Development of PHREEQC database for Surface complexation modelling of Arsenic on Nano magnetite

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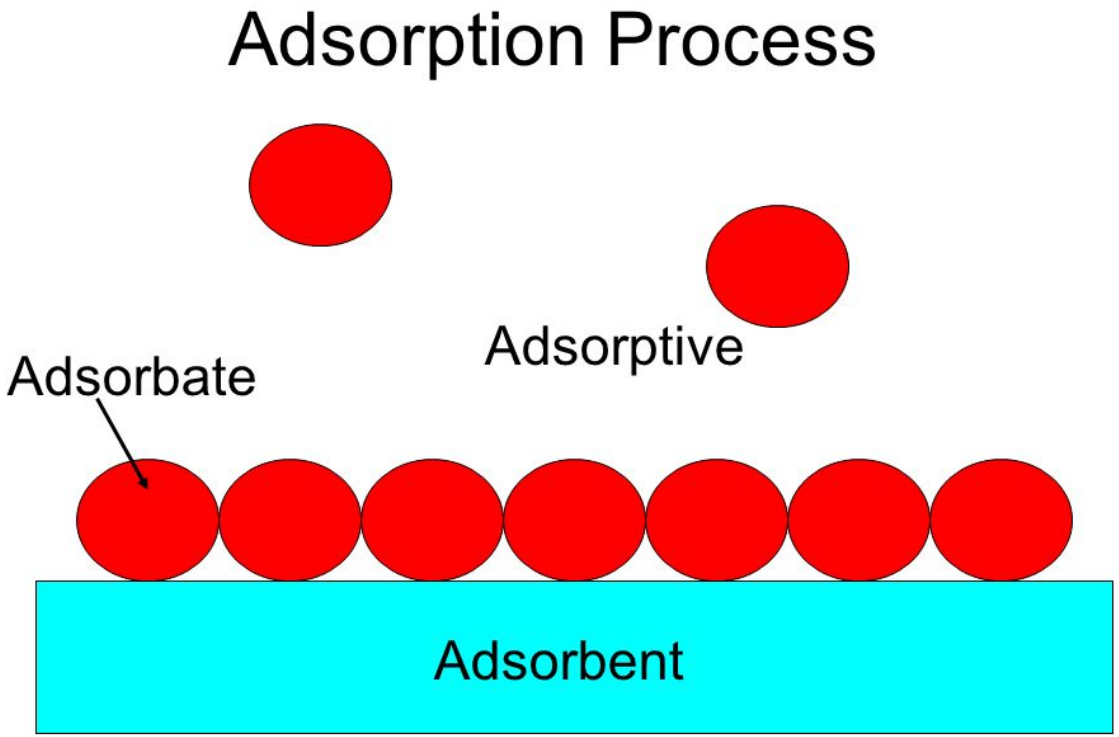
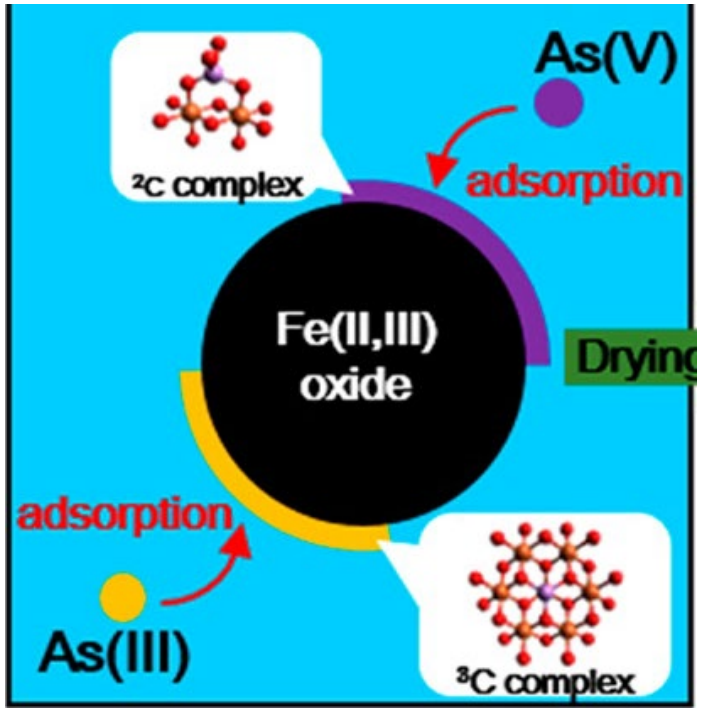
Adsorption



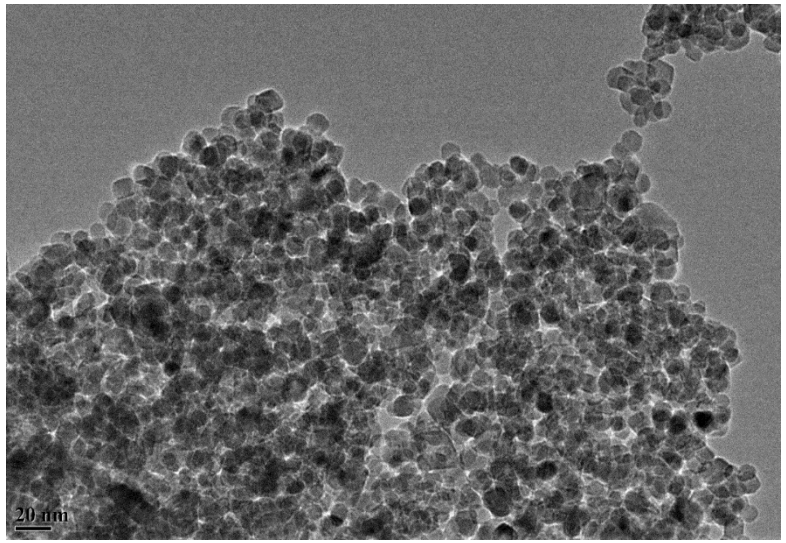
https://www.google.com/search?q=adsorption+process&tbm:

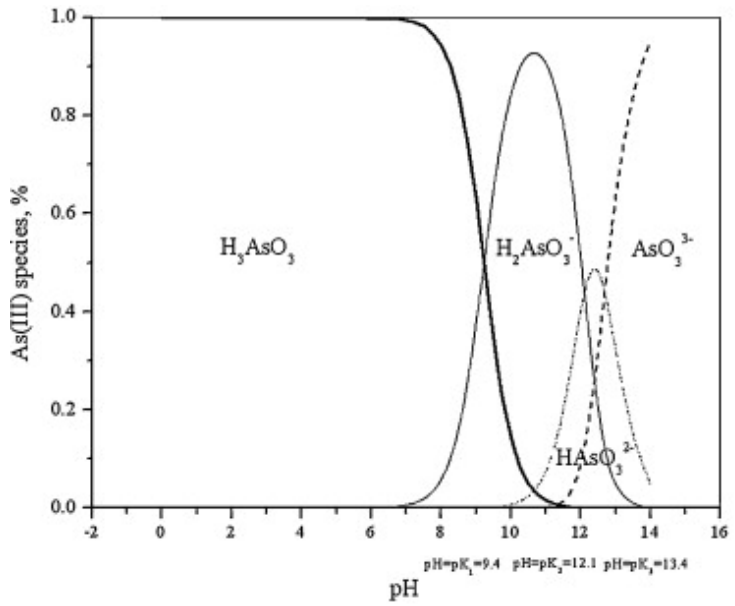


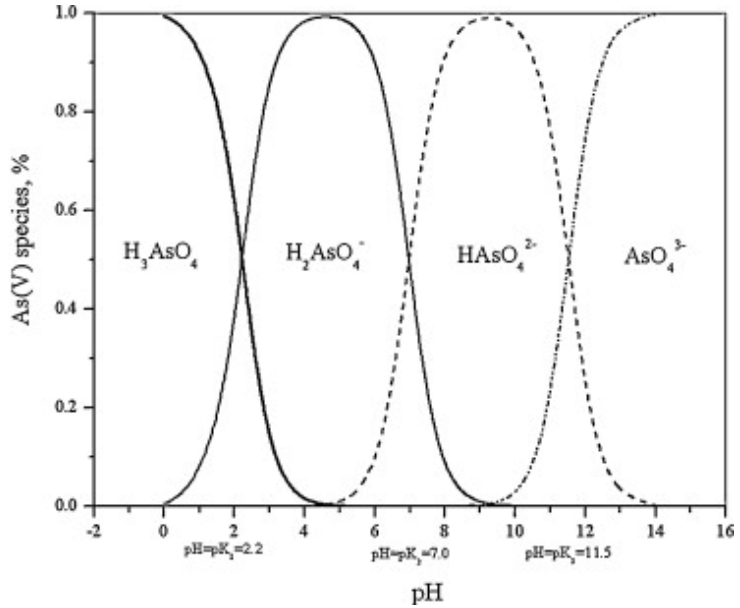
Liu *et al.*, 2015

Important factors for Adsorption

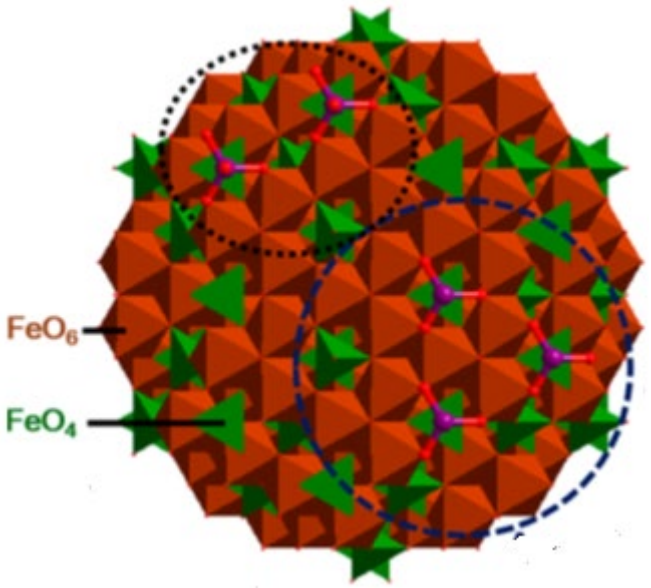
- Adsorbent surface
- Adsorbate species
- Removal Mechanisms

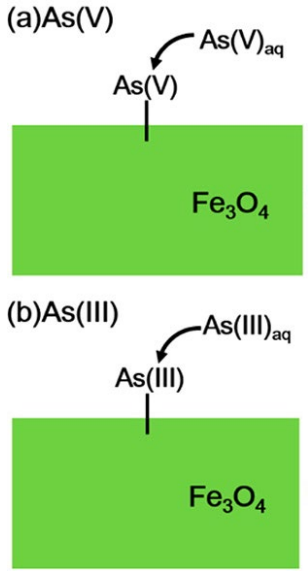




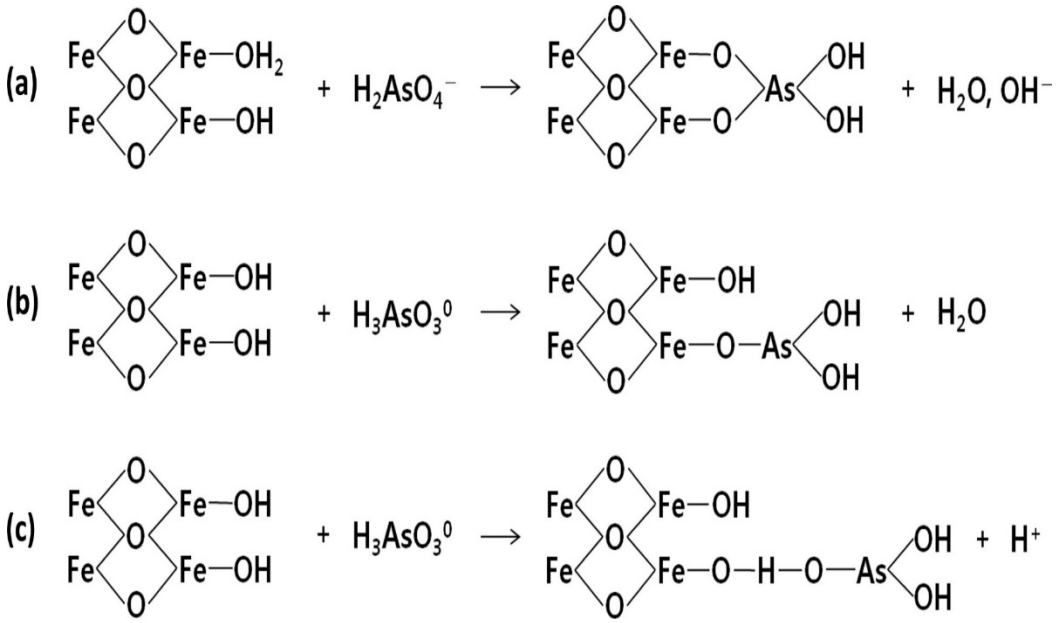


Magnetite Nanoparticles





Liu *et al.,* 2015



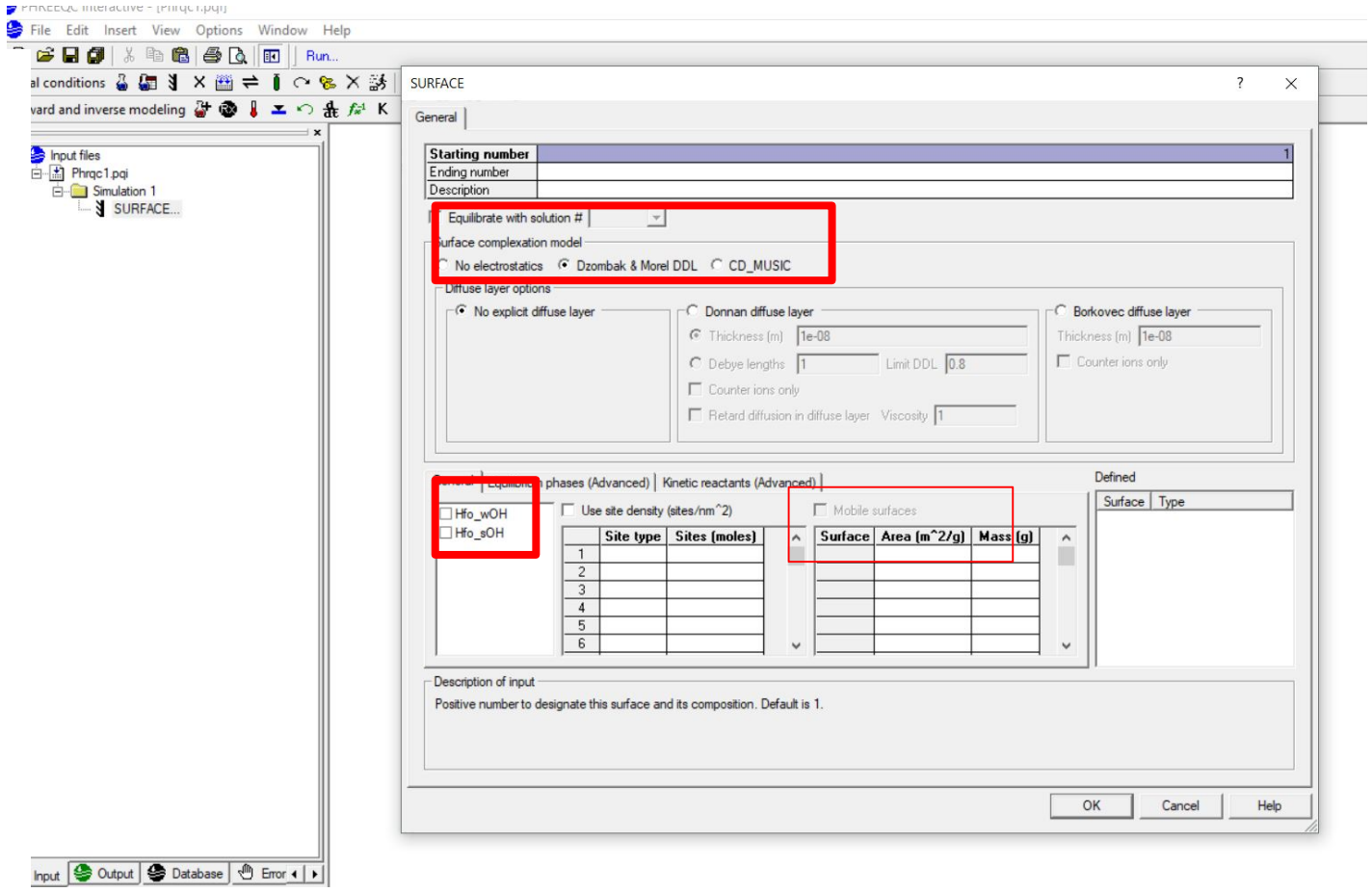
(a) bidentate binuclear–bridging complex for As(V), (b) monodentate complex for As(III), (c) outer-sphere complex for As(III).

Yahoon *et al.,* 2016

Surface Complexation in PHREEQC

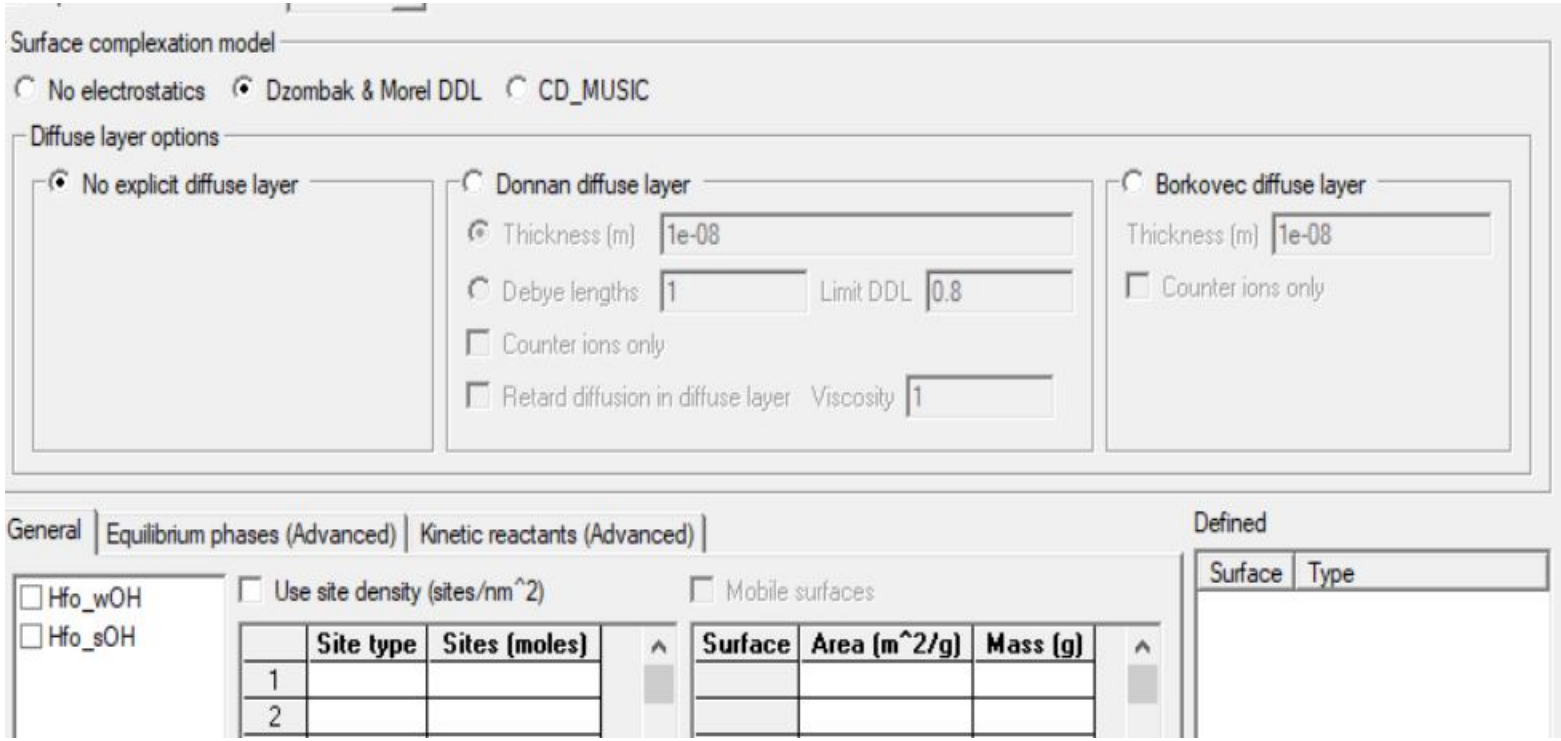
Minteq database

```
Hfo_sOH + H3AsO3 = Hfo_sH2AsO3 + H2O
        log_k   5.41
Hfo_wOH + H3AsO3 = Hfo_wH2AsO3 + H2O
        log_k   5.41
Hfo_sOH + H3AsO4 = Hfo_sH2AsO4 + H2O
        log_k   8.67
Hfo_wOH + H3AsO4 = Hfo_wH2AsO4 + H2O
        log_k   8.67
Hfo_sOH + H3AsO4 = Hfo_sHAsO4- + H2O + H+
        log_k   2.99
Hfo_wOH + H3AsO4 = Hfo_wHAsO4- + H2O + H+
        log_k   2.99
Hfo_sOH + H3AsO4 = Hfo_sAsO4-2 + H2O + 2H+
        log_k   -4.7
Hfo_wOH + H3AsO4 = Hfo_wAsO4-2 + H2O + 2H+
        log_k   -4.7
Hfo_sOH + H3AsO4 = Hfo_sOHAsO4-3 + 3H+
        log_k   -10.15
Hfo_wOH + H3AsO4 = Hfo_wOHAsO4-3 + 3H+
        log_k   -10.15
```



Surface Complexation in PHREEQC

- Complexation Model:
  - No electrostatic:
  - Dzombak and Morel Model:
  - CD Music: Charge distribution model
- Surface Area
- Site density



Why database modification?

- Surface of magnetite different than Hfo: site density, specific surface area
- Adsorption and reaction kinetics is different : having different Log K value
- Surface complex may be different
- Approximation of Hfo to magnetite leads to wrong modelling results

Modification Framework

- Getting log K value for the reaction : Log K calculated from the Langmuir K by using;

$K=K_L*C_w$ $C_w = 5.56*10^4$

Table 1. Fitted Langmuir Isotherm Parameters and Thermodynamic Calcu

arsenic species	temperature (K)	Langmuir parameters		
		q_{max} (mmol g^{-1})	K_L (L $mmol^{-1}$)	R^2
As(V)	283	0.195	15.5	0.979
	298	0.214	27.8	0.995
	313	0.225	32.8	0.996
	328	0.246	36.1	0.995
As(III)	283	0.212	6.59	0.971
	298	0.222	9.00	0.980
	313	0.227	11.4	0.989

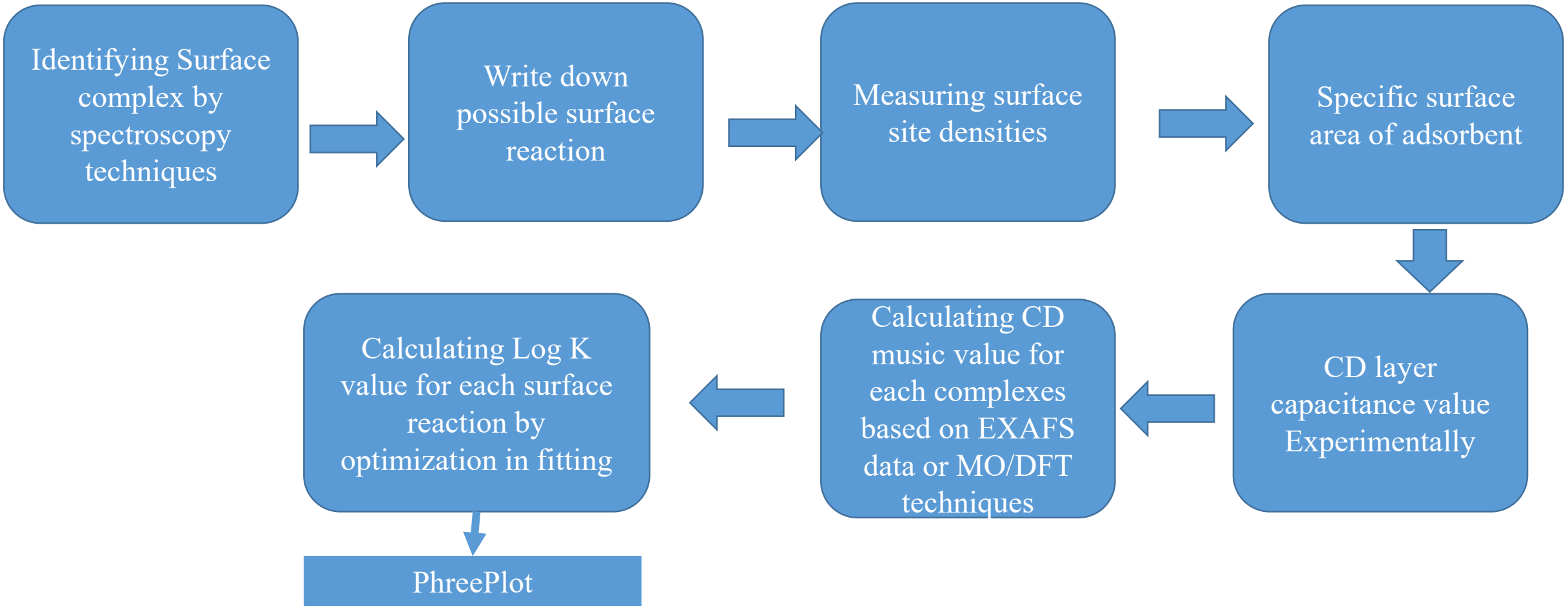
Liu *et al.*, 2015

As (V): Log K= 6.19

As(III): Log K=5.70

Modification Framework

Using CD-music model:



CD-MUSIC Reaction Database for Modeling (2009 EPRI Report)

Modification Framework

Optimization of CD-music model Parameter for Magnetite:

	Surface sps	**=FeOH site no**	**ΔZ0**	**ΔZ1**	**Log K**	**R2**
Arenite						
Arsenate						

CD-MUSIC Reaction Database for Modeling (2009 EPRI Report)

Developed data base

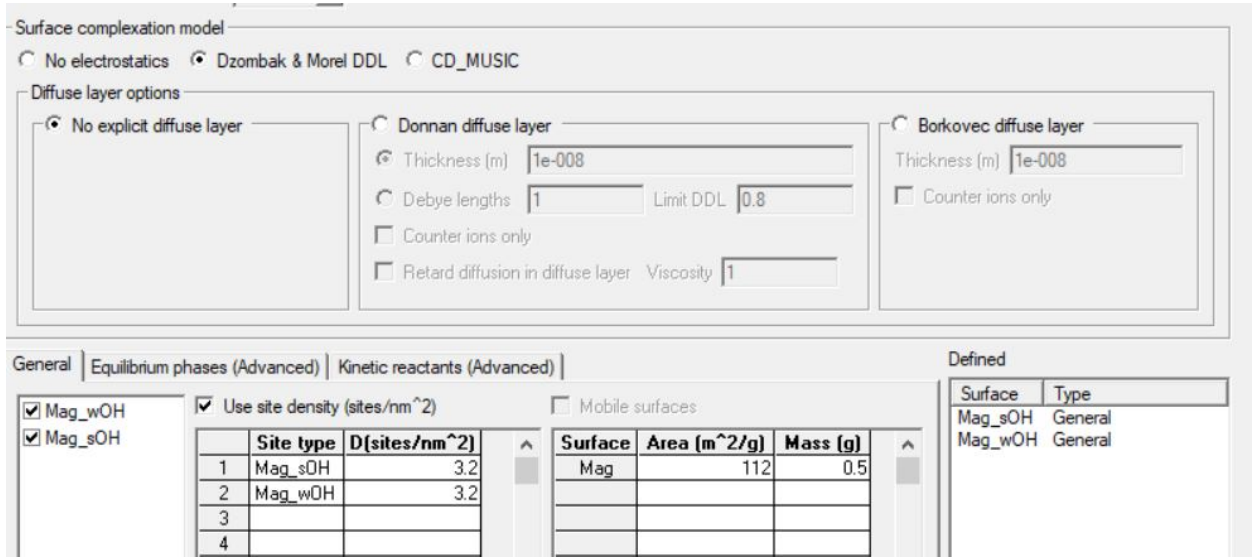
```
SURFACE_MASTER_SPECIES

Mag_uni Mag_uniOH-0.5 # =FeO site on Magnetite
Mag_tri Mag_triO-0.5 # =Fe3O site on Magnetite

SURFACE_SPECIES
#
# Magnetite
#
Mag_triO-0.5 = Mag_triO-0.5
-cd_music 0 0 0 0 0
log_k 0
Mag_triO-0.5 + H+ = Mag_triOH+0.5
-cd_music 1 0 0 0 0
log_k 9.20
Mag_uniOH-0.5 = Mag_uniOH-0.5
-cd_music 0 0 0 0 0
log_k 8.76

# H3AsO3
Mag_uniOH-0.5 + H3AsO3 = Mag_uniOAs(OH)2-0.5 + H2O
log_k 5.69 # Stachowicz et al 2006
-cd_music 0.16 -0.16 0 0 0
2Mag_uniOH-0.5 + H3AsO3 = (Mag_uniO)2AsOH- + 2H2O
log_k 5.69 # Stachowicz et al 2006
-cd_music 0.34 -0.34 0 0 0
# AsO4-3
Mag_uniOH-0.5 + 2H+ + AsO4-3 = Mag_uniOAsO2OH-1.5 + H2O
log_k 6.19
-cd_music 0.30 -1.30 0 0 0
2Mag_uniOH-0.5 + 2H+ + AsO4-3 = (Mag_uniO)2AsO2-2 + 2H2O
log_k 6.19
-cd_music 0.47 -1.47 0 0 0
```

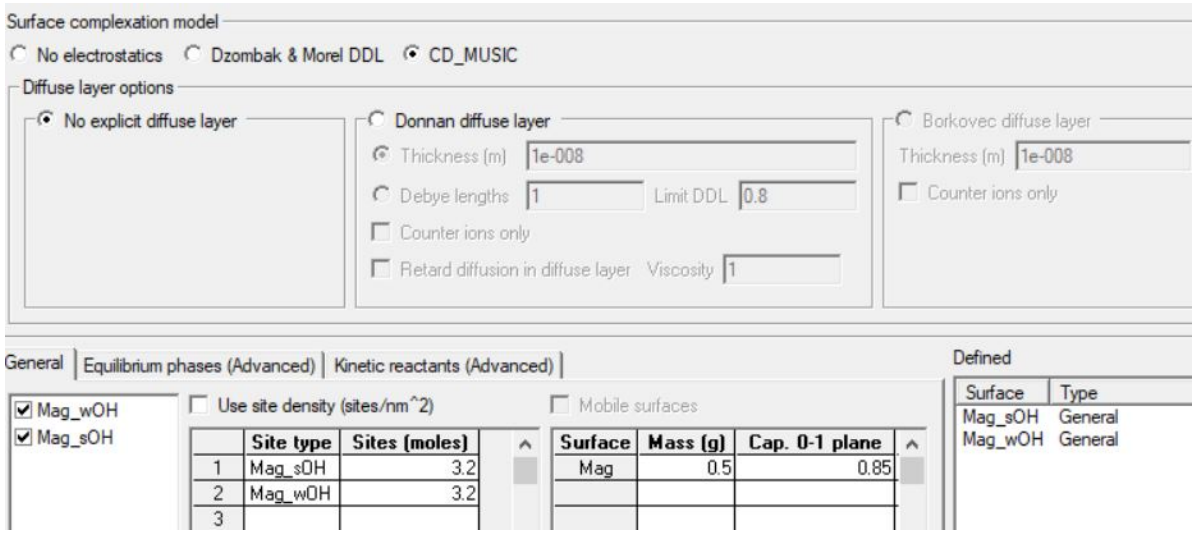
Minteq data base

```
#    Arsenate
         Mag_wOH + AsO4-3 + 3H+ = Mag_wH2AsO4 + H2O
         log_k   6.19

         Mag_wOH + AsO4-3 + 2H+ = Mag_wHAsO4- + H2O
         log_k   6.19

         Mag_wOH + AsO4-3 = Mag_wOHAsO4-3
         log_k   6.19
#
#    Anions from table 10.7
#
#    Arsenite
         Mag_wOH + H3AsO3 = Mag_wH2AsO3 + H2O
         log_k   5.70
```

Wateq4f data base

Model Run






```
SOLUTION 1
    temp      25
    pH        7
    pe        4
    redox     pe
    units     mmol/l
    density   1
    As(5)     0.5
    Cl        100
    Na        100
```

Output

Mag_s

2.975e-04 moles

Species	Moles	Mole Fraction	Molality	Log Molality
Mag_sOH	2.089e-04	0.702	2.089e-04	-3.680
Mag_sOH2+	7.534e-05	0.253	7.534e-05	-4.123
Mag_sO-	1.328e-05	0.045	1.328e-05	-4.877

Mag_w

2.975e-04 moles

Species	Moles	Mole Fraction	Molality	Log Molality
Mag_wOH	1.843e-04	0.620	1.843e-04	-3.734
Mag_wOH2+	6.647e-05	0.223	6.647e-05	-4.177
Mag_wOHAsO4-3	3.503e-05	0.118	3.503e-05	-4.456
Mag_wO-	1.171e-05	0.039	1.171e-05	-4.931
Mag_wH2AsO3	4.363e-14	0.000	4.363e-14	-13.360
Mag_wHAsO4-	1.202e-20	0.000	1.202e-20	-19.920
Mag_wH2AsO4	2.223e-28	0.000	2.223e-28	-27.653

DM model

Mag_s

3.200e+00 moles

Species	Moles	Mole Fraction	Molality	Log Molality
Mag_sOH	2.456e+00	0.768	2.456e+00	0.390
Mag_sOH2+	3.719e-01	0.116	3.719e-01	-0.430
Mag_sO-	3.716e-01	0.116	3.716e-01	-0.430
Mag_sOHAsO4-3	2.513e-04	0.000	2.513e-04	-3.600
Mag_sHAsO4-	1.295e-07	0.000	1.295e-07	-6.888
Mag_sH2AsO4	2.412e-12	0.000	2.412e-12	-11.618
Mag_sH2AsO3	2.730e-31	0.000	2.730e-31	-30.564

Mag_w

3.200e+00 moles

Species	Moles	Mole Fraction	Molality	Log Molality
Mag_wOH	2.456e+00	0.768	2.456e+00	0.390
Mag_wOH2+	3.719e-01	0.116	3.719e-01	-0.430
Mag_wO-	3.716e-01	0.116	3.716e-01	-0.430
Mag_wOHAsO4-3	2.513e-04	0.000	2.513e-04	-3.600
Mag_wHAsO4-	1.295e-07	0.000	1.295e-07	-6.888
Mag_wH2AsO4	2.412e-12	0.000	2.412e-12	-11.618
Mag_wH2AsO3	2.730e-31	0.000	2.730e-31	-30.564

CD Music

Importance of Surface complexation modelling

- Nano magnetite used for water filtration treatment unit
- Predicting adsorption in variable water quality
- Injecting nano-iron for in-situ stabilization of contaminant
- Sorption-desorption on adsorbent surfaces in the soil/aquifer matrix variable geochemical situation

Thank YOU!!!

Comments and Question !

-cd_music 0.46 -1.46 0 0 0

Arsenate

$$\equiv FeOH^{-1/2} + 2\,H^{+} + AsO_4^{-3} = \equiv FeOAsO_3H^{-3/2} + H_2O$$

$$2\,\equiv FeOH^{-1/2} + 2\,H^{+} + AsO_4^{-3} = (\equiv FeO)_2AsO_2^{-2} + 2\,H_2O$$

$$2\,\equiv FeOH^{-1/2} + 3\,H^{+} + AsO_4^{-3} = (\equiv FeO)_2AsO_2H^{-} + 2\,H_2O$$

```
Goe_uniOAs(OH)2-0.5 + H2O
# Stachowicz et al 2006
16 0 0 0
 (Goe_uniO)2AsOH- + 2H2O
# Stachowicz et al 2006
4 0 0 0

4-3 = Goe_uniOAsO2OH-1.5 + H2O

0 0 0 0
O4-3 = (Goe_uniO)2AsO2-2 + 2H2O

47  0 0 0
O4-3 = (Goe_uniO)2AsOOH- + 2H2O
```

Arsenite

$$\equiv FeOH^{-1/2} + H_3AsO_3 = \equiv FeOAs(OH)_2^{-1/2} + H_2O$$

$$2\,\equiv FeOH^{-1/2} + H_3AsO_3 = (\equiv FeO)_2AsOH^{-} + 2\,H_2O$$