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Use of Fenton reagent combined with humic acids for the removal of PFOA from contaminated water

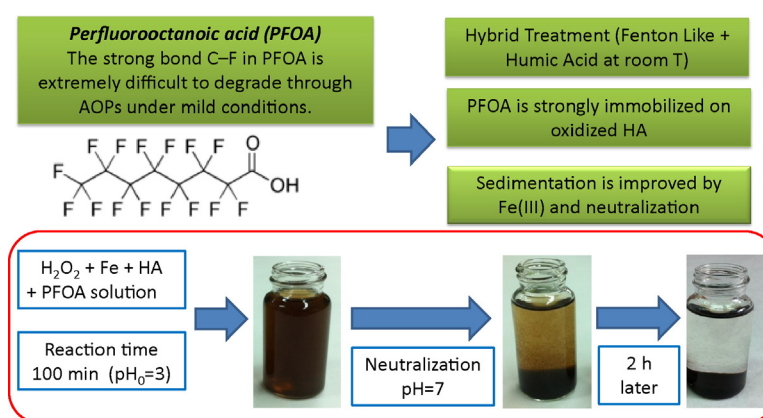
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HIGHLIGHTS

- PFOA was not degraded when Fenton-like or persulfate were used at mild conditions.
- Thermal activation of PS at 70 °C allows PFOA removal and defluorination after 18 h.
- Application of thermally activated persulfate is limited by energy costs.
- Proposed hybrid adds humic acid and Fenton-like reagent at 25 °C to the PFOA solution.
- PFOA was irreversibly entrapped during humic acid oxidation and precipitation.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluorinated compounds (PFCs) are receiving significant attention due to its global distribution, high persistence, and bioaccumulation properties. Among them, perfluorooctanoic acid (PFOA) is one of the most commonly found in the environment. The strong bond C–F in PFOA is extremely difficult to degrade, therefore advanced oxidation processes (AOPs) at room temperature and pressure are not able to oxidize them, as was noticed here using Fenton like reagent (FR) or persulfate (PS) at 25 °C. On the contrary, by using persulfate activated by heat (100 mM and $T = 70\text{ °C}$) a complete defluorination of PFOA 0.1 mM was noticed after 18 h, with a sequential degradation mechanism of losing one CF_2 unit from PFOA and its intermediates (perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPA) and perfluorobutanoic acid (PFBA)). Since this thermal treatment is not usually desirable from an economical point of view, alternative process has been tested. For this scope, a hybrid process is proposed in this work, by adding humic acid, HA, (600 mg L^{-1}) and FR, (165 mM in H_2O_2 and 3 mM in Fe^{3+}) to the 0.1 mM PFOA solution. It was found that the HA was oxidized by FR. PFOA was entrapped quantitatively and irreversibly during HA oxidation, resulting PFOA non-available to the aqueous phase. Oxidized HA with PFOA entrapped precipitates. Both, the leftover Fe(III) acting as a coagulant and neutral pH enhance the separation of this solid phase. The precipitation noticed by adding HA to the PFOA solution in absence of FR was negligible.

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1. Introduction

Perfluorinated compounds (PFCs) are a family of anthropogenic organofluoride compounds found in the environment, which consist of carbon chains saturated with fluorine atoms. Perfluorooctanoic acid (PFOA) and perfluorooctanoic sulfonate acid (PFOS) are the most commonly found PFCs in the environment. Due to their hydrophobic properties and thermal stability they have been widely used in a variety of applications over the last five decades, such as inert surfactants, as thermally stable lubricants, water-and-stain proof-coating for paper and textiles, as aqueous films forming foams, etc. (Giesy and Kannan, 2001, Schultz et al., 2003). Moreover, due to their physicochemical properties, PFCs have been found to be environmentally persistent and bioaccumulative and pose human health concerns (Johanson et al., 2009, EPA 2009). PFCs are water soluble, nonvolatile, and persistent in the environment, due to the strength of the highly polarized carbon-fluorine bond. Therefore, PFOS can easily migrate in water environments, and they have been detected in the hydrosphere, atmosphere, and biosphere. Low concentrations (ng L^{-1}) have been found in lakes, rivers and groundwater (Zareitalabad et al., 2013) and concentrations as high as mg L^{-1} have been measured in groundwater collected from some industrial sites (Moody et al., 2002, Schultz et al., 2004).

PFOS was categorized as a persistent organic pollutant under the Stockholm Convention in May 2009 and the United States (U.S.) Environmental Protection Agency (EPA) has classified perfluorooctanoic acid (PFOA) as a “likely carcinogen”.

Because of their physicochemical properties, they are difficult to treat using conventional remediation technologies. Thermal, physical and chemical treatments have been studied for this scope. Thermal methods include incineration (Taylor et al., 2014) and sonication (Moriwaki et al., 2005), having both high energy consumption and being applied as ex-situ treatment after excavation or water extraction.

Physical methods are based mainly on adsorption (Ochoa-Herrera and Sierra-Alvarez, 2008, Du et al., 2014), nanofiltration (Hang et al., 2015) and reverse osmosis (Tang et al., 2006, Tang et al., 2007). Granular activated carbon (GAC) is the most common adsorbent tested at field scale (MPCA 2009) although other adsorbent have been tested in literature (Ochoa-Herrera and Sierra-Alvarez, 2008, Senevirathna et al., 2010, Tang et al., 2010, Wang and Shih, 2011, Wang et al., 2012, Deng et al., 2008). Usually long times are needed to meet cleanup goals and the pollutants are merely transferred to other phase that require further treatment. Spent adsorptive media typically must be incinerated, with the corresponding impact to the overall management cost. Other sorbents can require disposal in landfill.

Chemical treatment includes coagulation, oxidation and reduction. Deng et al. (2011) used polyaluminium chloride (PACl) to remove PFOA from surface water finding that most PFOA was adsorbed on the particles and removed via the suspended soils in the coagulation process. Chemical oxidation has the potential to destroy organic pollutants rather than transferring contamination to another waste stream or area. However, the strong bond C–F in PFOA is extremely difficult to degrade through advanced oxidation technologies under room temperature and pressure (Cheng et al., 2014). Because of this, more energetic treatments have been checked coupling physical and chemical oxidation processes, as Photochemical defluorination by VUV/ Fe^{3+} (Moriwaki et al., 2005, Cheng et al., 2008, Taylor et al., 2014), microwave-hydrothermal decomposition by zero valent iron-activated persulfate, at 60 and 90 °C (Lee et al., 2010), thermal activated PS up to 85 °C (Lui et al., 2012, Lee et al., 2012), etc. Recently, sunlight and ferric iron (Fe(III)) has also been proven to be effective in PFOA abatement (Liu et al., 2013).

However, in spite that sunlight is free cost, this technology also requires pump and treat of groundwater and adequate infrastructures for sunlight capture (Yang et al., 2014).

Reduction has been also tested but the high energy of the F–C bond requires high temperatures if ZVI is used as reductor (Hori et al., 2006).

The heating costs of the techniques above cited must be considered from an economical point of view as well as those from water extraction and cannot be applied in situ.

Because of this, in this work abatement of PFOA, as example of perfluorinated compounds, will be studied by Fenton like reagent enhanced by suspended solid (SS) addition. Humic acid has been selected as SS compound. Humic acids are composed of molecules rich in both acidic functional groups, mainly carboxyl and phenolic groups, and hydrophobic moieties such as alkyl chains and aromatic cores. Humic acids are complex mixtures of many different acids containing carboxyl and phenolate groups with elemental compositions of C (52–62%), H (3–5.5%), O (30–33%) and N (3.5–5%) (Kumada, 1955, Ikeya et al., 2015). However, other authors reported lower C percentages, close to 32% (Wang et al., 2015). As an example, the elemental compositions of humic acids from swamp's water phase contain 47.06–53.47% carbon on a dry basis, 3.71–5.55% hydrogen, 38.07–47.11% oxygen, and 1.51–4.32% nitrogen (Efremova et al., 2014).

Humic acids have been used in literature as an amendment to improve the abatement of organic compounds by Fenton reaction, although the mechanism is not totally comprehended. HA is proposed to act as an iron chelator or sorbent (Georgi et al. 2007), as forming a Fe(III)-humate catalytic complex resulting in a higher abatement rate of some organic pollutants (Vione et al., 2004). It was noticed a synergetic effect in COD removal and color removal when humic acid was selected as adsorbent and precipitant for physicochemical pretreatment in the abatement of a dye pollutant by using Fenton reagent. It has been also found that HA is oxidized by Fenton reagent, measuring a decrease on the HA concentration (measured by UV at 254 nm) explained by both oxidation and coagulation (Wu et al., 2011). It is assumed that humic substances react with OH^\bullet resulting in bleaching, mineralization and production of molecular size distribution profiles. Lower molecular size (<3 kDa) fractions are produced by oxidative degradation of humic acid and higher molecular size fractions have been also found (Bekbolet and Sen-Kavurmaci, 2015). That means that oxygenated groups appear and probably new C–H–O groups are created. However, the chemical nature of these changes is yet under researching. The abatement of PFOA by this hybrid system, Fenton reagent by HA addition, will be compared with PFOA abatement by using Fenton like, thermally activated persulfate and not oxidized humic acids.

Not only the elimination of the parent pollutant will be considered but the organic intermediates produced and defluorination achieved. Besides, the immobilization of PFOA in the oxidized humic acid will also be evaluated to assess its availability.

2. Experimental

2.1. Materials

Analytical reagent grade or better chemicals as well as Milli-Q water were used in the experiments. Perfluorooctanoic acid (PFOA), and four of its oxidation intermediates, perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPA) and perfluorobutanoic acid (PFBA) were purchased from Aldrich. Humic acid sodium salt was purchased from Acros (ref 12086000, CAS 68131-04-4).

Oxidants employed were sodium PS, (obtained from Sigma-Aldrich), and $\text{H}_2\text{O}_2 > 30\%$ (w/w) from Fisher Chemical. Ferric sulfate obtained from Fluka, was used as the catalytic iron specie. Acetonitrile from Riedel de Haën was employed in mobile phase in HPLC determinations.

Sulfuric acid >95%, from Fisher Chemical, and potassium permanganate 99.5%, from Panreac, were used in oxidant determinations. TISAB IV solution from Fluka was employed in fluoride determination.

Nitric acid 69.5%, obtained from Scharlau, was utilized as iron ions stabilizer in MP-AES analysis.

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