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Activation of persulfate by UV and Fe^{2+} for the defluorination of perfluorooctanoic acid

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Abstract. Efficient defluorination of perfluorooctanoic acid (PFOA) was achieved by integrating UV irradiation and Fe^{2+} activation of persulfate ($S_2O_8^{2-}$). It was found that the UV-Fe^{2+}, Fe^{2+}-$S_2O_8^{2-}$, and UV-$S_2O_8^{2-}$ processes caused defluorination efficiency of 6.4%, 1.6% and 23.2% for PFOA at pH 5.0 within 5 h, respectively, but a combined system of UV-Fe^{2+}-$S_2O_8^{2-}$ dramatically promoted the defluorination efficiency up to 63.3%. The beneficial synergistic behavior between Fe^{2+}-$S_2O_8^{2-}$ and UV-$S_2O_8^{2-}$ was demonstrated to be dependent on Fe^{2+} dosage, initial $S_2O_8^{2-}$ concentration, and solution pH. The decomposition of PFOA resulted in generation of shorter-chain perfluorinated carboxylic acids (PFCAs), formic acid and fluoride ions. The generated PFCAs intermediates could be further defluorinated by adding supplementary Fe^{2+} and, $S_2O_8^{2-}$ and re-adjusting solution pH in later reaction stage. The much enhanced PFOA defluorination in the UV-Fe^{2+}-$S_2O_8^{2-}$ system was attributed to the fact that the simultaneous employment of UV light and Fe^{2+} not only greatly enhanced the activation of $S_2O_8^{2-}$ to form strong oxidizing sulfate radicals ($SO_4^{\bullet-}$), but also provided an additional decarboxylation pathway caused by electron transfer from PFOA to in situ generated Fe^{3+}.

Keywords: perfluorooctanoic acid; synergism; persulfate; UV; ferrous ions

1. Introduction

Perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA) is recognized as ubiquitous contaminants in water, wildlife and humans. Because the strong C-F bond (Vecitis *et al*. 2009), this compound shows high physical and chemical stability (Hurley *et al*. 2004). Its bioaccumulation and toxicity have adverse effect on human health and ecosystem (Melzer *et al*. 2010, Walters and Wallace 2010). Therefore, PFOA is recognized as a new kind of environmentally persistent organic pollutants (POPs) (Wang *et al*. 2009). It is urgent to develop effective methods to degrade this compound into harmless species.

Several advanced oxidation processes (AOPs) based on the generation of hydroxyl radicals (•OH) have been conducted to degrade perfluorinated compounds (PFCs). However, these systems

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