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Carbonate component reduces o,oEDDHA/Fe sorption on two-line ferrihydrite

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The o,oEDDHA/Fe is the most common and effective iron chelate used as fertilizer in calcareous soils. Several authors have reported that the anionic o,oEDDHA/Fe complex is adsorbed to soil components such as ferrihydrite. The bicarbonate anion may be a competing ion for this sorption, however no studies have yet identified the extent and mechanism of this interaction. The aim of this work was to study the carbonate (bicarbonate + carbonate) effect on EDDHA/Fe adsorption on two-line ferrihydrite. Two-line ferrihydrite was synthetized adding NaOH on a nitrate iron (III) solution up to a final pH to be 8.0 and allowing to age for 22 hours at 20ºC. Dialyzed ferrihydrite was characterized by determining specific parameters such as Fe/OH ratio, BET surface, point zero of charge and x-ray diffraction. The sorption was performed at three pH levels (5, 7.5 and 9.5) and three initial carbonate concentrations (from 0 to 2 mM). Initial EDDHA/Fe, ferrihydrite and ionic strength concentrations were adjusted to 0.18 mM, 10 g•L-1 and 5 mM respectively. Total dissolved FeEDDHA concentrations were quantified at 480 nm. The o,oEDDHA/Fe isomers (rac-o,oEDDHA/Fe and meso-o,oEDDHA/Fe) were separated and quantified by High Performance Liquid Chromatography (HPLC) fitting a photodiode array detector (PDA). Distribution factor (KD) and sorbed o,oEDDHA/Fe concentration were determined. Actual carbonate concentration was determined using a multi N/C analyzer. Ferrihydrite samples showed a typical XRD pattern of two-line ferrihydrite, two broad peaks at about 35 and 62º respectively. The BET surfaces (two replicates) were 259.2 ± 3.1 m^2/g and 256.0 ± 2.5 m^2/g. The Point Zero of Salt Effect (PZSE) was 7.9 ± 0.2 as bibliographically supported for all fresh and thus not rigorously de-carbonated ferrihydrite samples. The KD of the o,oEDDHA/Fe increased from 27.4 ± 0.6 to 304 ± 6 l/kg by decreasing pH from 9.5 and 5.0 when no carbonate was added. Increasing equilibrium carbonate concentrations between 8.6•10-2 and 76•10-2 mM decreased the KD about two-fold at pH 7.5. The KD values from meso-o,oEDDHA/Fe were up to 1000 fold larger than those of rac-o,oEDDHA/Fe at highest carbonate concentration at pH 7.5 and pH dependency suggests that former binds as inner sphere whereas latter binds as outer sphere. Despite the carbonate competition is unlikely to largely affect the net sorption of the chelate in soil, clear differences between meso-o,oEDDHA/Fe and rac-o,oEDDHA/Fe sorption rate on ferrihydrite in presence of carbonate were found.