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Removal of Perfluorinated Compounds From Water using Nanoscale Zero-Valent Iron.

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Abstract

Perfluorinated Compounds (PFCs) are persistent micropollutants that have been detected in various environmental and biological matrices, worldwide. During the last decade, these compounds have also been detected in municipal wastewater and tap water. Due to the stability of C-F bond, the application of biological and conventional physicochemical treatment methods does not seem to remove sufficient these compounds from water and wastewater. In the current study, the removal efficiency of four PFCs using three different types of nanoscale zero-valent iron (nZVI) was investigated. Influencing factors such as, initial pH solution, reaction temperature and nZVI dosage were also studied. According to the results, target compounds were removed in the presence of chemically synthesized nZVI modified with Mg-aminoclay (MgAC) than under commercial iron powder and chemically synthesized uncoated nZVI, under the same experimental conditions. Removal efficiencies of PFCs using MgAC coated nZVI were enhanced under acidic conditions and lower reaction temperature, as well as nZVI concentration increased. Based on removal mechanism experiments, it was demonstrated that PFCs removal can be accomplished by simultaneous sorption and degradation. Although the production of F^- was observed to aqueous solution, no formation of byproducts was detected.

Keywords
PFCs, nanoscale zero-valent iron, mechanism reaction, removal

INTRODUCTION

Perfluorinated Compounds (PFCs) are persistent micropollutants that have been detected in various environmental and biological matrices worldwide. This has resulted in the inclusion of PFCs to the Persistent Organic Pollutants (POPs) list of the Stockholm Convention. For over 50 years, they are widely used in several industrial and household applications due to their unique physicochemical properties, i.e. thermal and chemical stability. They are extensively used in firefighting foams, food packing, waterproof breathable fabrics and Teflon production [Ahrens, 2011]. Monitoring studies in Sewage Treatment Plants (STPs) have shown that these compounds are not significantly removed during conventional wastewater treatment [Arvaniti et al., 2012].

At present, many methods have been reported for the removal of PFCs from aqueous solutions [Hori et al., 2004, Hori et al., 2005, Hori et al., 2007, Yu et al., 2009], including adsorption and photochemical oxidation processes (UV, UV/H_2O_2, UV/$S_2O_8^{2-}$, UV/Fe^{3+}). Beside the significant PFCs removal observed in some of these studies, their applicability is limited either by the extreme laboratory conditions used (e.g. in Advanced Oxidation Processes; AOPs) or by the need of a following step for complete PFCs destruction (e.g. in adsorption processes).

In recent years, scientific research has been focusing in the application of zero-valent iron (ZVI) in the field of water and wastewater treatment. Due to its suitable redox potentials, it has been applied to the removal of a wide variety of environmental pollutants [Zhang et al., 2009, Fang et al., 2011, Chen et al., 2012]. Regarding the use of microsized ZVI on degradation of PFCs, to our knowledge, excepting from two reports [Hori et al., 2006, Lee et al., 2010], no other published data exist for PFCs removal with reductive treatment. According to these reports, it seems that reductive decomposition of PFCs by ZVI occurred only under extreme conditions.

On the other hand, the adaptation of nanoscale zero valent iron (nZVI) provides several advantages including an increase of reaction rate and generation of a nontoxic end product [Choe et al., 2000]. Moreover, application of surface coating on the nZVI surface has brought higher stability and reactivity compared to unmodified nZVI [Hwang et al., 2014]. To the best of our knowledge, so far, no data is available for the removal of PFCs using uncoated or/and coated nZVI.

Based on the above, the main objective of this study was to evaluate the removal efficiency of Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA) and Perfluorooctane sulfonate (PFOS) in aqueous solution using three different types of nZVI. The commercial nZVI powder was purchased from NANO IRON, s.r.o (Czech republic), while the chemically synthesized uncoated nZVI and modified nZVI with Mg-aminoclay (MgAC) were prepared as stated in previous research [Hwang et al., 2014]. Furthermore, the effects of initial pH, reaction temperature and nZVI dosage on PFCs removal by MgAC coated nZVI were investigated. Last, the removal mechanism was studied and discussed.

MATERIALS AND METHODS

Experimental set-up
To investigate the effect of three different types of nZVI on the removal of PFCs, batch experiments were carried out in 100 mL reactor containing 20 mM citric buffer solution, a mixture of PFCs at initial concentration of 200 μg L^{-1} and 1000 mg L^{-1} nZVI. Each reactor was capped with rubber stoppers and mixed on a rotary shaker at certain temperature for a period of time. At selected reaction time interval, 5 mL of the supernatant phase after filtration was withdrawn and the concentration of PFCs was determined.

Batch experiments were also performed using MgAC coated nZVI in order to study the effect of solution's pH (3, 5, 7), and temperature (20 °C, 55 °C) and nZVI concentration (ranging from 10 mg L^{-1} to 1000 mg L^{-1}) on PFCs removal.

To investigate the removal mechanism of PFCs, a mass balance experiment was performed in the presence of PFOS. The reactors were filled with 8 mL of citric buffer, given a final concentration of 20 mM (pH 3). The total volume of reaction solution was 30 mL and the initial concentration of nZVI and PFOS were 3 g L^{-1} and 40 mg L^{-1}, respectively. At selected reaction time intervals (10 min, 20 min, 24 hours), PFOS was determined in the particulate and dissolved phase. The experiment was performed in triplicate.

In each of the experiments described above, control runs without nZVI were performed to estimate the impact of other processes (e.g., sorption onto reactor walls) on PFCs removal. Additionally, control experiments (only with nZVI) were carried out in parallel.

Analysis of PFCs
All samples were analyzed using Liquid Chromatography (LC) - Mass Spectrometry (MS) technique. HPLC separation was performed on an Agilent-1200 high performance liquid chromatography system (Agilent, Palo Alto, CA, USA). Detection was performed with an Agilent 1100 MSD ion-trap system (Agilent, Palo Alto, CA, USA) using electrospray ionization (ESI) and measuring in negative ion mode. A 10 μL aliquot of standard solution/sample was injected into a guard column (Luna C18, Phenomenex, 2.0 mm i.d. x 4 mm, 5 μm) which was sequentially connected to a XTerra MS C18 column (2.1 mm i.d. x 100 mm, 3.5 μm; Waters), both held at 25 °C. The mobile phase was comprised of 5 mM ammonium formate aqueous solution (solvent A) and methanol (solvent B) and was applied at a gradient, starting at 70% methanol and increasing linearly at a flow rate of 100 μL min^{-1}. Operating conditions in the ESI source and the ion trap were: capillary voltage at 3500 V, source temperature at 350 °C, drying gas at 8 L min^{-1} and nebulizer gas at 30 psi. The instrumental limit of quantification (LOQs) of the target compounds varied from 0.23 μg L^{-1} (PFOS) to 0.66 μg L^{-1} (PFUdA).

For the determination of fluoride ions in order to investigate the reaction mechanism using a Dionex ion chromatography (ICS-3000, Dionex Corporation) interfaced with a suppressed conductivity detector; whereas a liquid chromatography (Thermo Dionex Ultimate 3000) coupled with a quadrupole time of flight mass spectrometry (QTOF, Brucker Maxis Impact) operated under negative ESI mode is used for the separation and identification of byproducts.

RESULTS
According to the results, the target compounds were removed in the presence of chemically synthesized nZVI modified with Mg-aminoclay, while no significant removal was observed using commercial nZVI and chemically synthesized nZVI without surface modification. Specifically, 3 out of 4 examined PFCs were presented high removal ($\geq$ 70%) by MgAC coated nZVI, whereas only PFOA was appeared partial removal.

The removal of PFCs was higher when the concentration of MgAC coated nZVI was increased. According to the results, when the dosage of nZVI increased from 10 to 100 mg L^{-1}, a significant difference was observed on PFCs removal after 1 h reaction, whereas no significant difference was observed in removing of all target compounds when testing 100 and 1000 mg L^{-1} nZVI. Moreover, this study demonstrated that the value of pH is one of the most critical factors for the removal efficiency of the target

compounds. When the initial solution pH was lower, the removal rate was increased. On the other hand, no removal of PFCs was observed between pH 5 and 7. Additionally, a maximum removal rate of PFCs was achieved at low temperature, whereas an apparently lower effect of high temperature on PFCs removal was observed for the most target compounds. In Figure 1 the effect of these parameters on PFOS removal by MgAC coated nZVI is presented.

Regarding the investigation of reaction mechanism, mass balance experiment showed that PFOS removal be accomplished by simultaneous sorption and degradation. Specifically, mass balance experiment showed that 30% of PFOS was adsorbed on iron surface, 30% was found in the dissolved phase, whereas the remaining 40% can was degraded. Although, no formation of byproducts was observed, this decomposition of PFOS can be revealed with release of F^- to aqueous solution.
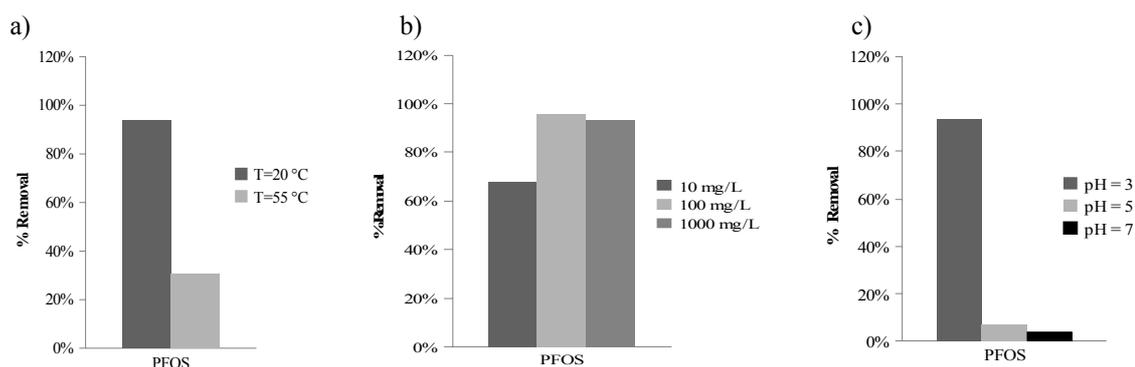
Figure 1. Effect of a) reaction temperature; b) nZVI dosage; and c) initial pH on PFOS removal by MgAC coated nZVI.

CONCLUSIONS
In this study the removal of PFCs by different types of nZVI and the effect of some parameters on their removal were investigated. Higher removal of PFCs was achieved by chemically synthesized nZVI modified with Mg-aminoclay. A maximum PFCs removal efficiency was observed under acidic conditions and lower reaction temperature using MgAC-nZVI. PFCs removal efficiencies increased with increasing the concentration of nZVI. According to the results of a mass balance experiment, the removal of PFOS by MgAC-nZVI can be achieved through degradation and sorption processes. Last, the appearance of F^- to aqueous solution, indicating the degradation mechanism.

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