

Co-sorption mechanisms of heavy-metal cations and oxyanions on iron (oxyhydr)oxides

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(Oxyhydr)oxides show particularly high sorption affinity towards heavy metals and oxyanions, and hence have received great interests. Of particular concern is the co-sorption of heavy metals (e.g., Cu^{2+} , Cd^{2+} or Zn^{2+}) and oxyanions (e.g. phosphate, sulfate or arsenate) on (oxyhydr)oxides as the sorption capacity can be greatly affected. The complex co-sorption of heavy metals and oxyanions varied with the physicochemical properties contaminants, solution pH, (oxyhydr)oxides surface properties, etc.

This work aims to elucidate the effects of the properties of oxyanions on the co-sorption behaviors. The co-sorption of Cd(II) with phosphate and sulfate on ferrihydrite (Fh) were compared. Batch sorption experiments showed that both sulfate and phosphate could be synergistically sorbed with Cd(II) by Fh, with the desorbed percentage of the contaminants in the P+Cd co-sorption systems much lower than those in S+Cd systems. *in situ* attenuated total reflectance Fourier transform infrared spectroscopy combining with the two-dimensional correlation spectroscopic analysis was used to explore the interaction mechanisms in the sorption system. The results showed that in the single sorption systems, sulfate primarily formed outer-sphere complexes, while phosphate mainly formed bidentate nonprotonated inner-sphere complexes, accompanied with minor outer-sphere complexes. In the co-sorption systems, the synergistic sorption of Cd(II) and sulfate was mainly attributed to the electrostatic attraction; nonetheless, the formation of Fe-Cd-S (i.e., Cd bridged) ternary complexes might also occur. On the other hand, Fe-P-Cd (i.e., phosphate bridged) ternary complexes were detected in all of the synergistic sorption systems, and the electrostatic interaction also contributed to the co-sorption process. The co-existence of the two types of contaminants could be beneficial for their immobilization on Fh, and phosphate was more efficient than sulfate for the long term immobilization of Cd(II).

This work could provide new information for understanding the distribution of contaminants on the (oxyhydr)oxides-water interfaces.