

ADSORPTION PROPERTIES OF PERFLUOROHEXANOIC ACID ONTO ANION EXCHANGE POLYMERS IN INDUSTRIAL WASTEWATER

Wilaingam K*, Tanaka S, Chularueangakorn P, Suzuki Y, Ono R, Fujii S

Graduate School of Global Environmental Studies, Kyoto University, Yoshida Campus, Sakyo-ku, Kyoto, Japan

Introduction

Concern about perfluorinated compounds (PFCs) is increasing due to their adverse effects on animals and humans. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are dominant PFCs which are used in a variety of industrial products such as plating, semiconductor production and fluoropolymer manufacturing¹. In 2009, PFOS was listed as a persistent organic pollutant in Annex B of the Stockholm Convention. PFOA and related chemicals are currently being phased out by eight major manufacturers through a voluntary stewardship agreement with USEPA. Some companies have switched to C6 PFCs such as perfluorohexanoic acid (PFHxA) to replace C8 chemicals such as PFOS and PFOA. Therefore, the trend of using PFHxA in industries is increasing.

Biological treatment process was not effective to remove PFCs in wastewater². Recently, high levels of PFHxA were detected in the downstream of PFHxA related industries. Thus, the development of effective PFHxA removal techniques in industrial wastewater is required. Adsorption is one of the effective techniques to remove PFCs in water/wastewater³. **Figure 1** shows the number of previous research works on adsorption of PFHxA compared to PFOS and PFOA. Activated carbon is used to remove PFOS and PFOA in synthetic wastewater. Recently, some researchers reported that anion exchange polymers have higher adsorption capacities of PFOS and PFOA than activated carbon⁴. Previous studies mostly developed adsorption treatment techniques for synthetic wastewater. The adsorption of PFHxA onto anion exchange polymers has not been studied in wastewater.

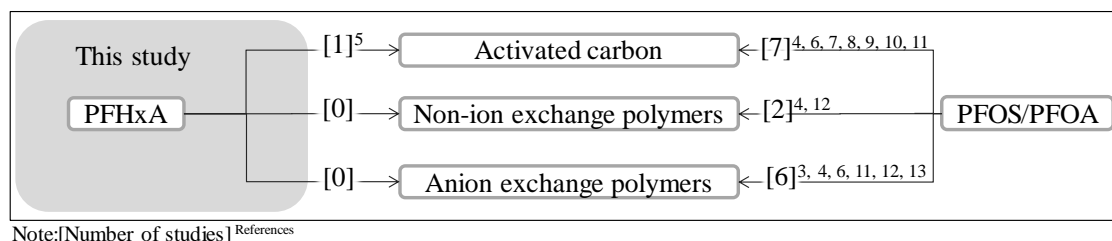


Fig. 1 The number of previous research works on adsorption of PFHxA compared to PFOS and PFOA

In this study, adsorption capacities and rates of PFHxA onto five anion exchange polymers, non-ion exchange polymers and granular activated carbon (GAC) were investigated in industrial wastewater.

Materials and methods

Fluorochemicals wastewater source and wastewater characteristics

In this study, a sample was collected from the treated wastewater of a fluorochemical industry in Japan on June 17th, 2013. This wastewater was treated by the coagulation process (using polyaluminium chloride as a coagulant) followed by the adsorption process (using GAC as an adsorbent). The sample was filtrated through a Whatman GB/F and stored at 4^oC. **Table 2** shows the wastewater characteristics in this study

Table 2 Wastewater characteristics in this study

| Parameter | Value | Analytical instrument |
|---------------------------------|-------|--|
| PFHxA (mg/L) | 50.3 | High-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS, Agilent 1200SL) |
| Chloride ion (mg/L) | 243 | Ion chromatograph (Dionex ICS-2000) |
| Sulfate ion (mg/L) | 360 | Ion chromatograph (Dionex ICS-2000) |
| Dissolved organic carbon (mg/L) | 54.2 | TOC analyzer (TOC-V _{CSN} , Shimadzu) |
| pH | 7.2 | pH meter (Horiba D-51S) |

Chemicals and adsorbents

PFHxA (98%), methanol (LC/MS grade) and acetonitrile (LC/MS grade) were purchased from Wako Chemicals (Japan). Anion exchange polymers, non-ion exchange polymers and GAC were purchased from Puro-lite Company, Sigma Aldrich and Calgon Mitsubishi Chemical. **Table 2** shows properties of these adsorbents. The polymeric adsorbents were washed with *Milli-Q* water followed by methanol to remove dirt and PFCs. Then, they were washed again by *Milli-Q* water to remove the remaining methanol and dried at 50°C. The GAC was washed with *Milli-Q* water (25°C) several times, and boiled at 80°C in *Milli-Q* water for two hours to remove impurities. The GAC was dried at 105°C for 48 hours followed by being crushed and sieved through 1.0-1.4 mm meshes. The total pore volume was 0.61 cm³/g and the pore size distributions of macropores, mesopores and micropores were 0.04, 0.09 and 0.48 cm³/g, respectively.

Table 2 Properties of anion exchange polymers, non-ion exchange polymers and GAC

| Type of adsorbent | Name of adsorbent ^a | Matrix | Functional group | Diameter (mm) | Exchange capacity (eq/L) | Surface area (m ² /g) |
|---------------------------|--|---|--|---------------|--------------------------|----------------------------------|
| Anion exchange polymers | PFA300 ^a | Polystyrene crosslinked with divinylbenzene | R-(CH ₃) ₂ (C ₂ H ₄ OH)N ⁺ (Dimethylethanolaminium) | 0.56 | 1.4 | - |
| | PFA400 ^a | | R-(CH ₃) ₃ N ⁺ (Trimethylbenzylammonium) | 0.57 | 1.3 | - |
| | A860 ^a | Macroporous polyacrylic | | 0.3-1.2 | 0.8 | - |
| | BA103 ^a | Macroporous polystyrene crosslinked with divinylbenzene | R-(CH ₃) ₂ N (Tertiary-amine) | 0.3-1.2 | 1.5 | - |
| | MN102 ^a | | | | 0.3 | - |
| Non-ion exchange polymers | XAD4 ^b | Macroreticular crosslinked aromatic polymer | - | 0.35-1.18 | - | > 750 |
| Granular activated carbon | GAC ^c (Filtrisorb 400, coal based) | Stacked layers of fused hexagonal ring of C atoms | - | 0.25-0.5 | - | 900-1,100 |

Note: a. Puro-lite company (www.puro-lite.com), b. Sigma Aldrich company (www.sigmaldrich.com), c. Calgon Mitsubishi Chemical (www.calgoncarbon.com)

Adsorption experiments

Adsorption isotherm and kinetics experiments were conducted by using seven adsorbents. **Table 3** shows the summary of experimental conditions of the adsorption isotherm and kinetics experiments. The adsorption isotherm experiments were carried out using a bottle-point technique. Different amounts of each adsorbent (1-25 mg) were placed into polypropylene (PP) bottles containing 50 mL of fluorochemical wastewater (50.3 mg/L of PFHxA). Adsorbents were not added into the bottles of controlled samples. All samples were shaken at 120 rpm and 25°C for 96 hours using a thermo shaker (*n*=2). The samples were diluted with 40% acetonitrile in *Milli-Q* water and analyzed using HPLC-MS/MS. For kinetics experiments, 50 mg of adsorbents was placed into 100 mL of the fluorochemical wastewater with the same shaking condition. The samples were collected at different contact times and analyzed using HPLC-MS/MS. The instrumental detection limit and instrumental quantification limit were 0.02 and 0.07 µg/L, respectively.

Table 3 Summary of experimental conditions in this study

| Experiment | Adsorbent | Adsorbent amount (mg) | Wastewater volume (mL) | Shaking condition |
|--|--|----------------------------------|------------------------|---|
| Adsorption isotherm ^a (<i>n</i> = 2) | PFA300, PFA400, A860, BA103, MN102, XAD4 and GAC | 1, 2, 4, 6, 8, 10, 15, 20 and 25 | 50 | 120 rpm and 25°C for 96 h |
| Adsorption kinetics (<i>n</i> = 2) | PFA300, PFA400, A860, BA103, MN102, XAD4 and GAC | 50 | 100 | 120 rpm and 25°C for 1, 3, 6, 12, 18, 24, 48, 72 and 96 h |

Note : a. Controlled samples were not added adsorbent (*n* = 2).

Results and discussion

Adsorption isotherms

The adsorption isotherms of adsorbents were determined from the adsorption equilibrium data with the *Freundlich* equation. The *Freundlich* equation is defined by

$$q_e = K_f \cdot C_e^{1/n} \quad (1)$$

where q_e (mg/g) is the concentration of PFHxA in solid phase and C_e (mg/L) is the equilibrium concentration of PFHxA in solution. K_f ((mg/g)/(mg/L)^{1/n}) is the *Freundlich* adsorption constant related to adsorption capacity. n is the *Freundlich* exponent. The *Freundlich* isotherm constants of PFHxA adsorbed onto the adsorbents in this study are shown in **Table 4**. The *Freundlich* equation fitted all adsorbents with squared correlation coefficients (R^2) ranging from 0.782 to 0.980.

Table 4 The *Freundlich* isotherm constants and pseudo-second order model kinetic parameters for the adsorption of PFHxA

| Name of adsorbent | <i>Freundlich</i> isotherm constants | | | Pseudo-second order model kinetic parameters | | | |
|-------------------|---------------------------------------|------|-------|--|-------------------|-------------------|-------|
| | K_f (mg/g)/(mg/L) ^{1/n} | 1/n | R^2 | q_e (mg/g) | k_2 (g/mg/h) | V_0 (mg/g/h) | R^2 |
| PFA300 (◆) | 36.33 | 0.52 | 0.980 | 88.9 | 0.0103 | 81.3 | 0.997 |
| PFA400 (×) | 24.55 | 0.59 | 0.974 | 85.3 | 0.0080 | 58.2 | 0.991 |
| A860 (●) | 0.05 | 1.68 | 0.881 | 7.3 | 0.0101 | 0.5 | 0.914 |
| BA103 (▲) | 37.12 | 0.56 | 0.980 | 96.7 | 0.0108 | 101.3 | 0.998 |
| MN102 (+) | 0.73 | 1.08 | 0.846 | 23.3 | 0.0202 | 11.0 | 0.998 |
| XAD4 | 0.04 | 1.79 | 0.782 | 9.8 | 0.0365 | 3.5 | 0.980 |
| GAC | 1.66 | 0.92 | 0.860 | 58.5 | 0.0057 | 19.4 | 0.985 |

The amounts of PFHxA adsorbed onto the adsorbents are K_f values at an equilibrium concentration ($C_e = 1$ mg/L). Anion exchange polymers had different types of polymeric matrix, functional group, ion exchange capacity, and porosity that affected their PFHxA adsorption capacities. Among five anion exchange polymers, styrene polymers (PFA300, PFA400, BA103 and MN102) had higher adsorption capacities of PFHxA than acrylic polymers (A860). The PFHxA adsorption capacities of styrene polymers were related to their exchange capacities as shown in **Table 1**. BA103 had the highest adsorption capacity of PFHxA (37.12 mg/g) because it had the highest exchange capacity (1.5 eq/L). PFA300 had higher adsorption capacity than PFA400 because type II polymers have a slightly higher adsorption capacity than types I polymers¹⁴. XAD4 is white translucent beads characterized by a macroreticular porous structure. The polystyrene matrix of XAD4 is highly hydrophobic. This means that XAD4 is difficult to contact with solutions. As a result, XAD4 had a small adsorption capacity of hydrophilic organic compounds from solutions¹⁵. XAD4 exhibited the lowest adsorption capacity of PFHxA (0.04 mg/g). GAC had a lower PFHxA adsorption capacity than anion exchange polymers except for A860 and MN102. On the other hand, GAC had a higher adsorption capacity than non-ion exchange polymers (XAD4). It can be explained that the bonding forces between adsorbates and adsorbents of non-ion exchange polymers were usually weaker than those of GAC¹⁶.

The 1/n values indicate linearity/nonlinearity in the *Freundlich* equation. The 1/n values were closer to 1 for GAC than for anion exchange polymers (PFA300, PFA400, A860 and BA103) and non-ion exchange polymers (XAD4). It means that these anion exchange polymers had more nonlinearity than GAC due to the heterogenous adsorption sites on the polymers such as ions exchange and polymeric matrix, and the electrostatic repulsion⁵.

Adsorption kinetics

To understand the behavior of adsorption kinetics, the pseudo-second order model was introduced to explain the adsorption rates. This model assumes that that adsorption rate is controlled by chemical adsorption and the adsorption capacity is proportional to the number of active sites on the adsorbent. Base on the pseudo-second order model, the adsorption rate can be expressed by

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} = \frac{1}{v_0} + \frac{t}{q_e} \quad (2)$$

where k_2 (g/mg/h) is the rate constant of pseudo-second order model adsorption. q_e and q_t (mg/g) are the amounts of PFHxA adsorbed onto the adsorbents at equilibrium and at time t . v_0 (mg/g/h) represents the initial adsorption rate. **Table 4** shows the kinetics data of all adsorbents fitted with the pseudo-second order model ($R^2 = 0.914 - 0.998$).

The values of q_e and v_0 depend on polymeric matrix, functional group and porosity of the adsorbents. BA103 had the highest values for the initial adsorption rate, followed by PFA300, PFA400, GAC, MN102, XAD4 and

A860. The macroporous polymers of BA103 had a faster initial adsorption rate than the gel ones (PFA300 and PFA400). PFA300 had a faster adsorption rate than PFA400 because the functional group of PFA300 (type II) has an ethanol group ($-C_2H_4OH$). The ethanol group possesses more open structures than PFA400¹⁷. GAC had a slower initial adsorption rate than BA103, PFA300 and PFA400 because it had a high proportion of micropores.

Figure 2 shows the relationships of exchange capacities with the *Freundlich* adsorption constant and with the initial adsorption rate. The adsorbents with higher exchange capacities had higher values of K_f and v_0 . This means that the higher exchange capacities of anion exchange polymers caused the higher adsorption capacities and faster initial adsorption rates.

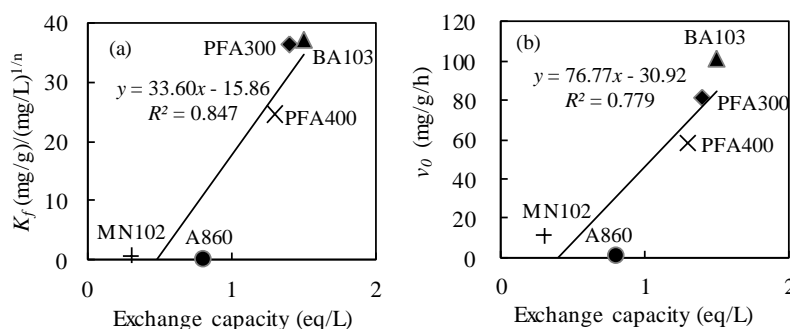


Fig. 2 The relationship between exchange capacities and (a) the *Freundlich* adsorption constant, (b) initial adsorption rate

In summary, adsorption capacities and rates of PFHxA onto five anion exchange polymers, non-ion exchange polymers as well as GAC in industrial wastewater were investigated. All adsorption data were fitted with the *Freundlich* isotherms and the pseudo-second order model. Adsorption capacities of PFHxA onto BA103, PFA300 and PFA400 were higher than those of GAC. BA103 had the highest PFHxA adsorption capacity (37.12 mg/g) and the fastest initial adsorption rate (101.3 mg/g/h). BA103 is a suitable adsorbent to remove PFHxA in industrial wastewater. The factors affecting adsorption (interferences, pH and temperature) followed by continuous experiments should be further investigated.

Acknowledgements

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