Surface Complexation Modeling of Arsenic Adsorption on Iron Oxide Minerals

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Geochemistry 628
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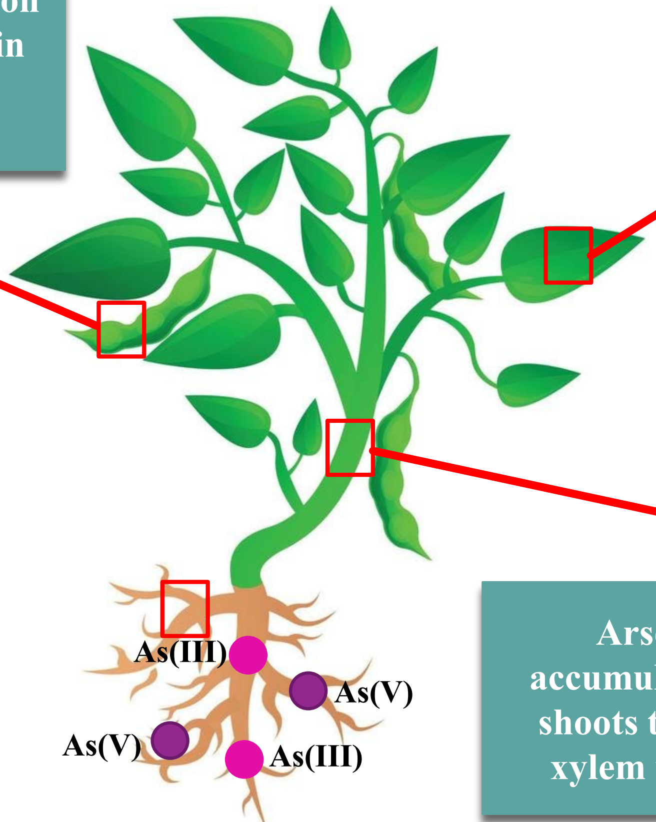
Outline

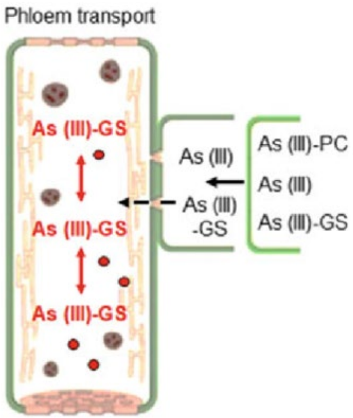
https://www.mindat.org/element/arsenic

Introduction
Case Study
Objectives
Results
Conclusion
References

Arsenic - Highly Toxic Groundwater Contaminant

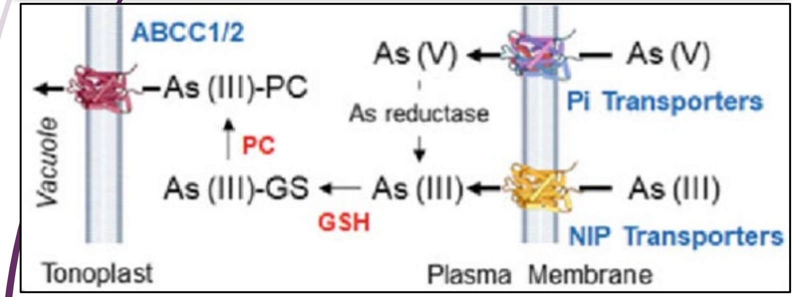
Accumulation of arsenic in seeds

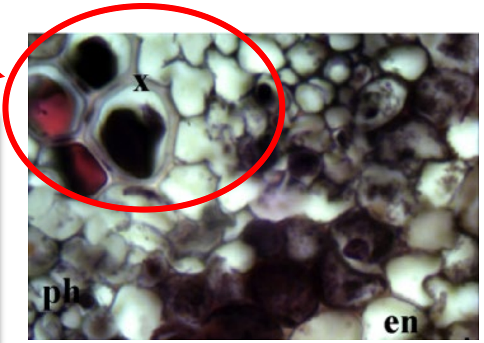




Arsenic accumulation in leaves through the phloem pathway

Roots uptake arsenic and translocate them to different parts of the plant



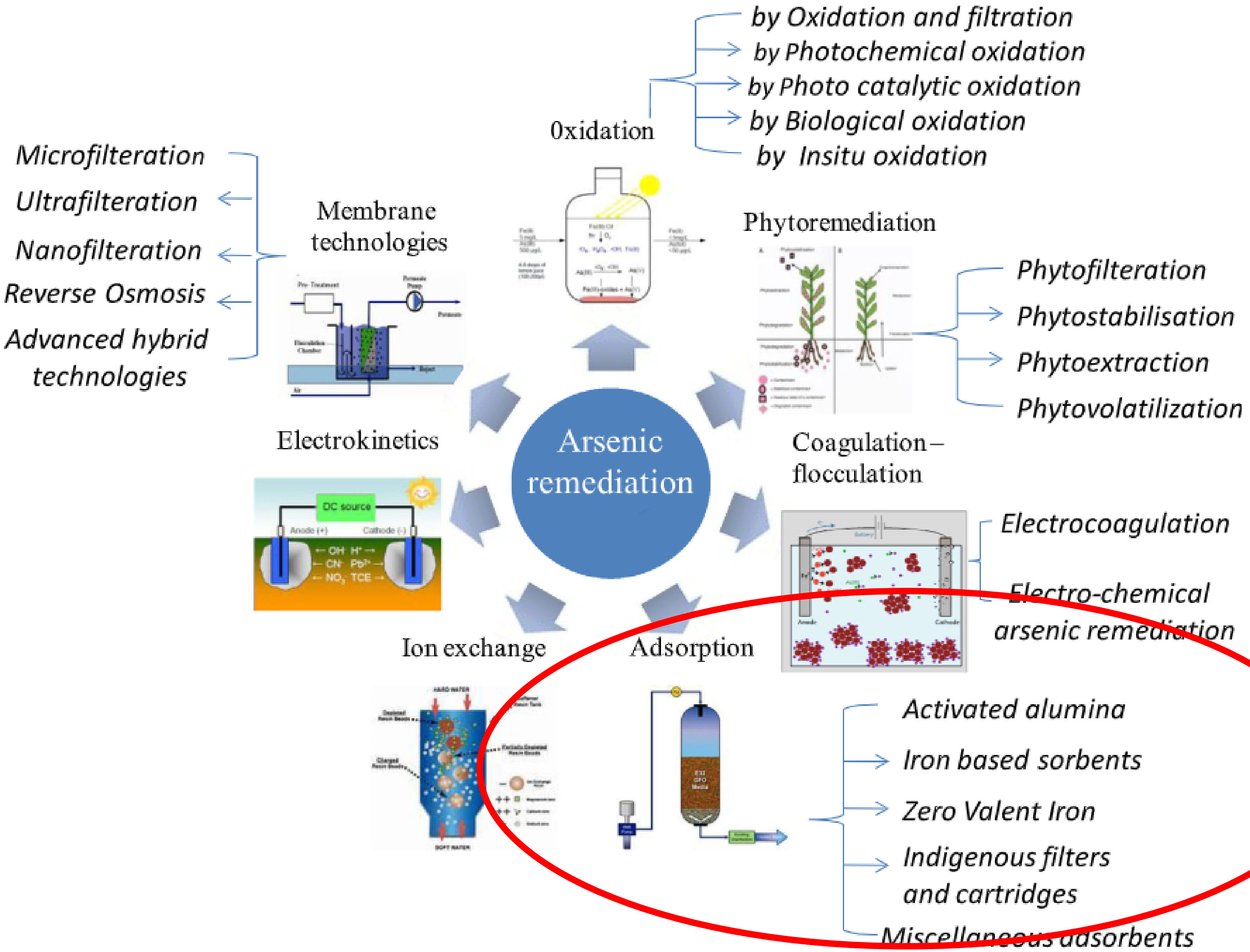


Arsenic accumulation in shoots through xylem uptake

Uptake of arsenic from soil/water

Upadhyaya and Roychoudhury (2022)

Different Mitigation Strategies



Arsenic remediation

0xidation
- by Oxidation and filtration
- by Photochemical oxidation
- by Photo catalytic oxidation
- by Biological oxidation
- by Insitu oxidation

Membrane technologies
- Microfilteration
- Ultrafilteration
- Nanofilteration
- Reverse Osmosis
- Advanced hybrid technologies

Phytoremediation
- Phytofilteration
- Phytostabilisation
- Phytoextraction
- Phytovolatilization

Coagulation–flocculation
- Electrocoagulation
- Electro-chemical arsenic remediation

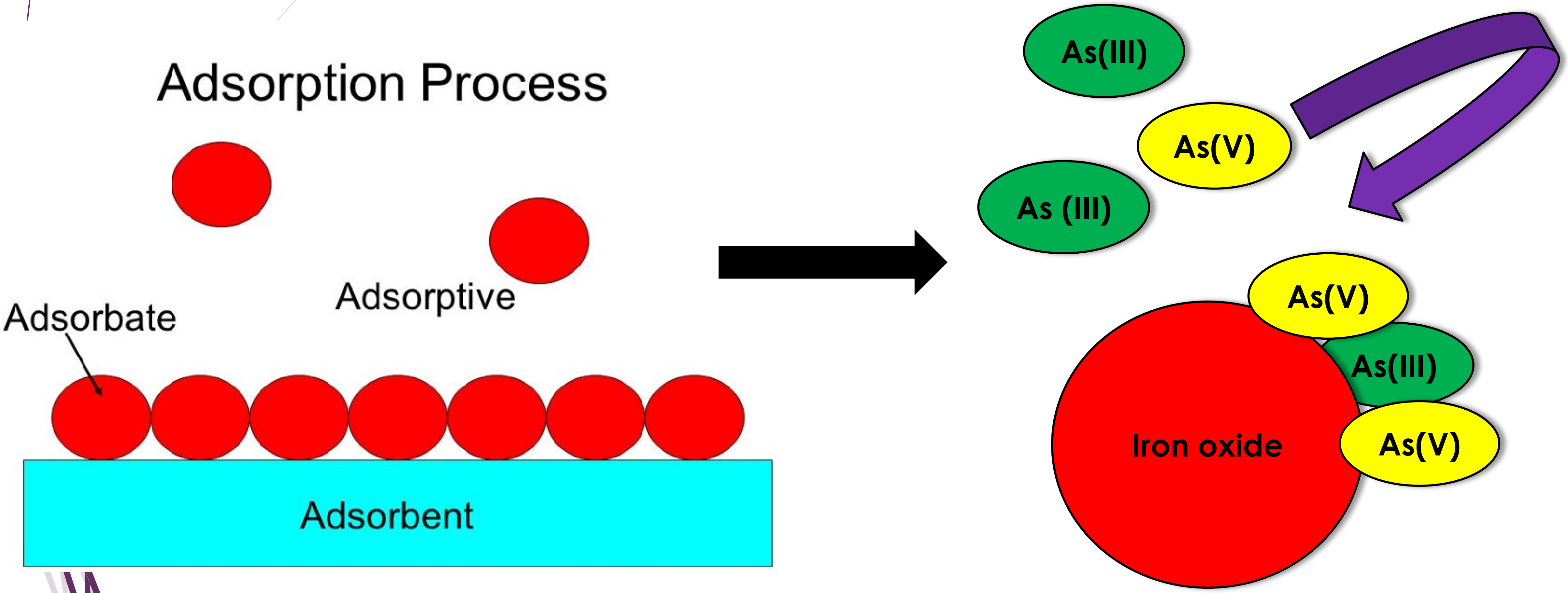
Electrokinetics

Ion exchange

Adsorption
- Activated alumina
- Iron based sorbents
- Zero Valent Iron
- Indigenous filters and cartridges
- Miscellaneous adsorbents

(Raturi et al., 2023)

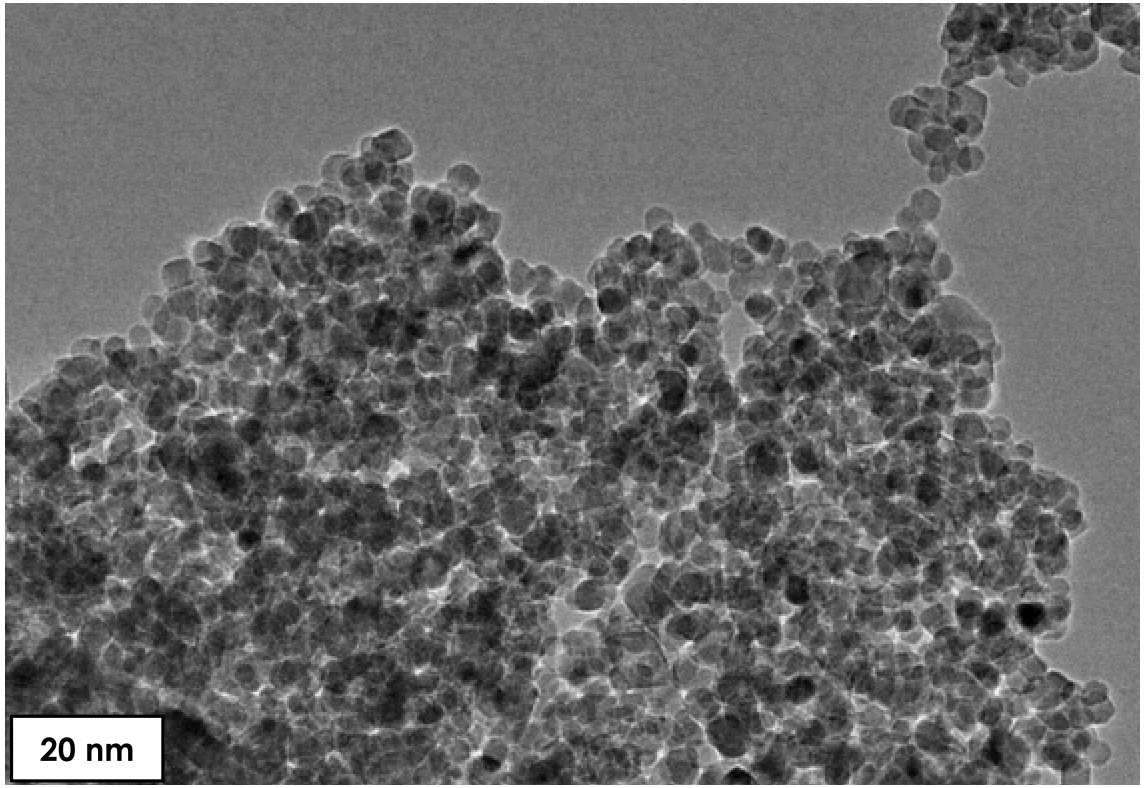
Adsorption



(Siddiqui & Chaudhry, 2017)

Nano Iron for Arsenic Adsorption

Particle Size: 1–100 nm with high surface area
Removes: As(III), As(V), Cr(VI), Pb(II), organic pollutants
Application: Nano iron oxides show high arsenic affinity (Das & Bezbaruah, 2021; Das et al., 2020)



Das et al., 2020

Surface Complexation Model in PHREEQC

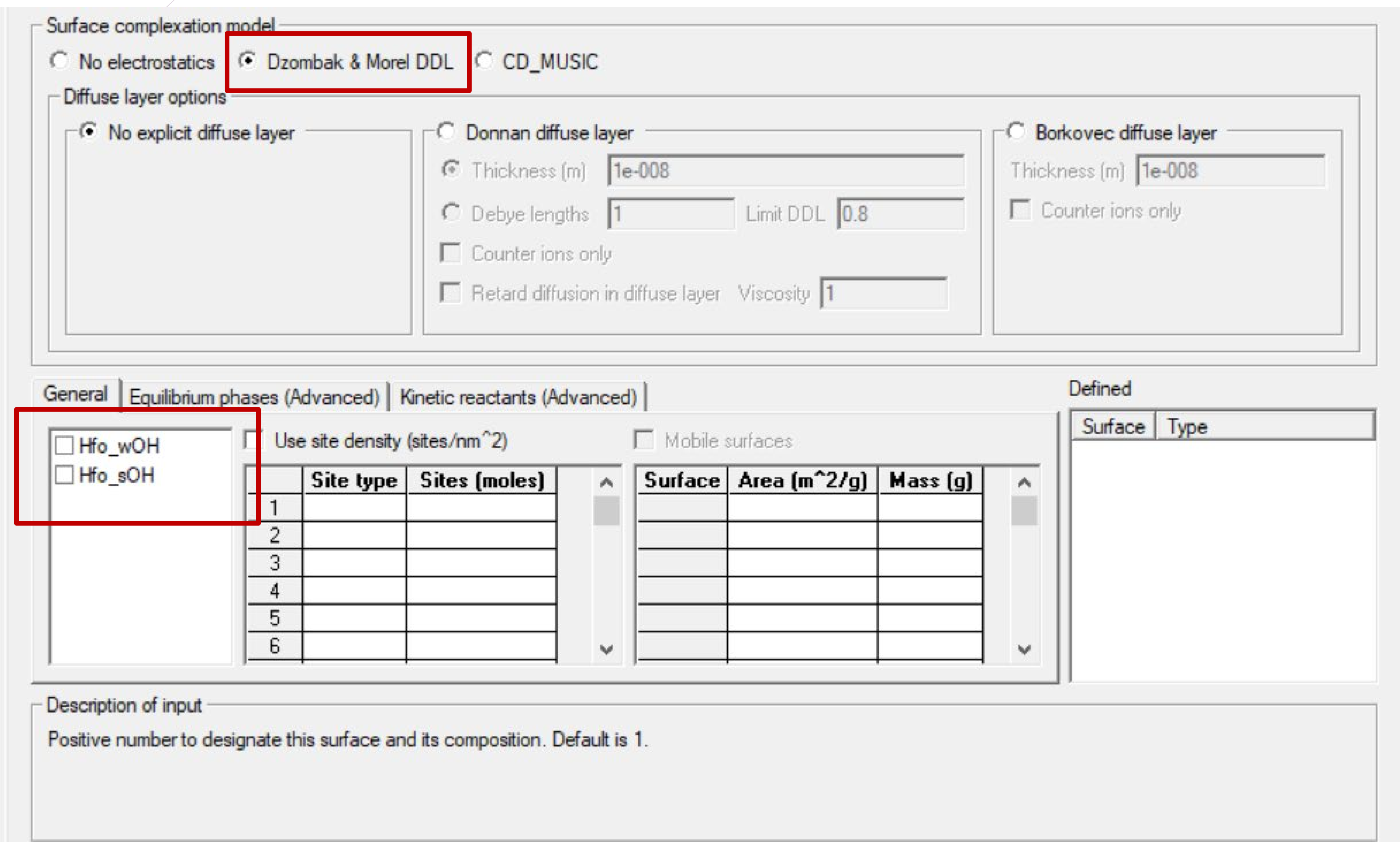
In all surface complexation models, sorption is a function of both chemical and electrostatic energy as described by the free energy relationship:

$$\Delta G_{tot} = \Delta G_{ads} + zF\psi$$

PHREEQC has two models for surface complexation:

- ❖ Dzombak and Morel,1990
- ❖ CD-MUSIC

Surface Complexation Model in PHREEQC



Surface complexation model

○ No electrostatics ● Dzombak & Morel DDL ○ CD_MUSIC

Diffuse layer options

● No explicit diffuse layer

○ Donnan diffuse layer

● Thickness (m) 1e-008

○ Debye lengths 1 Limit DDL 0.8

☐ Counter ions only

☐ Retard diffusion in diffuse layer Viscosity 1

○ Borkovec diffuse layer

Thickness (m) 1e-008

☐ Counter ions only

☐ Hfo_wOH

☐ Hfo_sOH

☐ Use site density (sites/nm^2)

☐ Mobile surfaces

	Site type	Sites (moles)
1		
2		
3		
4		
5		
6		

Surface	Area (m^2/g)	Mass (g)

Defined

Surface	Type

Description of input

Positive number to designate this surface and its composition. Default is 1.

CASE STUDY

Omoregie et al. 2013,
Arsenic bioremediation by biogenic iron oxides and sulfides,
Applied and environmental microbiology, 79(14), 4325-4335

CASE STUDY

Objective:

To model arsenic (As) removal from groundwater via sorption onto biogenic iron (Fe(III)) oxides formed by microbial oxidation of Fe(II), using PHREEQC geochemical modeling.

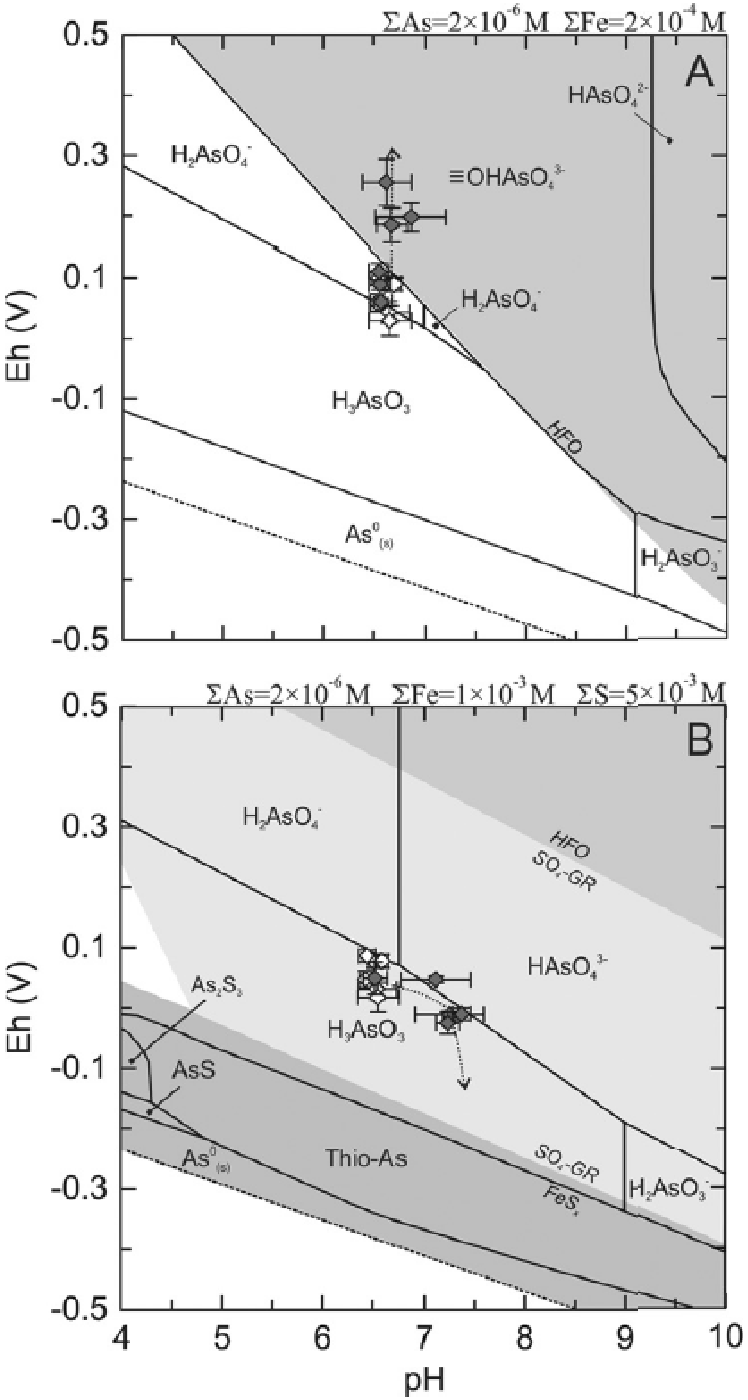
Methodology:

- ❖ Developed a 1D reactive transport model in PHREEQC.
- ❖ Simulated microbial oxidation of Fe(II) and subsequent precipitation of Fe(III) as Hfo (hydrous ferric oxide).
- ❖ Modeled arsenic adsorption onto the formed Hfo using surface complexation.

CASE STUDY

Reactions of Surface Species

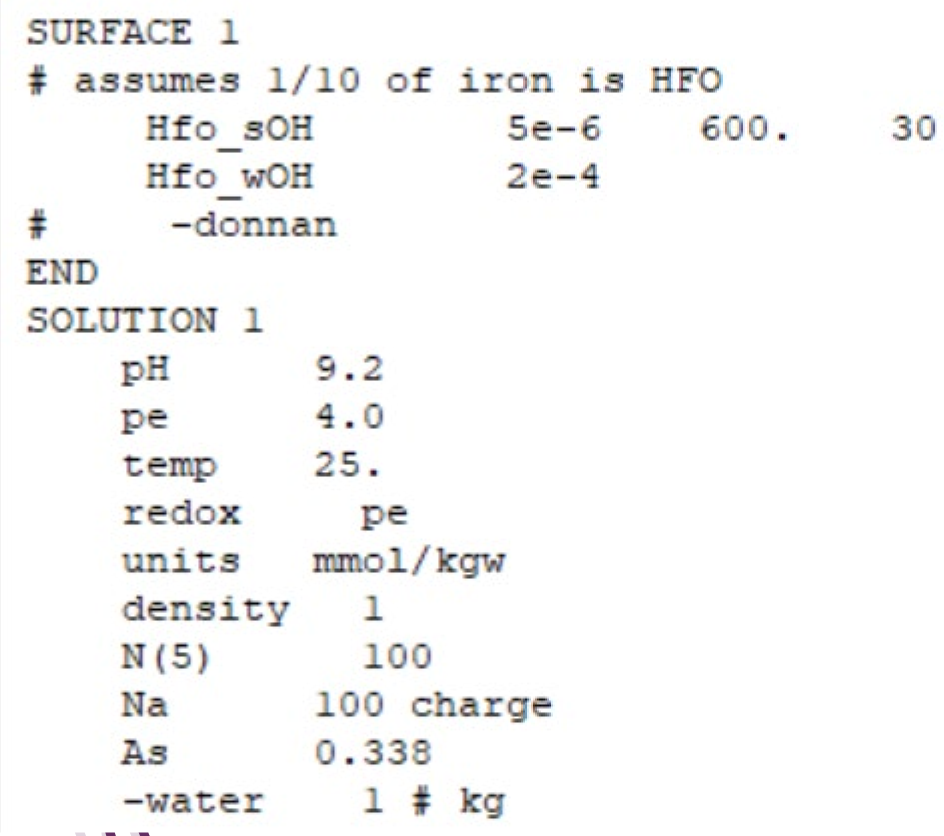
Reaction	Log K
$\text{Hfo\_sOH} + H^+ = \text{Hfo\_sOH}^{2+}$	7.29
$\text{Hfo\_wOH} + H^+ = \text{Hfo\_wOH}^{2+}$	7.29
$\text{Hfo\_sOH} = \text{Hfo\_sO}^- + H^+$	−8.93
$\text{Hfo\_wOH} = \text{Hfo\_wO}^- + H^+$	−8.93
$\text{Hfo\_sOH} + H_3AsO_3 = \text{Hfo\_sH}_2AsO_3 + H_2O$	5.41
$\text{Hfo\_wOH} + H_3AsO_3 = \text{Hfo\_wH}_2AsO_3 + H_2O$	5.41
$\text{Hfo\_sOH} + H_3AsO_4 = \text{Hfo\_sH}_2AsO_4 + H_2O$	8.61
$\text{Hfo\_wOH} + H_3AsO_4 = \text{Hfo\_wH}_2AsO_4 + H_2O$	8.61
$\text{Hfo\_sOH} + H_3AsO_4 = \text{Hfo\_sHAsO}_4^- + H_2O + H^+$	2.81
$\text{Hfo\_wOH} + H_3AsO_4 = \text{Hfo\_wHAsO}_4^- + H_2O + H^+$	2.81
$\text{Hfo\_sOH} + H_3AsO_4 = \text{Hfo\_sOHAsO}_4^{-3} + 3H^+$	−10.12
$\text{Hfo\_wOH} + H_3AsO_4 = \text{Hfo\_wOHAsO}_4^{-3} + 3H^+$	−10.12



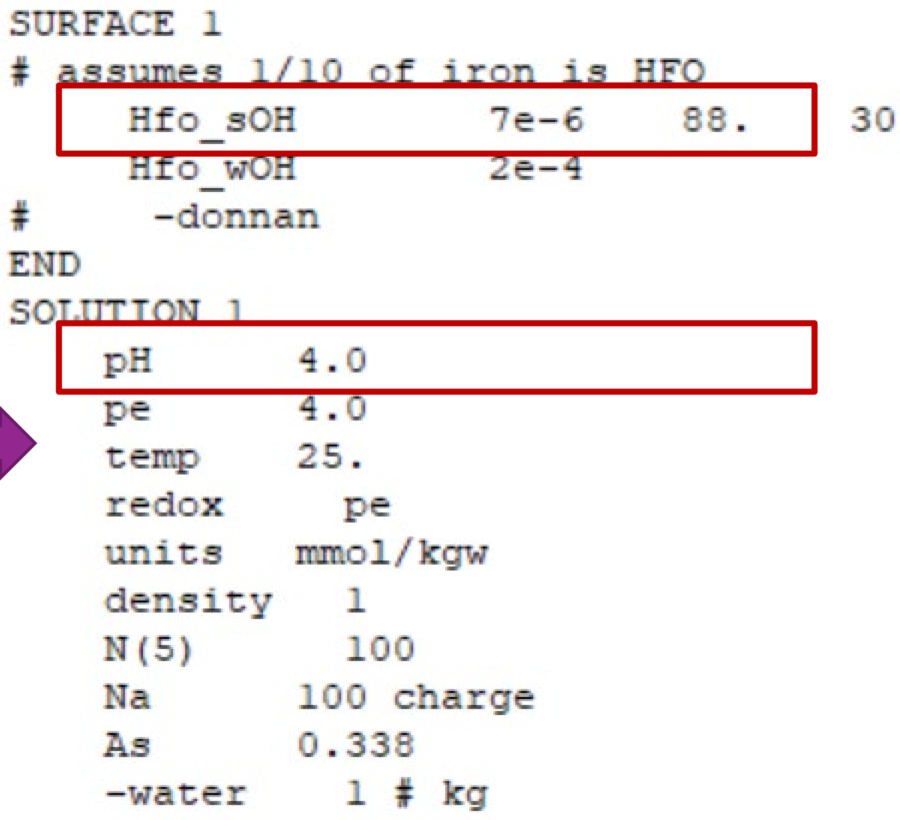
OBJECTIVE

- Change the pH of the solution
- Track the change in surface area of the Hfo
- Compare with experimental results (Das et al., 2020)

RESULTS



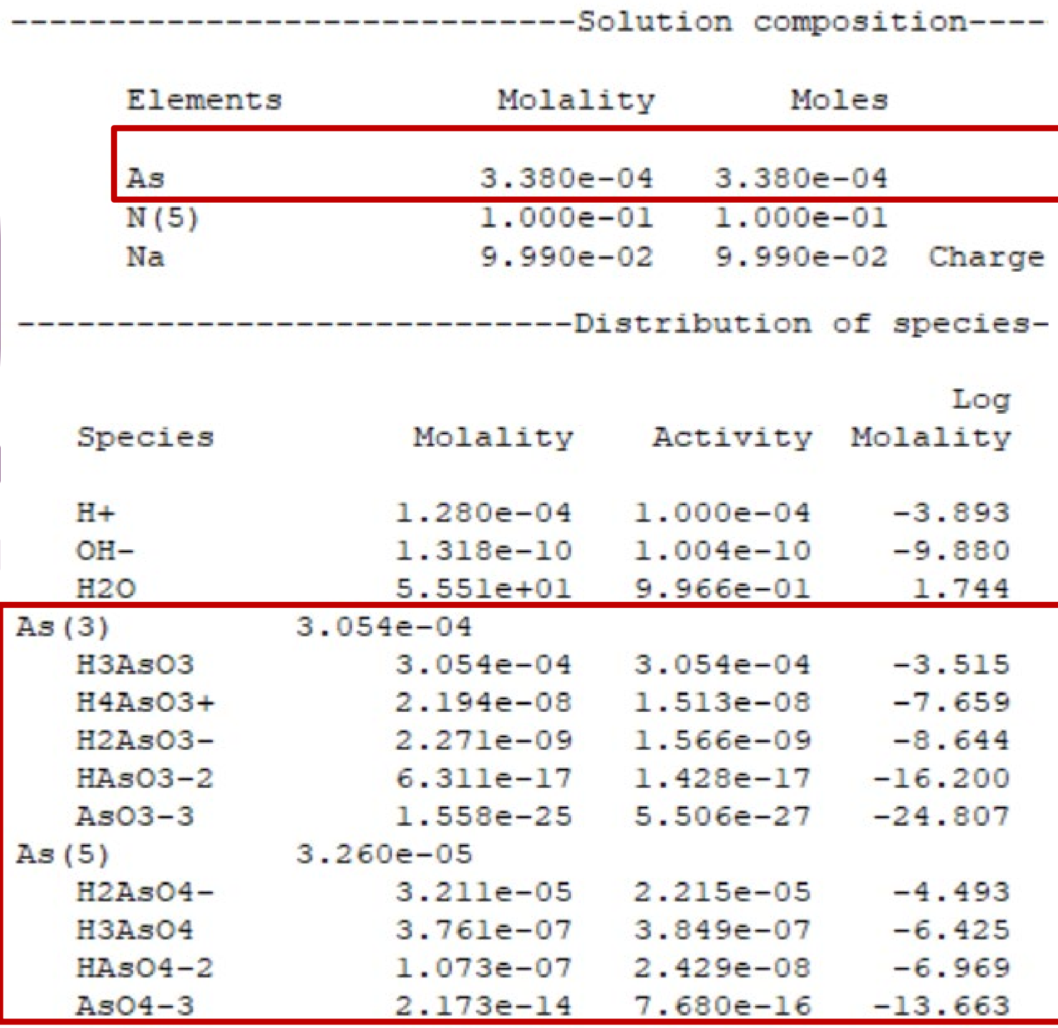
```
SURFACE 1
# assumes 1/10 of iron is HFO
     Hfo_sOH          5e-6    600.    30
     Hfo_wOH          2e-4
#     -donnan
END
SOLUTION 1
    pH      9.2
    pe      4.0
    temp    25.
    redox     pe
    units   mmol/kgw
    density    1
    N(5)      100
    Na      100 charge
    As      0.338
    -water     1 # kg
```



```
SURFACE 1
# assumes 1/10 of iron is HFO
     Hfo_sOH          7e-6    88.     30
     Hfo_wOH          2e-4
#     -donnan
END
SOLUTION 1
    pH      4.0
    pe      4.0
    temp    25.
    redox     pe
    units   mmol/kgw
    density    1
    N(5)      100
    Na      100 charge
    As      0.338
    -water     1 # kg
```

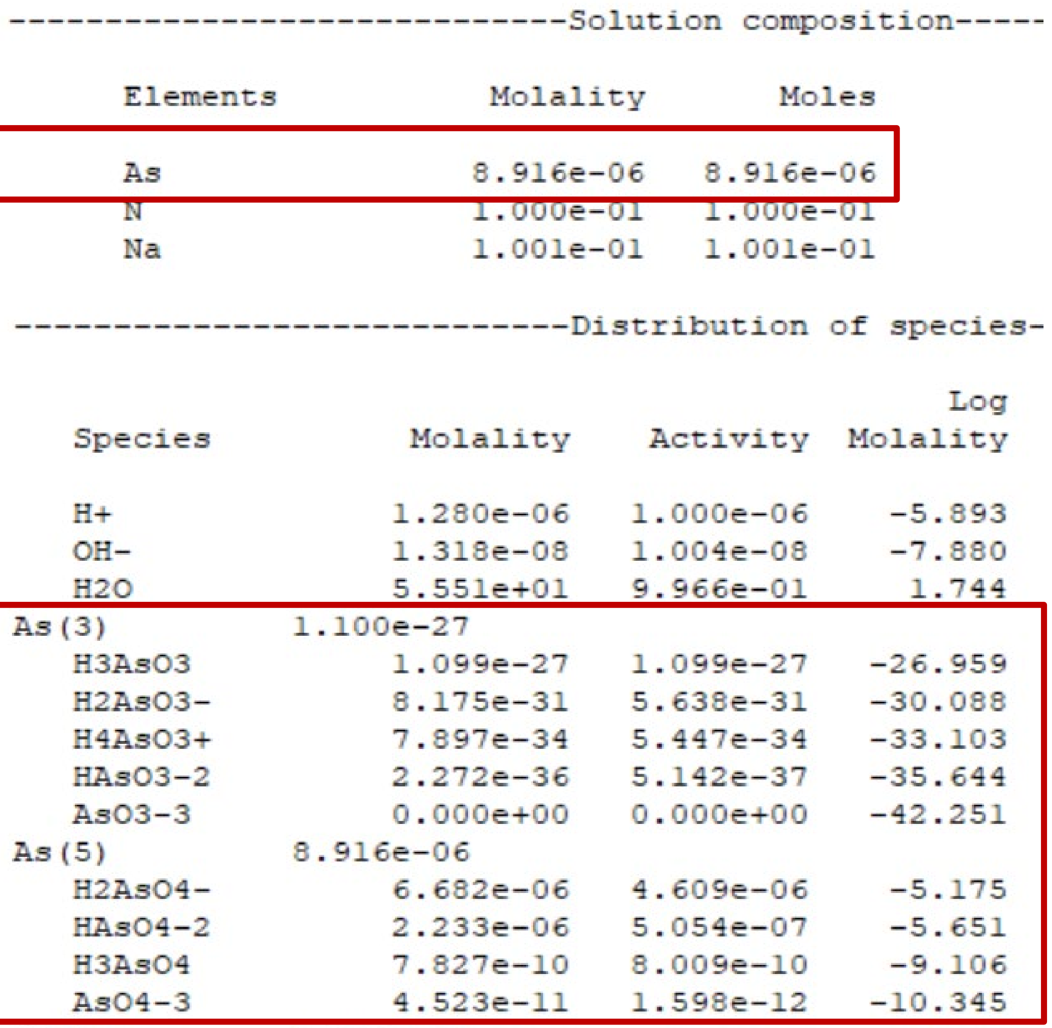
RESULTS

Initial solution



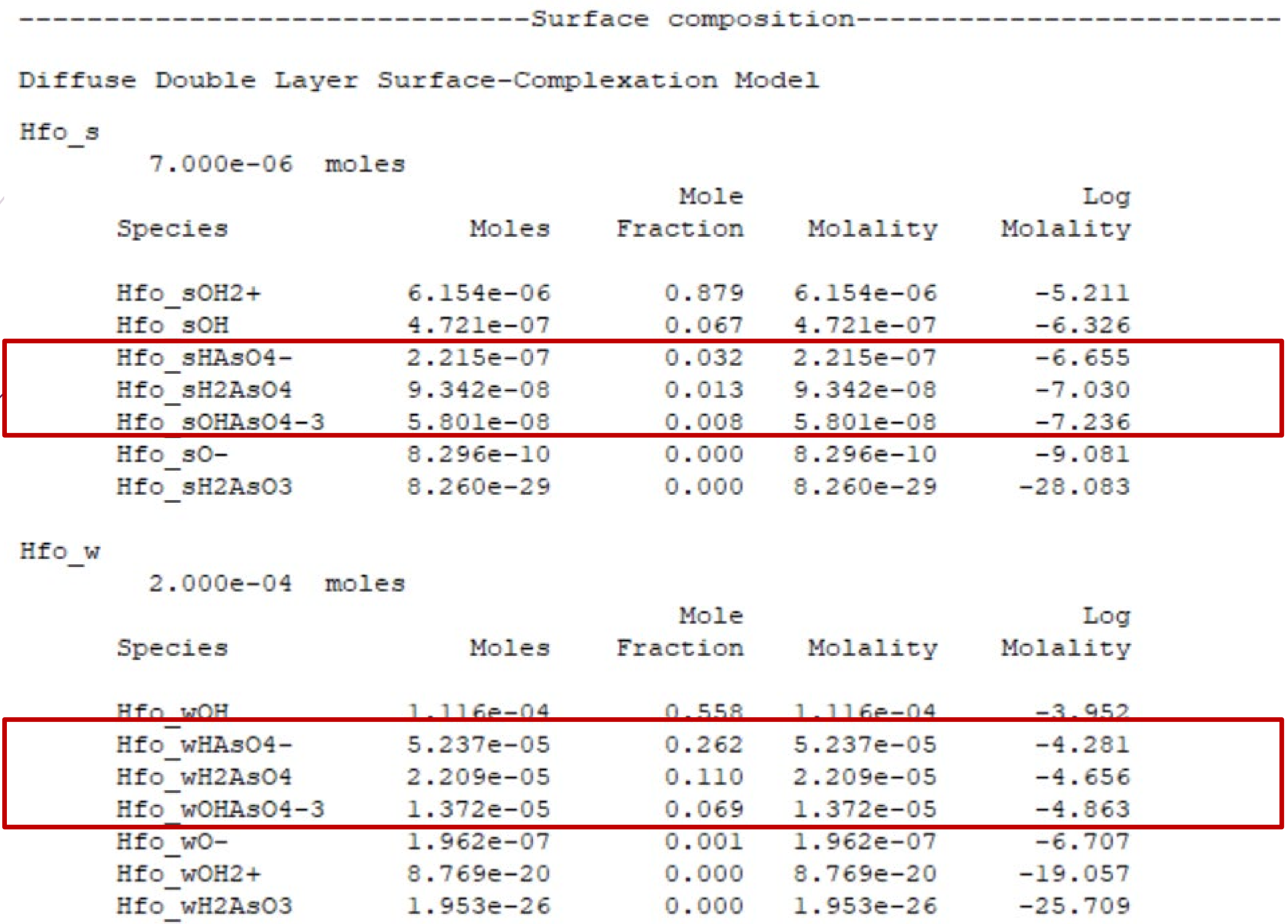
```
----------------------------Solution composition----

     Elements             Molality       Moles

     As                  3.380e-04   3.380e-04
     N(5)                1.000e-01   1.000e-01
     Na                  9.990e-02   9.990e-02  Charge

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

                                                Log
   Species               Molality     Activity  Molality

   H+                   1.280e-04   1.000e-04    -3.893
   OH-                  1.318e-10   1.004e-10    -9.880
   H2O                  5.551e+01   9.966e-01     1.744
As(3)         3.054e-04
   H3AsO3               3.054e-04   3.054e-04    -3.515
   H4AsO3+              2.194e-08   1.513e-08    -7.659
   H2AsO3-              2.271e-09   1.566e-09    -8.644
   HAsO3-2              6.311e-17   1.428e-17   -16.200
   AsO3-3               1.558e-25   5.506e-27   -24.807
As(5)         3.260e-05
   H2AsO4-              3.211e-05   2.215e-05    -4.493
   H3AsO4               3.761e-07   3.849e-07    -6.425
   HAsO4-2              1.073e-07   2.429e-08    -6.969
   AsO4-3               2.173e-14   7.680e-16   -13.663
```

Final solution



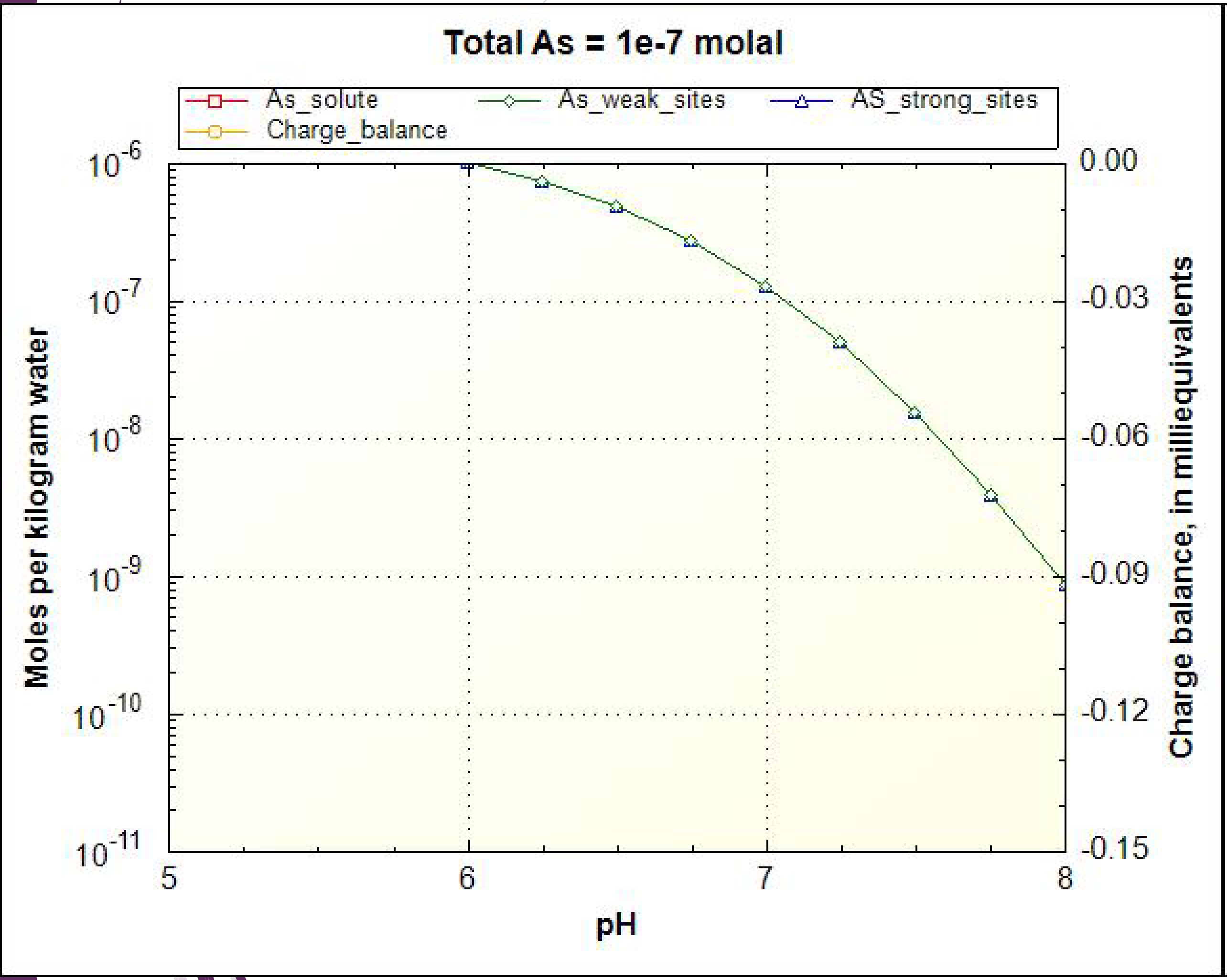
```
----------------------------Solution composition-----

     Elements             Molality       Moles

     As                  8.916e-06   8.916e-06
     N                   1.000e-01   1.000e-01
     Na                  1.001e-01   1.001e-01

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

                                                Log
   Species               Molality     Activity  Molality

   H+                   1.280e-06   1.000e-06    -5.893
   OH-                  1.318e-08   1.004e-08    -7.880
   H2O                  5.551e+01   9.966e-01     1.744
As(3)         1.100e-27
   H3AsO3               1.099e-27   1.099e-27   -26.959
   H2AsO3-              8.175e-31   5.638e-31   -30.088
   H4AsO3+              7.897e-34   5.447e-34   -33.103
   HAsO3-2              2.272e-36   5.142e-37   -35.644
   AsO3-3               0.000e+00   0.000e+00   -42.251
As(5)         8.916e-06
   H2AsO4-              6.682e-06   4.609e-06    -5.175
   HAsO4-2              2.233e-06   5.054e-07    -5.651
   H3AsO4               7.827e-10   8.009e-10    -9.106
   AsO4-3               4.523e-11   1.598e-12   -10.345
```

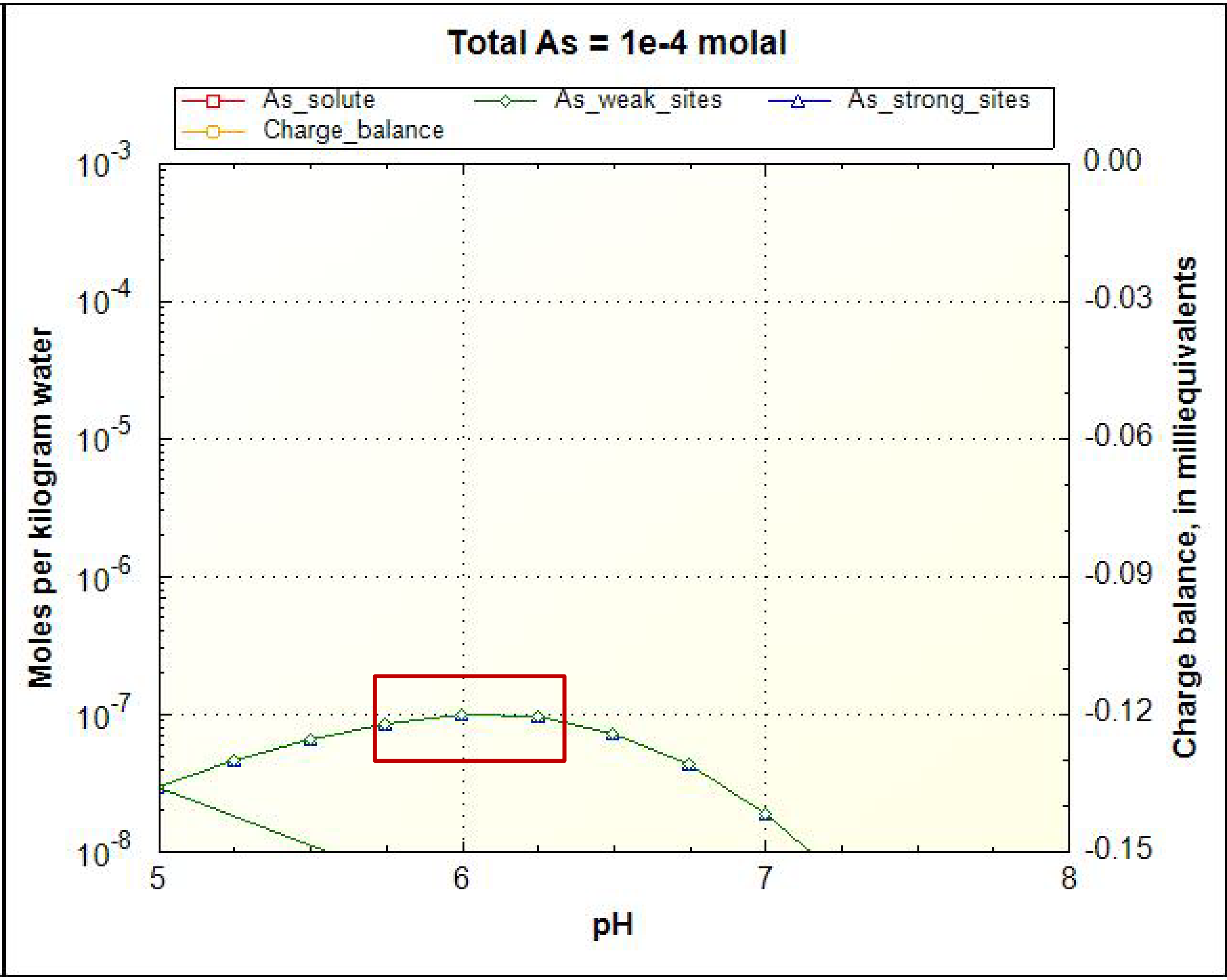
RESULTS



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

Diffuse Double Layer Surface-Complexation Model

Hfo_s
        7.000e-06  moles
                                             Mole                     Log
      Species                 Moles      Fraction    Molality    Molality

      Hfo_sOH2+           6.154e-06         0.879   6.154e-06      -5.211
      Hfo_sOH             4.721e-07         0.067   4.721e-07      -6.326
      Hfo_sHAsO4-         2.215e-07         0.032   2.215e-07      -6.655
      Hfo_sH2AsO4         9.342e-08         0.013   9.342e-08      -7.030
      Hfo_sOHAsO4-3       5.801e-08         0.008   5.801e-08      -7.236
      Hfo_sO-             8.296e-10         0.000   8.296e-10      -9.081
      Hfo_sH2AsO3         8.260e-29         0.000   8.260e-29     -28.083

Hfo_w
        2.000e-04  moles
                                             Mole                     Log
      Species                 Moles      Fraction    Molality    Molality

      Hfo_wOH             1.116e-04         0.558   1.116e-04      -3.952
      Hfo_wHAsO4-         5.237e-05         0.262   5.237e-05      -4.281
      Hfo_wH2AsO4         2.209e-05         0.110   2.209e-05      -4.656
      Hfo_wOHAsO4-3       1.372e-05         0.069   1.372e-05      -4.863
      Hfo_wO-             1.962e-07         0.001   1.962e-07      -6.707
      Hfo_wOH2+           8.769e-20         0.000   8.769e-20     -19.057
      Hfo_wH2AsO3         1.953e-26         0.000   1.953e-26     -25.709
```

RESULTS


Total As = 1e-7 molal
As_solute
As_weak_sites
AS_strong_sites
Charge_balance
Moles per kilogram water
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
Charge balance, in milliequivalents
0.00
-0.03
-0.06
-0.09
-0.12
-0.15
5
6
7
8
pH


Total As = 1e-4 molal
As_solute
As_weak_sites
As_strong_sites
Charge_balance
Moles per kilogram water
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Charge balance, in milliequivalents
0.00
-0.03
-0.06
-0.09
-0.12
-0.15
5
6
7
8
pH

RESULTS

- Smaller HFO particles and lower pH conditions led to significantly higher arsenic adsorption.
- The PHREEQC model predicted an increase of ~75% arsenic removal under these conditions.
- This is less compared with experimental results from Das et al. (2020), which reported >95% arsenic removal.

Das et al., 2020

CONCLUSION

- Differences in predicted vs. observed values may be due to the approximation of HFO as nano iron in the model
- Nano iron and HFO have different surface complexation constants (log K), which affects adsorption predictions
- Accurate modeling of arsenic adsorption on nanomaterials (e.g., nZVI, graphene oxide, nano-magnetite) requires a comprehensive and standardized thermodynamic database

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Thank you!