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Preparation of a functional silica membrane coated on Fe_3O_4 nanoparticle for rapid and selective removal of perfluorinated compounds from surface water sample

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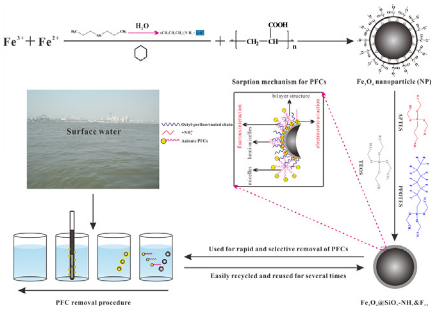
HIGHLIGHTS

- A novel magnetic nanocomposite was prepared in one step by a sol-gel process.
- The composite possessed good selectivity and rapid sorption kinetics for PFCs.
- The composite exhibited high removal efficiency for PFCs in surface water sample.
- The composite presented favorable reusability and stability for PFC removal.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel silica membrane functionalized with amino group and octyl-perfluorinated chain was prepared on the periphery of Fe_3O_4 nanoparticle (NP). The obtained nanocomposite ($Fe_3O_4@SiO_2$-NH_2&F_{13}) exhibited good selectivity for perfluorinated compounds (PFCs) by electrostatic and fluorine-fluorine (F-F) interaction with the addition of size exclusion effect. In ethanol, the monolayer coverage of PFCs occurred on most of the binding sites and the adsorption capacity were in the range of 13.20–111.14 mg g^{-1}. In aqueous solution, due to the hydrophobicity of perfluoroalkane chain, some PFCs ($C \geqslant 8$) may also stick together on the composite surface, which made the sorption amounts of these PFCs greatly enhanced. Thereafter, $Fe_3O_4@SiO_2$-NH_2&F_{13} was used for rapid and selective removal of nine PFCs from surface water sample. In 1 L of spiked water samples fortified at 0.5–50 ng L^{-1} levels, the composite showed a better removal efficiency (86.29%) for PFCs than that (58.61%) of powdered activated carbon (PAC). In addition, high concentrations (5–50 mg L^{-1}) of humic acid (HA) had no significant influence on the removal performance of the composite for PFCs. Furthermore, $Fe_3O_4@SiO_2$-NH_2&F_{13} could be reused for several times with no obvious decrease in the removal efficiency. Thus, the magnetic nanocomposite could be used as an effective adsorbent for PFC removal from aquatic environment.

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1. Introduction

Since the 1950s, perfluorinated compounds (PFCs) have been used in a wide range of industrial and commercial applications for several decades due to their unique properties [1,2]. Because of the extreme stability of C–F bond, PFCs are highly persistent in the environment. Up to now, they have been detected in several environmental matrices, i.e., oceans, rivers, lakes, food products and air particles [3–6]. Human are exposed to PFCs by the routes of drinking water, ingestion of food products and inhalation of household dust [7–9]. PFCs accumulate mainly in blood, liver and kidney rather than adipose tissue attributed to their high water-solubility [10]. PFCs are associated with numerous adverse effects for human health. For instance, perfluorooctanoic acid (PFOA) is described as a likely human carcinogen [11] and linked to two types of cancer in the general population [12]. In addition, perfluorooctane sulfonate (PFOS) is negatively associated with testosterone level, semen quality or sperm morphology [13,14]. At present, the occurrence of PFCs in the world spread aquatic environment has been recognized as one of the emerging issues in the public health [15,16]. Therefore, drinking water is considered as an important transfer route of PFCs [7,17] and an effective strategy for the removal of PFCs from contaminated water is highly required.

Some conventional treatments, such as activated sludge process, sand filtration, flocculation and chlorination, can hardly remove PFCs from contaminated water [18–20]. Recent studies showed that some advanced techniques, such as ultrasonic and ultraviolet irradiation, and some novel oxidation processes, could effectively decompose PFCs in water [21–23]. In addition, reverse osmosis has been used in drinking water treatment and showed good removal efficiency for PFOS and PFOA [19]. However, the inherent weaknesses of these strategies, for example, high energy consumption, harsh reaction conditions and complicated operation, hamper their large-scale application. Taking environment protection and cost saving into consideration, adsorption is considered as a suitable and effective technique for PFC removal from aquatic environment [24]. Among various adsorbents reported in the literatures, activated carbon (AC) is the most popular and widely used material due to its low cost and easy acquisition. In a drinking water production chain, Eschauzier et al. found granular activated carbon (GAC) could effectively remove PFOS, while PFOA only decreased about 50% after the GAC filtration. In addition, a decreasing removal efficiency of GAC was observed with increasing carbon loading and decreasing C–F length of the PFCs [25]. The removal capacity of PFOA with the fresh GAC calculated by Takagi et al. was only 0.52 $\mu g\ g^{-1}$. On the other hand, the GAC used for more than a year was not efficient to remove PFOS and PFOA from water [20]. Mailler et al. pointed out high concentration levels of other pollutants or organic matters in aquatic environment might interfere the removal performance of powdered activated carbon (PAC) for most of PFCs [26]. Therefore, it requires further study to develop an effective adsorbent to remove PFCs from ambient water and it would be attractive if the sorbent has high and selective adsorption efficiency for PFCs in a complex matrix. Moreover, rapid sorption for PFCs and easy separation of the adsorbent should be also taken into account.

A fluorous separation technique is a methodology that isolates fluorous or fluorous-tagged molecules from other types of molecules by fluorine-fluorine (F-F) interaction that occurs between a fluorous medium and a fluorous portion of a molecule [27–29]. Fe_3O_4 nanoparticles (NPs) have many unique properties, including good biocompatibility, low toxicity, high surface area, rapid magnetic susceptibility and ease of preparation [30]. During the past years, it was demonstrated that Fe_3O_4 NPs with appropriate modification can be used as effective magnetic materials for environmental decontamination [31,32]. In this study, a novel magnetic nanocomposite ($Fe_3O_4@SiO_2\text{-}NH_2\&F_{13}$) was initially prepared by coating a functional silica membrane on the surface of Fe_3O_4 NP, which combined the rapid magnetic separation property of Fe_3O_4 NP and selective recognition ability of F-F interaction. The sorption behavior of the prepared composite for PFCs was evaluated systematically. Furthermore, the composite was applied for rapid and selective removal of PFCs from surface water sample and the elimination efficiency of PAC for PFCs was used for comparison. To the best of our knowledge, this research is the first attempt to prepared a novel $Fe_3O_4@SiO_2\text{-}NH_2\&F_{13}$ composite for the application of rapid and selective removal of PFCs from environmental water sample.

2. Material and methods

2.1. Chemicals and reagents

Nine PFCs involved in this study included perfluorohexane sulfonate (PFHxS, purity 98%), PFOS (98%), perfluoroheptanoic acid (PFHpA, 99%), PFOA (96%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 98%), perfluoroundecanoic acid (PFUnDA, 96%), perfluorododecanoic acid (PFDoDA, 95%) and perfluorotetradecanoic acid (PFTA, 97%), purchased from Sigma-Aldrich Company (St. Louis, MO, USA). Six standard substances used as reference compounds contained 1H,1H,2H,2H-perfluoro-1-octanol (6:2 FTOH, 98%), *n*-octanoic acid (*n*-OA, 99%), 2-fluorophenylacetic acid (2-FPAA, 98%), 3,4-dihydroxyphenylacetic acid (3,4-DHPAA, 98%), florfenicol (FTAP, 98%) and erythromycin (ERY, 98%), bought from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). These chemicals' structures are seen in Fig. 1.

Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), cyclohexane, di-*n*-propylamine were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Poly(acrylic acid) (PAA, M.W. $\approx$ 3000) was supplied by Aladdin Industrial Corporation (Los Angeles, CA, USA). Tetraethyl orthosilicate (TEOS, 99%), (3-aminopropyl)triethoxysilane (APTES, 99%) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES, 98%) were bought from Sigma-Aldrich Company. PAC (200 mesh) and humic acid (HA) were obtained from Aladdin Industrial Corporation. Three-fold distilled water was used throughout the whole experiment.

2.2. Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs were synthesized according to a facile interfacial coprecipitation method [33] with some modifications. $FeCl_3{\cdot}6H_2O$ (5 mmol) and $FeSO_4{\cdot}7H_2O$ (2.5 mmol) were dissolved in 90 mL of distilled water by ultrasonic, used as iron solution. PAA (1.75 mL, $\approx$30 mmol AA) was added into 10 mL of water, used as dispersing solution. Di-*n*-propylamine (5 mL) was mixed with 45 mL of cyclohexane in a three-necked round-bottomed flask. Under a continuous stirring (700 rpm) and supersonic condition (200 W), iron solution was added dropwise into the flask at a rate of 1 drop per second. The stirring and ultrasonic were continued for 25 min after the process of dropping was completed. And then the dispersing solution was added (1 drop s^{-1}) into the reaction, and 30 min later, the Fe_3O_4 NPs were obtained (Fig. 2). The synthesis of Fe_3O_4 NPs was carried out at room temperature under the protection of N_2. The obtained Fe_3O_4 NPs were rinsed with distilled water for several times and further dispersed to form an aqueous colloid solution with a concentration of 25 mg mL^{-1}.

2.3. Prepartion of $Fe_3O_4@SiO_2\text{-}NH_2\&F_{13}$

APTES (0.125 mmol), PFOTES (0.125 mmol) and TEOS (1 mmol) were dissolved in 1 mL of anhydrous ethanol, used as silica precur-