

1. PURPOSE OF THE VISIT

The research stay aim was to measure and model iron chelates adsorption onto Iron (hydr)oxydes surfaces using CD-MUSIC model. In addition, Fe-EDDHA adsorption rate onto ferrihydrite was studied for both Fe-EDDHA diastereoisomers (rac-EDDHA/Fe and meso-EDDHA/Fe)

2. DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT

Following steps will be met during research stay.

2.1. CHELATING AGENTS ADSORPTION TO IRON (HYDR)OXYDES

Firstly, all related VMinteq databases were updated in order to include all related equilibrium constants.

2.1.1. ADSORPTION MODEL FOR EDDHA/FE USING EQUILIBRIUM VMINTEQ PROGRAM

Firstly distribution constants values (Kd) were determined with speciation VMinteq program and modeled Kd results were compared with those experimental data in order to evaluate the Kd consistency. Once Kd values were tested, EDDHA/Fe adsorption model can be stated. More than 70 models were done to check the effect that parameters such as; intrinsic constants (Log Kint), ionic strength; FeEDDHA concentration; solid phase concentration (Ferrihydrite concentration); electrostatic components; carbonate content and CO₂ could be affecting on EDDHA-Fe adsorption rate. Both adsorption rate (in terms of sorbed percentage) and Log KD values were analyzed as resulting parameters.

2.1.2. IRON (HYDR)OXYDES SYNTHESIS

Three approaches were performed in order to get two-lines ferrihydrite following different procedures from bibliography. First one was done following the methodology proposed by Li et al. (2011) in which two-lines ferrihydrite was synthesized in one step because air flow was continuously bubbled during NaOH addition on Fe(III) salt (nitrate). NaOH (1M) was slowly added on Fe(NO₃)₃·9H₂O salt vigorously stirring up to final pH to be 7.80. Sample suspension was allowed to age for 18 hours in a temperature controlled bath at 18 ± 2°C. The resulting suspension was repeatedly washed until the conductivity was around 3 µS/cm.

Second and third ferrihydrite synthesis was performed in accordance with Swedlund and Webster (1999) and Schwertmann and Cornell (2000). NaOH solutions (5M or 1M depending on curve zone) was slowly added on Fe(NO₃)₃·9H₂O salt allowing pH stabilization between NaOH additions. NaOH molarity and volumes and pH value were recorded for each volume addition up to final pH to be 8.0 (in accordance with Gustaffson et al 2009, Gustaffson 2003 and Antelo et al. 2010). The resulting sample suspension was allowed to age for 22 hours in a temperature controlled room at 20°C. The resulting suspension was repeatedly washed until conductivity was lower than 10 µS/cm. Ferrihydrite characterization was performed by determining of several specific ferrihydrite parameters, namely BET surface, point zero of charge and x-ray diffraction.

2.1.3. BATCH EXPERIMENTS FOR EDDHA-FE ADSORPTION ASSESSMENT

Five batch adsorption experiments were arranged to obtain adsorption isotherms. Commercial EDDHA-Fe was used in batch adsorption experiments. Effect of several parameters such as pH,

ionic strength, carbonate concentration, iron chelate concentration and ferrihydrite concentration were evaluated using batch experiments. In fact, EDDHA-Fe solutions at desired conditions were mixed with ferrihydrite solutions in 50 mL polyethylene bottles. The pH of the resultants suspensions was previously adjusted. Tubes were allowed to interact for 96 hours at a controlled temperature room at 20°C in the dark on an end-over-end shaker. After that, the pHs were registered, the suspensions were centrifuged for 15 min at 12000 rpm and at 20°C and filtered through 0.45 µm membrane filters. Total dissolved FeEDDHA concentration was quantified at 480 nm, where the red color formed due to iron phenolate bound is measured, using a Perkin Elmer Lambda 20 uv/vis Spectrometer equipped with a 1-cm quartz cell. Total added FeEDDHA concentration was quantified from those FeEDDHA blanks prepared for each pH value. Potential colour interference from Ferrihydrite suspension was corrected using the Ferrihydrite blanks. In addition, chelate separation into its isomers (rac-EDDHA/Fe and meso-EDDHA/Fe) and their quantification was analyzed by High Performance Liquid Chromatography (HPLC) technique following the Lucena et al. (1996) chromatographic method. Waters 2690 separation module (Alliance) and a Waters 996 photodiode array detector were used fitting a Symmetry RP =18, i.d. 150 x 3.9 mm and $d_p=5$ µm column. The injection volume was of 20 µL, and flow rate was 1.5 mL/min. The mobile phase contained 0.03 M tetrabutylammonium hydroxide (40% solution in water, 1.5 M, Sigma) and 30% acetonitrile (HPLC-grade, Fisher chemicals) at pH 6.0. Data were processed using Empower chromatography data system (Waters). Detection limit is 0.1 µmol L⁻¹ for each isomer. Distribution constant (K_D) and adsorption rate (in terms of sorbed Fe-EDDHA concentration) were determined for each bath experiment as adsorption parameters. Statistical analyses were performed by using the SPSS statistical software (version 19.0; SPSS Inc., Chicago, IL). Data were statistically evaluated by one-way analysis of variance (ANOVA). Levene variance homogeneity test was previously evaluated as well and, then, Duncan or Games-Howell post-hoc tests at $p \leq 0.05$ were used, as parametric and non-parametric appropriate tests respectively.

3. DESCRIPTION OF THE MAIN RESULTS OBTAINED

3.1.1. ADSORPTION MODEL FOR EDDHA/FE USING EQUILIBRIUM VMINTEQ PROGRAM

Relevant results were obtained after EDDHA-Fe was modeled with VMinteq. As Intrinsic Constant is larger sorbed percentage increase. Ionic Strength is largely affecting on adsorption rate. As ionic strength increase adsorption rate decrease. No great effect on adsorption rate were found when FeEDDHA concentration modified. Just (FeEDDHA) > 5000 mM on significantly affecting on adsorption rate. As expected as Ferrihydrite content increase (total sites increase) adsorption rate increase. Adsorption rate at pH 4 was > 90% at solid phase > 6 g/L. Lowest adsorption rate is found when total outer sphere adsorption is assumed (as expected), i.e. hydrogen charge is located in inner sphere and total ligand is in outer sphere. Adsorption rate is greatly affected by CO₂ concentration in agronomic pHs (5.5 – 8). Adsorption rate drop more than 50% when CO₂ goes from three to 15 times atmospheric conditions at pH 6.5. Similar result is found for log KD values. No carbonate content is affecting on either adsorption ratio or KD values. This fact should be confirmed through corresponding batch experiment. Once different models were done to check the effect of parameters such as pH, Ionic strength, ferrihydrite content, iron chelate concentration and carbonate content, corresponding batch experiments should be performed in order to confirm the proposed model.

3.1.2. FERRIHYDRITE CHARACTERIZATION

The structure and chemical composition of the resultant ferrihydrite synthesized was confirmed by the XRD pattern. Each ferrihydrite exhibits a typical XRD pattern of 2-lines ferrihydrite, which shows two broad peaks at about $2\theta = 35$ and 62° , respectively.

BET surface area were determined by N₂ adsorption. Resulting BET surface area were around 259 m²/g. No significant differences were found among two freshly ferrihydrites. Typical values of the BET surface area for Ferrihydrite were reported by Dzombak and Morel (1990) to be around 200–350 m²/g.

Point Zero of Salt Effect (PZSE) was determined by mixing an amount of ferrihydrite suspension with stock solutions of NaNO₃ salt to obtain three solutions with an ionic strength of 0.005 M, 0.05 M and 0.5 M. PSZE for synthesized ferrihydrite was **7.90 ± 0.17**. This result is in accordance with those reported by other authors. Villalobos and Antelo(2011) compiled several reported PZC (see following table). They noted that all fresh and thus not rigorously de-carbonated FH samples show consistently low values (7.9-8.1), whereas all dialyzed and N₂-purged samples after synthesis tend towards higher values (8.6-8.7). In our case, ferrihydrite was synthesized at room atmosphere and, therefore, the PZC is consistent with reported.

3.1.3. BATCH EXPERIMENTS FOR EDDHA-Fe ADSORPTION ASSESSMENT

3.1.3.1. PH EFFECT ON EDDHA-Fe ADSORPTION RATE.

Adsorption rate of both EDDHA/Fe diastereoisomers is totally different. Meso-EDDHA/Fe is much more adsorbed than rac-EDDHA/Fe. Thus, meso-EDDHA/Fe remains totally adsorbed up to pH around 7. Moreover, around 75% of meso-EDDHA/Fe is adsorbed onto ferrihydrite at pH around 8 (calcareous soils). On the other hand, rac-EDDHA/Fe diastereoisomer remains totally dissolved at pH 8. In accordance with these results, two intrinsic constants related to both EDDHA diastereoisomers should be determined and modeled. Similar results were found when distribution constants (K_D) for both FeEDDHA diastereoisomers were determined. K_D for rac-FeEDDHA was higher than that of meso-FeEDDHA.

3.1.3.2. IRON CHELATE CONCENTRATION EFFECT ON EDDHA-Fe ADSORPTION RATE.

Typical adsorption isotherms were obtained when adsorbed concentration versus equilibrium concentration was plotted for each ionic strength level. Langmuir isotherm parameters (C_m and K) were determined for both FeEDDHA diastereoisomers as well. No good fitting between experimental and modeled Langmuir isotherms was found for rac-FeEDDHA diastereoisomer as adsorption rate onto ferrihydrite was very low. However, as expected, Langmuir constant for meso-FeEDDHA was large and good fitting plots were found for each tested ionic strength level (see following table and figures).

3.1.3.3. CARBONATE CONCENTRATION EFFECT ON FEEDDHA ADSORPTION RATE.

Fe-EDDHA adsorption rate and distribution constants at different pH values and at the three carbonate concentrations were plotted at the following figures. As carbonate concentration increases adsorption rate decrease, even no large adsorption decreasing is observed. This fact may be explained since no large carbonate concentrations were tested. Anyway significant differences were observed for each pH value when carbonate concentration was increased. Similar results were observed when distribution constants were analyzed. When adsorption rate changes respect to no exogenous carbonate treatment were analyzed, around 30% less of adsorption rate is observed as carbonate concentration (2000 μM) is added. Significant differences were observed for each pH level.

3.1.3.4. IONIC STRENGTH CONCENTRATION EFFECT ON FEEDDHA ADSORPTION RATE.

FeEDDHA sorption percentage is greatly affected by ionic strength. Thus, sorption percentage is decreasing as ionic strength increase. At pH 4, sorption rate is decreasing from 80 to 50% when ionic strength is varied increased by 100 times Ionic strength is greatly affecting on adsorption rate regardless diastereoisomer. As ionic strength is increased from 0.005M to 0.5M adsorption rate is decreased. In calcareous soils (pH around 8) meso-FeEDDHA remains adsorbed around 70% at ionic strength 0.005M but only 50% at ionic strength 0.5M. In case of rac-FeEDDHA, adsorption rate is greatly affected as ionic strength increased. Thus no adsorption rate is found at ionic strength 0.5M along pH. Same pattern is observed when Log Kd values for each ionic strength for both FeEDDHA diastereoisomers are calculated

3.1.3.5. FERRIHYDRITE CONCENTRATION EFFECT ON FEEDDHA ADSORPTION RATE.

As previously modeled, as ferrihydrite concentration increases Fe-EDDHA adsorption rate increases due to number of adsorption sites increases. Thus meso-FeEDDHA adsorption rate goes from around 40% for ferrihydrite concentration to be 5 g·L⁻¹ to around 90% for ferrihydrite concentration to be 20 g·L⁻¹. Same pattern may be found when distribution constant (Log Kd) is analyzed

1. FUTURE COLLABORATION WITH HOST INSTITUTION (IF APPLICABLE)

Currently we are in contact with Peter Gustafsson (person in charge of VMinteq updating) in order to include EDDHA-Fe intrinsic constants. In order to reach this objective short visit to Uppsala University will be done to share results.

2. PROJECTED PUBLICATIONS RESULTING OR TO RESULT FROM THE GRANT

Following scientific publications are being managing form the grant:

- Publication on VMinteq database updating has been already sent to be published in European Journal of Soil Science.
- Publication to be sent to Journal of Colloid and Interface Science is being arranged. All batch experiments and models will be included in this work
- Submit an abstract to the EGU General Assembly 2012 (22-27 April 2012, Vienna, Austria) Session SSS2.1 "Nanosized iron oxides in soils: agronomic, environmental and palaeoenvironmental significance" at the Soil System Sciences Programme Group.