Combined Experimental and Atom Level Simulation Studies of Cadmium Adsorption at Goethite-Water Interfaces

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Cadmium and its compounds are highly toxic to human beings and many other organisms. We consider goethite α-FeO(OH), as an adsorbent not only for its ability to trap Cd(II) but also for its abundance in the earth's crust and as a good model system for computational investigations. Co-adsorption between phosphate and Cd(II) was discovered experimentally with ferrihydrite surfaces, a precursor of goethite (Liu *et al.*, 2018). We strongly suspected that a similar relationship will be found on goethite surfaces as well. Hence we combine computational simulations with experimental studies to invetigate the anticipated co-adsorption behavior.

We have simulated the structures of three common surfaces of goethite: {100}, {110} and {021}; studied their surface characteristics; and proposed likely adsorption mechanisms. Then, we performed atomic simulations with Monte Carlo simualtions (Brukhna *et al*., 2019) to mimic an aqueous mixture of Cd(II) and phosphate at fixed chemical potentials, for screening the possible coordinations between the surface and the two ions. The result from the simulations allowed us to evaluate the effect of surface composition on the free-energies of adsorption.

The laboratory works utilised spectroscopic (*i.e* XAFS, ATR-FTIR, etc.) and microscopic analysis to confirmed that co-adsorption occurs and provides an enhancement of the immobilisation of Cd(II) on goethite. The comparison between experimental work and simulations have given us more comprehensive understanding towards the synergistic adsorption of Cd(II) with phosphate on goethite surfaces.

Reference for supplementary information

1. Liu, J., Zhu, R., Liang, X., Ma, L., Lin, X., Zhu, J., He, H., Parker, S.C. and Molinari, M., 2018. Synergistic adsorption of Cd (II) with sulfate/phosphate on ferrihydrite: An in situ ATR-FTIR/2D-COS study. *Chemical Geology*, *477*, pp.12-21.
2. Brukhno, A.V., Grant, J., Underwood, T.L., Stratford, K., Parker, S.C., Purton, J.A. and Wilding, N.B., 2019. DL_MONTE: a multipurpose code for Monte Carlo simulation. *Molecular Simulation*, pp.1-21.