
PFOA and PFOS removal using nano-sized palladium spots coated zero-valent iron microparticles (nPd- μ ZVI)

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ABSTRACT

Per- and polyfluoroalkyl substances, PFAS, are known to be toxic for human health and represent a major environmental concern. Rodrigues *et al.*^{1,2} showed a complete dechlorination of hexachlorobutadiene and hexachloroethane by the reduction of C-Cl bond, facilitated by the generation of highly reactive H[•] radicals by the galvanic corrosion of well characterised nano-sized palladium spots coated zero-valent iron microparticles (nPd- μ ZVI). The goal of this study was to apply this successful for C-Cl bond reduction method to reduce the C-F bond into the **perfluorooctanoic acid (PFOA)** and **perfluorosulfonic acid (PFOS)**.

The PFOA and PFOS removal were individually investigated in sealed batch at 10 or 50 mg/L in 10 mL CH₃COOH/CH₃COONa buffer at pH 4, by using 0.1 or 1 g of nPd- μ ZVI. Experiments were also conducted in the pH range 1-14, using 10 mg/L of PFOA or PFOS and 1 g of nPd- μ ZVI. For this purpose, HCl (pH 1), CH₃COOH/CH₃COONa (pH 5), drinking water (pH 7) and NaOH solutions (pH 9, 10, 11 and 14) were used as reactive media. For all experiments, samples were vortexed and placed in a heated ultrasonic bath (45 kHz, 90°C) during 72 hours to pursue the PFAS-nPd- μ ZVI interaction under homogenised slurries. The liquid reactive media was then withdrawn and centrifuged. All nPd- μ ZVI solids were washed with 10 mL of methanol to differentiate adsorption from defluorination process. For a better insight, the washing procedure was repeated 5 times. The liquid reactive media and the methanol from the washes were analysed by Ultra-high-Pressure Liquid Chromatograph coupled with Mass Spectrometer (UPLC-MS) to quantify PFOA and PFOS contents. SEM-EDS allowed us to characterize the nPd- μ ZVI after interaction.

Experiments clearly showed the predominance of PFOS and PFOA adsorption process onto nPd- μ ZVI. It was confirmed by SEM-EDS analysis: adsorbed PFAS films were observed on nPd- μ ZVI. The PFOS and PFOA adsorption process reached 99% and 80% respectively with 1 g of nPd- μ ZVI, regardless of the tested concentrations (10 or 50 mg/L) at pH 4. With 0.1 g of nPd- μ ZVI, it decreased to 80% and 40% respectively for both concentrations. Experiments showed significant effectiveness at pH 1: PFOS and PFOA adsorption reached 99% and over 80% respectively. At pH 5, it decreased to 65% for both pollutants. At pH 7, 9, 10 and 11, the PFOA adsorption decreased between 15 and 4%; it decreased between 40 and 18% for the PFOS. At pH 14, the PFOA adsorption remained at 10%, while it reached 60% for the PFOS.

The adsorption processes are driven by the **anaerobic galvanic corrosion of nPd- μ ZVI (AGC-nPd- μ ZVI)**. In the pH range 1-4, **AGC-nPd- μ ZVI** intensity remains in the same order of magnitude; the massive production of free Fe²⁺ is responsible for **PFAS complexation adsorption process (PFAS-CAP)** onto nPd- μ ZVI. In the pH range 5-11, AGC-nPd- μ ZVI decreasing kinetic induces PFAS-CAP drop. From pH 8.7 to 11, Fe^{II} hydrolyses, as Fe(OH)⁺, and precipitates, as Fe(OH)₂, onto nPd- μ ZVI that compete with the PFAS-CAP, which drastically decreased. At pH 14, the increase of AGC-nPd- μ ZVI results in Fe^{II} redissolution as FeO₂²⁻ that should prevent PFAS-CAP, which is not the only occurring sorption phenomenon. The influence of the functional group onto the surprising adsorption process of PFOS is still under investigation.

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References:

- (1) Rodrigues, R., S., Betelu, C. Colombano, G., Masselot, T., Tzedakis and I. Ignatiadis. *Ind Eng Chem Res.*, 56:12092–12100 (2017). <https://doi.org/10.1021/acs.iecr.7b03012>
- (2) Rodrigues, R., S., Betelu, C. Colombano, G., Masselot, T., Tzedakis and I. Ignatiadis. *Environ. Sci. Pollut. Res.*, 26:7177–7194 (2019). <https://doi.org/10.1007/s11356-019-04128-y>

