Modeling the removal of Arsenic by nano-scale zero valent iron

Umma Salma Rashid

Geol 628 - Geochemistry

Fall 2014

Outline

- Introduction
- Mechanism
- Case study
- Objective
- Results
- Conclusion
- Future works
- References

Introduction

- Arsenic:
  - One of the most toxic, naturally occurring groundwater contaminants.
  - Sources: Natural and anthropogenic.
  - Speciation: Arsenate (As(V)) oxyanions ($H_2AsO_4^{-1}$ and $HAsO_4^{-2}$) and arsenite (As(III)) (H_3AsO_3, As^{3+}).
  - Health effect: Causes different types of health problems in human including cancer, uterine function damage (Akram et al., 2010), higher heart stroke rates, bladder cancer (Marshall et al., 2007)etc.
  - WHO drinking water safety limit for As is 10µg/L.

Introduction

- Nano-scale zero valent iron:
  - Size: 1 to 100 nm
  - High surface area
  - NZVI particles are able to treat chlorinated compounds, heavy metals, dichromate and pesticides.
  - NZVI particles and their corrosion products are suitable for remediation of both As (III) and As (V) (Kanel et al., 2005; Bezbaruah et al., 2014)

Mechanism of As removal by NZVI:

- Adsorption
  - Formation of iron hydroxides: oxidation

    $Fe(OH)_2$, $Fe(OH)_3$, FeOOH
- Reduction
  - NZVI core

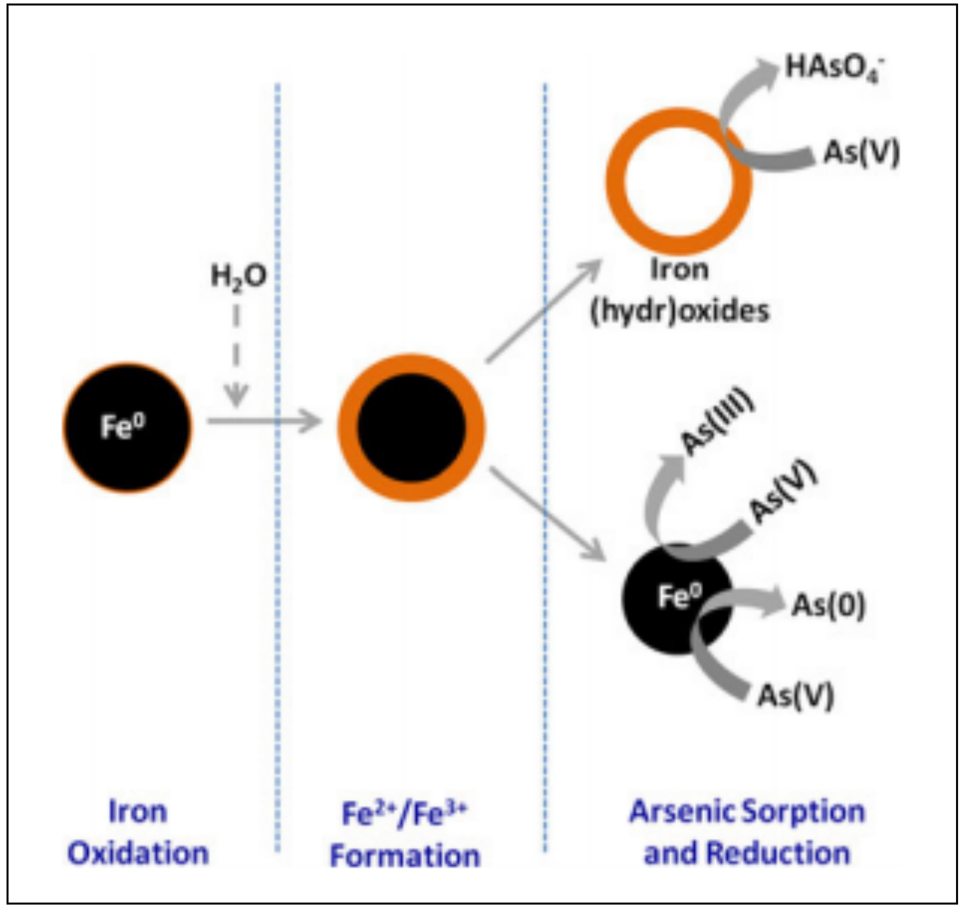


Figure. Schematic of possible mechanisms of As removal by NZVI. (Bezbaruah et al., 2014)

Surface Complexation Model

- In all surface complexation models, sorption is a function of both chemical and electrostatic energy as described by the free energy relationship:

  $\Delta Gtot = \Delta Gads + zF\psi$

where ΔG is the Gibbs energy (J/mol), z is the charge number (unitless) of the sorbed species, F is the Faraday constant (96,485 C/mol), ψ is the potential (V).

- PHREEQC has two models for surface complexation:
  - Dzombak and Morel,1990
  - CD-MUSIC

The paper researched

- Rozell D. 2010 Modeling of removal of Arsenic by iron oxide coated sand. Journal of Environmental Engineering. 136:246-248.

Case Study

Methodology:

- An arsenic filtration experiment using iron oxide coated sand was modeled using the USGS geochemical program PHREEQC.
- PHREEQC software uses the Dzombak and Morel (1990) model for surface complexation of iron oxide.
- Assumption:
  - Ferrichydrite or hydrous ferric oxide Hfo is the primary iron oxide surface due to its large surface area and number of binding sites.
  - weak sites 0.2 mole/mole Hfo, 0.005 mole/mole Hfo.

Case Study

- PHREEQC input values:

Fe(OH)3	0.0336 moles
Strong binding sites	0.000168 moles
Weak binding sites	0.00671 moles
Mass	3.59
Temperature	25 degree C
pH	7.5
pe	4
As	0.00000538 moles

Case Study

- Results:

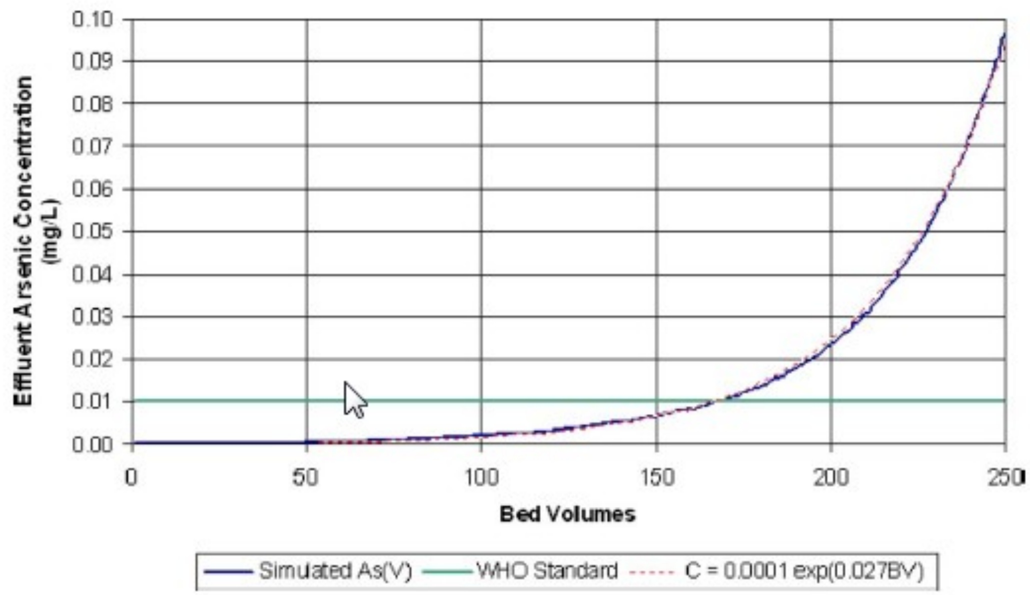


Figure. Iron oxide coated sand removal of As(V) during simulated column test

- The original experiment filtered 165 bed volumes to concentrations less than 0.01 mg/L As and approximately 210 bed volumes to 0.05 mg/L As. The model filtered 168 bed volumes to 0.01 mg/L As and 228 bed volumes to 0.05 mg/L.

Objective

- To model the removal of arsenic by adsorption on surfaces of NZVI particles
- Compare with experimental results (Bezbaruah et al., 2014)

Modeling Procedure

- Using PHREEQC model from USGS, the adsorption of As on iron hydroxide surface of NZVI was modeled.
- Input values used for modeling:

As(V)	0.000135 moles
NZVI	0.00855 moles
Weak sites	0.00171 moles
Strong sites	0.000043 moles
Total Hfo	0.91 gram
pH	5.0
pe	4
Temperature	25 deg C

- Database: WATEQ4F

Modeling Procedure

```
TITLE Example 8.--Sorption of arsenic on hydrous iron oxides layer of NZVI.
SURFACE_SPECIES
     Hfo_sOH  + H+ = Hfo_sOH2+
     log_k  7.18
     Hfo_sOH = Hfo_sO- + H+
     log_k  -8.82
     Hfo_sOH + H3AsO4 = Hfo_sOHAsO4-3 + 3H+
     log_k  -10.12
     Hfo_wOH  + H+ = Hfo_wOH2+
     log_k  7.18
     Hfo_wOH = Hfo_wO- + H+
     log_k  -8.82
     Hfo_wOH + H3AsO4 = Hfo_wHAsO4- + H+ + H2O
     log_k  2.81
     Hfo_wOH + H3AsO4 = Hfo_wH2AsO4 + H2O
     log_k  8.61
     Hfo_wOH + H3AsO4 = Hfo_wOHAsO4-3 + 3H+
     log_k  -10.12
SURFACE 1
     Hfo_sOH        4.27e-5    54.    0.91
     Hfo_wOH        1.71e-3
#     -donnan
END
SOLUTION 1
     -units  mmol/kgw
     pH      8.0
     As      0.135
     Na      100.    charge
     N(5)    100.
SELECTED_OUTPUT
     -file As1.35e_4
     -reset false
USER_PUNCH
  10 FOR i = 5.0 to 8 STEP 0.25
  20 a$ = EOL$ + "USE solution 1" + CHR$(59) + " USE surface 1" + EOL$
  30 a$ = a$ + "EQUILIBRIUM_PHASES 1" + EOL$
  40 a$ = a$ + "    Fix_H+ " + STR$(-i) + " NaOH 10.0" + EOL$
  50 a$ = a$ + "END" + EOL$
```

Reaction and thermodynamic constant for calculation of surface-complexation reactions in PHREEQC.

	Adsorption reaction	LogK
Case 1 to -3	$H_3AsO_4 + Hfo\_wOH = Hfo\_wOHAsO_4^{3-} + 3H^+$	−10.12
	$H_3AsO_4 + Hfo\_sOH = Hfo\_sOHAsO_4^{3-} + 3H^+$	−10.12
Case4	$H_3AsO_4 + Hfo\_wOH = Hfo\_wHAsO_4^- + H^+ + H_2O$	2.81
	$H_3AsO_4 + Hfo\_wOH = Hfo\_wH_2AsO_4 + H_2O$	8.61
	$H_3AsO_4 + Hfo\_wOH = Hfo\_wOHAsO_4^{3-} + 3H^+$	−10.12
	$H_3AsO_4 + Hfo\_sOH = Hfo\_sOHAsO_4^{3-} + 3H^+$	−10.12

Hfo = Oxidized iron.

(Allison et al., 1990)

Results

Initial solution

--------------------------Solution composition--------------

Elements	Molality	Moles	
As	1.350e-04	1.350e-04	
N(5)	1.000e-01	1.000e-01	
Na	1.003e-01	1.003e-01	Charge balance

Final Solution

--------------------------Solution composition-----

Elements	Molality	Moles
As	7.038e-11	7.038e-11
N	1.000e-01	1.000e-01
Na	9.984e-02	9.984e-02

- So, 99.99 % As has been removed by the adsorption on NZVI surfaces
- Bezbaruah et al., 2014 found 99.57% removal of As with the same amount of NZVI and same initial concentration of As.

Results

```
------------------------------Surface composition------------------------------

Hfo
         1.500e-04  Surface charge, eq
         2.945e-01  sigma, C/m²
         1.423e-01  psi, V
        -5.538e+00  -F*psi/RT
         3.934e-03  exp(-F*psi/RT)
         5.400e+01  specific area, m²/g
         4.914e+01  m² for   9.100e-01 g


Hfo_s
         4.270e-05  moles
                                             Mole                   Log
      Species                   Moles    Fraction    Molality    Molality

      Hfo_sOH               2.415e-05       0.565   2.415e-05      -4.617
      Hfo_sOH2+             1.438e-05       0.337   1.438e-05      -4.842
      Hfo_sOHAsO4-3         3.249e-06       0.076   3.249e-06      -5.488
      Hfo_sO-               9.290e-07       0.022   9.290e-07      -6.032

Hfo_w
         1.710e-03  moles
                                             Mole                   Log
      Species                   Moles    Fraction    Molality    Molality

      Hfo_wOH               9.660e-04       0.565   9.660e-04      -3.015
      Hfo_wOH2+             5.751e-04       0.336   5.751e-04      -3.240
      Hfo_wOHAsO4-3         1.300e-04       0.076   1.300e-04      -3.886
      Hfo_wO-               3.717e-05       0.022   3.717e-05      -4.430
      Hfo_wHAsO4-           1.718e-06       0.001   1.718e-06      -5.765
      Hfo_wH2AsO4           4.264e-08       0.000   4.264e-08      -7.370
      Hfo_wH2AsO3           3.910e-32       0.000   3.910e-32     -31.408
```

Results

Initial Solution

----------------------------Distribution of species----------------------------

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mo cm
OH-	1.310e-06	9.977e-07	-5.883	-6.001	-0.118	
H+	1.212e-08	1.000e-08	-7.917	-8.000	-0.083	
H2O	5.551e+01	9.966e-01	1.744	-0.001	0.000	
As(3)	3.248e-16					
H3AsO3	2.973e-16	3.042e-16	-15.527	-15.517	0.010	
H2AsO3-	2.758e-17	2.154e-17	-16.559	-16.667	-0.107	
HAsO3-2	1.155e-23	4.297e-24	-22.937	-23.367	-0.429	
H4AsO3+	1.930e-24	1.507e-24	-23.714	-23.822	-0.107	
AsO3-3	7.932e-31	8.574e-32	-30.101	-31.067	-0.966	
As(5)	1.350e-04					
HAsO4-2	1.262e-04	4.695e-05	-3.899	-4.328	-0.429	
H2AsO4-	8.690e-06	6.787e-06	-5.061	-5.168	-0.107	
AsO4-3	9.725e-08	1.051e-08	-7.012	-7.978	-0.966	
H3AsO4	1.323e-11	1.354e-11	-10.878	-10.868	0.010	
H(0)	1.384e-27					
H2	6.918e-28	7.079e-28	-27.160	-27.150	0.010	
N(5)	1.000e-01					
NO3-	1.000e-01	7.531e-02	-1.000	-1.123	-0.123	
Na	1.003e-01					
Na+	1.003e-01	7.845e-02	-0.999	-1.105	-0.107	
O(0)	1.614e-38					
O2	8.072e-39	8.261e-39	-38.093	-38.083	0.010	

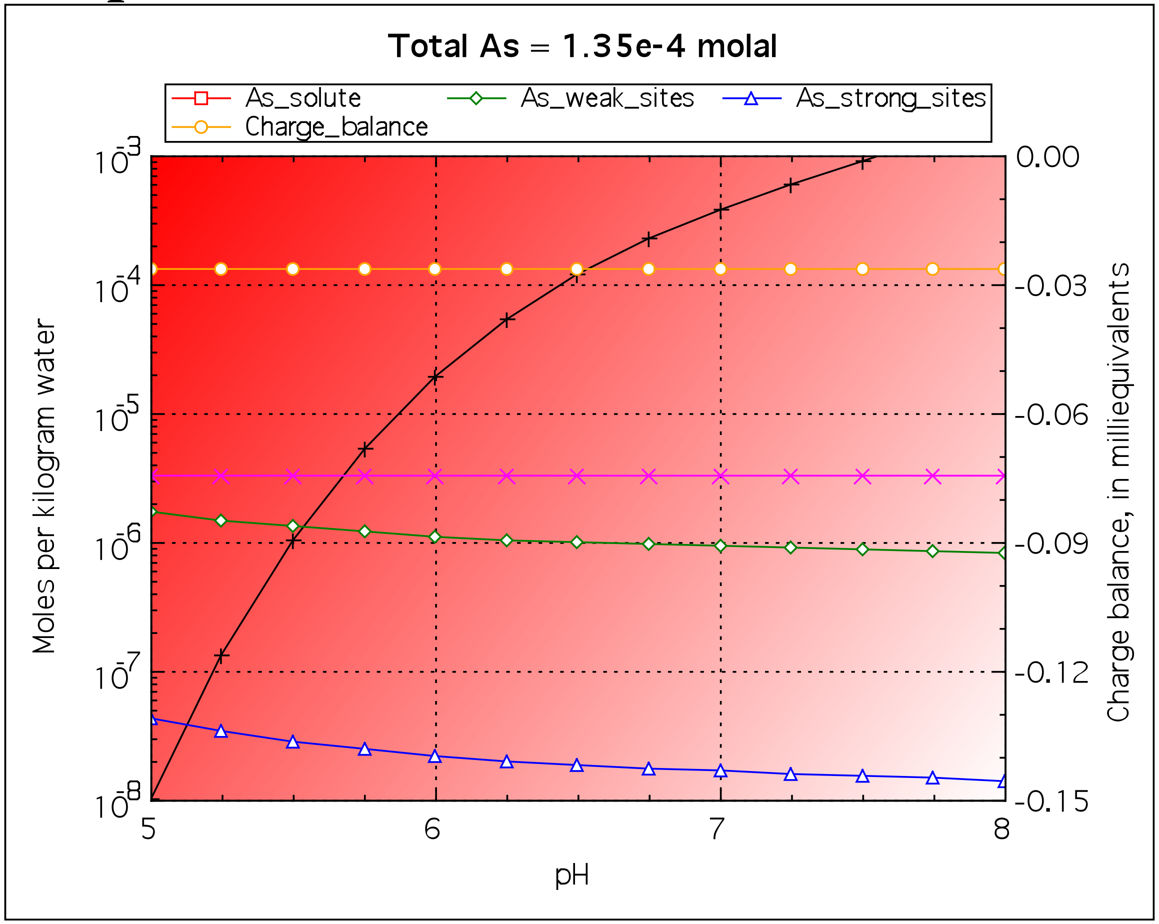
Final Solution

----------------------------Distribution of species----------------------------

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V cm³/mol
H+	1.212e-05	1.000e-05	-4.917	-5.000	-0.083	0.00
OH-	1.310e-09	9.977e-10	-8.883	-9.001	-0.118	(0)
H2O	5.551e+01	9.966e-01	1.744	-0.001	0.000	18.07
As(3)	1.534e-34					
H3AsO3	1.534e-34	1.569e-34	-33.814	-33.804	0.010	(0)
H2AsO3-	1.422e-38	1.111e-38	-37.847	-37.954	-0.107	(0)
H4AsO3+	9.952e-40	7.775e-40	-39.002	-39.109	-0.107	(0)
HAsO3-2	0.000e+00	0.000e+00	-47.225	-47.654	-0.429	(0)
AsO3-3	0.000e+00	0.000e+00	-57.389	-58.354	-0.965	(0)
As(5)	7.038e-11					
H2AsO4-	6.927e-11	5.412e-11	-10.159	-10.267	-0.107	(0)
HAsO4-2	1.005e-12	3.744e-13	-11.998	-12.427	-0.429	(0)
H3AsO4	1.055e-13	1.080e-13	-12.977	-12.967	0.010	(0)
AsO4-3	7.731e-19	8.382e-20	-18.112	-19.077	-0.965	(0)
H(0)	0.000e+00					
H2	0.000e+00	0.000e+00	-43.349	-43.339	0.010	(0)
N(-3)	0.000e+00					
NH4+	0.000e+00	0.000e+00	-52.691	-52.798	-0.107	(0)
NH3	0.000e+00	0.000e+00	-57.042	-57.042	0.000	(0)
N(0)	1.543e-06					
N2	7.716e-07	7.895e-07	-6.113	-6.103	0.010	(0)
N(3)	2.326e-13					
NO2-	2.326e-13	1.817e-13	-12.633	-12.741	-0.107	(0)
N(5)	1.000e-01					
NO3-	1.000e-01	7.535e-02	-1.000	-1.123	-0.123	(0)
Na	9.984e-02					
Na+	9.984e-02	7.814e-02	-1.001	-1.107	-0.106	(0)
O(0)	3.858e-06					
O2	1.929e-06	1.974e-06	-5.715	-5.705	0.010	(0)

Results

- Effect of pH:



Results

- Effect of pH:

pH	Final As concentration(molality)
5.0	7.043e-11
6.0	3.805e-10
7.0	6.062e-09
8.0	3.204e-07

Conclusion

- The model yeilded 99.99% removal of arsenic by NZVI whereas the experimental results yielded 99.57% removal of arsenic by NZVI
- Removal efficiency decreases with the increase of pH.
- More realistic results can be found by using the real K values for NZVI, sample of groundwater and also by incorporating reduction process in the model.

References

1. Maji SK, Kao YH, Wang CJ, Lu GS, Wu JJ, Liu CW. 2012 Fixed bed adsorption of As(III) on iron oxide coated natural rock (ICNOR) and application to real arsenic bearing groundwater. Chemical Engineering Journal. 203: 285-293.
2. Bezbaruah AN, Kalita H, Almeebi T, Capecchi CL, Jacob DL, Ugrinov AG and Payne SA. 2014 Ca–alginate-entrapped nanoscale iron: arsenic treatability and mechanism studies. J Nanopart Res. 16:2175.
3. Kanel SR, Manning B, Charlet L, Choi H (2005) Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. Environ Sci Technol 39:1291–1298.
4. Akram Z, Jalali S, Shami SA, Ahmad L, Batool S, Kalsoom O (2010) Adverse effects of arsenic exposure on uterine function and structure in female rat. Exp Toxicol Pathol. 62:451–459
5. Marshall G, Ferreccio C, Yuan Y, Michael NB, Steinmaus C, Selvin S, Liaw J, Smith HA (2007) Fifty-year study of lung and bladder cancer mortality in Chile related to arsenic in drinking water. J Natl Cancer Inst 99:920–928.
6. Allison JD, Brown DS, Novo-Gradac KJ. 1990 MINTEQA2/PRODEFA2–A Geochemical Assessment Model for Environmental Systems, US Environ. Protec. Agency, Athens, Georgia,