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Olga S. Arvaniti[1,2,3], Yuhoon Hwang[2], Henrik R. Andersen[2*], Athanasios S. Stasinakis[1], Nikolaos S. Thomaidis[3], Maria Aloupi[1]

[1]Department of Environment, Water and Air Quality Laboratory, University of the Aegean, Mytilene 81100, Greece
[2]Department of Environmental Engineering, Technical University of Denmark, Miloevej, B 113, 2800 Kgs. Lyngby, Denmark
[3]Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Zografou, Athens 15771, Greece*
Corresponding author. Tel.: +45 45 25 15 83; fax: +45 45 93 28 50. E-mail address: hran@env.dtu.dk (H.R. Andersen).

HIGHLIGHTS

- Different nanosized zero valent iron (nZVI) types were tested for PFCs degradation.

- Only nZVI coated with a cationic surface modifier removed PFCs effectively.

- The order of PFCs degradability was PFOA < PFNA < PFOS ≈ PFDA.

- Low pH and temperature favored degradation of PFCs by surface modified nZVI.

- Fluoride formation confirmed PFCs degradation while partial sorption was observed.

Graphical abstract
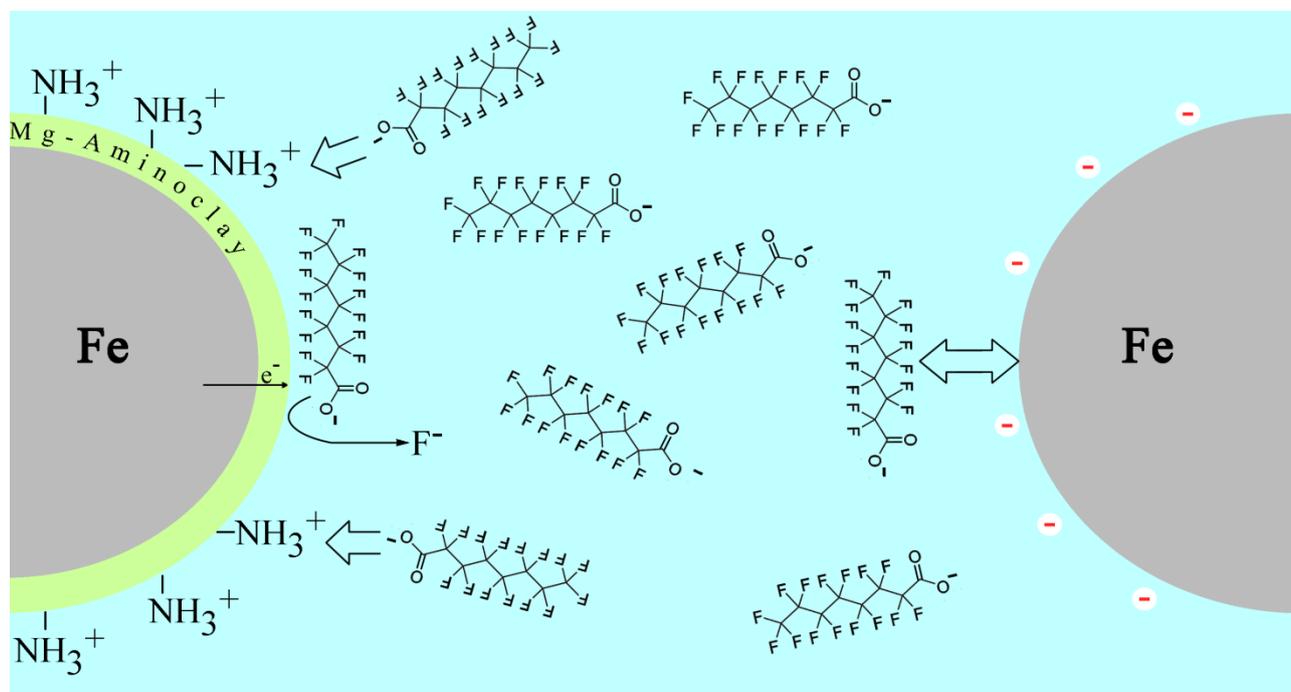
ABSTRACT

Perfluorinated Compounds (PFCs) are extremely persistent micropollutants that are detected worldwide. We studied the removal of PFCs (perfluorooctanoic acid; PFOA, perfluorononanoic acid; PFNA, perfluorodecanoic acid; PFDA and perfluorooctane sulfonate; PFOS) from water by different types of nanoscale zero-valent iron (nZVI). Batch experiments showed that an iron dose of 1 $g \cdot L^{-1}$ in the form of Mg-aminoclay (MgAC) coated nZVI, at an initial pH of 3.0 effectively removed 38 % to 96 % of individual PFCs. An increasing order of removal efficiency was observed of PFOA < PFNA < PFOS ≈ PFDA. Compared to this, PFCs removal was less than 27 % using a commercial air stabilized nZVI or freshly synthesized uncoated nZVI, under the same experimental conditions. The effectiveness of PFCs removal by MgAC coated nZVI was further investigated at various initial pH, nZVI dosage, temperature and age of the nZVI. A maximum removal was observed for all PFCs with high nZVI concentration, freshly synthesized nZVI, low pH and low temperature. A mass balance experiment with PFOS in a higher concentration of nZVI revealed that the removal was due to both sorption and degradation. Fluoride production partially matched the observed degradation, while no organic byproducts were detected using LC-QTOF-MS.

Keywords: Perfluorochemicals; Nanoscale Zero-Valent Iron; Mechanism; Reduction; Removal

1. Introduction

Perfluorinated Compounds (PFCs) are a new class of Persistent Organic Pollutants. They consist of a hydrophobic perfluorinated carbon tail and a hydrophilic ionic head. Due to the unique structure of fluoride-carbon bond, they present significant thermal and chemical stability. As a result, they have a wide variety of applications in firefighting foams, food packing, waterproof breathable fabrics and Teflon production [1,2].

Recently, the scientific interest has been grown over the PFCs, due to their widespread occurrence in the environment [2-4] as well as their environmental persistence, bioaccumulation potential and potential toxicity [2].

According to published findings, no PFCs biodegradation has been observed during conventional biological treatment of wastewater [2,5]. So far, several physicochemical methods have been investigated in laboratory scale in order to remove PFCs from water and wastewater. Most of the studies have been performed mainly for perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Amongst them, adsorption on powdered activated carbon (PAC), granular activated carbon (GAC), goethite/silica and alumina, as well as filtration techniques such as nanofiltration and reverse osmosis demonstrated significant PFCs removal [6-9]. However, the aforementioned methods aim to transfer PFCs to another medium (e.g. GAC, PAC, Alumina) and a following step such as incineration of sorbents or further treatment of the membrane concentrate is required to achieve full PFCs' destruction, thereby adding to the overall management cost.

On the contrary, destructive treatment technologies including different advanced oxidation processes (AOPs), photolysis and use of zero valent iron (ZVI) have also been investigated in laboratory scale for direct degradation of PFCs. Hori et al. [10] reported a removal of PFOA equal to 90 % (72 h irradiation), using direct photolysis under experimental conditions. Other studies have also found that persulfate and Fenton reagent can effectively degrade perfluorocarboxylic acids (PFCAs) to fluoride ions, carbon dioxide and shorter chain PFCAs [11-13]. Regarding the use of microsized ZVI, Hori et al. [14] reported that PFOS can partially be degraded by elemental iron, Fe(0), in water under subcritical water conditions (> 250 ^{o}C) and high pressure (20 MPa). Moreover, Lee at al. [15] demonstrated that at 90 ^{o}C PFOA was degraded up to 67.6 % using persulfate activated by ZVI and by 9 % using ZVI only. However, the above studies were performed under extreme laboratory conditions (e.g. high pressure and temperature). This indicates that PFCs' degradation using ZVI could be lower under conditions commonly applied during water and wastewater treatment. Overall the published procedures of degradation of PFCs involve extreme conditions which would be unrealistically costly to apply to municipal water or wastewater treatment.

In recent years, nanoscale ZVI (nZVI) has emerged as one of the most innovative technology for the removal of several environmental pollutants through reductive reaction mechanisms [16,17]. The high reactivity of nZVI is due to the high specific surface area originated from its small particle size. Therefore nZVI seems a promising and flexible reagent for *in situ* remediation of wastewater/water contaminants that are amenable to reduction by electron donation of ZVI [18]. However, uncoated nZVI particles have limited stability and reactivity in water due to aggregation which causes loss of reactive surface area [19]. For this reason, over the last years many studies have focused on creating more stable particles by attaching stabilizing molecules onto nanoparticles [20].

Recently, Hwang et al. [21] used water solubilized Mg-aminoclay (MgAC) as a stabilizing agent for the synthesis of nZVI. MgAC has been applied for several environmental applications, e.g. soil-flushing agent [22], flocculant [23], etc., and it has been reported not to have cytotoxicity to animal cells [24] and aquatic ecotoxicity towards marine bacteria, microalgae, and daphnia [25]. MgAC coated nZVI showed increased feasibility, compared to uncoated nZVI, for applications in water treatment, where high stability and mobility as well as high reactivity for degradation of

contaminants are desired. To the best of our knowledge, so far, no data is available for the removal of PFCs using uncoated or/and coated nZVI.

The main objectives of this study were to investigate the removal of four PFCs (PFOA, PFOS, perfluorononanoic acid; PFNA and perfluorodecanoic acid; PFDA) using MgAC coated nZVI in comparison with commercial nZVI powder and freshly synthesized uncoated nZVI. Furthermore, the effects of initial pH, reaction temperature, and nZVI dosage on PFCs removal by MgAC coated nZVI were investigated. A comparison of fresh and aged MgAC coated nZVI for removal of PFOS was also examined. Last, the removal mechanism through i) a mass balance experiment; ii) the observation of release F^- ions to the aqueous reaction solution; and iii) the separation and identification of byproducts, was studied and discussed.

2. Materials and methods

2.1 Chemicals and reagents

PFOS ($C_8F_{17}SO_3H$) (> 98 %) was obtained from Sigma Aldrich (Seelze, Germany). All other standards ($\geq$ 95 %), were obtained from Alfa Aesar (Karlsruhe, Germany). Two isotopically labeled standards (> 98 %) were purchased from Wellington Laboratories (Guelph, Ontario, Canada) and used as internal standards. Properties of all analytical standards are summarized in Table S1. Ferrous sulfate heptahydrate ($\geq$ 99.0 %) and sodium borohydride ($\geq$ 98.0 %) were used for the nZVI synthesis, according to protocols reported in previous studies [21,26]. Commercial air-stable nZVI powder (NANOFER STAR) was purchased from NANO IRON, s.r.o (Czech republic). MgAC was synthesized using a previously utilized method [27]. Sodium fluoride, sodium carbonate and sodium bicarbonate were obtained from Sigma Aldrich (Seelze, Germany), all with purity > 99 %. Anhydrous citric acid and sodium citrate dehydrate were purchased from Sigma Aldrich (Seelze, Germany) and were used for pH adjustment. Methanol (HPLC-MS grade) was obtained from Merck (Frankfurt, Germany); whereas ammonium formate was supplied by Fluka (Buchs, Switzerland). Ultrapure water was provided by a MilliQ system (Milli-Q Gradient A10, Molsheim, France).

2.2 Preparation of nZVIs

In this study, several kinds of nZVI were prepared and applied to investigate the effect of nZVI properties on PFCs degradation. A stock dispersion (4 g L^{-1}) of the commercial nZVI powder was prepared in deoxygenated deionized water (DDIW) followed by ultrasonication for 30 min to break aggregates formed during storage.

The uncoated nZVI and MgAC coated nZVI were prepared as described in a previous research, using a MgAC:Fe weight ratio of 7.5, which was found to be optimal for both stability and reactivity [21]. The uncoated nZVI was synthesized as the modified nZVI except the addition of MgAC. The nZVI was collected via centrifugation, and then washed with DDIW.

To investigate the removal mechanism of PFCs, pre-oxidation (aging) of MgAC coated nZVI was performed. The prepared fresh MgAC coated nZVI slurry was stored in water-saturated atmosphere under oxic conditions at room temperature for 3 days. After 3 days of aging time, the slurry was taken out and the washed aged nZVI was characterized and tested for PFCs degradation.

2.3 Physical characterization of nZVI

The visual morphology of the nZVI particles, uncoated and coated nZVI, was obtained using a transmission electron microscope (TEM, Tecnai F20 model, Eindhoven, Netherlands). In order to prepare TEM samples, a droplet of diluted sample suspension was put on a carbon-coated Cu grid (300-mesh), and immediately dried under anaerobic conditions for 12 h.

Stability of as-prepared MgAC coated nZVI was determined by sedimentation analysis using a UV-Vis spectrophotometer (Cary 50, Agilent Technologies Inc., USA), as previously described [21]. Freshly prepared samples were diluted with 1mM $NaHCO_3$ to obtain identical initial

absorbance of 2.25 ± 0.25. Then, the samples were transferred into a 1-cm plastic cuvette and capped to prevent further oxidation during the sedimentation test. The absorbances of diluted samples were monitored as a function of time, with the optical absorbance at 508 nm, to obtain the sedimentation curve.

Hydrodynamic size of nZVI aggregate was measured by dynamic laser light scattering (DLS, Malvern Zetasizer NanoZS, USA), where the diluted sample (identical to that used in the sedimentation test) was applied for analysis. Zeta potential measurements were also carried out, using the same DLS unit. All measurements were performed triplicate at room temperature.

The content of reactive iron in as-prepared MgAC coated nZVI was determined by measuring the hydrogen (H_2) gas produced by acid digestion, as previously described [21]. The amount of Fe(0) was calculated from the produced hydrogen determined by gas chromatography (Mikrolab GC82, Mikolab Aarhus A/S, Denmark). The Fe(0) content in the sample was compared with the total iron concentration measured by atomic absorption spectrometry (AAnalyst 200, PerkinElmer, USA).

2.4 Batch experiments

Batch experiments were performed to compare the removal efficiency of PFCs by commercial nZVI, freshly synthesized uncoated nZVI and MgAC coated nZVI. Citric buffer was initially added in a 100 mL reactor at a final concentration of 20 mM, to adjust pH to 3. PFCs compounds were added to the reactor and the solution was purged under nitrogen gas before the addition of nZVI, in order to achieve anaerobic conditions. Afterwards, 20 mL of 4 g L^{-1} nZVI was added to the reactor and the total volume of reaction solution was 80 mL. The final concentrations of nZVI and PFCs compounds were 1 g L^{-1} and 200 μg L^{-1}, respectively. Each reactor was capped and shaken at 130 rpm at 20.0 ± 1.0 °C. Samples of 5 mL were taken after 1 h of treatment time, filtered with 0.45 μm syringe filter and stored at 4 ˚C until analysis.

Additionally, the influence of initial solution's pH and reaction temperature on PFCs removal by MgAC coated nZVI were examined for three pH values (3.0 ± 0.1, 5.0 ± 0.1, 7.0 ± 0.1) and two different temperatures (20.0 ± 1.0 °C and 55.0 ± 1.0 °C), respectively, at a concentration level of 200 μg L^{-1} for each analyte. Further, batch experiments were performed to study the role of different concentrations of MgAC coated nZVI. The concentration of MgAC coated nZVI ranged between 10 and 1000 mg L^{-1}, while initial PFCs concentration was equal to 200 μg L^{-1}. Further details on the experimental design are described in Table S2.

To investigate PFCs removal mechanism, mass balance experiments were performed in triplicate using PFOS as target compound. The reactors were filled with 8 mL of citric buffer at a final concentration of 20 mM (pH 3). The total volume of the reaction solution was 30 mL and the initial concentration of nZVI and PFOS were 3 g L^{-1} and 40 mg L^{-1}, respectively. The reaction solutions were incubated at 20.0 ± 1.0 °C and shaken at 130 rpm. Samples were collected at 10 min, 20 min and 24 h. PFOS was determined in dissolved and particulate phase. Furthermore experiments with fresh and aged MgAC coated nZVI were also performed at the same experimental conditions. Fresh nZVI was prepared on the same day of the experiment, whereas aged nZVI three days before. Samples were collected at 20 min, 1, 3, 24 and 48 h.

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. Further, control runs with only nZVI were also conducted in parallel.

2.5 Analysis

Analysis of PFCs in liquid and solid samples was performed using our previously described analytical method with some modifications [28,29]. Briefly, an aliquot of each liquid sample was mixed with an equal volume of methanol, containing final concentration of each internal standard at 20 μg L^{-1}, filtered through a 0.2 μm filter and then a 10 μL aliquot was injected into a XTerra MS

C18 column (2.1 mm i.d. x 100 mm, 3.5 μm; Waters) maintained at 25 °C. An Agilent 1100 MSD ion-trap mass spectrometer (Agilent, Palo Alto, CA, USA) equipped with an electrospray interface operated in negative ion mode was used for quantification.

Particulate samples of 15 mg were extracted using 7.5 mL of 1% v/v acetic acid and 1.5 mL of methanol. Solids samples were spiked with internal standard ($^{13}C_4$-PFOS) before extraction. Extracts were analyzed as described for liquid samples. The instrumental limit of quantification (LOQs) of the target compounds varied from 0.23 μg L^{-1} (PFOS) to 0.50 μg L^{-1} (PFDA) (Table S3). During each batch analysis, procedure blanks served as quality control for contamination during sampling and analysis.

The concentrations of fluoride ions in the aqueous reaction solutions were determined using a Dionex ion chromatography system (ICS-3000, Dionex Co., Sunnyvale, CA, USA) with suppressed conductivity detection. A 25 μL aliquot of each sample was injected into an Ion Pac, AS9-HC column (4 mm i.d. x 250 mm) protected by a guard column (Ion Pac, AG9-HC, 4 mm i.d. x 50 mm). A solution containing 2.7 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ was used as the eluent with flow rate set at 1.2 mL min^{-1}. The limit of detection (LOD) of F$^-$ was 20 μg L^{-1}.

For the tentative identification of degradation byproducts, a liquid chromatography (Thermo Dionex Ultimate 3000) coupled with a quadrupole time of flight mass spectrometry, LC-QTOF-MS, (Bruker Maxis Impact, Bremen, Germany) operated under negative ESI mode was used. An Acclaim RSLC 120 C18 column (2.1 mm i.d. x 100 mm, 2.2 μm; Thermo Dionex) was used. The software Data Analysis and Metabolite Detect from Bruker Daltonics was used for data evaluation.

2.6 Calculations
For each PFC, the degree of removal efficiency was calculated using Eq. 1:

$$Removal\ (\%) = \frac{C_0 - C_w}{C_0} \times 100 \qquad (1)$$

where, C_0 is the measured concentration of each PFC (μg L^{-1}) in flasks without nZVI addition (control run) and C_w is the analyte concentration (μg L^{-1}) in the dissolved phase at different time intervals.

Moreover, the mass load of target compound that was lost due to the reduction process (M_{lost}) was calculated according to Eq. 2:

$$M_{in} = M_d + M_s + M_{lost} \qquad (2)$$

where, M_{in} is the measured mass of target compound (μg) in flasks without nZVI addition (control run), M_d and M_s are the masses of target compound in dissolved and particulate phase, respectively (μg).

3. Results and discussion

3.1 Effect of surface modification with Mg-aminoclay on reactivity toward PFCs

No PFCs loss due to sorption on the reactors or volatilization was observed in control runs. The removal efficiencies of PFCs were compared using 1.0 g·L^{-1} of either commercial air stabilized nZVI, freshly synthesized nZVI or freshly synthesized MgAC coated nZVI, under the same conditions (Fig. 1). The removal rates of PFCs by MgAC coated nZVI ranged from 38 % (PFOA) to 96 % (PFDA) after 1 h reaction. Furthermore, based on these results, it was observed that PFCAs removal rate increased with the increase of the perfluorocarbon chain length, while PFOS had a higher removal rate than PFOA. PFCs were slightly or not at all removed by the other two types of nZVI. These data agree with our previous finding of better reductive effectiveness of MgAC coated nZVI for another anionic target, nitrate [21]. In our previous study, we attributed the better removal by reduction of contaminants by MgAC coated nZVI compared to the uncoated nZVI to its higher stability in water, as aggregation is inhibited by the highly cationic surface coating compared to the

uncoated nZVI, as well as to its higher reactivity towards degradation that stems from the dispersed nZVI aggregate, achieved by synthesizing the nZVI in a matrix of MgAC.
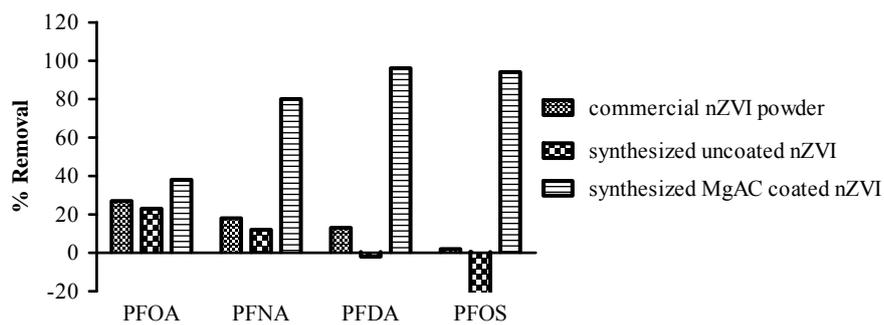
a)

b)
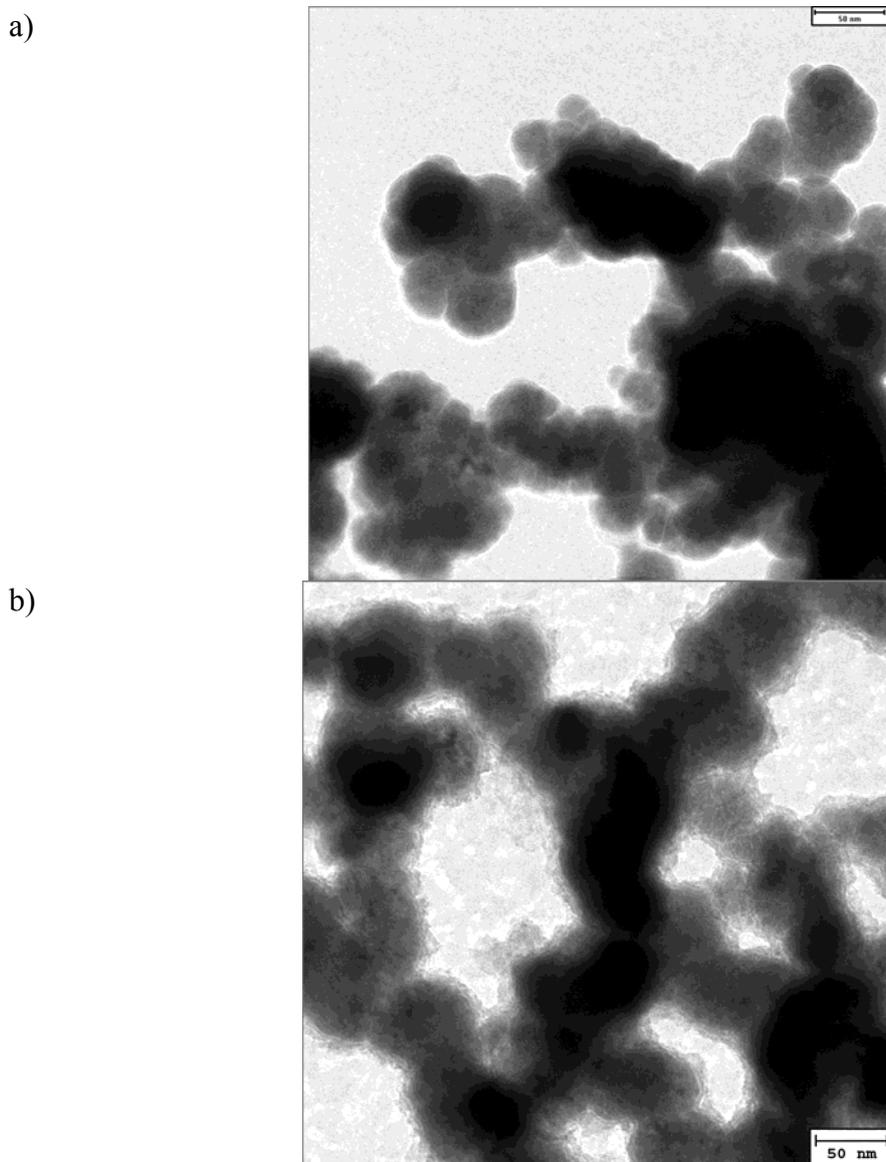
Fig. 2 shows the morphologies of the prepared nZVI with and without MgAC coating. The

surface coating by MgAC can be clearly seen in Fig. 2b. The individual particle size of nZVI itself was not significantly changed by addition of MgAC. It exhibited chain-linked and amorphous spheres as nanoclusters conventionally do, ranging from 30 nm to 100 nm, and with a broad particle size distribution. However, MgAC coating allows less aggregation of individual nZVI particles as illustrated in Fig. S1. Because the positively charged MgAC exhibit electrostatic repulsion, the individual MgAC coated nZVI particles remain dispersed as individual nZVI particles, rather than aggregated particles. The hydrodynamic size of MgAC coated nZVI (508 nm) was 10-fold smaller than uncoated nZVI (5,130 nm).

Moreover, the surface charge of nZVI is an important property determining nZVI reactivity by the aqueous-solid partition of target molecules [30]. The higher zeta potential of MgAC coated nZVI (+25.3 mV) than uncoated nZVI (+ 14.5 mV) also revealed the formation of MgAC coating on the surface of nZVI and its effectiveness on changing surface properties of nZVI [21]. The positively charged surface of MgAC-nZVI attracted PFCs anions; therefore, higher removal of PFCs can be achieved.

3.2 Effect of pH on the removal of PFCs

Target compounds were removed only at pH 3 (Fig. S2). No removal for all PFCs was observed at pH 5 and 7. These results confirmed that the removal of micropollutants in the presence of nZVI is enhanced under acidic conditions, verifying the important role of pH in removal experiments with nZVI [31,32]. In ZVI system, following equations are known as main reaction mechanisms for pollutant degradation.

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (anode)} \qquad (3)$$
$$2H^+ + 2e^- \rightarrow 2[H]_{abs} \rightarrow H_2 \text{ (cathode)} \qquad (4)$$
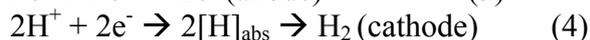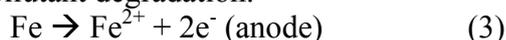
According to Eqs. (3)-(4), the reaction rate is determined by H^+ concentration in the solution. Thus the PFCs removal efficiencies increased with the decrease of the initial pH [32].

Moreover, the surface charge of nZVI is another important factor determining PFCs removal. Due to the extreme pKa values of PFCAs (< 3.13) and PFOS (3.27) (Table S1), target compounds exist mainly as anions in the examined pH range (3-7). On the contrary, at low pH values the surface of MgAC coated nZVI is positively charged [22] and the free amine groups are ionized (-NH_3^+) and thus are available for ionic interaction with the negatively charged PFCs. At near neutral pH, amine groups are neutral and do not interact with anionic PFCs.

3.3 Effect of temperature on PFCs removal

The effect of temperature on the removal of PFCs by MgAC coated nZVI was studied at temperature of 20 °C and 55 °C. According to Fig. 3, PFCs removal decreased with increasing temperature of the reaction solution. These results indicate that the removal rate of PFCs is greatly affected by the temperature and at ambient temperatures this process could be applied for water/wastewater decontamination. These findings are contrary to a previous study [33], reporting that the removal rate for reaction (reduction) of contaminant (2,4,6-trinitrotoluene) with nZVI is enhanced by increased temperature. It should be mentioned that the aforementioned study was conducted using uncoated nZVI [33]. The contradictive result on the effect of temperature could be an evidence of adsorption as a first step before their reduction. According to Valsaraj [34], pollutants removal using ZVI/nZVI involves the following steps; mass transfer of the pollutant to the Fe(0) surface, adsorption and chemical reaction of the pollutant on ZVI surface, desorption and mass transfer of the reaction product(s) into the solution. Previous study for the effect of temperature on PFCs sorption using activated sludge has shown that sorption decreased with temperature increase for a certain range of temperatures [35]. Since the removal of PFCs by MgAC coated nZVI is probably a multimodal mechanism which includes adsorption in its initial steps, a more thorough study on the effect of temperature is needed to provide plausible evidence on the process.

Figure 3. *Effect of different reaction temperature on PFCs removal by MgAC coated nZVI. (Experimental conditions: C_oPFCs = 200 µg L^{-1}, nZVI dosage = 1000 mg L^{-1}, initial pH = 3, reaction time = 1 h).*

3.4 Effect of nZVI concentration on PFCs removal
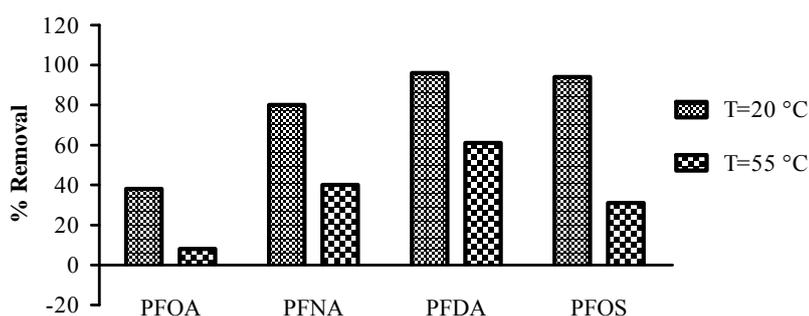
The effect of the initial concentration of freshly synthesized MgAC coated nZVI was investigated at pH 3 and 20 °C. As shown in Fig. 4, for all target compounds the removal rate increased with the increase of nZVI concentration. According to the results, when the dosage of nZVI increased from 10 to 100 mg L^{-1}, a significant increase on the removal was observed for all PFCs. Specifically for PFOA and PFNA, the removal efficiency was increased almost 2-fold from 8 % to 15 % and from 35 % to 77 %, respectively, when 100 mg L^{-1} MgAC-nZVI were used. This behavior is in agreement with previous reports [31,33], where nZVI was applied to remove other micropollutants and can be attributed to the increase of total surface area with increase of nZVI dosage. On the contrary, with the exception of PFOA, further increase of nZVI concentration from 100 to 1000 mg L^{-1} did not significantly affect PFCs removal. A similar trend was also observed in a previous study [36], where Wu et al. observed no significant difference on removal of other anions (phosphate) with increase of nZVI concentration from 400 to 600 mg L^{-1}.
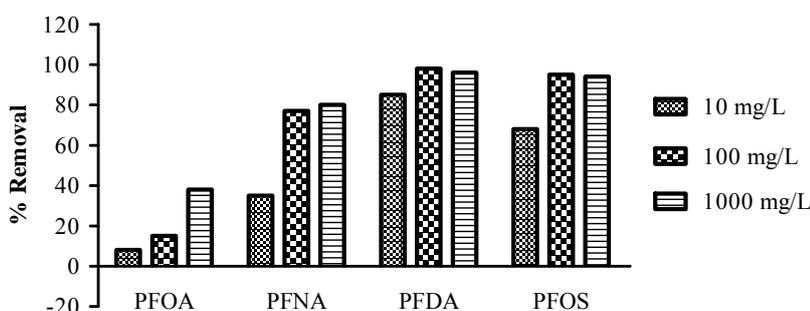
Figure 4. *Effect of different nZVI dosage on PFCs removal by MgAC coated nZVI. (Experimental conditions: C_oPFCs = 200 µg L^{-1}, initial pH = 3, reaction temperature = 20 °C, reaction time = 1 h).*

3.5 Effect of fresh and aged nZVI on PFOS removal

To investigate the role of reactive iron content [Fe(0)] on PFCs removal, experiments were performed with fresh and aged nZVI (3 days interval) using PFOS. The reactive iron contents were

determined as 95.1 % and 10.1 % for fresh and aged MgAC coated nZVI, respectively. According to Fig. S3, both materials presented significant ability to remove PFOS, while PFOS removal was almost completed during the first 20 min (0.33 h) of the experiment. Among different materials, an almost 15 % higher removal efficiency was observed for fresh nZVI during the whole duration of the test. The higher removal efficiency of fresh nZVI revealed that the reduction is one of the main mechanisms for PFCs removal. However, more than 60 % of PFOS could be removed by aged MgAC coated nZVI even though it mainly consisted of oxidized forms of iron. The remaining PFCs removal ability of aged nZVI clearly showed that adsorption of PFCs on the nZVI surface could be another important removal mechanism. These findings on removal mechanisms agree with other experimental results about the effect of reaction conditions, e.g. pH, temperature and type of nZVI, on PFCs removal. Therefore, it was required to conduct more quantitative analysis for obtaining mass balance of removed PFCs.

3.6 Mechanism responsible for PFOS removal by Mg-aminoclay coated nZVI

According to recently published papers [37,38], the removal of micropollutants by nZVI can be attributed to the following main mechanisms: i) adsorption onto iron surface and ii) reduction via dehydrohalogenation. To investigate the fate of PFOS in aqueous solution with MgAC coated nZVI against the reaction time and to clarify the removal mechanisms, a mass balance experiment was performed. As it can be seen in Fig. 5, after 20 min reaction time, 34 % ± 8.4 % of PFOS was found in the dissolved phase, 28 % ± 9.0 % was adsorbed on iron surface, while the remaining 38 % ± 13 % of PFOS was lost. Taking into account that PFOS is not volatile and it was not adsorbed on the reactors in control runs, this loss is possibly due to its reductive degradation. These results reveal that adsorption and reduction are two main reaction mechanisms involving in PFOS removal using MgAC coated nZVI. A similar behavior was also observed at 10 min and 24 h that samples were also taken, indicating that PFOS removal is completed very rapidly under the experimental conditions used.
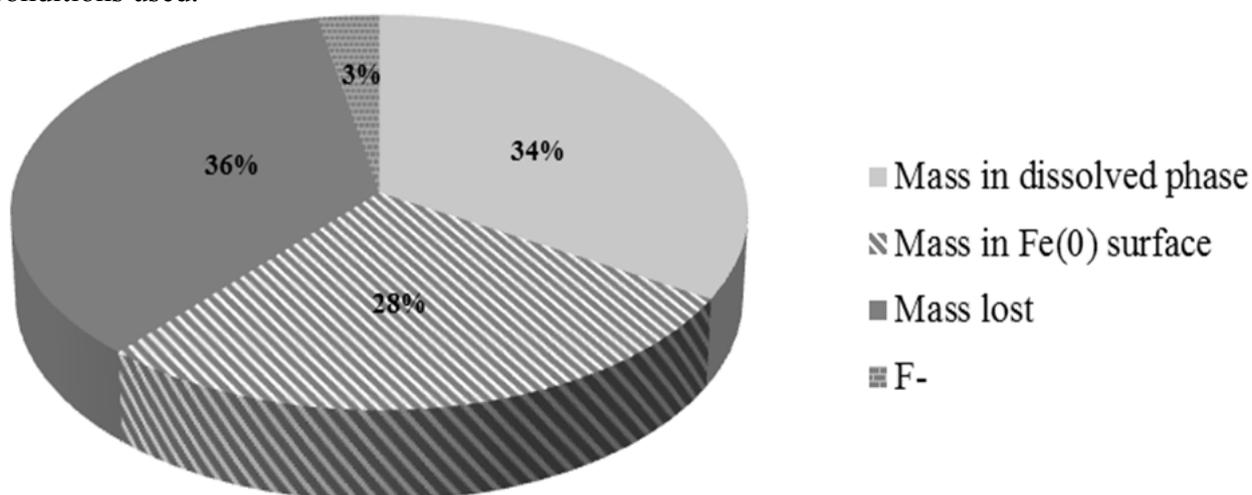

Figure 5. Mass balance during PFOS reduction by MgAC coated nZVI after 20 min reaction time. (Experimental conditions: C_0PFOS = 40 mg L^- ^{1}, nZVI dosage = 3 g L^{-1}, initial pH = 3, reaction temperature = 20 °C).

To confirm that this loss of PFOS was due to degradation, samples were analyzed for degradation products using LC-TOF-MS and the concentration of fluoride was quantified by IC. Comparison of control sample (MgAC coated nZVI, 20 min reaction time) with fortified sample (PFOS with MgAC coated nZVI, 20 min reaction time) revealed the same eluted peak at $R_t = 1.1$ min (Fig. S4). Moreover, the MS spectrum of this peak was similar in both the control and the fortified sample, indicating that this peak was attributed to the matrix (nZVI) (Fig. S5). By analyzing the fortified samples and after substraction of the control sample, no other peaks were

observed (Fig. S4c), except for the eluted peak at 7.2 min, which is attributed to PFOS (Fig. S4d). A similar analytical procedure was followed for samples taken at different time points (10 min, 24 h) during the experiment and no degradation products were identified as well. It is possible that either PFOS intermediates are not stable in ZVI - H_2O system or the ionization of the possible formed degradation products in the present aqueous solution is insufficient under negative electrospray ionization. It should be mentioned that in previous studies, where oxidation processes have been used for PFCs destruction, volatile unstable degradation products such as CHF_3, CF_4, were identified using GC-MS technique [10,12]. Such neutral polyfluorinated products aren't expected to be ionized and thus to be detectable by electrospray ionization.

For the detection of fluoride ions, control and diluted PFOS samples in experiments with MgAC coated nZVI were analyzed. Analysis of control samples showed that no analytical or procedural contamination was observed. As it can be shown in Fig. S6a, fluoride ions were detected in aqueous solution after 20 min reaction time. To ensure the identification of F^- peak, the sample was spiked with a known amount of F^-. As it was expected, this addition resulted to a pronounced increase of the F^- peak (Fig. S6b). Moreover, a spike with acetic acid revealed that the peak eluted at 3.953 min was due to acetate (Fig. S6c). Similar results for the F^- production were obtained for different reaction times (1, 3, 24 and 48 h). Back-calculating the measured concentration of fluoride to the theoretical maximal concentration of fluoride that would have occurred if all the lost PFOS was degraded, explained only 3 % of the observed PFOS removal (Fig. 5). It is possible that sorption of fluoride to either MgAC [39] or iron hydroxides [40] contributed to its low recovery. Specifically, Lee et al. [39] reported fluoride adsorption by MgAC and suggested that this removal is mainly due to electrostatic interactions between anion and aminoclay. Moreover, Sujana et al. [40] observed fluoride adsorption on metal hydroxides (iron, aluminum) and reported that adsorption was an exothermic reaction.

4. Conclusions
The main conclusion of this study is that MgAC coated nZVI can be used for the efficient removal of PFCs, while no removal was achieved using commercial nZVI powder and uncoated nZVI. The maximum PFCs removal efficiency was observed under acidic conditions (pH = 3) and lower reaction temperature. Furthermore, PFCs removal efficiencies sharply increased with increasing nZVI concentrations from 10 to 100 mg L^{-1}. The removal ability of MgAC coated nZVI was slightly decreased (by 15 %) when 3 days old nZVI was used. Use of mass balance experiments indicated that the mechanism of PFCs removal includes adsorption as a first step followed by reduction. The degradation of target compound was assured by the identification of F^- to aqueous reaction solution. Further experiments should be performed to investigate the formation of other degradation products, using GC-MS technique.

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Supporting information

Table S1. Target compounds and internal standards that were used in the present study.

Compounds	Molecular Structure	Molecular Weight	LogK$_{ow}$	pKa
Target compounds				
Perfluorooctanoic acid (PFOA)	CF$_3$(CF$_2$)$_6$COOH	414.07	3.60[1]	2.5[2]
Perfluorononanoic acid (PFNA)	CF$_3$(CF$_2$)$_7$COOH	464.08	4.84[3]	2.66[1]
Perfluorodecanoic acid (PFDA)	CF$_3$(CF$_2$)$_8$COOH	514.09	5.40[1]	2.606[4]
Perfluorooctanesulfonate (PFOS)	CF$_3$(CF$_2$)$_7$SO$_3$Na	522.11	4.30[1]	3.27[5]
Internal Standards				
Perfluoro-n-[1,2,3,4-^{13}C$_4$]octanoicacid (MPFOA)	CF$_3$(CF$_2$)$_3$(^{13}CF$_2$)$_3$^{13}COOH	418.04	3.60[1]	2.5[2]
Sodium perfluoro-1-[1,2,3,4-^{13}C$_4$]octanesulfonate (MPFOS)	CF$_3$(CF$_2$)$_3$(^{13}CF$_2$)$_4$SO$_3$Na	526.08	4.30[1]	3.27[5]

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Table S2. Experimental set up for PFCs removal by nZVI (all samples were taken from the reactor after 1h).

Objectives	nZVI type	nZVI dosage (mg L^{-1})	Initial PFCs concentration (μg L^{-1})	Reaction temperature (°C)	Initial pH
Effect of nZVI type	Commercial nZVI powder	1000	200	20 ± 1.0	3.0 ± 0.1
	Freshly synthesized uncoated nZVI				
	Freshly synthesized MgAC coated nZVI				
Effect of nZVI concentration	Freshly synthesized MgAC coated nZVI	10	200	20 ± 1.0	3.0 ± 0.1
		100			
		1000			
Effect of reaction temperature	Freshly synthesized MgAC coated nZVI	1000	200	20 ± 1.0	3.0 ± 0.1
				55 ± 1.0	
Effect of initial pH	Freshly synthesized MgAC coated nZVI	1000	200	20 ± 1.0	3.0 ± 0.1
					5.0 ± 0.1
					7.0 ± 0.1
Control run	-	-	200	20 ± 1.0	3.0 ± 0.1
					5.0 ± 0.1
					7.0 ± 0.1
Control run	-	-	200	55 ± 1.0	3.0 ± 0.1

Table S3. Analytical characteristics of the developed LC-MS method for the determination of each analyte, as well as instrumental limits of detection (LOD) and limit of quantification (LOQ).

Target Analytes	Linearity range (ng L^{-1})	Correlation coefficient (r^2)	LOD (µg L^{-1})	LOQ (µg L^{-1})
PFOA	1-100	0.9980	0.12	0.36
PFNA	1-100	0.9910	0.11	0.35
PFDA	1-100	0.9991	0.17	0.50
PFOS	1-100	0.9996	0.07	0.23
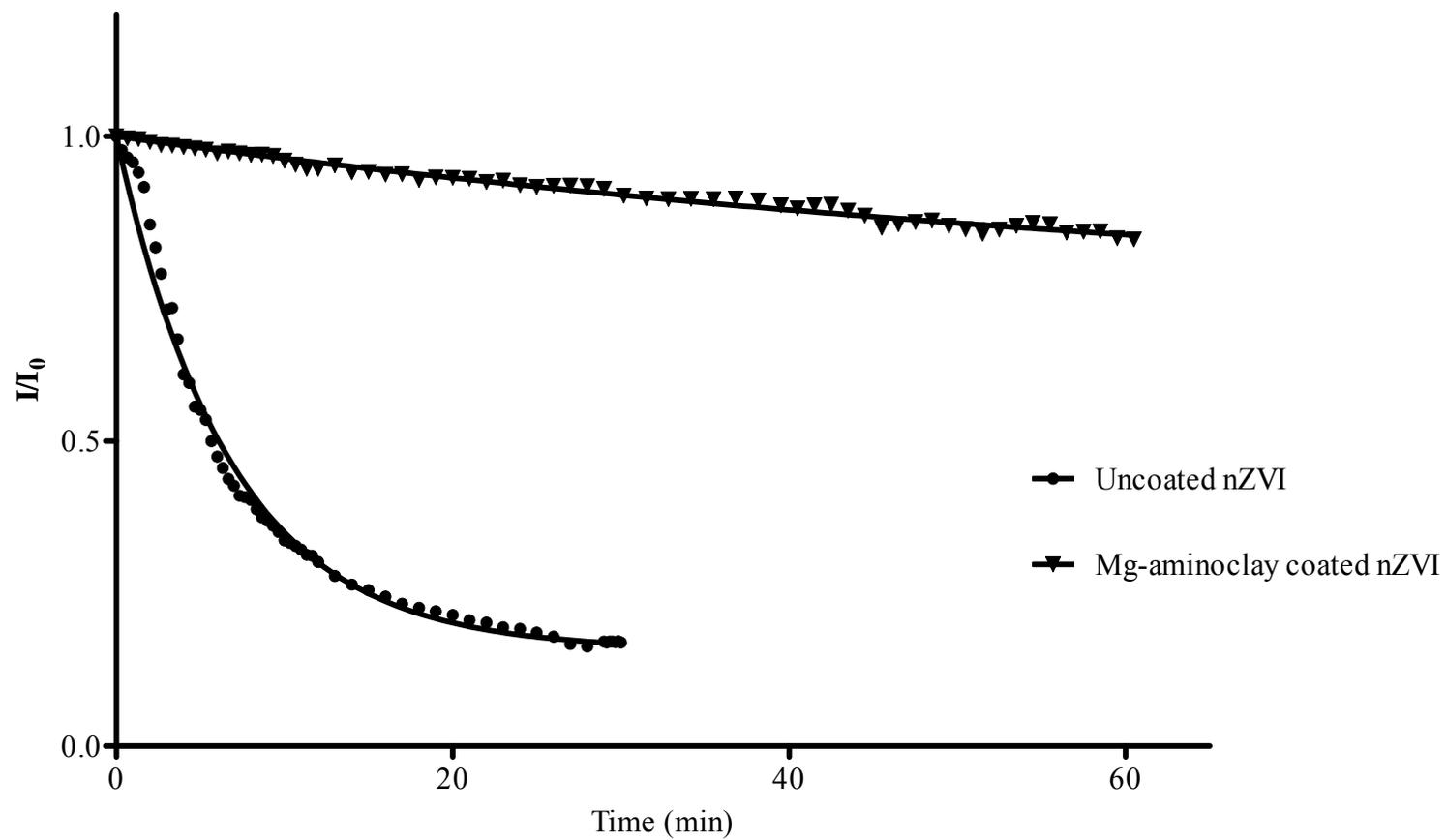
Figure S1. Enhancement of particle stability by Mg-aminoclay coating under MgAC:Fe weight ratio of 7.5. (Where I is the absorbance of solution at each time t and I_0 is the initial absorbance).
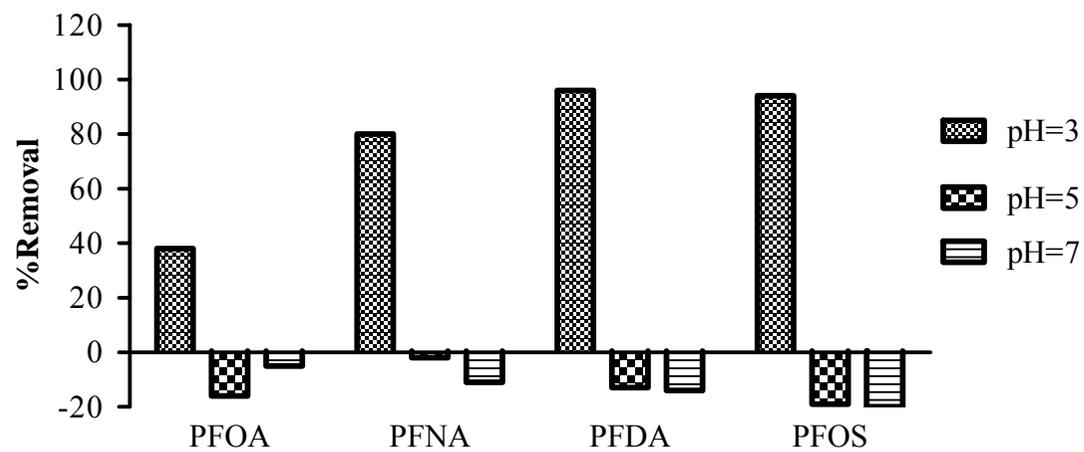
Figure S2. Effect of initial pH on PFCs removal by MgAC coated nZVI. (Experimental conditions: C_0PFCs = 200 µg L^{-1}, nZVI dosage = 1000 mg L^{-1}, reaction temperature = 20 °C, reaction time = 1 h). (Negative values are due to analytical errors).
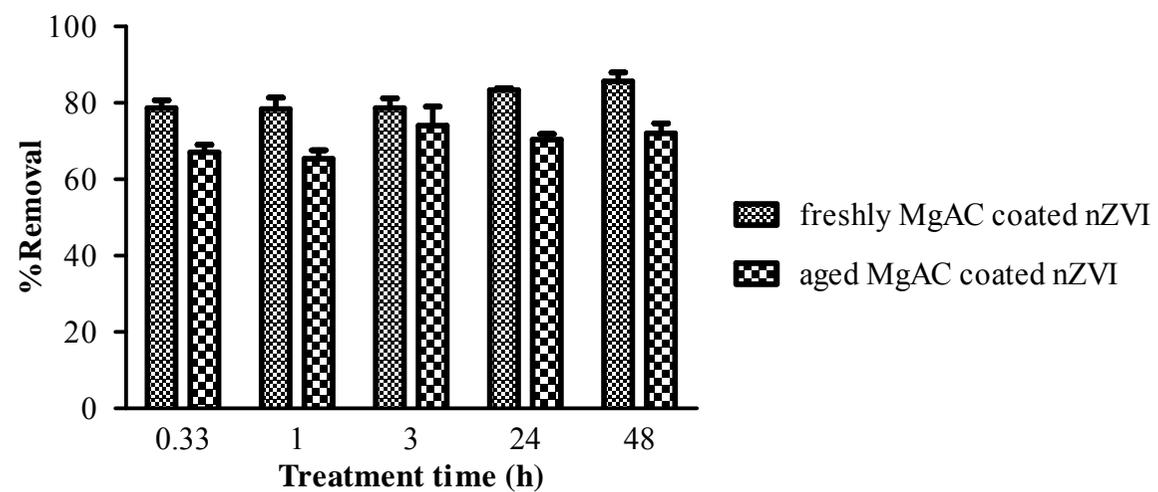
Figure S3. Comparison of PFOS removal using fresh and aged MgAC coated nZVI. (Experimental conditions: C_0PFOS = 40 mg L^{-1}, nZVI dosage = 3 g L^{-1}, initial pH = 3, reaction temperature = 20 °C). Error bars represent the standard deviation on each result (n = 3).
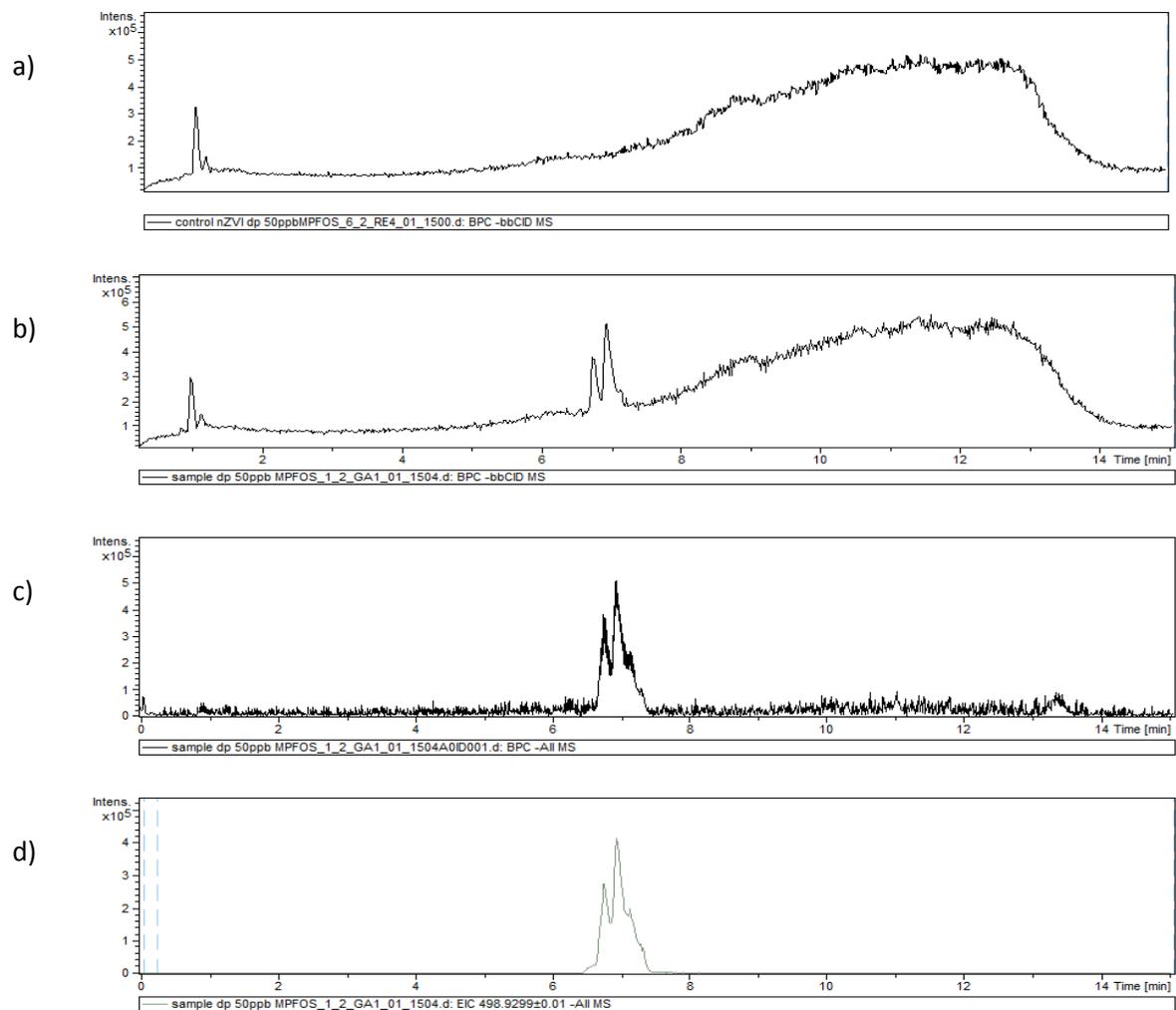
Figure S4. UHPLC-QTOF MS chromatograms after 20 min reaction time: a) TIC chromatogram of control sample (MgAC coated nZVI); b) TIC chromatogram of fortified sample (PFOS with MgAC coated nZVI); c) TIC chromatogram of the fortified sample after substraction of the control sample; and d) MRM chromatogram of PFOS.
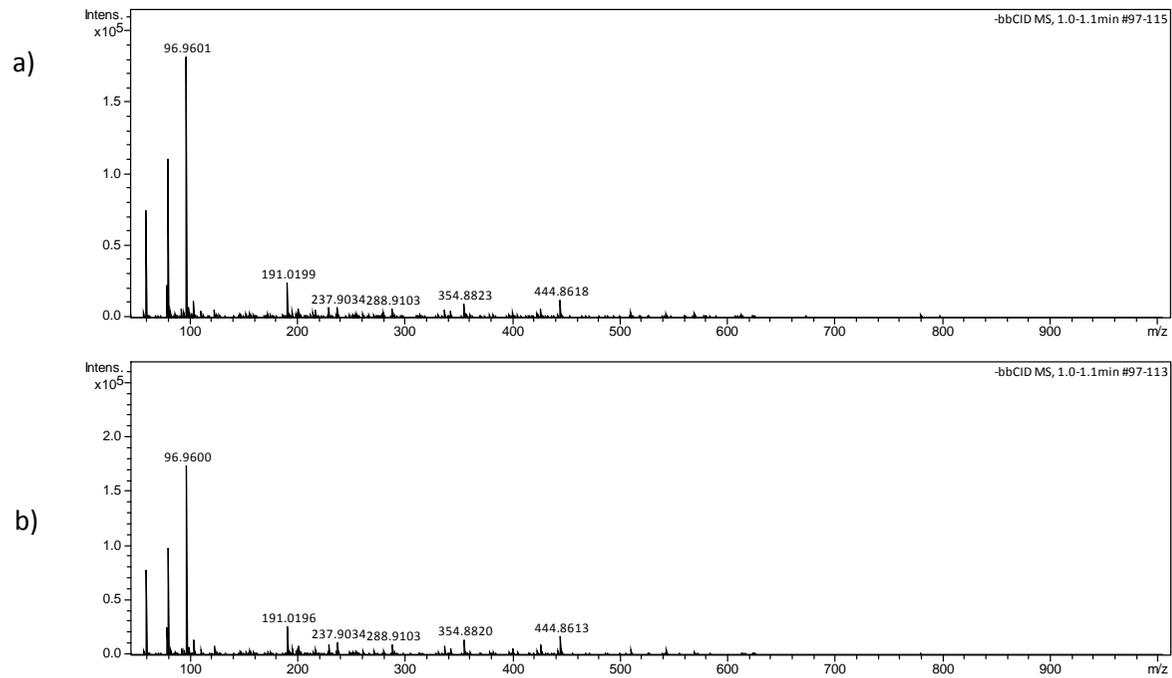
Figure S5. MS spectrum of peak at R_t = 1.1 min of: a) control sample (MgAC coated nZVI); and b) fortified sample (PFOS with MgAC coated nZVI), after 20 min reaction time.
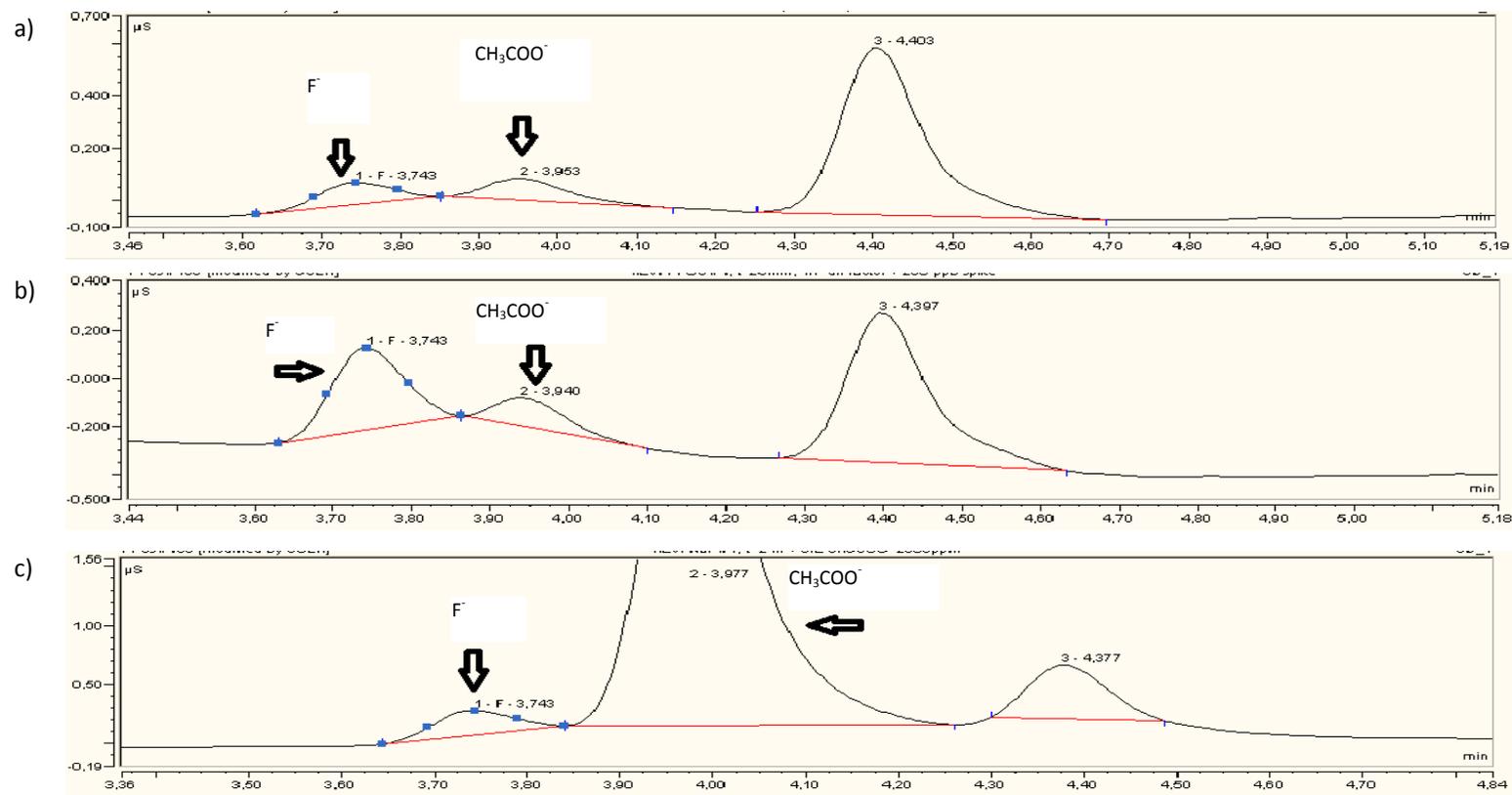
Figure S6. IC chromatograms for the detection of fluoride ions (T_R = 3.74 min) at various samples: a) diluted sample after 20 min reaction (7 times dilution); b) fortified sample with F^- standard solution, and c) fortified sample with aqueous CH_3COOH (T_R = 3.95 min) standard solution. (Experimental conditions: C_0PFOS = 40 mg L^{-1}, nZVI dosage = 3 g L^{-1}, initial pH = 3, reaction temperature = 20 °C).

9