High-efficiency removal of perfluorooctanoic acid from water by covalently bound hybrid coagulants (CBHyC) bearing a hydrophobic quaternary ammonium group

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ABSTRACT

Perfluorooctanoic acid (PFOA) is one of global persistent organic pollutants (POPs). The currently available PFOA removal techniques are of high cost and only limited to bench scale. In the present work, a novel covalently bound hybrid coagulant (CBHyC) bearing a hydrophobic quaternary ammonium group was prepared and characterized. Its excellent PFOA removal performance was demonstrated. Compared with the conventional coagulants, it is a thicker, larger and more irregular aggregate with much higher zeta potential. CBHyCs with different Si/Al molar ratio (0.15, 0.3 and 0.6) and basicity (B) values (1.0, 2.0 and 2.5) were tested for the PFOA removal from a water solution containing 100 μg/L PFOA. The results indicate that CBHyCs can remove 99.6% PFOA and its Si/Al molar ratio and B value can affect its PFOA removal performance. The CBHyC with Si/Al = 0.3 and B = 2 showed the best PFOA removal performance and highly tolerance to pH of the PFOA solution. A PFOA removal mechanism including counter-ion attraction from quaternary ammonium groups, hydrophobic interaction between PFOA and the long chain alkyls of CBHyCs and hydrolytic polymerization on aluminum species was proposed. In all, CBHyCs is a very promising coagulant for the removal of PFOA in the drinking water and wastewater treatments.

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1. Introduction

Persistent organic pollutants (POPs) can stay in environment for yeas and accumulate in fatty tissue, which is a massive threaten to both water sources and human health [1]. Perfluorooctanoic acid (PFOA) is one of emerging POPs [2]. It is a class of perfluorinated compounds that have been produced and used in numerous industrial and consumer products in the past 60 years [3]. PFOA is highly chemically and biologically stable and toxic towards human and animals and ubiquitously exists in the environment. The solubility of PFOA in water is 8 mM/L at 20–25 °C [4]. Therefore, it can be often transported by water movement such as the rain and surface run off [5] and easily pollutes water sources. For example, up to 105 μg/L PFOA was found in the ground water from the wells near a fire-training area six years after it was last used [6]. Wastewater is one of major source of PFOA because the regular wastewater treatment plants (WWTPs) cannot effectively remove PFOA. Studies have shown that the concentration of PFOA gets even higher in the effluent than in the influent in some WWTPs due to its resistance to the traditional water treatment technologies and the degradation of its precursors [7–9]. For example, the maximum PFOA concentration in the effluent water of WWTPs in Chinese mainland was reported to be 160 μg/L [10]. Therefore, effective and feasible technologies to remove PFOA from water, especially from WWTP effluents are strongly desired.

Several technologies for the PFOA removal, such as photocatalytic degradation [11–13], persulfate oxidation [14–16], electrochemical degradation [17–19], adsorption [20–22], and sonochemical decomposition [23–25], have been reported. However, PFOA degradation requires substantial energy and extreme reaction condition due to its strong C–F bond. For example, the conventional photocatalyst, titanium dioxide, showed very low activity for decomposition of PFOA [26]. Therefore, more active photocatalysts, such as indium oxide [12], β-gallium oxide [27], potassium iodide [28] have been developed for the photocatalytic degradation of PFOA. Compared with other techniques, the PFOA

degradation by persulfate oxidation is more effective in acidic pH [29] at temperatures lower than 80 °C [15]. Electrochemical degradation of PFOA is the most efficient on the anodes with high chemical stability such as boron-doped diamond (BDD) electrode [30,31] and SnO$_2$-based electrode [17,18]. However, all these technologies are unfeasible for conventional WWTPs due to the high cost and issues for large-scale application.

Coagulation is one of the most important water treatment processes and the performance of coagulation highly depends on the coagulant used for the process. There are three classes of coagulants including inorganic coagulants [32–34], organic coagulants [35,36] and inorganic/organic composite coagulants [37–39]. Particulate and colloidal impurities in water can be destabilized and removed by coagulants through double electric layer compression, charge neutralization, polymer bridging and sweep flocculation [40,41]. However, the soluble POPs with low molecular weight [42], especially PFOA (C$_8$HF$_{15}$O$_2$, 414.07 g/mol), cannot be removed by these conventional coagulants [43,44]. Recently, a novel covalently bound inorganic–organic hybrid coagulant (CBHyC) was prepared by the covalent bonding of C–Si with Si–O–Al [45]. By choosing the proper silicon source, the organic functional groups can be coupled to the inorganic component to improve the charge neutralization and adsorption and increase its molecular weight for the rapid removal of the soluble POPs with low molecular weights.

In the present work, a CBHyC was prepared using the silane coupled with an octadecyl-ammonium group as the Si source and characterized with X-ray photoelectron spectrometer (XPS), TEM, zeta potential and octanol/water partition coefficients (K_{ow}) analysis. Its performance for the removal of PFOA was investigated. The effect of basicity (B = OH/Al molar ratio) value and Si/Al molar ratios on its performance were determined. The conventional coagulants including polyaluminum chloride (PACl), polyaluminum silicate chloride (PASiC), poly-diallyl-dimethyl-ammonium chloride (PDADMAC) and PACl/PDADMAC composites were used for a comparison. A possible PFOA removal mechanism for the CBHyC was proposed.

2. Experimental

2.1. Materials

PFOA (CAS No. 335-67-1), PDADMAC (40%, CAS No. 26062-79-3) and HPLC grade methanol were purchased from J &K Scientific Ltd. (USA), Shandong Binzhou Jiayuan Environmental Protection Ltd., (China) and Agilent Technologies Co. (USA), respectively. The ultra-pure water from a Millipore-MilliQ system was used for the preparation of PFOA standard solution and the mobile phase for HPLC–MS analysis. Other chemicals were of analytical grade.

PACl (aluminum concentration (Al$_T$) = 0.2 mol/L, B = 2.0) and PASiC (Al$_T$ = 0.2 mol/L, Si/Al = 0.3 and B = 2.5) were prepared according to the procedure reported by Zhao et al. [45]. PACl/PDADMAC coagulant was prepared by injecting a certain amount of PDADMAC into a PACl solution (Al$_T$ = 0.2 mol/L). The mixture was vigorously stirred at room temperature until a uniform solution was formed. The mass ratio of Al to PDADMAC was set to 4:1 based on the conclusion that the coagulant with this ratio had more favorable coagulation performance and relatively lower residual Al concentration [38].

3-(Trimethoxysilyl)propyl-n-octadecyldimethyl-ammonium chloride was prepared according to the procedure reported by Mebes and Ludi [46] and used as the Si source for the preparation of CBHyCs. CBHyCs were prepared as described in our previous report [47]. A certain amount of 1.0 mol/L AlCl$_3$ solution and the Si source were mixed in a 500 mL triflask to obtain a Si/Al molar

ratio of 0.15, 0.3 and 0.6, respectively, and titrated with NaOH solution under vigorous stirring to obtain B values of 1.0, 2.0 and 2.5. The solutions were diluted with water to obtain a final Al$_T$ of 0.2 mol/L. The hybrid coagulants were denoted hereafter as CBHyC followed by the values of Si/Al molar ratio and B in succession; for example, the hybrid coagulant with Si/Al = 0.3 and B = 1.0 was referred as CBHyC-0.3–1.0.

2.2. Jar test

The test solution was prepared by dissolving PFOA in deionized water to obtain the final concentration of 100 μg/L. The pH of the solution was adjusted to 7.0 with NaHCO$_3$, providing a certain buffer capacity and ionic strength. The coagulation experiments were performed in a program-controlled jar test apparatus with six paddles. Five CBHyCs with different Si/Al molar ratios and B values, PACl, PASiC, PDADMAC and PACl/PDADMAC, with doses in the range of 1×10^{-5} –2×10^{-4} Al mol/L (except PDADMAC dose ranging from 1 to 10 mg/L) were tested. The test solution (1 L) was mixed with the coagulant, vigorously stirred at 250 rpm for 1.5 min, slowly stirred at 50 rpm for 15 min and settled for 30 min. Samples (1 mL) were taken from 2 cm under the surface and filtered with 0.22 μm membrane filters for further analysis. The pH of the solution was adjusted to 5.0 and 9.0 to investigate the effect of pH on the performance of coagulants. All of the coagulation experiments were conducted in triplicate and the mean values were reported.

2.3. Analysis

The concentrations of PFOA in each were determined by HPLC–MS on an Agilent 1100 series HPLC (Agilent, USA) coupled to an ion trap mass spectrometer with an electrospray ionization (ESI) source. Chromatographic separation was performed by injecting 5 μL of sample onto a 2.7 μm particle 2.1 × 150 mm Agilent Poroshell 120 EC-C18 column. The column temperature was set to 50 °C. The mobile phase was methanol/water (80:20, v/v) at the flow of 0.18 mL/min. Mass spectra were acquired in the negative ESI mode and the spectrometer parameters were optimized by tuning on the [M−H]$^-$ and [M-COOH]$^-$ ions of PFOA at 413 m/z and 369 m/z, respectively. The experimental parameters were set as following: nebulizer 40 psi, dry gas 12 mL/min and dry gas temperature 330 °C. The PFOA ions were monitored in selected ion monitoring (SIM) mode and the data were acquired by LC/MCD Trap software 5.3.

Zeta potential was measured with a Malvern Zetasizer 2000 (U. K.) at 25 °C. The sample cell was rinsed with ultrapure water 3 times followed by the test sample twice before the measurement. One millimeter test solution was put in the sample cell and the average of three readings was reported to avoid the variation of species and particle size distribution.

K_{ow} values of PACl, PASiC and CBHyCs were determined at 25 °C by a shake-flask method. Briefly, 0.5 mL coagulant (Al$_T$ = 0.2 mol/L) was dissolved in 5 mL n-octanol-saturated water in a flask, followed by the addition of 5 mL water-saturated n-octanol. The initial concentration of coagulant in octanol phase was measured as C_0 (expressed as Al). The mixture was shaken until the equilibration was reached. The equilibrium concentration of coagulant in water phase was measured as C_w (expressed as Al). K_{ow} was calculated with $K_{ow} = (C_0V_0 - C_wV_w)/C_wV_0$, where V_0 and V_w were the volumes of octanol and water, respectively. Two parallel tests were carried out with 2.5 mL and 5 mL coagulant solution. The value of log K_{ow} was reported.

The morphologies of the coagulants were imaged with 10-time MQ water-diluted CBHyCs, PASiC and PDADMAC solutions on a Hitachi H9000NAR (Japan) TEM with a point resolution of