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Fast Reductive Defluorination of Branched Perfluorooctane Sulfonic Acids by Cobalt Phthalocyanine: Electrochemical Studies and Mechanistic Insights

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Abstract : Branched perfluorooctane sulfonic acid (PFOS) is recognized as a threatening environmental pollutant due to its high persistence and bioaccumulation in various environmental matrices as well as for its toxic effects on humans and wildlife, even at very low concentrations. This study reports the first investigation of branched PFOS defluorination catalyzed by metal phthalocyanines. The reaction conditions were optimized using the different reductants and temperatures. Cobalt phthalocyanine, when combined with Ti citrate as a reducing agent, was able to defluorinate 10.9% of technical PFOS within 8 hours. In contrast, vitamin B12 only showed 2.4% defluorination during the same period under similar conditions. The defluorination mediated by cobalt phthalocyanine and Ti citrate system corresponds to 54.5% of all branched PFOS isomers (br-PFOS isomers). Isomer-specific degradation was also investigated via high-resolution LC-orbitrap, followed by their relative rates. The difference in catalytic efficacy of various phthalocyanine complexes is rationalized by their structures and electrochemical response. Lastly, a new defluorination mechanism is proposed based on the newly detected degradation products after the phthalocyanines treatment and the previous studies.

Keywords: branched isomers, catalyst, reductive defluorination, water remediation

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