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Removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from water by coagulation: Mechanisms and influencing factors

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ABSTRACT

In this study, alum ($Al_2(SO_4)_3{\cdot}18H_2O$), ferric chloride ($FeCl_3{\cdot}6H_2O$) and polyaluminium chloride (PACl) were used to remove perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from water. The influencing factors, including pH and natural organic matter (NOM), were investigated. A positive correlation was found between the size of the flocs and the removal efficiency of PFOX (X = S and A). The removal ratios of PFOS and PFOA were 32% and ~12%, respectively, when 50 mg/L of $FeCl_3{\cdot}6H_2O$ was added as the coagulant at the initial pH. Coagulation achieved high removal ratios for PFOX under acidic conditions (~47.6% and 94.7% for PFOA and PFOS at pH 4, respectively). In addition, increasing NOM concentrations decreased the removal rates of PFOX because of the existence of competitive adsorption between NOM molecules and PFOX on the surface of the coagulants and flocs. The combination of adsorption by powdered activated carbon (PAC) and coagulation increased the removal ratios up to >90% for PFOX at the initial concentration of 1 mg/L, implying that the adsorption enhanced coagulation. Meantime, the experiments with natural water showed that coagulation is a feasible method to remove PFOS and PFOA from surface water.

1. Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are typical perfluorinated compounds (PFCs) that have been used in many industries including surfactants and fire retardants for decades [1,2]. Due to their high-energy carbon–fluorine bond (C—F, 116 kcal/mol) and low reactivity [3], these compounds are persistent in the natural environment and have been widely observed in sediments, sludge, municipal wastewater, drinking water and even human blood throughout the world [4,5]. Although several considerable advancements have been made in order to understand the environmental fate and toxicity of these compounds, challenges still remain because of their particular chemical properties [6]. In addition, PFOS was categorized as one of the new persistent organic pollutants in the Stockholm Convention in 2009 [7]. While PFOA has been used as an additive in the production of fluoropolymers for years and is still produced and used in many industries [8]. In contrast to other persistent organic pollutants (POPs), PFOS and PFOA have higher water solubility (680 mg/L for PFOS in pure water and 3400 mg/L for PFOA) [9,10], and they are easy to transport into the aquatic environment, resulting in acute and chronic toxicity to aquatic organisms [10]. The physicochemical properties of PFOS and PFOA are shown in Table S1. In our previous study, the toxicity effects of PFOS and PFOA on *Brachionus calyciflorus* (*B. calyciflorus*) were tested, and the results displayed the changes of *B. calyciflorus* both at the single level and at the population level when they were exposed to PFOS and PFOA [11]. Other studies showed that PFOS and PFOA had been found in the blood of virtually all Americans tested during the last decade [12], and higher serum levels of PFOS and PFOA were associated with a higher prevalence of hyperuricemia [13]; at the same time, they were related to current disease in the U.S. general adult population [14]. Therefore, it was necessary to develop reliable and effective methods for the removal of PFOS and PFOA from aqueous environments.

In previous studies, PFOS and PFOA were reported to be resistant to oxidation [5,15–17]. Some researchers studied the adsorption behaviors of PFOS and PFOA on different adsorbents [18–22], indicating that physicochemical treatments played an important role on the removal of these compounds. Conventional physicochemical technologies, such as adsorption [23–26], membrane filtration [9,27,28] and sonochemistry [29–31], have been confirmed to be effective for PFOS and PFOA removal at a relatively high

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concentration (tens to hundreds mg/L) in wastewater. However, these technologies are not effective and economic for lower concentrations of PFOS and PFOA in surface water. Therefore, it is still meaningful to find an effective method for the removal of PFOS and PFOA with relatively low concentrations.

Coagulation has been widely employed in drinking water and wastewater treatment processes for removing various particulates and natural organic matter (NOM) [32,33]. The process of coagulation is influenced by the source of water and the nature of the organic constituents existing in the water (including suspended, colloidal and dissolved organic matter). Coagulation by adding hydrolyzing chemicals, such as alum and iron salts, mainly involves: (i) destabilization of small suspended and colloidal particulate matter; (ii) adsorption or reaction of portions of the colloidal and dissolved NOM to particles; and (iii) creation of flocculent particles that sweep through the water to be treated, enmeshing small suspended, colloidal, and dissolved material as they settle. In prior study, PFOA was reported to be removed up to 90% from water by polyaluminium chloride (PACl, $Al_2O_3 = 29\%$). In the coagulation process, PFOA was adsorbed on the particles in water at the first step, which was the crucial one, and then removed via the removal of suspended solids (SS) [34]. However, in other literature, the removal of PFOS and PFOA by coagulation was verified by the adsorption onto the freshly formed fine Al hydroxide flocs during the initial stage of coagulation [35]. Until now, the removal mechanism for PFOS and PFOA in water has not been fully understood. Thus, it is necessary to examine the effects of different coagulants in removing PFOS and PFOA from water. The different influencing factors such as pH and NOM are also needed to be investigated to interpret the removal mechanism of perfluorinated compounds from water by coagulation.

In this study, the removal abilities of different coagulants for PFOS and PFOA, including alum ($Al_2(SO_4)_3{\cdot}18H_2O$), PACl and ferric chloride ($FeCl_3{\cdot}6H_2O$), were investigated. The aims of this present study were: (i) to investigate the effect of influencing factors, including pH and NOM; (ii) to explore the removal efficiency of PFOS and PFOA in natural water and the combined coagulation with powdered activated carbon (PAC); and (iii) to interpret the removal mechanisms between perfluorinated compounds and coagulants.

2. Experimental section

2.1. Materials

All chemicals used in the experiments were of reagent grade or higher and were used as received without further purification. PFOS and PFOA were supplied by Sigma–Aldrich Chemical Co. Humic acid (HA), fulvic acid (FA), kaolinite clay, sodium hydroxide (NaOH), ammonium acetate (CH_3COONH_4), and other chemicals, such as $Al_2(SO4)_3{\cdot}18H_2O$, $FeCl_3{\cdot}6H_2O$ and PACl, were obtained from Sinopharm (Beijing, China). The pH values were adjusted by adding HCl (5%, v/v) and NaOH (5%, m/m). A stock solution of HA was prepared by adding 2.5 g HA into 250 mL 0.1 mmol/L of NaOH solution, whereas FA was dissolved directly into deionized (DI) water. All solutions used in our experiments were prepared with deionized (DI) water supplied by a Milli-Q Gradient-A 10 Millipore (resistance of 18.25 MΩ).

2.2. Jar tests

Coagulation of PFOS and PFOA was performed in a series of jar tests at different initial pHs and concentrations of HA or FA. Unless otherwise specified, the synthetic water was prepared by adding kaolinite clay (10 mg/L) for turbidity, which was proven to have a negligible effect on the adsorption of PFOS and PFOA in our previous study. Meanwhile, 1.0 mmol/L $NaHCO_3$ and 1.0 mmol/L NaCl were added to provide alkalinity and ionic strength [35]. A given amount of PFOS or PFOA was added into the synthetic water, and the mixture was stirred for 30 min before the coagulation experiments. The synthetic water containing PFOS or PFOA was used to conduct the coagulation experiments, including the effects of coagulant dose (1–100 mg/L), solution pH (4–9), concentration of HA or FA (0–50 mg/L) and PAC (0–1000 mg/L), on the removal of PFOS or PFOA and turbidity. To investigate the effect of PAC, different amounts (0–1000 mg/L) of PAC were added into the synthetic water, and the mixture was stirred for 30 min to allow PFOX to adsorb on the PAC and reach the sorption equilibrium. During the coagulation experiments, the changes of pH values, as well as the turbidity, were measured in each of the batch experiments.

Coagulation experiments were performed in 500 mL plastic beakers on a conventional jar test apparatus. The coagulants were added into each 500 mL solution with an initial concentration of 1.0 mg/L PFOS or PFOA to study the removal efficiency. Before coagulation, the mixture was stirred for 30 min to examine the adsorption of the plastic beaker. The jar test procedures consisted of a 30 s rapid mix (300 rpm), a 15 min slow mix (50 rpm), and a 15 min settling period. The obtained supernatants were collected for PFOS and PFOA determination, as well as the changes of pH and turbidity.

2.3. Characterization

The FA used in the experiments was characterized by Fourier transform infrared spectroscopy (FT-IR, Nexus 670, Nicolet, USA), and the main functional groups were determined. The flocs formed in the coagulation were characterized by transmission electron microscopy (TEM, H600, Hitachi, Japan), and the particle sizes of the flocs were measured by a particle size analyzer (S3500, Microtrac, USA). The surface area of PAC used in the experiment was measured with a surface area analyzer (Quadrasorb SI, Quantachrome, USA) as 1280 m^2/g with the use of nitrogen, and its point of zero charge (pHpzc) was determined to be pH 7.8, according to the method reported before [36,37]. The pH values and turbidity changes were recorded by a microprocessor pH meter (pH 211, EUTECH Co, USA) and a turbidimeter (WGZ-1B, Xinrui, China).

2.4. Analytical method of PFOS and PFOA

After the coagulation process, 1.0 mL of PFOS solution taken from the supernatant was diluted with 1.0 mL methanol (v/v = 1:1). The mixture was then filtered with a 0.2 μm inorganic membrane filter, whereas the sample of PFOA was directly filtered with a 0.2 μm inorganic membrane filter without dilution [21]. The concentrations of PFOS and PFOA were measured by a high performance liquid chromatography coupled with a triple-stage quadrupole mass spectrometer (HPLC-MS/MS, API 3200, Applied Biosystems, USA). The HPLC separation was performed with a HPLC BEH C18 column (2.1 × 50 mm, 1.7 μm) at 40 °C. The mobile phases were composed of methanol and 10 mmol/L CH_3COONH_4. The total analysis time was 7 min, and the flow rate was set at 0.8 mL/min. The details of the analytical method can be found in our previous study [38].

3. Results and discussion

3.1. Removal of PFOS and PFOA by coagulation

As ferric or aluminum ions are added into the water, a number of parallel and sequential reactions occur. Initially, when a salt of