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PFOA binding at the Goethite-Water Interface: Experimental data and Mechanistic Interpretation using the Charge Distribution and Multi-Site Complexation (CD-MUSIC) Model in combination with DFT

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Understanding the adsorption behavior of per- and polyfluoroalkyl substances (PFAS) on metal (hydr)oxides is essential for assessing their mobility and risk in the environment. In this study, batch adsorption experiments were conducted to investigate the binding of the frequently detected PFAS perfluorooctanoic acid (PFOA) at the goethite-water interface under variable chemical conditions. The charge distribution and multi-site complexation (CD-MUSIC) model combined with density functional theory (DFT) were employed to interpret mechanisms involved in PFOA binding. The experimental results indicate that PFOA adsorption is inversely related to pH. This being due to the decrease in positive charge on the goethite surfaces with increasing pH, weakening the electrostatic attraction by the goethite surface to the anionic PFOA molecules. In the presence of adsorbed phosphate, the adsorption of PFOA decreased, further validating the importance of surface charge. Increasing ionic strength with $NaNO_3$ decreased the adsorption of PFOA. Adding Ca^{2+} to the system decreased PFOA adsorption similarly without any indication of specific interaction with PFOA. Modeling results indicated PFOA binding can be described with a single inner-sphere complex formed between the carboxylic group on PFOA and the hydroxy group on the goethite surface. With this model the decreased binding with increasing electrolyte concentration and pH could be described accurately. The configuration of PFOA in the interface was optimized using DFT modelling. The charge distribution calculated based on the with DFT calculated bond length agreed well with the freely fitted charge distribution using CD-MUSIC. This further strengthened the reliability of the used CD-MUSIC approach. These findings help to improve our understanding of how environmental conditions influence PFOA adsorption on metal (hydr)oxide, providing valuable insights for predicting the geochemical behavior of PFOA in nature soil and water systems.

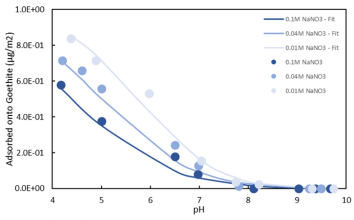

Figure 1. Measured and predicted 200 µg/L PFOA pH-dependent adsorption edges onto 2 g/L goethite at three ionic strengths (0.01M, 0.04 M and 0.1M NaNO3).

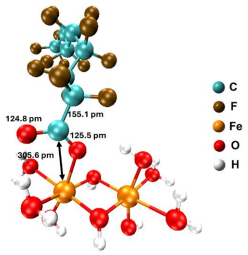

Figure 2. Schematic representation of the surface structure of PFOA on iron dimer clusters optimized by DFT calculations.