Removal of aqueous perfluorooctanoic acid (PFOA) using starch-stabilized magnetite nanoparticles

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HIGHLIGHTS

- First study on adsorption of PFOA by starch-stabilized magnetite nanoparticles
- The stabilized nanoparticles offer much greater capacity than other sorbents.
- The nanoparticles remove PFOA mainly by inner-sphere surface complexation.
- The nanoparticles perform well at typical pH, ionic strength, and HA concentrations.
- The nanoparticles significantly reduced biological toxicity of PFOA.

GRAPHICAL ABSTRACT
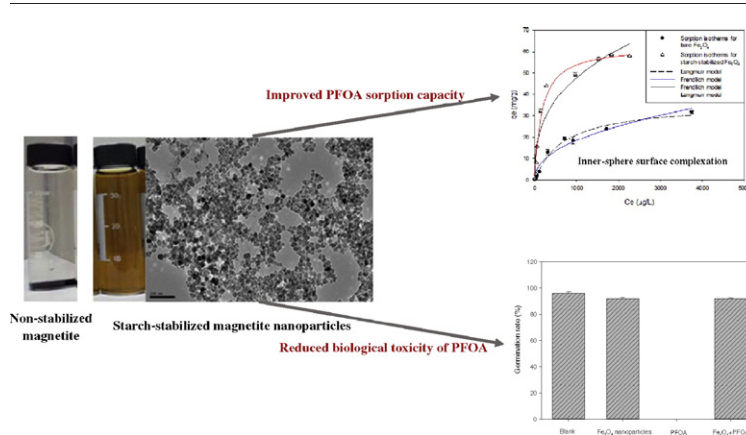
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ABSTRACT

Fully stabilized magnetite (Fe_3O_4) nanoparticles were prepared with a water-soluble starch as a stabilizer and tested for removal of aqueous perfluorooctanoic acid (PFOA). The presence of starch at ≥0.2 wt% can fully stabilize 0.1 g/L as Fe of the Fe_3O_4 nanoparticles. The particle stabilization technique resulted in 2.4 times higher PFOA uptake. Fourier transform infrared spectra suggested that the main PFOA removal mechanism was inner-sphere complexation. Batch kinetic experiments revealed that the starch-stabilized nanoparticles facilitated a rapid PFOA uptake with a sorption equilibrium time of 30 min, and the sorption process followed a pseudo-second-order kinetic model. The Langmuir model was able to well interpret the adsorption isotherm, with a maximum adsorption capacity of 62.5 mg/g. Increasing pH from 4.7 to 9.6 led to a sharp increase (by 2.6 times) in PFOA uptake. The presence of 12 mg/L humic acid inhibited PFOA uptake by 96%, while effect of ionic strength ($CaCl_2 = 0$–2 mmol/L) was negligible. The nanoparticles significantly reduced the biological toxicity of PFOA. The results demonstrated promise of starch-stabilized Fe_3O_4 nanoparticles as a "green" adsorbent for effective removal of PFOA in soil and groundwater.

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1. Introduction

Perfluorooctanoic acid (PFOA) is one of the most common perfluorinated compounds (PFCs). It has been widely used as surfactants, fire retardants, lubricants, wetting agents, and polymer additives for its unique chemical and physical properties such as hydrophobicity, oleophobicity, and extraordinary chemical stability (Fricke and Lahl, 2005; Key et al., 1997; Li et al., 2012; Loos et al., 2008).

PFOA has been frequently detected in various environmental media, including surface waters, groundwater, soils/sediments, livers of human beings, and wildlife species. It has been of an emerging health concern due to its persistence, bioaccumulation, toxicity, and resistance to typical environmental degradation processes due to the highly stable carbon-fluorine bonds (Saez et al., 2008).

Sorption has been one of the most cited methods to remove PFOA (Du et al., 2014). Various adsorbents have been investigated for removal of PFOA, including activated carbon (Deng et al., 2015; Yu et al., 2009), carbon nanotubes (Deng et al., 2012a), polymeric resins (e.g., commercial anion-exchange and non-ionic resins) (Yu et al., 2009; Deng et al., 2010), and biomaterials (Deng et al., 2012b; Deng et al., 2013; Zhang et al., 2011). However, these adsorbents bear with some critical drawbacks, such as low adsorption capacity, long equilibrium time, high cost, and/or potential secondary pollution. Consequently, more effective and environmentally friendly adsorbents which can overcome the abovementioned drawbacks have been consistently sought.

A number of studies have shown that iron oxides such as magnetite (Fe_3O_4), goethite (α-FeO(OH)), and maghemite (γ-Fe_2O_3) can effectively adsorb PFCs (Zhao et al., 2011). For instance, Gao and Chorover (2012) found that nanoparticulate hematite (α-Fe_2O_3) can adsorb PFOA via electrostatic interactions and inner-sphere Fe-carboxylate complexation. Tang et al. (2010) found that perfluorooctane sulfonate (PFOS) adsorption onto goethite is governed by PFOS-surface electrostatic attraction and PFOS-PFOS electrostatic repulsion.

Magnetite is a well-known adsorbent for its versatile properties, e.g., highly active sites, low toxicity, biocompatibility, good chemical stability, strong superparamagnetic properties, and easy separation from water (Hu et al., 2009). Synthetic Fe_3O_4 is generally prepared via co-precipitation of Fe^{2+} and Fe^{3+} ions in a highly alkaline media under an oxygen-free environment (An et al., 2011). However, in the absence of a stabilizer, the resultant magnetite particles tend to aggregate, resulting in limited adsorption capacity.

Compared to bulk materials or natural minerals, nanoscale Fe_3O_4 particles are expected to offer much greater sorption capacity due to their larger specific surface area and potentially greater reactivity. Recently, Liang et al. (2012) found that a water-soluble starch (a modified polysaccharide) can effectively prevent agglomeration of Fe_3O_4 nanoparticles, and the stabilized nanoparticles increased maximum Langmuir capacity for arsenate by 2.3 times compared to non-stabilized magnetite; moreover, they observed that starch-stabilized magnetite nanoparticles offered a much faster adsorption kinetics than non-stabilized magnetite.

The overall goal of this study was to test the effectiveness of starch-stabilized magnetite nanoparticles for removing PFOA from water. The specific objectives were to: (1) synthesize stabilized magnetite nanoparticles in the presence of various concentrations of starch; (2) characterize the starch-stabilized nanoparticles; (3) investigate the effects of starch concentration, reaction time, initial PFOA concentration, solution pH, ionic strength, and humic acid (HA) on PFOA sorption by the nanoparticles; (4) elucidate the underlying PFOA removal mechanisms; and (5) test the effects of PFOA and the magnetite nanoparticles before and after the PFOA sorption to seed germination.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade or higher. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), NaOH, HCl, and $CaCl_2$ were purchased from Jiangtian Chemical Commercial Ltd. (Tianjin, China). Methanol (HPLC grade) was purchased from Anpel Laboratory Technologies Inc. (Shanghai, China). Sodium perfluorooctanoate was purchased from J&K Scientific Ltd. (Beijing, China). A water soluble starch was obtained from Dingguo Changsheng Biotechnology Commercial Ltd. (Beijing, China). HA (sodium salt, 50–60% as HA, CAS 68131-04-4) was purchased from Beijing InnoChem Science & Technology Commercial Ltd. (Beijing, China). Wheat seeds (Weimai-8) were kindly supplied by Shandong Wuyue Taishan Seeds Co., Ltd (Taian, China).

2.2. Preparation and characterization of starch-stabilized magnetite nanoparticles

Starch-stabilized magnetite nanoparticles were prepared in 500 mL glass bottles following the procedure as described previously (An et al., 2011; Liang et al., 2012). In brief, first, a 1 wt% starch stock solution was prepared. Meanwhile, pre-determined masses of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ were dissolved in N_2-purged deionized (DI) water to form a ferrous-ferric stock solution at an Fe^{2+}:Fe^{3+} molar ratio of 1:2. Second, a fraction of starch stock solution was added into the Fe^{2+}–Fe^{3+} solution to yield a final concentration of 0.1 g/L as total Fe and 0.2 wt% starch, and the mixture was mixed under N_2 purging for 15 min. The pH of the solution was then raised to ~11 by adding a 1.5 M NaOH solution, and the nanoparticle suspension was sealed and aged for 24 h to allow for full growth. Then, the pH was lowered to 6.8–7.2 by 1.2 M HCl. The resulting nanoparticle suspension was used in the subsequent characterization and PFOA adsorption experiments. For comparison, non-stabilized magnetite particles were prepared in the absence of starch but under otherwise identical conditions.

X-ray powder diffraction (XRD) (D/max-2500, Rigaku, Tokyo, Japan) was carried out to investigate the crystalline compositions of non-stabilized and starch-stabilized magnetite particles. The prepared magnetite samples were collected by filtering the suspensions using a 25 nm membrane filter of mixed cellulose esters (Millipore Corp., Billerica, MA, U.S.A.). The solids were then rinsed three times with N_2-purged DI water, and subsequently freeze-dried under vacuum using a freezer dryer (FD5–3, SIM International Group CO., U.S.A.) at −60 °C for 48 h. The samples were placed in a zero background sample holder and scanned from 3 to 80° 2θ angles. Transmission electron microscope (TEM) analysis was carried out using a T-20 transmission electron microscope (Philips, Amsterdam, Holland). Ten μL of a sample suspension was placed on a 230 mesh copper grid, and then dried under a nitrogen stream. Fourier transform infrared (FTIR) spectroscopy measurements of the freeze-dried samples were carried out using a FTS6000 spectrometer (Bio-rad, Beijing, China) to explore the interactions between starch and magnetite, and between magnetite nanoparticles and PFOA. Neat starch and non-stabilized magnetite particles were also measured in the same manner. Zeta potential and hydrodynamic diameters of non-stabilized and starch-stabilized magnetite in the respective suspensions were measured using a Zetasizer Nano ZS 90 (Malvern, Malvern Instruments Corp., Worcestershire, U.K.). The magnetic properties of the samples were measured using a Squid-vsm magnetic measuring system. Specific surface area was measured using a Micrometritics ASAP 2460.

2.3. Effects of starch concentration on physical stability of magnetite nanoparticles

To investigate the effects of starch on the physical stability of Fe_3O_4 particles, the particles were prepared at a fixed Fe concentration of