



ELSEVIER

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Recovery of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from dilute water solution by foam flotation



Yu-Chi Lee^{a,b}, Po-Yen Wang^b, Shang-Lien Lo^a, C.P. Huang^{b,*}

^a Graduate Institute of Environmental Engineering, National Taiwan University, 71, Chou-Shan Rd., Taipei 106, Taiwan, ROC

^b Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

Article history:

Received 25 January 2016

Received in revised form 9 September 2016

Accepted 10 September 2016

Available online 21 September 2016

Keywords:

Perfluorooctanoic acid
Perfluorooctane sulfonate
Foam separation
Foam flotation
Metallic activators

ABSTRACT

The separation and recovery of surfactants, namely, Perfluorooctane sulfonate (PFOS) and Perfluorooctanoate (PFOA) was conducted using foam flotation process aided by metallic activators, including Al(III), Fe(III), La(III), Ca(II), Fe(II), and K(I). The PFOS removal efficiency followed the following decreasing order: Fe(III) \geq La(III) > Al(III) > Ca(II) > Fe(II) > K(I). Both PFOS and PFOA had a removal efficiency of >99% in the presence of 11.5 mM of Fe(III) in 5 min. High Fe(III) dose and elevated initial PFOS and PFOA concentration enhanced surfactant removal. PFOS and PFOA removal also increased with decreasing pH with maximum removal occurring at the lowest pH of 2.3 studied; whereas no significant removal was observed at pH \geq 6. At high pH, hydroxide ion (OH⁻) competed with PFOS or PFOA for Fe³⁺ and formed ferric hydroxo species that impeded surfactant removal. However, by adjusting the pH of the concentrate scum to 7.0, approximately 84–91% of PFOS and PFOA could be recovered. Foam flotation using ferric ion as activator, is a simple, fast, and cost-effective method of broad environmental-friendly applications for the separation and recovery of PFOS and PFOA from dilute water solutions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Perfluorochemicals (PFCs) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are anionic surfactants with high-energy carbon-fluorine (C-F) bonds that can render them persistent in the environment [1]. PFCs have been extensively used for over fifty years especially in many developing industries as surface treatment agents, polymers, metal coating, and fire retardants [2,3] due to their high surface activity, thermal and acid resistance, and hydrophobic and oleophobic properties [4]. Wastewater from photolithographic processes of semiconductor manufacturing can contain PFOS at concentration as high as 1650 mg/L [5], which could seriously impeded the operation of wastewater treatment processes and potentially pollute the receiving water bodies. PFOX chemicals (X = S or A) have been detected in the surface water [6], tap water [7], wildlife [8] as well as human blood [9]. The Stockholm Convention has identified PFOS as a persistent organic pollutant (POP) due to its marked resistance to degradation in the environment. Current research approaches on the control of PFOXs has been focused on chemical decomposition involving extreme temperature and/or pressure conditions such as thermal- or

UV-activated oxidation [10–12] and ultrasonic irradiation [13]. These treatment methods have technical and/or economic constraints, mainly due to high energy-consumption and severe reaction conditions. Therefore, treatment methods of low energy requirement and high potential for material recovery, in lieu of decomposition/destruction, can be cost-effective and highly desirable environmental-friendly alternatives.

Flotation separation has been widely utilized in industry for the recovery of minerals from ores as well as for the separation or concentration of surfactants, proteins, and metallic ions. Furthermore, flotation separation has numeral advantages including low energy and small space requirement, rapid, and easy operation, and low residual concentration of the contaminant in question [14,15]. Foam flotation processes are based on the premise of the ultimate concentration of surface-active compounds at the gas-liquid interface. When air is bubbled through a solution, the surface-active compounds adsorb onto the rising bubbles, which are then being separated from the solution. If the substance to be removed is not surface active, it can adsorb onto a surfactant (as a collector) first. In this study, PFOX chemicals are surfactants with C–F bonds that are more hydrophobic than the conventional surfactants such as dodecyl sulfates. Consequently, no additional surfactant to promote foams is need.

The primary objective of this study was to evaluate the removal and recovery of PFOXs by foam flotation. Batch experiments were

* Corresponding author at: Department of Civil and Environmental Engineering, University of Delaware, 352 Du Pont Hall, Newark, DE 19716, USA.

E-mail address: huang@udel.edu (C.P. Huang).

conducted to study the effect of different metal activators, solution pH, metal dose, initial PFOX concentration on PFOX separation exemplified by perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). To better understand the mechanisms of PFOX removal and recovery, the surface excess and stability constants of metal-PFOX complexes were determined.

2. Experimental

2.1. Materials

Perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), ferric chloride, potassium chloride (KCl), and lanthanum chloride (LaCl_3) were purchased from Aldrich. Ferric chloride (FeCl_3), ferrous chloride (FeCl_2), and aluminum chloride (AlCl_3) from Alfa Aesar and calcium chloride (CaCl_2) from Riedel-deHaën were used as received.

2.2. Methods

The foam flotation system was a simple batch-type column as illustrated in Fig. S1 (Supporting Information). The column was made of polyethylene, 30 cm in length and 4 cm in inside diameter. Air bubbles were introduced by passing compressed air through a gas diffuser having a pore size of 25–50 μm . The air flow rate was adjusted with a Hoke needle valve with a micrometer control and was measured with a soap film flow meter. The air flow rate was maintained at 7.5 L/min. The air was purified by passing through glass wool to remove particulates, ascarite to remove carbon dioxide, and distilled water to control humidity. The bottom of the column was sealed with a rubber stopper with holes for the gas diffuser and a stopcock for sampling and drainage. A lipped side-arm near the top of the column was the foam outlet.

Stock solutions of FeCl_3 , LaCl_3 , AlCl_3 , CaCl_2 , FeCl_2 , KCl, PFOS and PFOA were prepared with DI water and kept in polyethylene containers until use. The initial concentration of PFOX was 20 (0.04), 50 (0.1), 100 (0.2), 120 (0.24), 150 (0.3) and 200 (0.4) mg/L (mM) and the metal concentration was 0.115, 0.23, 0.46, 0.92, 1.15, 2.3, 4.6, 6.9, 9.2 and 11.5 mM in all tests. The initial solution pH was adjusted by NaOH (0.1 M) or H_2SO_4 (0.1 M). At pre-selected time intervals, samples were retrieved by a syringe through the sampling port and analyzed for residual PFOX concentration. In the similar way, the stability constants of Fe-PFOX complexes were obtained by mixing 200 mg/L (0.4 mM) of PFOX and ferric ion (at concentration as mentioned above) without aeration for 12 h with shaking. The surface tension of the solution was determined by a du Nouy interfacial tensiometer using the standard ring method (ASTMD1331-89). All experiments were conducted in triplicate.

2.3. PFOX analysis

The PFOX concentration was analyzed with a high-performance liquid chromatograph (HPLC) (DIONEX, UltiMate 3000, USA.) equipped with a conductivity detector and an anion self-regenerating suppressor (ASRS 300 2-mm U.S.A.). The PFOA was extracted using a 150×2.1 mm 3.5- μm column (Acclaim® Polar Advantage II, C18, DIONEX, USA.) maintained at 30 °C. Solutions of 70:30 (v/v) acetonitrile/Milli-Q water (Solution A), Milli-Q water (Solution B), and 9-mM NaOH/100-mM H_3BO_4 (Solution C) were mixed and introduced at 0.3 mL/min as the mobile phase. The gradient mode was operated as follows: 20% Solution A, 20% Solution B and 40% Solution C for the initial

5 min, 20–60% of Solution A for the next 15 min, and 60% Solution A for the period after 20 min. The limit of detection (LOD) using 50 μL samples, observed from a signal-to-noise (S/N) ratio of 3, was 0.11 mg/L for PFOS and 0.18 mg/L for PFOA.

3. Results

3.1. Metallic cations are effective activators

The removal of all PFOX increased sharply within the first few minutes of bubbling and reached a plateau in 3–5 min; consequently, a reaction time of 5 min was chosen in subsequent experiments. Fig. 1a,b show the PFOX removal in the presence of cationic activators, e.g. Fe^{3+} , La^{3+} , Al^{3+} , Fe^{2+} , Ca^{2+} and K^+ . In general, the extent of removal was dependent on the activator valence. Trivalent cations, more electrophilic than the di- and the monovalent cations and having stronger electrostatic attraction toward the anionic PFOX, had PFOX removal efficiency apparently higher than those of the divalent or monovalent metal ions. The highest PFOX removal percentage occurred in the presence of Fe^{3+} under otherwise identical operation conditions. The PFOS removal efficiency followed the order: $\text{Fe}^{3+} \geq \text{La}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+} > \text{Fe}^{2+} > \text{K}^+$, at approximately 99.5, 99.0, 90.2, 28.9, 25.2 and 3.1% removal, respectively, at a dose of 11.5 mM.

3.2. Initial PFOX and ferric concentration affected PFOX removal

Fig. 2a,b show the removal efficiency of PFOX as a function of the total concentration of Fe^{3+} and PFOX. Results showed that PFOX removal was enhanced at high PFOX concentration, in part, due to the elevated surface activity, which facilitated its separation from the aqueous solution under foam flotation. Furthermore, an increase in ferric dose also resulted in a high PFOX removal efficiency. Moreover, the PFOS removal efficiency was much greater than that of PFOA at similar ferric dose range. By decreasing the ferric dose, e.g., 0–1.15 mM, which was close to 1:1 M ratio of PFOX/ $\text{Fe}(\text{III})$, the PFOX removal efficiency dropped rapidly. The aggregates formed in highly-diluted PFOX solutions, e.g., 20–50 mg/L (or 0.04–0.1 mM), by keeping the ferric dose at less than 1.15 mM, were very fine and foam flotation seemingly became ineffective. However, by increasing $\text{Fe}(\text{III})$ dose to 11.5 mM, a high PFOX removal efficiency (exceed 99%) was observed in 5 min.

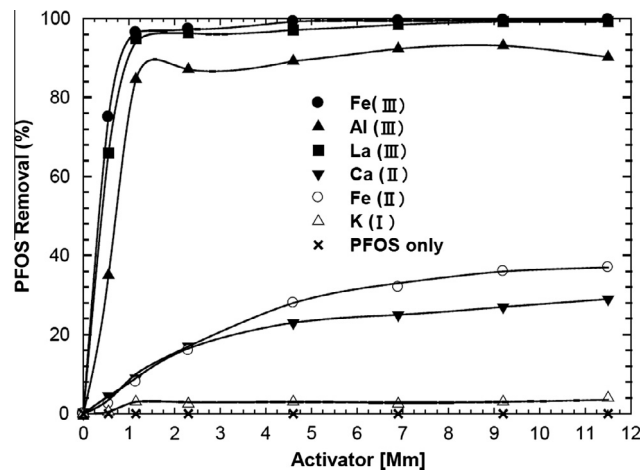


Fig. 1. The effect of different metal ions as activators on the removal of (a) PFOS, (b) PFOA. Experimental conditions: [PFOX] = 200 mg/L; pH = 2.3; reaction time = 5 min.

Download English Version:

<https://daneshyari.com/en/article/4990302>

Download Persian Version:

<https://daneshyari.com/article/4990302>

[Daneshyari.com](https://daneshyari.com)