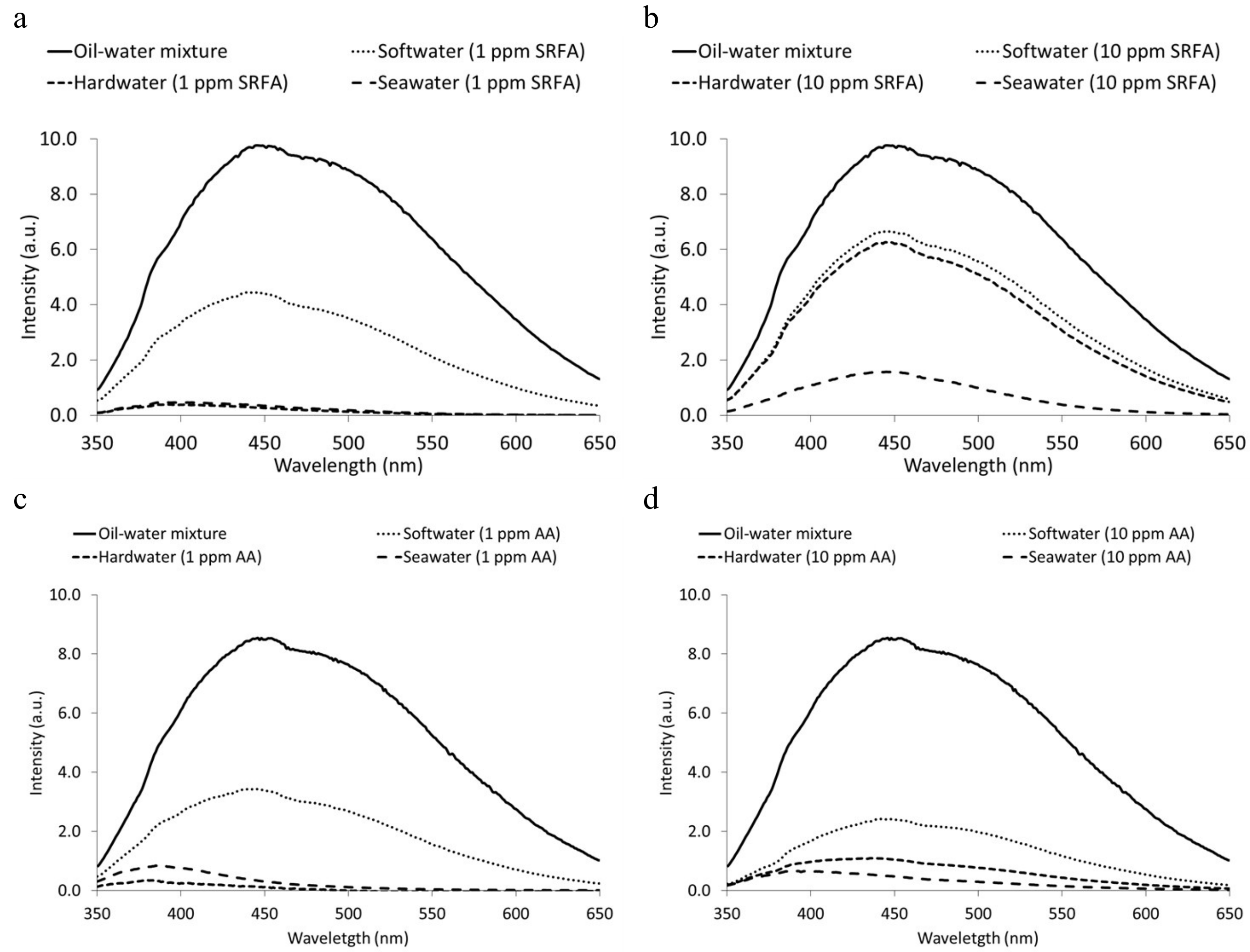

Figure S2. Fluorescence spectra before and after oil removal. Oil removal in the presence of (a) 1 ppm SRFA, (b) 10 ppm SRFA, (c) 1 ppm AA and (d) 10 ppm AA (Solution conditions: soft, hard and sea waters, NP concentration = 35.2 ppm and separation time = 18 h).

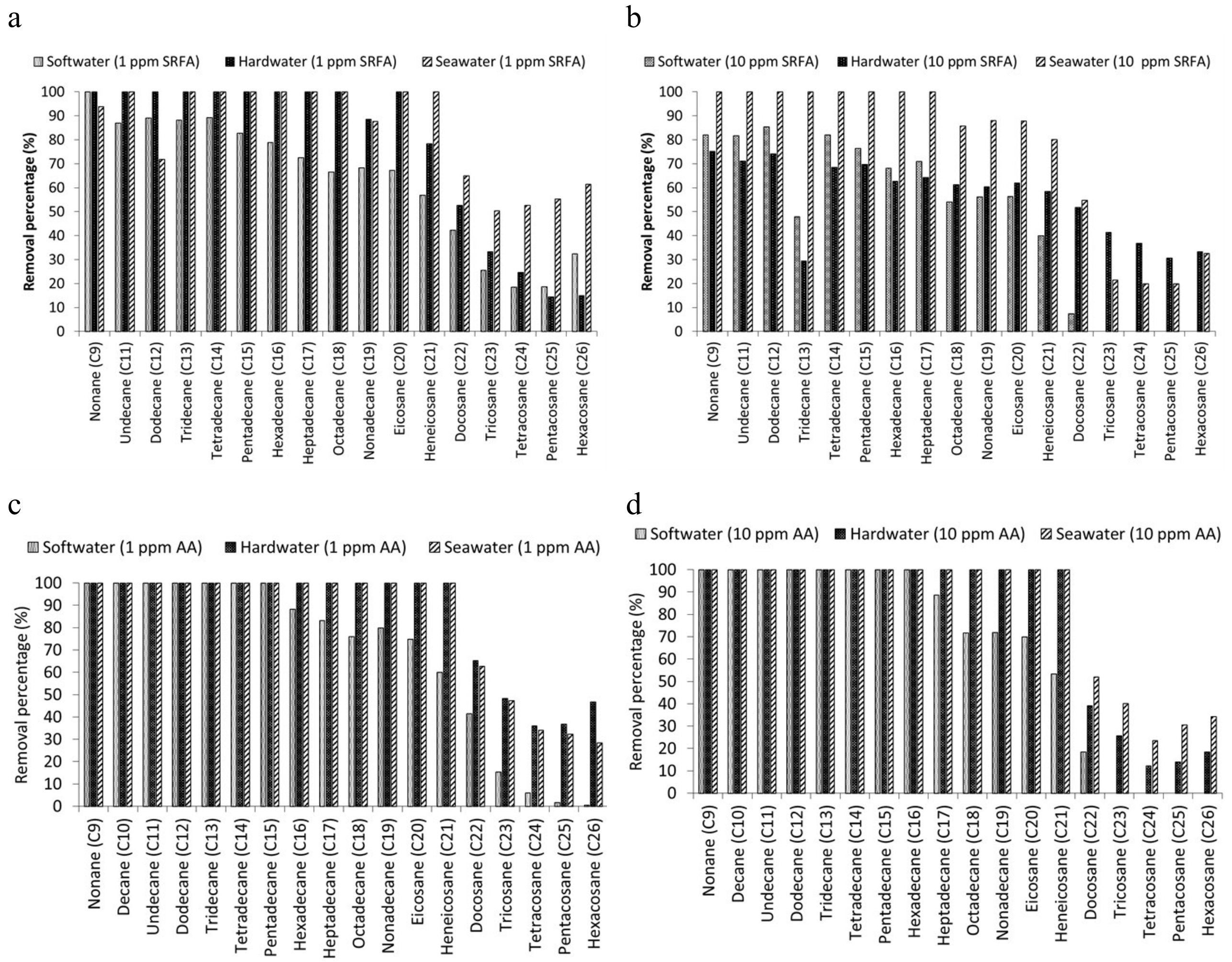

Figure S3. GC-MS removal percentages for oil removal in the presence of (a) 1 ppm SRFA, (b) 10 ppm SRFA, (c) 1 ppm AA and (d) 10 ppm AA. (Solution condition: soft, hard and sea waters, NPs concentration= 35.2 ppm and separation time= 18 h).

References

1. BP, *directory: Oil. subdirectory: Oil Characteristics – additional reference oils. filename: OilChemistry_O-04v01-01.zip*, 2014.
2. U.S.EPA, *Methods for measuring the acute toxicity of effluents and receiving water to freshwater and marine organisms. EPA-821-R-02-012, 1–266*, U.S. Environmental Protection Agency Office of Water, Washington, DC, 2002.
3. S. Mirshahghassemi and J. R. Lead, *Environ. Sci. Technol.*, 2015, DOI: 10.1021/acs.est.5b02687.
4. S. Palchoudhury and J. R. Lead, *Environ. Sci. Technol.*, 2014, **48**, 14558-14563.