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Comparative study of removing fluorine and perfluoroalkyl substances (PFAS) by the in situ formation process of Zn-based LDH: Interactions mechanism at a molecular level

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Per- and polyfluoroalkyl substances (PFAS) are emerging environmental contaminants with significant bioaccumulation potentials and health risks. Among these, perfluorooctanoic acid (PFOA) is widely detected in wastewater, especially in landfill leachate, where its concentration can exceed the WHO guideline of 500 ng/L by several orders of magnitude. Conventional removal methods are ineffective in complex wastewater containing interfering ions such as fluoride (F^-). Considering the complex components of real wastewater, in situ remediation of PFOA using layered double hydroxides (LDHs) is proposed. Currently, there is a lack of studies on the effects of pH, ionic strength, and dissolved CO_2 on the competitive behavior of F^- removal. Hence, this study investigates PFOA removal mechanisms by in situ formation of ZnAl-LDH via the co-precipitation method under varying conditions such as F^-/PFOA molar ratios (0–100), pH (6.5–9.5), and ionic strength (1–10 M). Molecular dynamics (MD) simulations and density functional theory (DFT) calculations have elucidated the mechanisms of the interfacial interactions. The results showed that the optimum removal efficiency of PFOA was 92.0% at pH 7.5 within 20 min. However, F^- addition with F^-/PFOA molar ratio of 10 reduced the PFOA removal efficiency to 76.0%, indicating competitive effects. The removal of PFOA was strongly affected by pH, carbonate, and ionic strength. For instance, a high ionic strength (10 M NaCl) reduced the removal efficiency by 44.2%, which was attributed to the electrical double-layer compression that reduced electrostatic attraction. Notably, the nitrogen atmosphere eliminated the carbonate effect and improved removal performance owing to an enhanced ion exchange process. MD analyses revealed that F^- preferentially occupied the LDH surface, thereby reducing the number of PFOA adsorption sites. DFT results confirmed the lower binding energy of F^- on the LDH surface, explaining its dominance in the competitive adsorption process. This study demonstrates that electrostatic interactions, including hydrogen bonding, mainly drive PFOA removal mechanisms by in situ LDH. By integrating experimental and computational approaches, this study provides a molecular-level mechanistic interpretation that offers a novel way to intuitively represent the nature of interactions. This advances our understanding of anion competition, contributing to the tailoring of LDHs for multicomponent wastewater treatment.