

Influence of Solution Chemistry on Adsorption of Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA) on Boehmite

Fei Wang, Kaimin Shih

Abstract—The persistent nature of perfluorochemicals (PFCs) has attracted global concern in recent years. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the most commonly found PFC compounds, and thus their fate and transport play key roles in PFC distribution in the natural environment. The kinetic behavior of PFOS or PFOA on boehmite consists of a fast adsorption process followed by a slow adsorption process which may be attributed to the slow transport of PFOS or PFOA into the boehmite pore surface. The adsorption isotherms estimated the maximum adsorption capacities of PFOS and PFOA on boehmite as $0.877 \mu\text{g}/\text{m}^2$ and $0.633 \mu\text{g}/\text{m}^2$, with the difference primarily due to their different functional groups. The increase of solution pH led to a moderate decrease of PFOS and PFOA adsorption, owing to the increase of ligand exchange reactions and the decrease of electrostatic interactions. The presence of NaCl in solution demonstrated negative effects for PFOS and PFOA adsorption on boehmite surfaces, with potential mechanisms being electrical double layer compression, competitive adsorption of chloride.

Keywords—PFOS; PFOA; adsorption; electrostatic interaction; ligand exchange

I. INTRODUCTION

PERFLUORO-CHEMICALS (PFCs) are a type of anionic surfactant with high-energy carbon-fluorine (C-F) bonds that render them persistent in the environment [1].

Within the PFC group, the compounds perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) have been widely found in sediment, sludge, municipal wastewater, coastal water, and even tap water [2]-[5]. Due to the wide distribution and bioaccumulation of PFOS and PFOA in the environment, they have been proposed as persistent organic pollutants (POPs) [6]. Different from other POPs, however, PFOS and PFOA are highly water-soluble; thus, they are easy to transport in an aquatic environment. At the same time, the hydrophobic chain and hydrophilic functional groups may provide opportunities for PFOS and PFOA to adsorb onto the surfaces of a variety of environmental solid matrices.

Because of the persistent nature of PFOS and PFOA in the environment and these compounds' harmful effects on human beings, studies to understand their fate and transport in aquatic environments is important [3], [7]-[9]. It was reported that both organic matter and minerals played important roles in the PFC sorption process [3]. In groundwater systems, the fate and transport of PFCs presumably has a strong dependence on interactions with surrounding mineral surfaces, however, the interactions between PFCs and minerals are not well characterized.

Kaimin Shih is with the University of Hong Kong, Hong Kong, China (phone: +852-28591972; fax: +852-28598987; e-mail: kshih@hku.hk).

Fei Wang is with the University of Hong Kong, Hong Kong, China (e-mail: wf1984@hku.hk).

Boehmite (AlOOH) is a common form of hydrated aluminum oxide that usually exists as fine-grained constituents in soils and sediments due to its thermodynamic stability under hydrous conditions [10]. Boehmite is also an important industrial mineral used as a catalyst or adsorbent because of its ability to retain high surface area [10]-[11]. As the point of zero charge (PZC) of boehmite has been determined to be between 7.7 and 9.4 [12], it is likely to exist with positive charges on its surface in nature. Boehmite's protonated surface renders it easy for compounds with negative charges to be attached by electrostatic attraction and thus PFOS and PFOA, which are anionic, are likely to be adsorbed on the surface of boehmite and this mechanism may play an important role in the fate and transport of these compounds in the environment.

The adsorption behavior of PFOS and PFOA on boehmite has not yet been systematically investigated; therefore the first goal of this study was to quantify the adsorption capacities of PFOS and PFOA on boehmite through sorption kinetics and isotherm experiments. Experiments observing the adsorption behavior of PFOS and PFOA on boehmite under different solution pH and ionic strengths were then performed to observe their effect on the adsorption process.

II. EXPERIMENTS

All sorption experiments were conducted in 50 ml polypropylene copolymer (PPCO) Nalgene centrifuge tubes (Rochester, NY) containing 0.1 g of boehmite and 20 ml of solution with varying PFOS or PFOA concentrations. The tubes were shaken at 150 rpm and kept at 25 °C for 72 h.

The pH was adjusted by 0.1 M HCl and 0.1 M NaOH solutions, and the ionic strengths were controlled by adding 1 M stock solutions of NaCl(aq). The kinetic sorption experiments used an initial PFOS or PFOA concentration of 200 $\mu\text{g}/\text{L}$.

The sorption isotherm experiments were carried out with PFOS or PFOA concentrations ranging from 50 $\mu\text{g}/\text{L}$ to 1000 $\mu\text{g}/\text{L}$. In preliminary tests, the standard deviations of quality control experiments are lower than 1%, which indicated the reproducibility of the experiment in current study.

After the adsorption experiments, 1.5 ml of sample solution was diluted with 3.5 ml methanol (v/v = 3/7). The mixture was then filtered with a 0.2 μm Whatman inorganic membrane filter (Maidstone, UK), and the initial 3 ml of the mixture was discarded to reduce the potential effect of membrane adsorption.

The concentrations of PFOS (or PFOA) were determined using a Waters Acquity ultra-performance LC/MS/MS system (UPLC/MS/MS) equipped with a $50 \times 2.1\text{-mm}$ Waters BEH C18 column (1.7- μm particle size) and tandem quadrupole mass spectrometers (Milford, MA).

III. RESULTS AND DISCUSSION

Fig. 1 shows the adsorption kinetics of PFOS and PFOA on boehmite, which indicates that approximately 48 h of agitation were required to reach the equilibrium for both PFOS and PFOA adsorption, similar to the ranges reported in studies of PFOS adsorption on a variety of minerals [7],[13].

This result shows that the mineral-water interfaces are accessible for PFOS and PFOA molecules, and thus equilibrium was rapidly reached. Overall, the kinetic behavior of PFOS or PFOA on boehmite consists of a fast adsorption followed by a slow adsorption, which is consistent with the two-step model for surfactant adsorption on solid surfaces [14].

Considering our cases, the slow adsorption process observed in this study may be attributed to the slow transport of PFOS or PFOA to the boehmite surface after the concentration of PFOS or PFOA in the aquatic phase dramatically decrease (around 70-80%) with a rapid adsorption within the initial 3h.

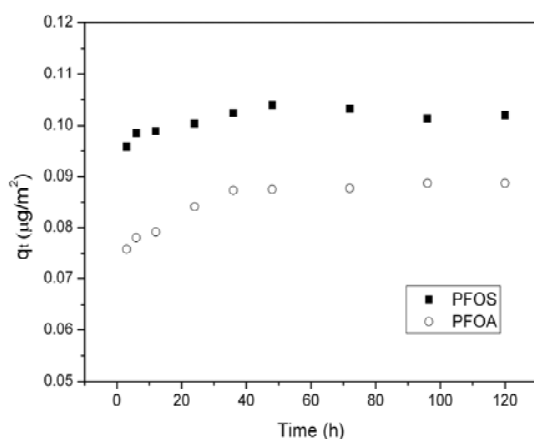


Fig. 1 PFOS and PFOA adsorption kinetics on boehmite

The adsorption isotherms of PFOS and PFOA on boehmite at pH 7 are shown in Fig. 2. The Langmuir and Freundlich equations [15] were applied to model the experimental data, and the derived constants are provided in Table 1. The model equations can be expressed as follows:

$$\text{Langmuir model: } q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (1)$$

$$\text{Freundlich model: } q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

where q_e is the adsorbate amount on the surface of the adsorbent at equilibrium [$\mu\text{g}/\text{m}^2$], C_e is the equilibrium concentration of adsorbate in solution [$\mu\text{g}/\text{L}$], q_m is the maximum sorption capacity [$\mu\text{g}/\text{m}^2$], and K_L is the Langmuir adsorption constant [$\text{L}/\mu\text{g}$]. K_F is the Freundlich adsorption constant [$(\mu\text{g}/\text{m}^2)(\mu\text{g}/\text{L})^{-n}$], which suggests the adsorption capacity, and n represents the measure of the nonlinearity involved.

Adsorbate	Langmuir constants		
	K_L ($\text{L}/\mu\text{g}$)	q_m ($\mu\text{g}/\text{m}^2$)	R^2
PFOS	0.00622	0.877	0.985
PFOA	0.00512	0.633	0.984
Adsorbate	Freundlich constants		
	$K_F [(\mu\text{g}/\text{m}^2)(\mu\text{g}/\text{L})^{-n}]$	n	R^2
PFOS	0.0139	0.678	0.969
PFOA	0.0155	0.559	0.980

NOTE: “ R^2 ” is the correlation coefficient of fitting result

The adsorption isotherms of PFOS and PFOA were found to fit well with both the Langmuir and Freundlich equation, judging from the correlation coefficients (R^2) in Table 1. The good fitness of Langmuir equation hints that the adsorption of PFOS and PFOA may occur on the boehmite surface with monolayer coverage. The good fitness of Freundlich equation as well as Langmuir equation indicates the concentration of PFOS and PFOA may also dominate the adsorption process.

It has been suggested that amphiphilic compounds may adsorb onto minerals in hemi-micelles when the organic ions are present at 0.001 to 0.01 of the critical micelle concentration [16]. The critical micelle concentration (CMC) of PFOS and PFOA was reported at around 8 mM and 25 mM [17], respectively. In this study, the PFOS and PFOA concentrations were all controlled below 1 ppm (around 0.002 mM) in experiment, and thus the hemi-micelles were unlikely to form during the adsorption processes. This condition also supports the monolayer adsorption behavior described by Langmuir model.

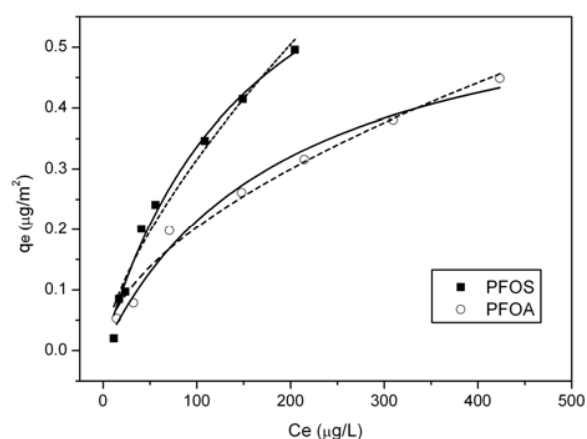


Fig. 2 PFOS and PFOA adsorption isotherms on boehmite. The solid lines are the fitted Langmuir isotherms, and the dashed lines are the fitted Freundlich isotherms

For adsorption on boehmite, the maximum adsorption capacities were estimated to be $0.877 \mu\text{g}/\text{m}^2$ for PFOS and $0.633 \mu\text{g}/\text{m}^2$ for PFOA.

This result is similar to our previous result that γ -alumina showed a higher affinity toward PFOS than PFOA. The different adsorption levels were attributed between perfluorosulfonate and perfluorocarboxylate to the slightly larger size of the sulfonate moiety as compared to the carboxylate moiety [3].

According to Pearson's concept of hard- and soft-acids/bases, the carboxylate group is a soft base while the sulfonate group is a relatively hard one, and a hard base is more readily adsorbed on oxide surfaces which are hard acids [18]-[19].

The effects of varying pH on the adsorption of PFOS and PFOA are shown in Fig. 3. Since the pKa values of PFOS and PFOA are lower than 1, PFOS and PFOA mainly existed in anionic forms within the pH range (4.0-7.5) tested in this study [20]-[21].

The PZC of the boehmite in this study was measured at around 8.4, and hence the surface of boehmite was positively charged in the tested pH range. The protonation reaction of boehmite and the electrostatic attraction between anionic PFOS or PFOA and protonated boehmite are as follows:



Therefore, the decrease of solution pH can increase the positive sites on the boehmite surface, which may lead to the increase of PFOS and PFOA adsorption we observed. The adsorption behavior within this pH range can be explained by the increase in electrostatic interactions and/or the formation of surface complexes by ligand exchange [22]. In our previous study, the adsorbed concentrations of PFOS or PFOA on γ -alumina ($\text{pH}_{\text{pzc}} = 8.5$) increased three to four times when pH decreased from 6.5 to 4.0.

However, only a 20%-30% increase of PFOS or PFOA adsorption levels on boehmite was observed when the pH decreased from 7.0 to 4.0. This comparison indicates that the adsorption behavior of PFOS and PFOA on boehmite may not be fully due to the electrostatic interaction mechanism. The increase of H^+ concentration not only increases Al-OH^{2+} sites, but also decreases the Al-OH sites on boehmite surfaces (Eq. 4).

Therefore, if the pH is decreased, the ligand exchange reaction (Eq. 3) will be decreased and the electrostatic interaction (Eq. 5) will be increased. The observed moderate increases of PFOS and PFOA adsorption following the decrease of solution pH may be attributed to electrostatic interaction counteracted by the reduced ligand exchange.

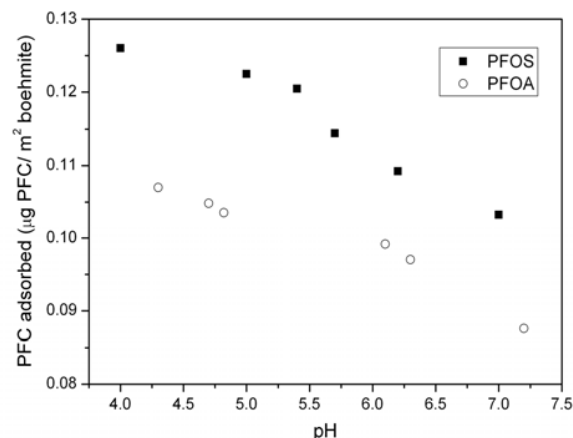


Fig. 3 Effect of pH on the adsorption of PFOS and PFOA on boehmite. The results illustrate that the increase of pH leads to a moderate decrease of PFC adsorption

Salts are abundant from natural and anthropogenic sources, and the salinity of surface water and groundwater can vary considerably. For example, NaCl can be used as a road de-icing agent and enters wetlands, lakes and rivers [23]. Thus, the influence of NaCl on PFOS and PFOA adsorption may be important in determining the environmental fates of PFOS and PFOA. Fig. 4 shows the influence of different NaCl concentrations on the PFOS and PFOA adsorption on boehmite surfaces, and indicates a decreasing trend of PFOS and PFOA adsorption with the increase of NaCl concentration. A possible explanation of this result is that the higher ionic strength causes a decrease of electrostatic attraction between the positively charged boehmite surface and the negatively charged PFC molecules, due to the compression of the electrical double layer (EDL), and the reduction in ζ -potential [9]. The adsorption of adsorbates (PFOS and PFOA) on adsorbents (boehmite) is usually associated with the free energy between adsorbate and adsorbent, which can be evaluated by the equation as follows:

$$G_{\text{electrostatic, adsorbate-adsorbent}} = zF\Psi_d = -F\Psi_d \approx -F\zeta \quad (6)$$

where z is the charge of PFOS or PFOA ions (-1), F is the Faraday constant (96,485 C/mol), and Ψ_d is the diffuse layer potential (V). Ψ_d can be approximated by the ζ -potential, as the shear plane is often located close to the inner boundary of the diffuse layer [23]-[25]. Thus, the reduction of ζ -potential can lead to the increase in free energy, which causes the reduction in PFOS and PFOA adsorption. In addition, It was reported their observation of minor direct uptake of chloride by aluminum oxide [26]. In such a case, the potential hindering effect due to the competitive adsorption of chloride ions on the active adsorption sites may also decrease the adsorption of PFOS and PFOA on the boehmite surface [27].

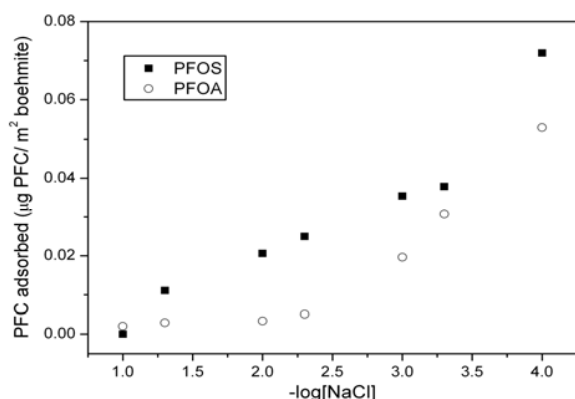


Fig. 4 Effect of NaCl concentration on the adsorption behavior of PFOS and PFOA

IV. CONCLUSION

Kinetic experiments showed that adsorption equilibrium can be achieved within 48 hours and the boehmite (AlOOH) surface is receptive to perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) adsorption. The sulfonate group in PFOS is a relatively harder base than the carboxylate group in PFOA, and a hard base is more readily adsorbed on boehmite surfaces. Therefore, in this study boehmite was observed to exhibit a higher affinity toward PFOS than PFOA. The experimental data suggest a moderate effect of solution pH on PFOS and PFOA adsorption on boehmite, resulting in the increase of electrostatic interaction and the decrease of ligand exchange reaction at lower pH. The NaCl concentrations showed a negative effect for PFOS and PFOA adsorption on boehmite, potentially due to EDL compression and the competitive adsorption of chloride ions. The results of this study indicate that environments of high salt content, such as subsurface pore water, will substantially hinder the adsorption of PFOS and PFOA on boehmite surfaces.

ACKNOWLEDGMENT

We gratefully acknowledge the funding for this research provided by the General Research Fund scheme (HKU 716809E, HKU 716310E) and Special Equipment Grant (SEG_HKU10) of the Research Grants Council of Hong Kong.

REFERENCES

- [1] J. P. Giesy, K. Kannan, "Perfluorochemical surfactants in the environment," *Environ. Sci. Technol.*, vol. 36, pp. 146A-152A, 2002.
- [2] M.K. So, S. Taniyasu, N. Yamashita, J.P. Giesy, J. Zheng, Z. Fang, S.H. Im, P.K.S. Lam, "Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea," *Environ. Sci. Technol.*, vol. 38, pp. 4056-4063, 2004.
- [3] C. P. Higgins, R. G. Luthy, "Sorption of perfluorinated surfactants on sediments," *Environ. Sci. Technol.*, vol. 40, pp. 7251-7256, 2006.
- [4] L.M. Yim, S. Taniyasu, L.W.Y. Yeung, G. Lu, L. Jin, Y. Yang, P.K.S. Lam, K. Kannan, N. Yamashita, "Perfluorinated compounds in tap water from china and several other countries," *Environ. Sci. Technol.*, vol. 43, pp. 4824-4829, 2009.
- [5] R. Ma, K. Shih, "Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong," *Environ. Pollut.*, vol. 158, pp. 1354-1362, 2010.
- [6] R. Loos, G. Locoro, T. Huber, J. Wollgast, E.H. Christoph, A. de Jager, B. Manfred Gawlik, G. Hanke, G. Umlauf, J.M. Zaldívar, "Analysis of perfluorooctanoate (PFOA) and other perfluorinated compounds (PFCs)

in the River Po watershed in N-Italy," *Chemosphere*, vol. 71, pp. 306-313, 2008.

- [7] R.L. Johnson, A.J. Anschutz, J.M. Smolen, M.F. Simcik, R. Lee Penn, "The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces," *J. Chem. Eng. Data*, vol. 52, pp. 1165-1170, 2007.
- [8] C.Y. Tang, Q. Shiang Fu, D. Gao, C.S. Criddle, J.O. Leckie, "Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces," *Water Res.*, vol. 44, pp. 2654-2662, 2010.
- [9] F. Wang, K. Shih, "Adsorption of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on alumina: Influence of solution pH and cations," *Water Res.*, vol. 45, pp. 2925-2930, 2011.
- [10] A. Navrotsky, "Thermochemistry of nanomaterials," *Rev. Mineral. Geochem.*, vol. 44, pp. 73-103, 2001.
- [11] T.H. Yoon, S.B. Johnson, C.B. Musgrave, G.E. Brown Jr, "Adsorption of organic matter at mineral/water interfaces: I. ATR-FTIR spectroscopic and quantum chemical study of oxalate adsorbed at boehmite/water and corundum/water interfaces," *Geochim. Cosmochim. Acta*, vol. 68, pp. 4505-4518, 2004.
- [12] B. Kasprzyk-Hordern, "Chemistry of alumina, reactions in aqueous solution and its application in water treatment," *Adv. Colloid Interface Sci.*, vol. 110, pp. 19-48, 2004.
- [13] Q. Zhou, S. Deng, Q. Yu, Q. Zhang, G. Yu, J. Huang, H. He, "Sorption of perfluorooctane sulfonate on organo-montmorillonites," *Chemosphere*, vol. 78, pp. 688-694, 2010.
- [14] R.F. Tabor, J. Eastoe, P.J. Dowling, "A two-step model for surfactant adsorption at solid surfaces," *J. Colloid Interface Sci.*, vol. 346, pp. 424-428, 2010.
- [15] W.J. Weber Jr, P.M. McGinley, L.E. Katz, "Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport," *Water Res.*, vol. 25, pp. 499-528, 1991.
- [16] R. P. Schwarzenbach, P. M. Gschwend, D. M. Imboden, "Environmental Organic Chemistry", first ed. John Wiley & Sons, New York, 1993.
- [17] K. Harada, F. Xu, K. Ono, T. Iijima, A. Koizumi, "Effects of PFOS and PFOA on L-type Ca²⁺ currents in guinea-pig ventricular myocytes," *Biochem. Biophys. Res. Commun.*, vol. 329, pp. 487-494, 2005.
- [18] V. Snoeyink, D. Jenkins, "Water Chemistry", John Wiley & Sons, New York, 1980.
- [19] F. H. Walters, "Design of corrosion inhibitors: Use of the hard and soft acid-base (HSAB) theory," *J. Chem. Educ.*, vol. 68, pp. 29, 1991.
- [20] D. Brooke, A. Footitt, T.A. Nwaogu, "Environmental Risk Evaluation Report: Perfluorooctanesulphonate (PFOS)." Environment Agency, Chemicals Assessment section, Wallingford, UK, 2004.
- [21] K. U. Goss, "The pKa values of PFOA and other highly fluorinated carboxylic acids," *Environ. Sci. Technol.*, vol. 42, pp. 456-458, 2008.
- [22] W. Stumm, "Aquatic colloids as chemical reactants: surface structure and reactivity," *Colloids Surf. A: Physicochem. Eng. Asp.*, vol. 73, pp. 1-18, 1993.
- [23] F. Xiao, X. Zhang, L. Penn, J.S. Gulliver, M.F. Simcik, "Effects of monovalent cations on the competitive adsorption of perfluoroalkyl acids by kaolinite: experimental studies and modeling," *Environ. Sci. Technol.*, vol. 45, pp. 10028-10035, 2011.



Kaimin Shih is currently an Assistant Professor in the Department of Civil Engineering at the University of Hong Kong. His main research interest is in engineering and employing material properties for innovative environmental technologies particularly for solid waste and water treatment, such as the stabilization of hazardous metal sludge/ash by ceramic materials and novel catalysts/membranes for water purification/ decontamination technology. Dr. Shih received his MS (2000) and PhD (2005) degrees in Environmental Engineering & Science from Stanford University (USA).

Before joining HKU in 2007, he was a Postdoctoral Scholar at Stanford University and has years of experience as a teaching assistant/guest lecturer in the environmental engineering courses at Stanford and its joint programs. Dr. Shih is currently also a Board Member of Hong Kong Waste Management Association, a Director of Overseas Chinese Environmental Engineers and Scientists Association, and serves as the editors/reviewers for a number of professional environmental publications. Fei Wang received the B.S., M.S. degrees in environmental science and technology from the Sun Yat-sen University, Guangzhou, China, in 2007 and 2009. Now he is the PhD candidate in civil engineering in Hong Kong University. His research topics are the fate and transport of PFCs in aqueous environment and sludge thermal treatment processes.