Electronic Supplementary Information

Modeling Performance of Rhamnolipid-Coated Engineered Magnetite Nanoparticles for U(VI) Sorption and Separation

Neha Sharma[†], Anushree Ghosh[†], John D. Fortner[✧], Daniel E. Giammar[†,*]

[†]Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States

[✧]Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06520, United States

*Corresponding Author:
Address: Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, USA
Phone: (314) 935-6849
Email: giammar@wustl.edu

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Supplementary Information

Table S1: Phase transfer efficiency achieved by variation of various parameters for obtaining aqueous stable suspensions using Rhamnolipids

Iron oxide volume (µL)	Rhamnolipid concentration (mg/L)	Time (min)	Amplitude (%)	Numbered Mean (nm)	Efficiency (%)
400	60	5-6	60-70	61.2	26.21
400	70	5-6	60-70	38.16	28.01
400	80	5-6	60-70	41.07	39.94
400	90	5-6	60-70	47.15	36.83
400	100	5-6	60-70	49.51	32.42
500	60	5-6	60	37.86	17.87
500	70	5-6	60	37.96	25.64
500	80	5-6	60	38.27	23.29
500	90	5-6	60	37.85	24.42
500	100	5-6	60	40.35	20.67
800	60	5-6	80-90	104.4	26.7
800	70	5-6	80-90	41.21	34.57
800	80	5-6	80-90	37.5	52.12
800	90	5-6	80-90	36.24	47.46
800	100	5-6	80-90	39.2	43.48
600	60	10-12	80-100	33.76	51.79
600	70	10-12	80-100	29.86	63.71
600	80	10-12	80-100	26.1	84.78
600	90	10-12	80-100	25.66	80.33
600	100	10-12	80-100	26.29	90.57
800	60	10-12	80-100	38.23	28.5
800	70	10-12	80-100	35.1	46.82
800	80	10-12	80-100	32.59	51.43
800	90	10-12	80-100	31.14	63.05
800	100	10-12	80-100	30.42	69.93

Table S2: Aqueous reactions considered for surface complexation modeling[1]

Reaction	log K^o
$H_2O = H^+ + OH^-$	-14.00
$UO_2^{2+} + H_2O = UO_2OH^+ + H^+$	-5.25
$UO_2^{2+} + 2H_2O = UO_2(OH)_2 + 2H^+$	-12.15
$UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	-20.25
$UO_2^{2+} + 4H_2O = UO_2(OH)_4^{2-} + 4H^+$	-32.40
$2UO_2^{2+} + H_2O = (UO_2)_2(OH)^{3+} + H^+$	-2.70
$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62
$3UO_2^{2+} + 4H_2O = (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.90
$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^{2+} + 5H^+$	-15.55
$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$	-32.20
$4UO_2^{2+} + 7H_2O = (UO_2)_4(OH)_7^+ + 7H^+$	-21.90
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3$ (aq)	9.94
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.61
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.84
$3UO_2^{2+} + 6CO_3^{2-} = (UO_2)_3(CO_3)_6^{6-}$	54.00
$2UO_2^{2+} + 3H_2O + CO_3^{2-} = (UO_2)_2CO_3(OH)_3^- + 3H^+$	-0.86
$3UO_2^{2+} + 3H_2O + CO_3^{2-} = (UO_2)_3CO_3(OH)_3^+ + 3H^+$	0.65

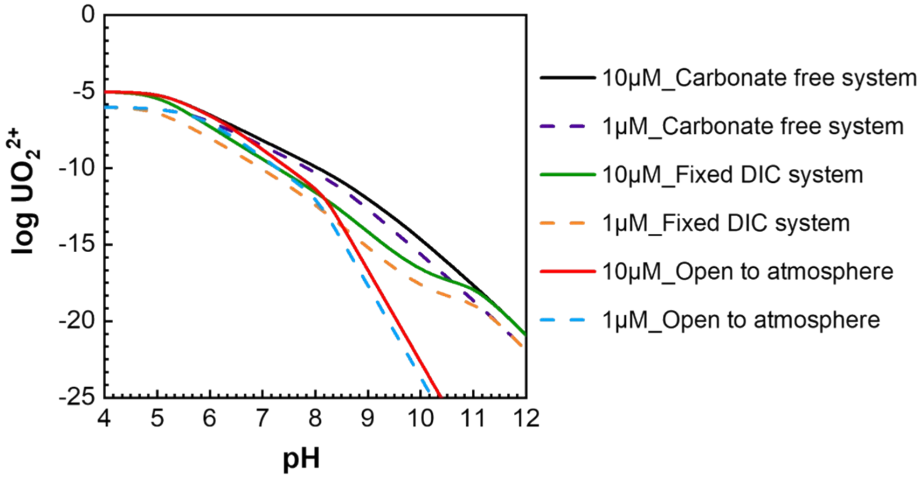

Figure S1: Variation of log UO_2^{2+} as a function of pH. The ionic strength is fixed at 0.01 M.

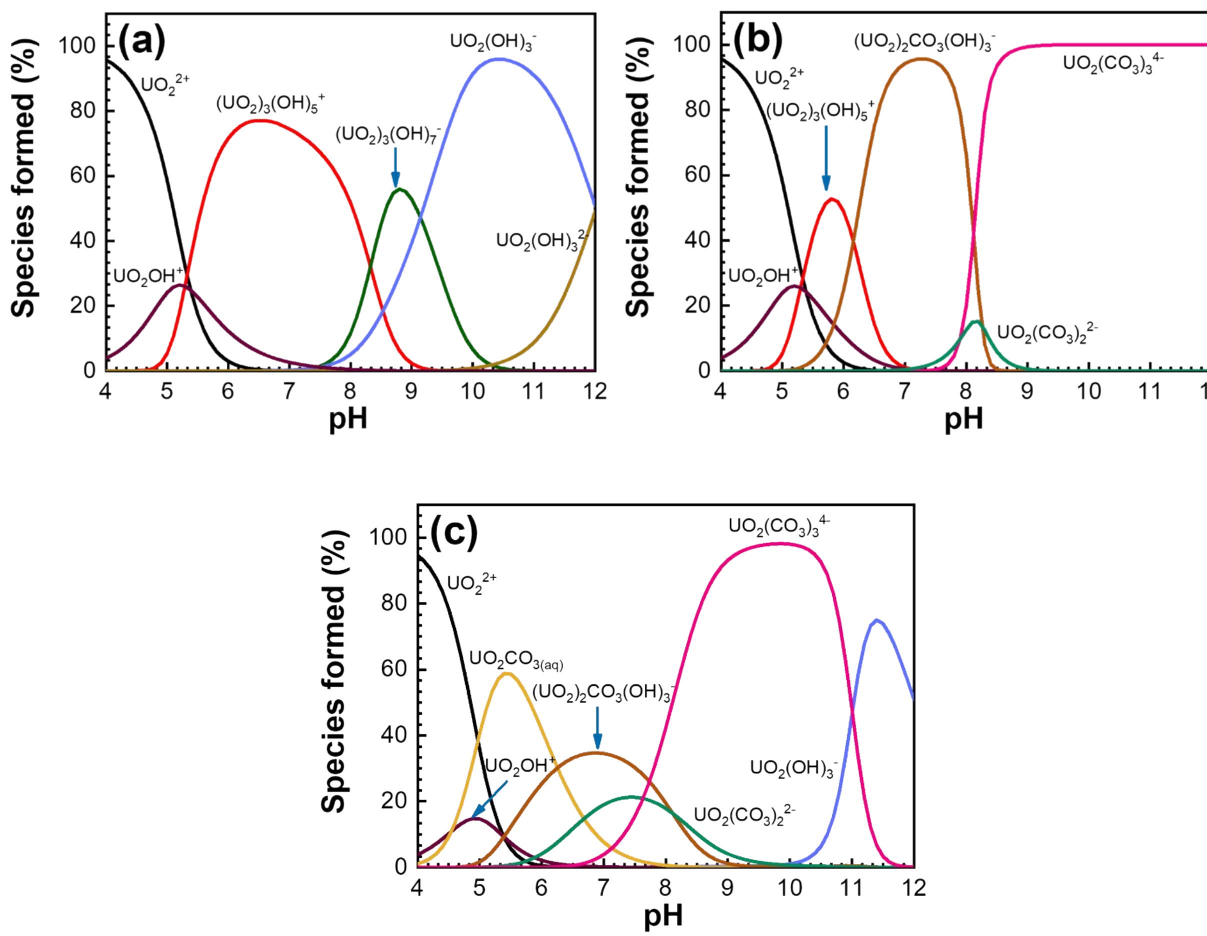

Figure S2: Speciation of U(VI) in (a) carbonate-free system, (b) open to atmosphere system, and (c) fixed dissolved inorganic carbon (DIC) system. U(VI) loading for all carbonate conditions is 10 μM and ionic strength is 0.01 M.

Calculation for estimating number of rhamnolipids attached per nanoparticle

Before ultracentrifuge (Rhamnolipid excess +Rhamnolipid attached to IONPs + Oleic acid attached to IONPs) = 84.48 mg/L as C

After ultracentrifuge, Rhamnolipid excess = 11.16 mg/L as C

Total carbon attached to IONPs = 73.32 mg/L as C

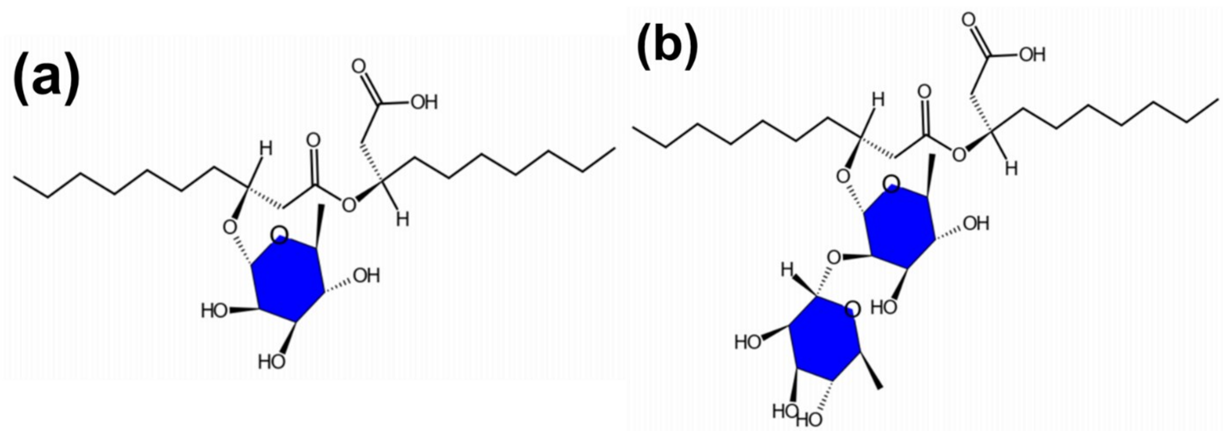

Figure S3: Structures of (a) Monorhamnolipid and (b) Dirhamnolipid

As rhamnolipids have two hydrophobic chains so it is assumed that one molecule of rhamnolipid gets attached to two nanoparticles. This will be considered as one entity in further calculations.

The total number of carbon atoms in one entity = 65.6 carbon atoms (as the standard obtained is a mixture of monorhamnolipid (40%) and dirhamnolipid (60%))

Density of IONPs as magnetite = 5 g/cm^3

The total volume of particles in V liter of suspension = 6.16*10^{-2} V cm^3

Assuming the diameter of 9 nm,

Number of IONPs in suspension = 1.51 *10^{17} V

Concentration of entities in the suspension= 73.32/ (65.6*12*1000) = 9.31 * 10^{-5} M

Moles of entities in suspension of Volume V = 9.31 * 10^{-5} mol/ liter* V (liters)= 9.31 * 10^{-5} * V moles

1 mole contains 6.022 * 10^{23} entities, hence total number of entities in suspension = 56.06 x 10^{18} V

Number of entities attached per nanoparticle = 371.2 entities per nanoparticle or 185.6 rhamnolipids per nanoparticle (as 1 rhamnolipid molecule gets attached to two oleic acid molecules)

Site density estimated per surface area of magnetite nanoparticle = 0.73 sites/nm^2

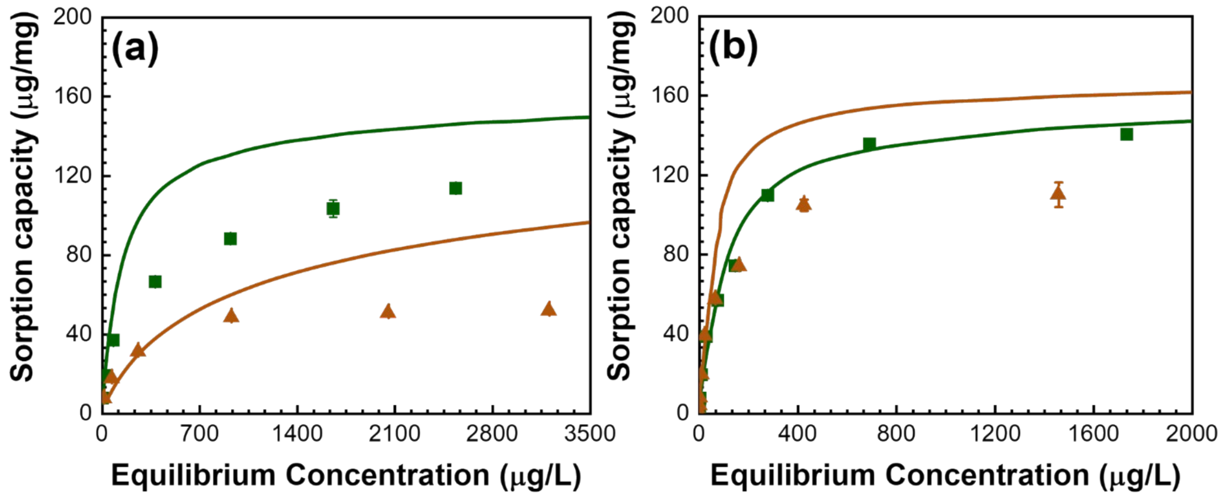

Figure S4: Fitting SCM obtained parameters to isotherm obtained for NEM model in (a) Open to atmosphere system and (b) Carbonate-free system. ▲ represent points obtained at pH =8 and ■ represent points obtained at pH=6. Solid lines are the fitting lines obtained using NEM at pH 6 and pH 8.

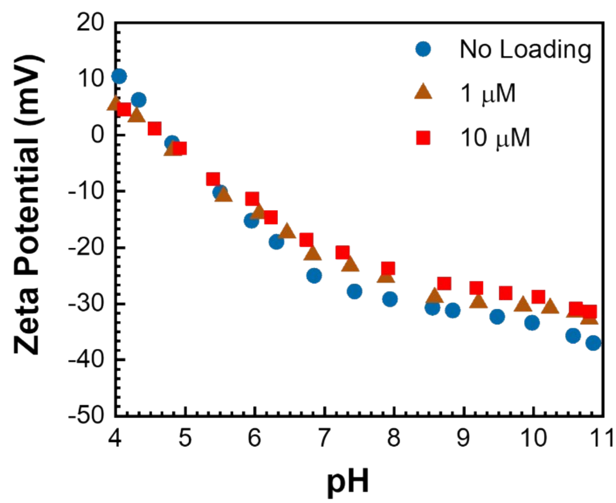

Figure S5: Effect of uranium loading on zeta potential of rhamnolipid-coated nanoparticles

References

1 R. Guillaumont, T. Fanghanel, V. Neck, J. Fuger, D. A. Palmer, I. Grenthe and M. H. Rand, *Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*, 2003, vol. 5.