How Should Freundlich Isotherms Be Compared

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The Freundlich equation \( \frac{x}{m} = K_C C_n^{1/\alpha} \) has been used widely in sorption studies in chemistry and environmental research. Two problems arise in comparing sorbate-sorbent systems if \( C_n = 1 \) or if \( 1/\alpha \) values differ. First, it is often not possible to compare \( K_C \) values from the literature if they were derived from different units of \( x/m \) and \( C_n \). Second, the exponent \( 1/\alpha \) determines the interpretation of \( K_C \). We propose a way to characterize sorption dynamics of Freundlich isotherms so that problems caused by comparing \( K_C \) values can be avoided. We will illustrate that: 1) The units of \( K_C \) are \( \mu\text{mol}1^{-1}\text{mg}^{-1} \) or \( \mu\text{g}1^{-1} \) \( \text{mg}^{-1} \) etc. depending on the units of \( x/m \) and \( C_n \). Therefore, \( K_C \) parameters cannot be compared among samples whenever the \( 1/\alpha \) parameters are different. 2) For \( K_C \) values that are associated with different units, the units-conversion factor for \( K_C \) is also a function of \( 1/\alpha \). It has the form of \( A^{1/\alpha} \), where \( A \) is the units-conversion factor if \( 1/\alpha = 1 \). 3) We propose a new variable, \( K_C^* \), to unify the units of \( K_C \) and to conduct sensitivity analyses of \( K_C \) and \( 1/\alpha \). Numerically \( K_C^* \) is the slope, \( (x/m)/C_n^* \) of the sorption isotherm at any value of \( C_n \) or \( x/m \) and has unit of \( \text{mg} \).}

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**Phosphorus Fraction dynamics in Amended Soils.**

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Phosphorus (P) fraction dynamics on high P (NH4Ox > 6000 mg kg^-1) Southern Delaware soils (0-30cm) was investigated. Short term (24h) P desorption (0.1M NaCl at soil pH) using a stirred-flow method on non-treated and treated (NH4Cl, NH4Cl + NH4Ox, and NH4Cl + NH4FeX)tration) soils showed that P releasable to significantly reduced in following treatment order (NH4Cl > NH4Cl+Fe > NH4Ox). More than 65 % of labile P in the high P soils was originated from NH4Ox and NH4Fe extractable P fractions. Long term (30d) P desorption, using a dilution method (0.1M NaCl at soil pH) coupled with sequential inorganic P extraction (NH4Cl, NH4Fe, NH4Ox, NaOH, Na2CO3, and H2SO4) on 15d and 30d desorption samples also showed a high correlation between labile P and NH4Ox + NH4Fe extractable P. P mineralization characterization of the P treated soils was also investigated using ex-situ spectroscopic techniques (FTR and EDX).

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Cadmium adsorption studies on biosolids-amended soils and their inorganic fractions have been conducted at various pH values. Soil samples were collected from five sites where biosolids (sewage sludge) had been applied. Adsorption of Cd on the biosolids-amended soils was significantly higher than the control soils. When organic carbon (1 to 6 % organic carbon) was removed by NaClO from the soils, the adsorption on the inorganic fractions for these soils showed a similar trend. Decreasing pH of adsorption media reduced adsorption of Cd on soils and inorganic fractions. However, the inorganic fractions of the biosolids-amended soils appeared to be less affected by pH than the controls. Adsorption of Cd on the biosolids samples and the inorganic fractions of biosolids suggested that application of biosolids into soils increased adsorption on soils, and that the contribution by the inorganic phases of biosolids is important.

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**ELUCIDATING REVERSIBLE SORPTION MECHANISMS FOR AROMATIC AMINES FROM SINGLE AND BINARY SORPTION DATA**

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Reversible sorption mechanisms of anilines and 1-naphthylamine were investigated using single and binary solute sorption data from soils at several pHs and employing a distributed parameter (DP) model. The DP model includes linear partitioning of each sorbate between the organic cation with exchange coefficients represented by a Gaussian mixed probability distribution. Sorption isotherms were nonlinear, which was attributed to cation exchange from DP model simulations. Both hydrophobic partitioning and cation exchange selectivity was greatest for 1-naphthylamine compared to aniline. Sorption of 1-naphthylamine was not impacted by aniline; however, 1-naphthylamine reduced aniline sorption. DP model simulations showed that contributions from hydrophobic partitioning increases with pH; however, cation exchange still contributes significantly to the total sorption even at soil-solution pH >> pKa + 2.

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**Effectiveness of phosphate and hydroxide for desorption of As and Se species from Fe oxides.** B.P. JACKSON and W.P. MILLER, Univ. of Georgia.

Phosphate and OH are often used for the extraction of As and Se from soils and sediments, either as single extractants or as part of a sequential extraction scheme. However, the effectiveness of either ligand to quantitatively desorb As and Se species, and the integrity of the resulting speciation in the extracting solution merits investigation. In this study the relative effectiveness of PO4 and OH to extract sorbed As(III), (As(V), dimethylarsinic acid, DMA, monomethylarsonic acid MMA, and Se(IV) and Se(VI)) from aqueous and an amorphous Fe oxide were compared and ion chromatography coupled to inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the speciation of As and Se in the resulting extract. Hydroxide was more effective in desorbing MMA, As(III) and Se(IV) from the amorphous Fe oxide and MMA and Se(IV) from goethite. Se(IV) was not recovered in the exchangeable fraction from goethite but the ligand-exchangeable fraction from the amorphous Fe oxide. Arsenite was not greatly desorbed (~10%) from the amorphous Fe oxide by either extractant. Oxidation of As(III) occurred in the hydroxide extractions and appeared to be correlated by the presence of the solid phase. Addition of 0.1 M PO4 to extractants used for the dissolution of the amorphous Fe oxide prevented the readsoption of As and Se to goethite.

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**Arsenite Surface Complexes on Metal Sulfides.** B.C. Bostick, S.E. Fendorf, Stanford University

Metal partitioning into the solid phase is an important means of limiting the bioavailability and transport of toxic elements such as arsenic. While there are considerable advances in the understanding of cation sorption on oxide surfaces, much less is known about sorption to sulfide minerals formed in anoxic soils and sediments. The purpose of this research was to obtain a molecular-scale description of arsenite surface complexes on pyrite and galena. The surface complexes that formed through sorption were studied using X-ray absorption spectroscopy (XAS) and Raman spectroscopy. Rapid sorption of arsenic results from the formation of sulfide complexes with As-S bond lengths near 2.4 Å. Arsenic and iron were also found in the center of surficial sulfur (S-Cu-S) lattice, suggesting the presence of surface clusters. Thus, arsenite undergoes a ligand-exchange process with sulfide derived from the surface. The resulting complex oxidized readily, possibly due to reaction with oxidized surface species.

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**In Situ Spectroscopic Studies of Sulfate and Selenate Adsorption on Iron (II) Hydroxides.** J.D. Peak, University of Delaware, D.L. Sparks, University of Delaware, E.J. Elzinga, University of Delaware

Recent research in our laboratory has determined that both inner- and outer-sphere surface complexes of both sulfate and selenate can occur simultaneously on iron oxides. The influence that pH, ionic strength, iron oxide identity, and oxygenation loading level has on the competition between sulfate and selenate will be explained using results from in situ spectroscopic studies. The results from ATR-FTIR spectroscopic studies of sulfate adsorption on iron oxides will be presented. Findings from EXAFS spectroscopic investigations at the Se K-edge will also be shown.

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**Adsorption/Desorption of Ba on Goethite.** S. E. Arthur, P. Zhang, R. T. Cygan, Sandia National Laboratories

Sorption of Ba on iron oxides must be understood to model its mobility in natural systems. Since Ra and Ba are similar in chemical reactivity, we used Ba, as an analogue, to study Ra sorption on goethite as a function of surface loading, pH, and ionic strength. Synchrotron X-ray absorption fine structure (XAFS) was used to characterize the local molecular bonding of sorbed Ba. At pH 12, Ba (15 mg/g) sorbed on goethite had bonding similar to Ba(OH)2(2H2O)(3H2O), with first and second shell Ba-O bonds and third shell Ba-Ba bonds, which indicates formation of an inner-sphere precipitate. The Ba (7 mg/g) goethite, in a goethite precipitated from ferricyanide aged with Ba at pH 12, had first and second Ba-O bonds, second shell Ba-Fe bonds and third shell Ba-Ba bonds perhaps indicating that Ba-O clusters were occluded in and/or adsorbed on goethite surfaces.

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**Actinide Interactions in Environmental Systems.** H. N. Heino Nitsche, University of California at Berkeley and Lawrence Berkeley National Laboratory.

Actinides can migrate in the environment mostly via aqueous media such as groundwater and surface, river, lake and sea water. Models predicting the hydrological transport through the environment require as input an actinide concentration, the true amount that is actually available for transport. It is defined as the actinide source term and not as true solubility, because it may be a...