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Sunlight-assisted degradation of perfluorooctanoic acid (PFOA) in the presence of various silicate clay minerals

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Per- and polyfluoroalkyl substances (PFAS), particularly perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$), have been extensively used in various industrial applications due to their exceptional chemical stability and thermal resistance. Although PFOA is highly recalcitrant under typical aqueous environmental conditions, it can be degraded in the presence of catalysts or strong oxidizing/reducing agents. Previous studies have reported that perfluorooctanesulfonamide (PFOSA) derivatives can be transformed into PFOA and shorter-chain perfluorocarboxylic acids (PFCAs) in the presence of montmorillonite under sunlight irradiation, suggesting the potential role of naturally occurring clay minerals as reactive matrices.

In this study, we investigated whether naturally abundant clay minerals can facilitate the degradation of PFOA under environmentally relevant conditions. Aqueous solutions containing PFOA and each clay minerals-kaolinite, montmorillonite, and hectorite-were exposed to simulated solar light for 31 days at neutral pH. PFOA loss, formation of shorter-chain PFCAs, and defluorination ratio were evaluated.

In the presence of kaolinite and montmorillonite, PFOA loss was observed under dark conditions; however, no shorter-chain PFCAs were detected and defluorination ratios remained low (2–4%). Notably, even under simulated solar light irradiation, no substantial enhancement in PFOA degradation was observed. These results indicate that PFOA loss in the presence of kaolinite and montmorillonite is predominantly attributable to adsorption rather than degradation, regardless of light exposure.

In contrast, the hectorite system exhibited distinctly different behavior. PFOA loss exceeded 95% under both dark and simulated solar light conditions, and significant defluorination ratio (~30%) was achieved in both cases. Although no shorter-chain PFCAs were detected under dark conditions, substantial defluorination occurred, suggesting that C-F bond cleavage may occur in the presence of hectorite even without light irradiation. Under simulated solar light irradiation, chain-shortening of PFOA was observed, with the formation of PFHpA, PFHxA, PFPeA, and PFBA, accompanied by substantial defluorination. Among the tested clay minerals, hectorite demonstrated the highest phototransformation among three clay minerals.

This study demonstrates that naturally occurring hectorite can partially degrade and defluorinate PFOA under neutral pH and simulated solar light conditions without the addition of excessive chemicals. These findings highlight the potential of clay minerals as naturally occurring reactive media for PFAS transformation under near-natural conditions.