

**Development of Effective Removal Procedures of  
Perfluorohexanoic Acid (PFHxA) from Industrial Wastewater  
by Adsorption and Regeneration**

**2015**

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## **Abstract**

Perfluorohexanoic acid (PFHxA) is one kind of perfluorinated chemicals (PFCs) which is widely used in various consumer products and industrial applications such as food packaging, cosmetics, fluorochemical manufacture, etc. It has been found to be toxic as well as persistent during natural degradation processes. Wastewater containing PFHxA from industries can cause severe pollution to the nearby water environments. Thus, it is of critical importance to remove PFHxA from industrial wastewater before discharging into water environments. Adsorption process was considered as an effective and economic technique to remove PFHxA from wastewater.

The main objective of this study was to develop the effective removal procedures of PFHxA from industrial wastewater by adsorption and regeneration. To achieve the main objective, the following survey and experiments were conducted. The PFCs contaminations and wastewater characteristics were examined in industrial wastewater. PFHxA adsorption performances in both synthetic and industrial wastewater were investigated onto granular activated carbon (GAC), non ion exchange polymers and anion exchange polymers. Factors affecting PFHxA adsorption efficiency were identified. Regeneration of spent adsorbents were studied. Continuous PFHxA removal experiments were conducted with both synthetic and industrial wastewater.

Wastewater samples were collected from ten central wastewater treatment plants (WWTPs) and a fluorochemical factory in Japan in order to know eleven PFCs concentrations and wastewater characteristics. Total PFCs concentrations in the effluent of central WWTPs ranged from 15 to 1,030 ng/L. Among ten WWTPs, WWTP7 had the highest total PFCs concentration and its predominant PFC was PFHxA. Totally, ten WWTPs discharged 28.7 g/day of PFCs into the environment. PFHxA concentrations detected in the treatment process for industrial wastewater in Japan ranged from 4 to 73 mg/L, while the others PFCs could not be detected. Wastewater samples from each industrial process had the different wastewater characteristics. Ionic strength and DOC concentration were higher than that total PFCs concentration resulting in a huge impact on the adsorption process.

Adsorption kinetics and isotherms of PFHxA onto GAC, non ion exchange polymers (XAD4) as well as five anion exchange polymers (PFA300, PFA400, A860, BA103 and MN102) were investigated in synthetic and fluorochemical wastewater. All adsorption kinetics and isotherms data were fitted with the *pseudo-second-order* equation and the *Freundlich* equation, respectively. BA103 showed the fastest initial adsorption rate and the highest adsorption capacity in synthetic wastewater, followed by PFA300, A860, PFA400, GAC, MN102 and XAD4. Initial adsorption rates of BA103 were 320 and 101 mg/g/h in synthetic and in fluorochemical wastewater, respectively. Adsorption capacities of BA103 were 412 and 37 mg/g in synthetic and fluorochemical wastewater, respectively. It is noted that adsorption rates and capacities of PFHxA in synthetic wastewater were higher than those in fluorochemical wastewater onto all adsorbents. Thus, effects of interferences on PFHxA adsorption capacity were investigated.

Effects of interferences (inorganic ions and DOC) and adsorption conditions (pH and temperature) on PFHxA adsorption capacities were identified onto seven adsorbents. Adsorption capacities of PFHxA onto GAC and anion exchange polymers decreased when increasing inorganic ions (NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>NO<sub>3</sub>, KCl, and CaCl<sub>2</sub>) in wastewater. BA103 showed the better performance than other adsorbents on removal of PFHxA in wastewater when inorganic ions present. DOC in humic acid and in fluorochemical wastewater affected the adsorption capacities of PFHxA onto GAC and anion exchange polymers. DOC had less effect on PFHxA adsorption capacity onto gel polymers (PFA300 and PFA400) than the other adsorbents. Adsorption of PFHxA was most effective at pH values between 5 to 7 and temperature during 30 to 40°C onto PFA300, PFA400, BA103 and MN102 while GAC had higher adsorption capacity at lower pH (2 to 4) and higher temperature (45°C). XAD4 showed the low adsorption capacity of PFHxA under various conditions.

Regeneration experiment under different types of regenerant (such as methanol, salt solution and mixture of them) were conducted with BA103 as it showed a fast adsorption rate and high adsorption capacity. Experimental results revealed that more than 99% of PFHxA was desorbed by 5% of NaOH and NaCl in MeOH:Milli-Q water (7:3) solutions. Regenerant of 5% NaCl in MeOH:Milli-Q water (7: 3) was selected to regenerate spent

BA103 for ten cycles with fluorochemical wastewater because it showed a faster regeneration rate than other regenerants. After regeneration for ten cycles, the adsorption capacity of BA103 was 91.8% of the original value. This suggested that BA103 could be reused in fluorochemical wastewater.

Continuous adsorption and regeneration of PFHxA were performed with synthetic wastewater (tap water containing PFHxA) and industrial wastewater in Japan and Thailand for practical applications. Breakthrough curves of PFHxA of each adsorbent were different in column experiments. The column data for PFHxA adsorption of four adsorbents were fitted to the linearized form of the *Thomas* model. BA103 showed the highest adsorption capacity in column experiment ( $q_{exp} = 275$  mg/g). Breakthrough curves of BA103 with different bed volumes were observed. A higher bed volume of BA103 could treat a larger amount of wastewater. Exhausted column of BA103 was regenerated by 5% NaCl in MeOH:*Milli-Q* water (7:3), the regeneration efficiency of PFHxA was more than 99%.

PFHxA was detected in industrial wastewater. Anion exchange polymers were able to remove PFHxA from industrial wastewater. Adsorption rates and capacities of PFHxA onto anion exchange polymers in synthetic wastewater were higher than those in industrial wastewater due to interferences. Influences of inorganic ions were more than those of DOC on the removal efficiency of PFHxA onto anion exchange polymers. In addition, anion exchange polymers were able to be regenerated and reused for wastewater treatment. Therefore, adsorption and regeneration were effective procedures to remove PFHxA from industrial wastewater.

### **Keywords**

Adsorption, industrial wastewater, perfluorohexanoic acid (PFHxA), regeneration

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### Abbreviations

AC	activated carbon	PACl	polyaluminium chloride
ACN	acetonitrile	PET	polyethylene terephthalate
AOP	advanced oxidation process	PFASs	perfluoroalkyl sulfonates
AS	activated sludge	PFBuS	perfluorobutane sulfonate
Ave	average	PFCAs	perfluorocarboxylates
CE	collision energy	PFCs	perfluorinated chemicals
CMC	critical micelle	PFDA	perfluorodecanoic acid
	concentration	PFDODA	perfluorododecanoic acid
DOC	dissolved organics carbon	PFHpA	perfluoroheptanoic acid
DVB	divinylbenzene	PFHxA	perfluorohexanoic acid
EBCT	empty bed contact time	PFHxS	perfluorohexane sulfonate
ESI	electrospray ionization	PFNA	perfluorononanoic acid
GAC	granular activated carbon	PFOA	perfluorooctanoic acid
HPLC	high performance liquid	PFOS	perfluorooctane sulfonate
	chromatography	PFOSF	perfluorooctane sulfonyl
ICP	inductively coupled		fluoride
	plasma	PFPeA	perfluoropentanoic acid
LC	liquid chromatograph	PFUnDA	perfluoroundecanoic acid
LOD	limits of detection	POPs	persistent organic
LOQ	limits of quantification		pollutants
MeOH	methanol	PP	polypropylene
MRM	multiple reaction monitoring	RO	reverse osmosis
MS/MS	tandem mass spectrometer	SS	suspended solids
MWCO	molecular weight cut-off	TOC	total organic carbon
NF	nanofiltration	UF	ultrafiltration
NOAEL	no observable adverse	UV	ultraviolet
	effect level	WWTP	wastewater treatment plant
NOM	natural organic matter		
PAC	powder activated carbon		

# Chapter 1 Introduction

## 1.1 Research Background

Perfluorinated compounds (PFCs) are produced and widely used for since 1950s in various industries and consumer products such as firefighting foams, paints, non-stick cookware, carpets, upholstery, cosmetics, semiconductors, photographic films, pesticide formulations, food packaging and waterproof coating (Kissa, 2001 and Prevedouros *et al.*, 2006). Due to their toxicity, persistence, bioaccumulation and global distribution in aquatic environments, PFCs have attracted attention in recent years (Flores *et al.*, 2013). The uses of PFOS and PFOA, fluorinated eight carbons (C8), they have been reduced manufacturers. PFOS was listed as a persistent organic pollutant at the United Nations Stockholm convention on persistent organic pollutants (Wang *et al.* 2009) while PFOA has also been out by eight major manufacturers through a voluntary stewardship agreement with USEPA (USEPA, 2011). Some industries switched to use C6 PFCs such as perfluorohexanoic acid (PFHxA) as the alternative of C8 PFCs such as PFOS and PFOA. Thus, trend of using PFHxA in industries is increasing.

According to PFCs survey in wastewater treatment plants (WWTPs) by Schultz *et al.* (2006) and Kunacheva *et al.* (2011), sedimentation and biological processes are ineffective to remove these compounds. Advanced treatments such as photoelectrocatalytic Jin *et al.* (2014), sonochemicals degradation (McNamara *et al.*, 2003), NF and RO membranes (Tang *et al.*, 2007; Zhao *et al.*, 2013) were studied to remove PFCs. However, these treatments are harsh chemical reactions and/or required high energy consumption. Adsorption and ion exchange treatment was able to remove PFCs (Yu *et al.* 2009; Lampert *et al.* 2007; Appleman *et al.* 2013).

Activated carbon (AC), in either powdered (PAC) or granular (GAC) form, have been studied to remove PFOS and PFOA in synthetic wastewater. Non ion exchange polymers could remove both compounds in synthetic wastewater (Senevirathna *et al.*, 2010; Yu *et al.*, 2012). Furthermore, some researchers reported that anion exchange polymers have higher adsorption capacities than AC and non ion exchange polymers for both PFOS and

PFOA (Chularueangaksorn, 2013). The adsorption of PFHxA onto GAC, non ion exchange polymers and anion exchange polymers have not been well studied.

In general, industrial wastewater contains both ions and dissolved organic matters. These ions and/or compounds affected the adsorption of target compounds. Before the implementation of adsorption process in industry, the effect of these compounds should be well studied. In this study, various commercial adsorbents such as GAC, non ion exchange polymers and anion exchange polymers were tested. Up to now, the information of effects of interferences (ions and dissolved organic matters) on adsorption of PFHxA is still not available. Thus, this study provided very a useful information in this field.

Spent polymeric adsorbents could be regenerated to reduce the cost. Previous studies showed that the spent non ion exchange polymers could be completely desorbed by pure methanol, while anion exchange polymers required the mixed salt solution and methanol (Chularueangaksorn, 2013). However, most of studies conducted regeneration experiments by adsorption of PFCs in synthetic wastewater and then regeneration through those regenerants. Regeneration experiments of adsorbents used to adsorb PFCs in industrial wastewater still has not been fully studied.

Several bench scale studies assessed the effectiveness of PFOS and PFOA adsorption onto GAC (Senevirathna *et al.*, 2011; Ochoa-Herrera and Sierra-Alvarez, 2008). These studies focused on adsorption in synthetic wastewater. Information of adsorption behavior of PFHxA in industrial wastewater is limited in bench scale experiments. This study provided continuous adsorption and regeneration to remove PFHxA in industrial wastewater.

## **1.2 Research objectives**

This study aims to develop the effective removal procedures of PFHxA from industrial wastewater by adsorption and regeneration. Specific objectives are as following.

1. To investigate PFCs contaminations and wastewater characteristics in industrial wastewater treatment plants in Thailand and Japan
2. To study adsorption properties of PFHxA in synthetic and fluorochemical wastewater
3. To examine factors affecting PFHxA adsorption in wastewater
4. To study regeneration efficiencies of PFHxA and reusability of spent adsorbents
5. To apply adsorption and regeneration techniques to remove PFHxA industrial wastewater by column experiments

## **1.3 Dissertation organization**

The organization of this dissertation is shown in **Fig. 1.1**. It contains of nine chapters and each chapter is described as below:

Chapter 1 stated the research background, objectives and dissertation organization.

Chapter 2 reviewed the current available publication related to the properties, toxicities occurrences of PFHxA. Removal techniques of PFCs such as advance oxidation process, membrane filtration and coagulation were briefly summarized. The adsorption behaviors and mechanisms of PFCs were focused.

Chapter 3 presented the materials and methods used in this research. The details of each experiment were given out in chapter 4 to 8.

Chapter 4 showed the results of the survey of PFCs contaminations in industrial wastewater in both Thailand and Japan and the wastewater characteristics were also provided. The results were compared with the results from previous researches.

Chapter 5 revealed adsorption rates and capacities of PFHxA onto different types of adsorbent (GAC, non ion exchange polymers and anion exchange polymers) in both synthetic and industrial wastewater.

Chapter 6 identified the effects of interferences (inorganic ions and DOC) and adsorption conditions (pH and temperature) on PFHxA adsorption.

Chapter 7 evaluated PFHxA regeneration efficiencies of spent absorbents and their reusability for wastewater treatment.

Chapter 8 applied adsorption and regeneration (chapter 5 and 7) techniques to remove PFHxA by column experiments with synthetic wastewater and actual wastewater in Thailand and Japan.

Chapter 9 summarized the main conclusions of this research and the recommendations for further researches were given out.



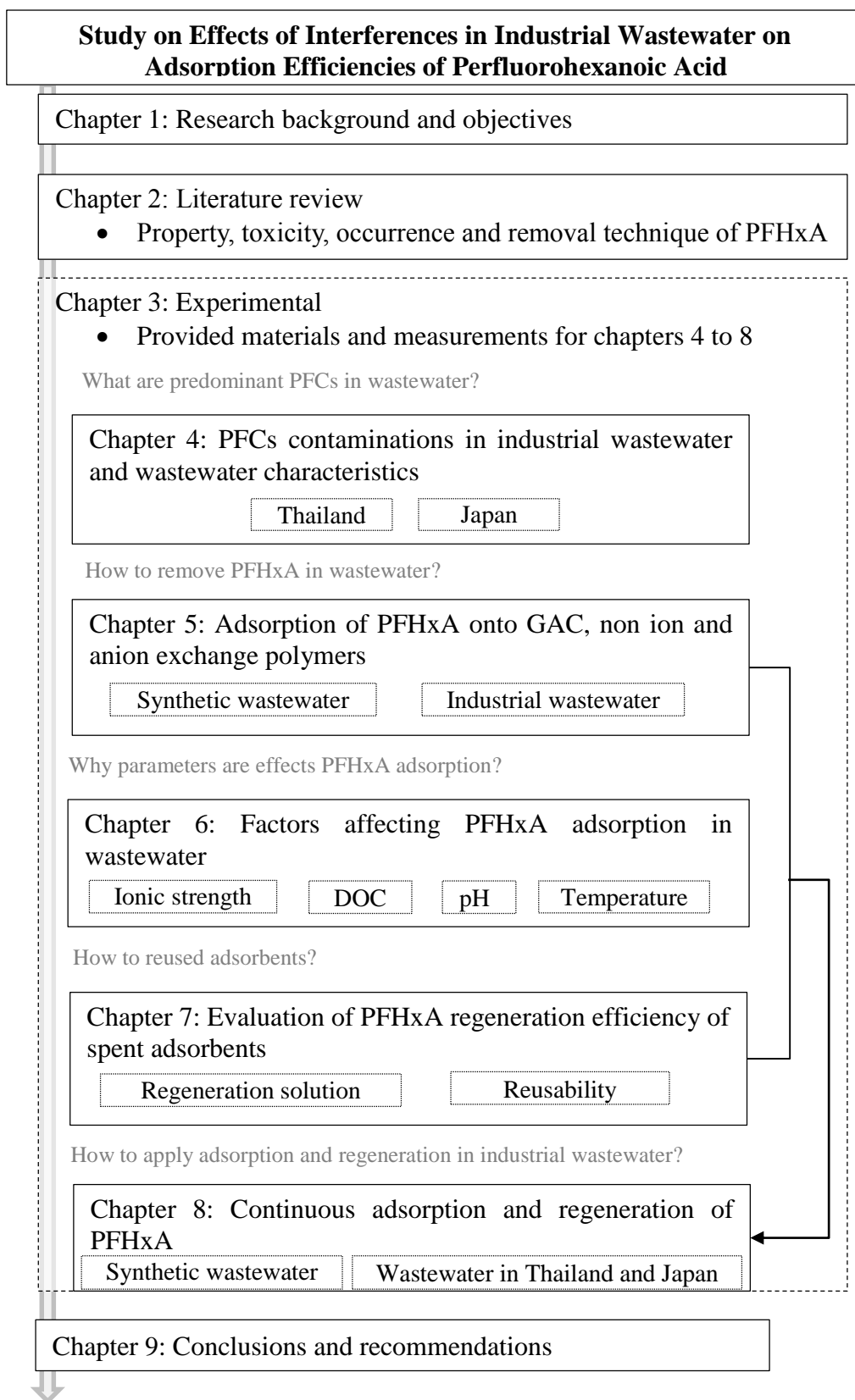


Figure 1.1 Dissertation organization

## Chapter 2 Literature review

### 2.1 Introduction of PFHxA

Perfluorohexanoic acid (PFHxA) is a member of perfluorinated chemicals (PFCs). PFHxA is a chemical containing a five-carbon perfluoroalkyl chain attached to a carboxylic acid functional group. PFHxA and other PFCs did not naturally occur, they were synthesized and used in industrial processes since the 1950s (3M Company, 1999). Their structures have useful properties including surfactant, oil and water repellency and resistance to heat and chemical reactions. They are used in water- and stain-resistant coatings for clothing, leather and carpets, oil-resistant for food packaging, aviation hydraulic fluids, firefighting foam, paints and cosmetics (Prevedouros *et al.*, 2006).

In the present, researchers focus on PFHxA as emerging environmental contaminants and they do research works about environmental occurrences and biota exposure, pharmacokinetics, epidemiology and toxicology. PFHxA is persistent and resistant to typical environmental degradation processes due to its carbon-fluorine bond (C-F). C-F bond is one of the strongest bonds in organic chemistry. PFHxA is found in environment including river water, lake, sea water, ocean, tap water, wastewater, rain water and groundwater, sludge, soil, sediment, dust and biota (Schultz *et al.*, 2006; Kunacheva, 2009; Shivakoti *et al.*, 2010; Zushi *et al.*, 2011; Cai *et al.*, 2012a; Takemine *et al.*, 2014).

PFHxA proposed as a replacement of an eight-carbon perfluoroalkyls: perfluorooctanoic acid (PFOA) and perfluorooctanoic sulfonate (PFOS) in industrial processes (Klaunig *et al.*, 2014). Biological wastewater treatment processes are ineffective to remove PFHxA form in industrial wastewater (Kunacheva, 2009). It can be expected that the environmental loading of PFHxA will be increased. The effective of PFHxA removal techniques are required to minimize adverse effects on humans and environment. To understand more about this research work, the literature review provides the relevant information of PFHxA including physicochemical properties, toxic effects, occurrences in environment and possible treatment techniques of PFHxA.

### 2.1.1 PFHxA properties

**Table 2.1** shows physico-chemical properties of PFHxA. PFHxA has moderate water solubility and it is a strong acid ( $pK_a < 1$ ) that is dissociated at environmentally relevant pH values (Kissa, 2001). The critical micelle concentration (CMC) is an important characteristic of a surfactant. PFHxA is a moderate CMC and easier to form hemi-micelles/micelles in water. In addition, it is still possible to form hemi-micelles on adsorbent surfaces when their concentrations are in the range of 0.01 to 0.001 time of CMC (Johnson *et al.*, 2007).

Table 2.1 Physicochemical properties of PFHxA

Property	Value	Reference
Chemical formula	$\text{CF}_3(\text{CF}_2)_4\text{COOH}$	-
Chemical structure	$  \begin{array}{c}  \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \\    \quad   \quad   \quad   \quad   \\  \text{F}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\    \quad   \quad   \quad   \quad   \\  \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F}  \end{array}  \begin{array}{l}  \text{O} \\  // \\  \text{C} \\  \backslash \\  \text{OH}  \end{array}  $	-
Molecular weight	314.05	-
CAS No.	307-24-4	-
Solubility (g/L)	< 29 mg/L	Ding and Peijnenburg, 2013
$pK_a$ at 25 °C	0.74	Moroi <i>et al.</i> , 2001 (Conductivity method)
Melting point at 1 atm (°C)	12 to 14	Huang <i>et al.</i> , 1987
Boiling point at 1 atm (°C)	155 to 157	Huang <i>et al.</i> , 1987
CMC at 25 °C (g/L)	28.26	Daikin, 1970 (Surface tension method)
Vapor pressure at 25 °C (Pa)	114 to 121	Arp <i>et al.</i> , 2006 <sup>1</sup>
Octanol-water partitioning (log $K_{ow}$ )	3.12 to 3.26	Arp <i>et al.</i> , 2006 <sup>1</sup>
Air-water partitioning (log $K_{aw}$ )	~ 2.2	Calculated using a vapor pressure of 115 Pa and a solubility
Octanol-air partitioning (log $K_{oa}$ )	~ 1	Calculated from $\log K_{oa} = \log K_{ow} - \log K_{aw}$

Note: <sup>1</sup>Modeled using property estimation software.

### 2.1.2 Toxic effects of PFHxA

The acute, subchronic and chronic toxicity of PFHxA were evaluated in mice, rats and monkeys by many researchers (**Table 2.2**). Loveless *et al.*, 2009 found that all rats can survive with dosed at 175 or 550 mg /kg of NaPFHxA, whereas one of four rats died on the day of dosing at 1,750 mg/kg of NaPFHxA. All three rats dosed died on the day of dosing or the day after dosing at 5,000 mg/kg of NaPFHxA. The clinical sign of systemic toxicity were observed from doses 175 to 5,000 mg/kg including an abnormal gait, dehydration, high or low posture, nasal discharge, salivation or lethargy in most of the rats.

There were four reports of subchronic dosing toxicity in mammals. Chengelis *et al.*, 2009a, and Gannon *et al.*, 2011 found that PFHxA was rapidly eliminate from blood plasma and serum of rats and mice with no appreciable gender differences. Loveless *et al.*, 2009 and Chengelis *et al.*, 2009b provided the different values of no observed adverse effect level (NOAEL) based on the criteria of adverse effects.

Iwai *et al.*, 2011 studied a two-year chronic toxicity, the study was carried out on rats which received oral doses of 2.5, 15 and 100 mg/kg/day for males and 5, 30 and 200 mg/kg/day for females. There were no PFHxA-related effects on body weight, food consumption, functional observational battery, hematology, serum chemistry, or hormone parameters. However, NOAELs were 15 mg/kg/day for males and 30 mg/kg/day for females based on non-neoplastic systemic toxicity.

The toxicity effects of PFHxA on human have not been fully understood yet. There was a study on elimination kinetics of PFHxA in humans (professional ski wax technicians) compared with mice, rats and monkeys (Russell *et al.*, 2013). They found that the elimination half-life of PFHxA in highly exposed humans ranged between 13 to 49 days with a geometric mean of 32 days. The half-life of PFHxA in mouse, rat and monkey and human were proportional to body weight with no differences observed between genders.

Table 2.2 Toxicity effects studies of PFHxA on mouse, rat and monkey

Study type	Dose	Duration	Exposure route	End points examined	Comments
<sup>1</sup> Acute and subchronic toxicity (rats)	Acute: 175, 550, 1750, 5000 mg/kg Daily: 0, 20, 100, or 500 mg/kg	Acute, 90-day	Oral (gavage)	Mortality and clinical sign of systemic toxicity	All three rats dosed died on the day of dosing or the day after dosing at 5,000 mg/kg of NaPFHxA
<sup>2</sup> Acute (monkeys, rats) and subchronic (rats) toxicity	10 mg/kg	24 hours, 25 days	Intravenous injection (acute), oral (gavage) (subchronic)	Rate of elimination, mortality, morbidity	In monkeys, the terminal half-lives of PFHxA in serum were 2.4 to 5.3 hours  In rats, the terminal half-lives of PFHxA in serum were 0.42 to 1.0 hours
<sup>3</sup> Acute and subchronic toxicity (rats)	2 or 100 mg/kg after single	14 day	Oral (gavage)	Absorption, distribution, Metabolism and excretion	The plasma elimination half-lives in male rats were 1.5 to 1.7 hours and female rats were 0.5 to 0.7 hours.
<sup>4</sup> Subchronic toxicity (rats)	10, 50 and 200 mg/kg/day	90 days	Oral (gavage)	Body weight, hematology data and histopathology	NOAELs for oral administration were 50 mg/kg/day for males and 200 mg/kg/day for females based on liver histopathology and liver weight changes
<sup>5</sup> Chronic toxicity	2.5, 15 and 100 mg/kg/d for males and 5,30, and 200 mg/kg/d for females	2 years	Oral (gavage)	Toxicity, carcinogenic, and clinical sign of systemic toxicity	NOAELs were 15 mg/kg/day for males and 30 mg/kg/day for females based on non-neoplastic systemic toxicity of PFHxA. NOAELs were 100 mg/kg/day for males and 200 mg/kg/day for females based on neoplastic findings.
<sup>6</sup> Genotoxicity	100 or 400 µM	24 hours exposure	-	Generation of reactive oxygen species (ROS), and DNA damage	PFHxA did not generate ROS or DNA damage

Note: <sup>1</sup> Loveless *et al.*, 2009, <sup>2</sup>Chengelis *et al.*, 2009a, <sup>3</sup>Gannon *et al.*, 2011, <sup>4</sup>Chengelis *et al.*, 2009b, <sup>5</sup>Iwai *et al.*, 2011 and <sup>6</sup>Eriksen *et al.*, 2010

### 2.1.3 Regulation related to PFHxA

There are no any regulations of PFHxA at this moment. On the other hand, there are some regulations of PFCs especially PFOS and PFOA (**Table 2.3**). Regulations have been proposed in many developed countries such as U.S, Canada, German, Norway and Japan to reduce the release of the abundant PFOS and PFOA into the environment. PFCs related manufactures changed from PFOS or PFOA to shorter carbon chains such as PFHxA (DuPont, 2012) because of less bioaccumulation. Using of PFHxA might be increased due to regulation of PFOS and PFOA. The most of regulations were regulated in developed countries. PFCs manufacturers have been shifted to developing countries resulting in large distributions of PFCs into water environments.

International regulations also are available such as Organization for Economic Co-operation and Development (OECD), Stockholm Convention, and Strategic Approach to Chemicals Management (SAICM). The summary of international settings is following.

#### Organization for Economic Co-operation and Development (OECD)

- In 2000, OECD developed a hazard assessment of PFOS and its salt
- In 2006, OECD released a survey on the production and use of PFOS, PFOA, PFAS, PFCA and related substances
- In 2006, OECD held a workshop on PFCs and precursors and published a workshop report in 2007
- In 2010, survey of product content and environmental release informations on PFCs

#### Stockholm Convention on Persistent Organic Pollutants (POPs)

- In May 2009, PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOSF) were added to Annex B, subjecting them to restrictions on production and use

Table 2.3 Summary of regulations or actions related to PFCs in different countries

Country	Action	Proposed date	Effective date
U.S.	• 2010/15 PFOA Stewardship program	January 2006	December 2015
	• Significant new use rules: Perfluoroalkyl sulfonates (PFASs) and long- chain perfluoroalkyl carboxylates (PFCAs) chemical substances	August 2012	Pending
Canada	• Government of Canada published its Action Plan for the Assessment and Management of PFCAs and their precursors	June 2006	Pending
	• Voluntary environmental performance agreement respecting PFCAs and their precursors in perfluorochemical products sold in Canada	March 2010	December 2015
	• Proposed risk management approach for PFOA, its salts and its precursors and long-chain (C9 to C20) PFCAs, their salts and their precursors	August 2012	Pending
Germany	• Proposed quality standards and reduction targets applicable to water bodies, wastewater, and soils to be introduced with respect to PFASs	July 2007 (first draft); July 2009 (revised)	Pending
Norway	• Proposed regulations to restrict the production, import, export or sale of consumer products that contain PFOA in consumer products if they exceed certain limit values.	December 2011	Pending
Japan	• PFOS and PFOA were listed in regulation of production and use under the chemical substances control law (Production or use of PFOS were prohibited except for essential uses; Production or use of PFOA were regulated under the law)	2010	Pending
	• PFOS was in Pollutant Release and Transfer Register, PRTR (Data on release and transfer of PFOS will be reported from industries)	2010	Pending
	• No effluent standards for PFOS and PFOA	-	-
Thailand	• Thailand is one party of Stockholm Convention	-	-

Source: OECD Portal on PFCs, 2014

## Strategic Approach to International Chemicals Management (SAICM)

- In May 2009, during the International Conference on Chemicals Management, delegates agreed to consider the development of stewardship programs and regulatory approaches to reduce emissions of PFASs and PFCAs in products and to work toward their elimination where feasible.

## 2.2 PFHxA occurrences in environment

### 2.2.1 Occurrences of tap water, precipitation, river water, lake, seawater, wastewater and landfill leachate

PFHxA are ubiquitously found in aquatic environments. **Table 2.4** shows PFHxA concentration in tap water, river water, lake, seawater and wastewater in different counties. From the table, it can be interpreted as following. PFHxA were detected in many types of aquatic environment over the world. Typical concentrations in aquatic environment are in ng/L range exception of contaminated areas. PFHxA concentrations in tap water depend on treatment technologies used to purify the water and sources of water. Tap water can be a major direct source of PFHxA exposure through ingestion (Yim *et al.*, 2009).

Precipitation such as rain and snow contained PFHxA, it suggested that an atmospheric is a source of PFCs (Loos *et al.*, 2007). Groundwater and surface water (river and lake) are used to produce drinking water which is a known exposure pathway of humans (Vestergren and Cousins *et al.*, 2009). In fact, PFHxA concentrations in tap water are usually similar to surface water because water treatment processes such as coagulation, sand filtration, sedimentation and chlorination are not effectively remove. PFHxA is discharged to sea via surface water, treated wastewater and precipitation. Main sources of PFHxA to the aquatic environment are municipal and industrial wastewater treatment plants and landfill leachate due to ineffective of biological treatment process (Kunacheva, 2009). Industrial wastewater treatment plants contained higher concentration of PFHxA than the others aquatic environments.



Table 2.4 Concentrations of PFHxA in tap water, precipitation, river water, lake, seawater, wastewater and landfill leachate in different counties

Type	Location	year	Concentration (ng/L)	Reference
Tap water	Niagara on the lake, Canada	2006	4	Yim <i>et al.</i> , 2009
	Shanghai, China	2006	19	Yim <i>et al.</i> , 2009
	Osaka, Japan	2006	8	Yim <i>et al.</i> , 2009
	Bangkok, Thailand	2007	<0.01-2.1	Kunacheva, 2009
Precipitation (Rain or snow)	Antarctica	2011	0.142-0.677	Cai <i>et al.</i> , 2012a
	China	2010	<0.07-9.5	Zhao <i>et al.</i> , 2013
	Tsukuba, Japan	2007	1.5-7.5	Taniyasu <i>et al.</i> , 2013
	Zandvoort, Netherlands	2008	<0.1-2.3	Eschauzier <i>et al.</i> , 2010
Ground water	Netherlands	2011	<0.4-19	Eschauzier <i>et al.</i> , 2013
	Stockholm, Sweden	2012	<0.5-900	Filipovic <i>et al.</i> , 2014
River water	Haihe River, China	2010	2.2-42	Li <i>et al.</i> , 2011
	Rivers of Tokyo basin, Japan	2009	<0.43-423.29	Zushi <i>et al.</i> , 2011
	Hyogo prefecture, Japan	2010	<0.5 -16,000	Takemine <i>et al.</i> , 2014
	Stockholm, Sweden	2012	<0.5-4.4	Filipovic <i>et al.</i> , 2014
	Chao Phraya, Thailand	2007	<0.02-5.72	Kunacheva, 2009
Lake	Antarctica	2011	<0.0083-0.026	Cai <i>et al.</i> , 2012a
	Ruhr Area, German	2005	<2-1,248	Skutlarek <i>et al.</i> , 2006
	Lake Shihwa, Korea	2004	<0.50-1.37	Rostkowski <i>et al.</i> , 2006
Seawater	East to South China	2010	<0.42-0.250	Cai <i>et al.</i> , 2012b
	Hyogo, Japan	2010	<0.5 - 510	Takemine <i>et al.</i> , 2014
	Gyeonggi Bay, Korea	2004	<0.50-0.60	Rostkowski <i>et al.</i> , 2006
Wastewater	WWTP, Germany	2007	3.7-54.4	Ahrens <i>et al.</i> , 2009
	WWTP, Japan	2008	<0.02-180	Shivakoti <i>et al.</i> , 2010
	WWTP, Thailand	2007	<0.02-325	Kunacheva, 2009
	WWTP, USA	2005	<0.50-20	Schultz <i>et al.</i> , 2006
Landfill leachate	Finland	2009	49-200	Perkola and Sainio, 2013
	Netherlands	2011	44-670	Eschauzier <i>et al.</i> , 2013

Table 2.5 Concentrations of PFHxA in biota

Type	Location	Year	Number of sample	Concentration	Reference
Eider duck	Poland	2003	16	<0.05 (ng/g, ww)	Falandysz <i>et al.</i> , 2007
Long-tailed duck	Poland	2003	10	<0.05 (ng/g, ww)	Falandysz <i>et al.</i> , 2007
Liver of beaver	Poland	2003	18	0.03–0.23 (ng/g, ww)	Falandysz <i>et al.</i> , 2007
Razorbill	Poland	2003	10	<0.05 (ng/g, ww)	Falandysz <i>et al.</i> , 2007
Velvet scoter	Poland	2003	5	<0.05 (ng/g, ww)	Falandysz <i>et al.</i> , 2007
Cod (whole blood)	Poland	2003	18	<0.05–0.69 (pg/mL)	Falandysz <i>et al.</i> , 2007
Waterbird Eggs	Quanzhou, China	2004	28	<0.01 -0.071 (ng/g, ww)	Wang <i>et al.</i> , 2008
Blood of wild rats	Japan	2007	700	<0.05–9.93 (ng/mL)	Taniyasu <i>et al.</i> , 2013
Gills Rockfish	West coast, Korea	2008	1	9.43 (ng/g, dw)	Naile <i>et al.</i> , 2010
Soft tissue of Asian periwinkle	West coast, Korea	2008	300	4.08-5.01 (ng/g, dw)	Naile <i>et al.</i> , 2010
Soft tissue of surf clam	West coast, Korea	2008	12	1.5 (ng/g, dw)	Naile <i>et al.</i> , 2010
Soft tissue of mussel	West coast, Korea	2008	15	4.97 (ng/g, dw)	Naile <i>et al.</i> , 2010
Soft tissue of oyster	West coast, Korea	2008	20	5.04 (ng/g, dw)	Naile <i>et al.</i> , 2010
Serum sample from male, human	Shenzhen, China	2009	133	<0.01-1.64 (ng/mL)	Li <i>et al.</i> , 2011
Serum sample from female, human	Shenzhen, China	2009	94	<0.01-2.36 (ng/mL)	Li <i>et al.</i> , 2011
Algae	Tierra del Fuego and Antarctica	2010	9	4.1 - 200 (ng/g, dw)	Llorca <i>et al.</i> , 2012
Guano	Tierra del Fuego and Antarctica	2010	6	1,190 – 2,480 (ng/g, dw)	Llorca <i>et al.</i> , 2012
Penguin dung	Tierra del Fuego and Antarctica	2010	6	19.9 - 237 (ng/g, dw)	Llorca <i>et al.</i> , 2012
Oysters and mussels	Hong Kong.	2010	3	< 0.02 (ng/g, dw)	Zhao <i>et al.</i> , 2014
Plasma from pregnant women	Japan	2011	6	<0.1-0.13 (ng/mL)	Okada <i>et al.</i> , 2013

Note: dw = dry weight, ww = wet weight

Aquatic system is regarded as a major sink and it is the most significant media of PFHxA and its precursors transport in the environment (Cai *et al.*, 2012a). PFHxA in the aquatic environment can be contributed to PFHxA in biological samples such as fish, reptiles, aquatic birds and humans. The summary is provided in the next section.

### 2.2.2 Occurrences of biota

Detected PFHxA in biota are shown in **table 2.5**. Researchers detected PFHxA in biota from various locations around the world including Poland, China, Korea and Antarctica. Detection of PFHxA in biota in a remote location might indicate a long-range transport. Falandysz *et al.* (2007) detected PFHxA in a liver of beaver (0.03 to 0.23 ng/g of wet weight) and blood of cod (<0.05 to 0.69 pg/mL). Velvet scoter, eider duck, long-tailed duck and razorbill which are predators of cod were also detected. PFHxA concentrations were less than 0.05 ng/g (wet weight). The lower concentrations in predators indicate that PFHxA has less bioaccumulation potential.

Li *et al.* (2011) detected PFHxA in non-occupational people living in areas where there is PFHxA exposure. PFHxA was determined in 227 serum samples from a population in Shenze, China. PFHxA concentrations in serum of male and female ranged from not detected to 1.64 ng/mL and not detected to 2.36 ng/mL, respectively. No significant gender differences were observed for PFHxA concentration as well as no significant correlations were observed between age and the concentrations of PFHxA.

### 2.3 PFCs removal techniques

The PFCs removal techniques can be further classified into two groups namely, decomposition and separation. Diagram of removal technologies for PFCs in wastewater is showed in **Fig 2.1**. PFCs removal efficiencies by different treatment techniques are shown in **Table 2.6**.

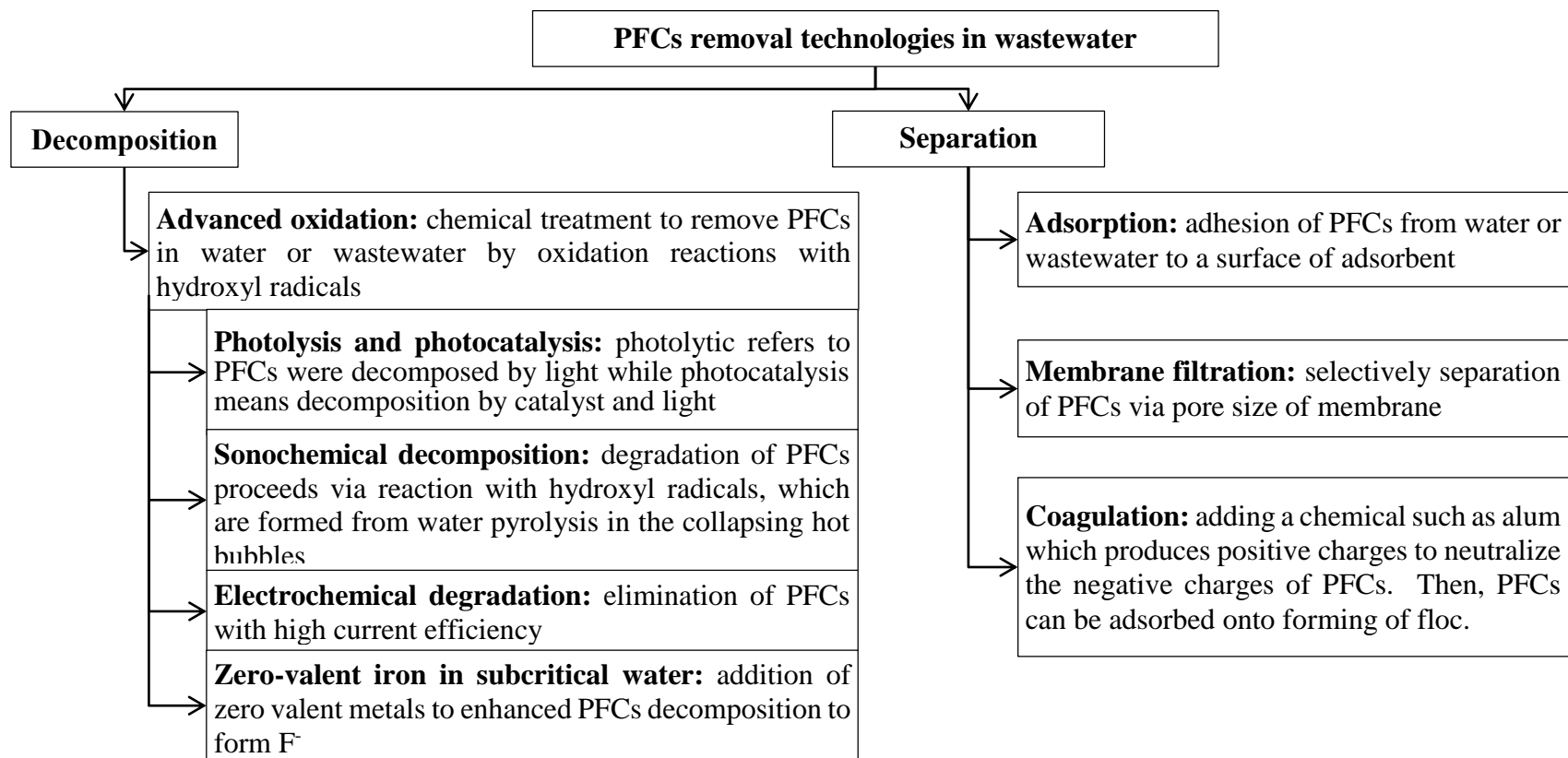


Figure 2.1 Removal technologies for PFCs in wastewater

Table 2.6 PFCs removal by different techniques

Technology	Treatment method	Target compound	Concentration (mg/L)	Condition	Efficiency (%)	Reference
Advanced oxidation	Photolysis	PFOS	10	23 W of UV light (254 nm) for 72 hours	12%	Jin <i>et al.</i> , 2014
	Photocatalysis	PFOA	8.26	9 W of UV lamp (254 nm) with 30 mM of H <sub>2</sub> O <sub>2</sub> , 2 mM of Fe <sup>2+</sup> and pH 3 (UV-Fenton)	95%	Tang <i>et al.</i> , 2012
	Photocatalysis	PFOA	10.3	15 W of UV light (254 nm) with 0.8 mM of KI at pH 9 for 14 hours	98%	Qu <i>et al.</i> , 2014
	Sonochemical	PFOA	20.6	150 W of ultrasonic (40 kHz) with 30 mM of NaHCO <sub>3</sub> for 4 hours, pH 8.65	99%	Phan <i>et al.</i> , 2014
	Sonochemical	PFOA	50	150 W of ultrasonic (40 kHz) with 25 mM of SO <sub>4</sub> <sup>2-</sup> for 2 hours, pH 4.3	99%	Lin <i>et al.</i> , 2015
	Electrochemical	PFOA	3,300	NaClO <sub>4</sub> (10 mM) was electrolyzed at a current density of 0.15 mA/cm <sup>2</sup> for 10 hours	52%	Ochiai <i>et al.</i> , 2011
	Electrochemical	PFOA	100	NaClO <sub>4</sub> (10 mM) was electrolyzed at a current density of 10 mA/cm <sup>2</sup> for 1.5 hours with Ti/SnO <sub>2</sub> -Sb, Ti/SnO <sub>2</sub> -Sb/PbO <sub>2</sub> and Ti/SnO <sub>2</sub> -Sb/MnO <sub>2</sub>	90.3%, 91.1%, and 31.7%, respectively	Lin <i>et al.</i> , 2012
	Zero-valent iron in subcritical water	PFSAs (C2-C8)	155-4,800	React with 9.6 mmol of iron powder at 350 °C for 6 hours	36-53%	Hori <i>et al.</i> , 2006
Membrane	RO	PFOS	0.5-1,500	Cross-flow was 1.37 L/min, at 200 psi	>99%	Tang <i>et al.</i> , 2006
	NF	PFCs	0.1	NF270, Dow/Filmtec, Ca <sup>2+</sup> concentration of 0 to 2 mM at 0.4 MPa	94 - 99%	Zhao <i>et al.</i> , 2013
Coagulation	Polyaluminium chloride (PACl)	PFCs	0.2-3	PACl concentration of 10 mg/L, 1 NTU	27%	Deng <i>et al.</i> , 2011 Xiao <i>et al.</i> , 2013

### 2.3.1 Advanced oxidation processes (AOPs)

AOPs involve the generation of hydroxyl radicals ( $\bullet\text{OH}$ ) in sufficient quantity to oxidize with target compounds (PFCs) in water/ wastewater. Hydroxyl radicals unselectively react with PFCs and they will be quickly converted into inorganic molecules such as  $\text{CO}_2$  and HF (Hori *et al.*, 2005). Hydroxyl radicals are produced from one or more primary oxidants (such as  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ ), energy sources (such as ultraviolet light, ultrasonic and microwave) and/ or catalysts (such as  $\text{TiO}_2$ , KI and  $\text{K}_2\text{S}_2\text{O}_8$ ). Flores *et al.* (2013) found that  $\text{O}_3$  and UV are ineffective to remove PFOS and PFOA in drinking water treatment plants. Different types of effective AOPs to remove PFCs described in subsequent sections.

#### Photolysis and photocatalysis process

Photolysis is decomposition of compound by light while photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In photocatalysis process, light is absorbed by an adsorbed substrate. Photocatalytic activity depends on the ability of the catalyst to create electron hole pairs, which generate free radicals (such as  $\bullet\text{OH}$ ) able to undergo secondary reactions. Jin *et al.* (2014) reported that the decomposition of PFOS (10 mg/L) with UV light (254 nm) was 12% at 72 hours. On the other hand, Tang *et al.* (2012) found that UV irradiation was found to be improved the PFOA degradation in the fenton reaction, resulting in almost complete degradation and substantial defluorination of PFOA within several hours. Short-chain PFCAs and fluoride ions were formed during degradation intermediates. The effective decomposition condition was 30 mM of  $\text{H}_2\text{O}_2$  and 2 mM of  $\text{Fe}^{2+}$  at pH 3 resulting in decreased by 95% under irradiation of 9 W of UV lamp (254 nm).

Similarly, Qu *et al.* (2014) studied decomposition of PFOA in aqueous phase with potassium iodide (KI) as a catalyst. The experiment was conducted under 254 nm irradiation at room temperature and pH 9 under anaerobic condition. Ultraviolet photolysis of iodide solutions led to the generation of  $\bullet\text{OH}$  which contributed to defluorination of PFOA. Defluorination was confirmed by fluoride release of 98%, indicating almost complete defluorination of PFOA. Fluoride ions and intermediates such

as formic acid, acetic acid,  $\text{CF}_3\text{H}$ ,  $\text{C}_2\text{F}_6$  and six short-chain PFCAs (C1 to C6) were detected. It means that the decomposition of PFOS is more effective when catalysts presence in photolysis process. However, further treatments are required for by-products.

### **Sonochemical process**

Sonochemical degradation is effective in treating PFOS and PFOA in aqueous solution over a wide range of concentrations. Acoustic cavitation induced by high frequency ultrasonic irradiation of aqueous solutions produces transient high temperatures and high pressures in the bubble vapor phase and at the bubble-water interface (McNamara *et al.*, 2003). The sonochemical degradation decomposes organic contaminants via reaction of  $\bullet\text{OH}$  from pyrolysis of water or via direct pyrolysis. The ultrasonic reaction is powerful, but it is not economical when used alone due to high input energy. To decrease input energy, sonochemical degradation of PFCs can be improved by the additive-assisted such as photocatalytic compounds (Panchangam *et al.*, 2009), ozone (Kidak and Ince, 2007)  $\text{H}_2\text{O}_2$  (Abbasi and Asl, 2008), iron (Hung *et al.*, 2000), carbonate (Merouani *et al.*, 2010), per sulfate (Liu *et al.*, 2012) and sulfate (Gayathri *et al.*, 2010 and Liu *et al.*, 2012). It is interesting that there are no any shorter chain PFCAs detected except fluorine ions in final reaction solution of sonochemical treatment with carbonate radical oxidant of PFOA (Phan *et al.*, 2014).

### **Electrochemical degradation**

Researchers mainly focused on “non-active” anodes such as tin oxide ( $\text{SnO}_2$ ), lead dioxide ( $\text{PbO}_2$ ), and boron-doped diamond which can produce larger amount of  $\bullet\text{OH}$  (Panizza, 2010). PFCs decomposition began with an electron transfer from carboxyl or sulfonate group to anodes, and the formed PFCs radicals were decarboxylated or desulfonated to yield the perfluoroalkyl radical which permitted a defluorination reaction between perfluoroalkyl radical and hydroxyl radical (Ochiai *et al.*, 2011). Boron-doped diamond electrode has better performance of electrochemical degradation than other anodes but boron-doped diamond electrode is expensive. Recently, Liu *et al.* (2012) investigated electrochemical degradation from aqueous solution using  $\text{Ti/SnO}_2\text{--Sb}$ ,  $\text{Ti/SnO}_2\text{--Sb/PbO}_2$ , and  $\text{Ti/SnO}_2\text{--Sb/MnO}_2$  electrodes. However, the toxic by-products formed were unknown.

### **Zero-valent iron in subcritical water**

Subcritical water is defined as hot water with sufficient pressure to maintain the liquid state. Iron is added to subcritical water which PFCs can be adsorbed on the surface of iron. The fluorinated species on the iron surface decomposed with rising temperature, with prominent release of fluoride ions to the solution. Hori *et al.* (2006) reported PFASs (C2 to C8) could be degraded (95 to 96%) by elemental iron in water under subcritical water conditions (350 °C) and high pressure (20 MPa) for 6 hours while formation of fluoride ions were about 36 to 62 %.

### **2.3.2 Adsorption**

Adsorption is a suitable technique for PFCs removal from water/ wastewater (Yu *et al.*, (2009; Deng *et al.*, 2013). Although some advanced oxidation processes are effective to decompose PFCs, they had some limitations such as high energy consumption, complicated operation and harsh reaction conditions for large-scale application. Properties of adsorbents, adsorption behaviors (adsorption rate and capacity) and adsorption mechanisms of PFCs were summarized.

#### **A. Types of adsorbents for removal of PFCs**

The adsorbents that used to remove PFCs in previous studies such as activated carbon, polymers, mineral materials and biomaterials are briefly explained. **Table 2.7** shows the adsorption capacity of different types of adsorbent.

#### **Activated carbon**

Granular activated carbon (GAC) and powder activated carbon (PAC) are widely used in water/wastewater treatment due to low cost. Activated carbon (AC) is non-polar with few functional groups, which is suitable for hydrophobic pollutants. Yu *et al.* (2009) found that the adsorption capacity of PAC was higher than GAC. The limitations of activated carbon were difficult to be desorbed by methanol or ethanol and safe disposal of saturated AC.



## **Polymers**

Anion exchange polymers (weak and strong base anion exchange polymers) and non ion exchange polymers were used to remove PFCs. Our research group found that the adsorption capacity of anion exchange polymers was higher than GAC and non ion exchange polymers (Senevirathna, 2010 and Chularueangaksorn, 2013). Moreover, they also reported that non ion exchange polymer and anion exchange polymers can be desorbed by methanol and high concentration of salts (NaOH and NaCl) in methanol: water (7:3), respectively. Polymers could be reused well after regeneration. However, regenerants are required to decompose or recycle. The method of recovering fluorinated acid surfactants from regenerants was reported by the United States Patent (Führer *et al.*, 2010).

## **Mineral materials and biomaterials**

Activated alumina, silica, hydrotalcite, zeolite and montmorillonite are mineral materials which are studied removal of PFCs (Punyapalakul *et al.*, 2013; Rattanaoudom *et al.*, 2013; Zhou *et al.*, 2010; Zhou *et al.*, 2013). The modifications of mineral materials have been studied to improve adsorption capacity and selectivity via specific interactions from the modified functionalities. Zhou *et al.* (2013) found that silica was modified with hexadecyltrimethylammonium bromide to improve the efficient removal of PFOS.

Maize straw-origin ash (Chen *et al.*, 2011), chitosan (Zhang *et al.*, 2011), cotton (Deng *et al.*, 2012), aminated rice husk (Deng *et al.*, 2013) are biomaterial used to remove PFCs. Among these adsorbents, the porous materials normally have high sorption capacity for PFCs, but the sorption velocity is very slow due to the slow intraparticle diffusion.

## **B. Adsorption rate**

Adsorption kinetics is affected by adsorbents and adsorbates. The adsorption kinetics of PFCs onto the porous adsorbents related to the particle diameter and pore size of adsorbents. Yu *et al.*, (2009) found that PAC reached the equilibrium concentration before GAC on the adsorption of PFOS. Punyapalakul *et al.* (2013) reported that mesoporous adsorbents had faster adsorption of PFOS and PFOA than microporous ones.

There are many mathematical models proposed to describe adsorption data of PFCs, which can be classified as adsorption reaction model and adsorption diffusion models. Adsorption diffusion models consisted of three consecutive steps (Lazaridis and Asouhidou, 2003). The first step is diffusion across the liquid film surrounding the adsorbent (film diffusion). The second step is diffusion in liquid contained in the pores (intraparticle diffusion) and the last step is adsorption and regeneration between the adsorbate and active sites of adsorbent. Adsorption reaction kinetics model are based on chemical reaction without considering these three steps.

### **C. Adsorption capacity**

The adsorption capacity depended on many factors such as properties of adsorbent (porosity, surface area and particle size) and adsorbate (structure, water solubility, ionic charge, functional groups,  $pK_a$ , polarity, functionality, molecular weight and size), solution conditions (solvent, pH, temperature, ionic strength, solute concentration and competition between solutes), interactions at the solid–liquid interface and types of experimental setup. **Table 2.7** and **Fig. 2.2** shows the adsorption capacity of PFCs onto different types of adsorbent.

### **D. Adsorption mechanisms of PFCs**

Adsorption mechanisms of PFCs on different adsorbents such as electrostatic interaction, hydrophobic interaction, ion exchange, and hydrogen bond are briefly summarized.

#### **Electrostatic interaction**

Electrostatic interaction of PFCs can be described as the electric force between negative charge of PFCs and positively charge of adsorbents. The functional head of PFC had the electrostatic negativity while the tail of PFC molecule exhibited the hydrophobic. PFCs showed an anionic at the common pH due to a low  $pK_a$  (Kissa, 2001). It means that the electrostatic interaction can be formed with positively charged at a certain pH (Zhang *et al.*, 2011).

Table 2.7 Adsorption capacities of PFCs on different adsorbents

Type	Adsorbents name	Adsorbates	Initial conc. (mg/L)	pH	Equilibrium time (hour)	Adsorption capacity (mg/g)	Reference
Powder activated	PAC <sup>1</sup>	PFOS	20-250	5	12	633	Yu <i>et al.</i> , 2009
	PAC <sup>1</sup>	PFOA	20-250	5	12	343	Yu <i>et al.</i> , 2009
Granular activated carbon	GAC <sup>1</sup>	PFOS	20-250	5	12	215	Yu <i>et al.</i> , 2009
	GAC <sup>1</sup>	PFOA	20-250	5	12	194	Yu <i>et al.</i> , 2009
	GAC <sup>2</sup>	PFOS	0.01-5	~7	96	163	Chularueangaksorn, 2013
	GAC <sup>2</sup>	PFOA	0.01-5	~7	96	40	Chularueangaksorn, 2013
	GAC <sup>2</sup>	PFHxA	0.01-5	~7	96	22	Senevirathna, 2010
Anion exchange polymers	AI400	PFOS	20-250	5	168	260	Yu <i>et al.</i> , 2009
	AI400	PFOA	20-250	5	168	1,383	Yu <i>et al.</i> , 2009
	IRA67	PFOS	35-500	3	48	2,844	Deng <i>et al.</i> , 2010
	IRA410	PFOS	35-500	3	48	364	Deng <i>et al.</i> , 2010
	PFA300	PFOS	0.01-5	~7	96	455	Chularueangaksorn, 2013
	PFA300	PFOA	0.01-5	~7	96	117	Chularueangaksorn, 2013
	PFA300	PFHxA	0.01-5	~7	96	150	Chularueangaksorn, 2013
Non ion polymers	XAD4	PFOS	0.01-5	~7	96	41	Senevirathna, 2010
	XAD4	PFOA	0.01-5	~7	96	88	Senevirathna, 2010
	Dow V493	PFOS	0.01-5	~7	96	38	Senevirathna, 2010
	Dow V493	PFOA	0.01-5	~7	96	92	Senevirathna, 2010
Mineral materials	Hydrotalcite	PFOS	1-1000	-	1	998	Rattanaoudom <i>et al.</i> , 2013
	Hydrotalcite	PFOA	1-1000	-	1	1,033	Rattanaoudom <i>et al.</i> , 2013
	Zeolites	PFOS	50-500	3.0-6.3	24	83-99	Zhou <i>et al.</i> , 2010
	Montmorillonite	PFOS	15-300	6.8-7.0	3	31	Ochoa-Herrera and Sierra-Alvarez, 2008

Note: <sup>1</sup> Sinopharm Chemical Regent Co., Ltd. (China) and <sup>2</sup> Calgon Carbon Asia Pte Ltd.

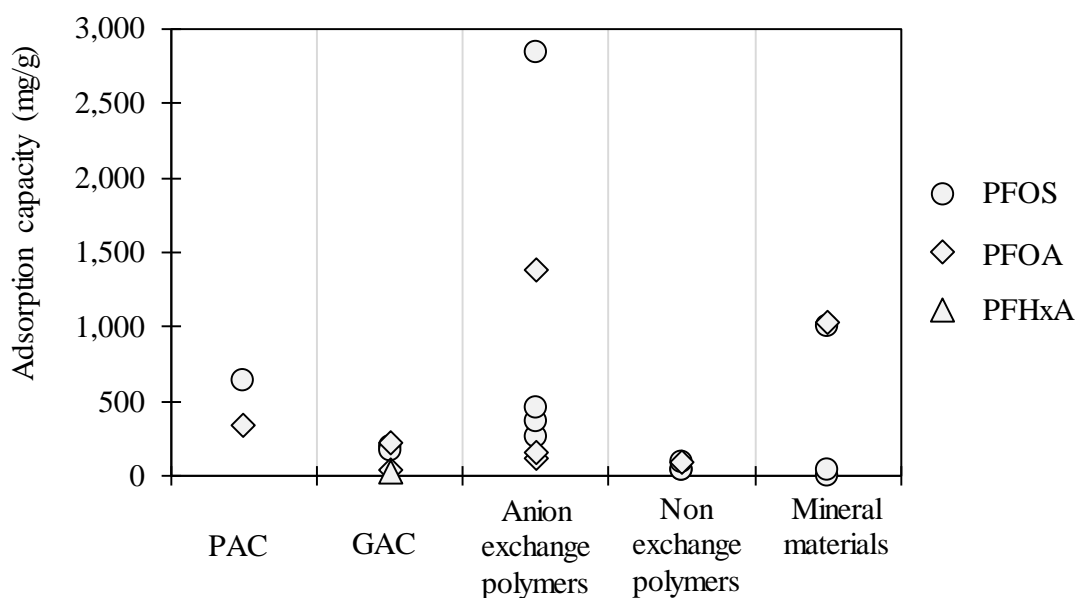


Figure 2.2 Removal technologies for PFCs in wastewater

Not only electrostatic interaction is generated by the direct adsorption between charge of surface and PFCs but also by the adsorbed on adsorbent surfaces (Xiao *et al.*, 2011 and Chen *et al.*, 2011). Adsorbents showed a negative charge after adsorbing PFC or NOM molecules. Then, the adsorbed molecule (PFC or NOM) repulsed with other anion molecule in the solution. On the other hand, divalent cations can shift the negative sites of adsorbent surface into positive ones and can attract PFC molecules (Zhou *et al.*, 2013 and Kwadijk *et al.*, 2013).

### Hydrophobic interaction

Hydrophobic interaction is interactions between hydrophobes (low water-soluble molecules). Hydrophobes are non-polar molecules and usually have long-chains of carbon that do not interact with water molecules. Ahrens *et al.*, (2011) and Jia *et al.*, (2010) found that PFCs can be adsorbed onto negatively charged surface of adsorbents overcoming electrostatic repulsion. A longer chain of PFCs showed more adsorption capacity onto hydrophobic adsorbents (Deng *et al.*, 2012).

Stronger hydrophobicity of PFCs had a lower CMC value and easily formed hemi-micelles/micelles in water (Rayne and Forest, 2009). CMC values of PFOS and PFOA

are 4,573 and 15,696 mg/L, respectively. The hemi-micelles can be formed in the range of 0.01 to 0.001 times of CMC (Johnson *et al.*, 2007).

### **Ion exchange**

The head of PFC molecule might be adsorbed via exchange reaction by functional group of ion exchange polymers. Deng *et al.* (2010) investigated the mobile ions of anion exchange polymers were exchanged with PFOS in solutions. The ratios of adsorbed PFOS to released mobile ions from the polymers were in the range of 1.0 to 1.28. It means that exchanging between mobile ions of anion exchange polymers and adsorbed PFOS were the dominant mechanism.

### **Hydrogen bond**

Many researchers reported that hydrogen bonding interaction related to PFC sorption (Takayose *et al.*, 2012; Gao and Chorover, 2012). Oxygen atoms contained in the functional head of PFCs can bond with hydrogen atom of adsorbents (Takayose *et al.*, 2012). The functional groups containing oxygen can bond with water molecules via hydrogen bonds from bulk solutions which lead to the competition between sorption of water and PFCs. Torn *et al.* (2003) reported that both hydrophobic and electrostatic interactions play important roles in sodium dodecylbenzenesulfonate adsorption onto kaolinite, and Dobson *et al.* (2000) suggested that interactions of sodium dodecylsulfate and positively charged minerals are dominated by electrostatic attraction and hydrogen bonding.

Thus, the role of hydrogen bond was significant in the adoption process of PFCs.

### **2.3.3 Membrane filtration**

Membrane filtration is a technique which used to separate target compounds from a liquid for the purpose of purifying them. Reverse osmosis (RO) and nanofiltration (NF) membranes are related to removal of PFCs. Tang *et al.* (2006) found that RO membrane rejected more than 99 % of PFOS at wide range of feed concentration (0.5 to 500 mg/L). Due to high energy consumption of RO membrane, many researchers studied NF membrane to remove PFCs. NF was tested at a feed concentration of 10 mg/L of PFOS

for four days, the PFOS rejection was related to NaCl rejection. The rejection efficiencies of NF membrane ranged from 90 to 99% (Tang *et al.*, 2007).

Recently, Zhao *et al.* (2013) have been investigated removal efficiency of PFOS from simulated surface water containing calcium ions by NF270. An increase of calcium chloride concentration enhanced PFOS rejection from 94.0 to 99.3% for the feed of 100 µg/L of PFOS with calcium concentration from 0 to 2 mM at 0.4 MPa. RO and NF membranes exhibited high efficient to remove PFCs in previous studies. However, matrixes in wastewater need to be removed from the wastewater prior to use these membranes. Retentate wastewater from membrane process is required further treatment.

#### **2.3.4 Coagulation**

Coagulation is an important technology to remove some suspended solids (SS) and soluble organic pollutants from water in water treatment plants. Deng *et al.* (2011) was the first research that studied on PFCs removal from water by coagulation. Coagulation is an efficient method to remove PFOA (initial concentration of 200 µg/L) from surface water, and its removal PFOA more than 90% at 10 mg/L of polyaluminium chloride (PACl). Most of PFOA was removed from surface water in the coagulation via the produced precipitate since the SS in water had strong sorption affinity for PFOA. The positive PACl coagulant would adsorb the negative PFOA in water in the coagulation process. Long-chain PFCs were easier to be adsorbed on the SS and removed by the coagulation.

Xiao *et al.* (2013) also tested removal of PFOS and PFOA by coagulation. Solution pH, coagulants (alum and ferric chloride), coagulant dosage, natural organic matter (NOM), initial turbidity, and flocculation time were considered. PFOS and PFOA (initial concentration of 100 and 82 µg/L, respectively) can be removed less than 20% at alum dosage of 10 to 60 mg/L and final pH of 6.5 to 8.0 while PFOS was not removed by ferric chloride coagulation (3.0 to 5.0 mg/L). Due to sorption of PFCs onto coagulant, contaminated coagulants were required proper treatment and disposal.

## Chapter 3 Experimental

This chapter summarized all materials and measurements to support methodology parts of chapter 4 to 8. It showed chemicals and reagents (such as PFCs standard, PFCs internal standard, solvents and chemicals) and adsorbents including GAC, non ion exchange polymers and anion exchange polymers. Moreover, this chapter presents procedures to analyze PFCs and wastewater parameters such anion, cation and DOC.

### 3.1 Materials

#### 3.1.1 Chemicals and reagents

##### PFCs

The eleven PFCs were selected as target chemicals which purchased from Wako Pure Chemicals (Osaka, Japan). Their stock solutions were prepared by mixing three perfluoroalkyl sulfonates (PFASs) and eight perfluoroalkyl carboxylates (PFCAs) into acetonitrile (LC/MS grade) and storing in polypropylene (PP) bottle at 4°C. The stock solutions were diluted at different concentrations by 40% acetonitrile (v/v) and used as PFCs standard. PFC internal standards were purchased from the Wellington Laboratory Inc. (Ontario, Canada). They were MPFHxA, MPFOA, MPFDA and MPFOS which prepared similar as PFCs standard. All target PFCs and internal standards are shown in **Table 3.1**.

##### Solvent and inorganic chemicals

Methanol, acetonitrile and ethanol were purchased from Wako Pure Chemicals (Osaka, Japan) which both solvent were HPLC grade. Inorganic chemicals also purchased from Wako Pure Chemicals (Osaka, Japan). **Table 3.2** shows the details of solvents and inorganic chemicals.

Table 3.1 Details of standards and internal standards of PFCs in this study

Compounds	Abbreviation	Supplier
Perfluorobutane sulfonate	PFBS	Wako Pure Chemicals
Perfluorohexane sulfonate	PFHS	Wako Pure Chemicals
Perfluorooctane sulfonate	PFOS	Wako Pure Chemicals
Perfluoropentanoic acid	PFPeA	Wako Pure Chemicals
Perfluorohexanoic acid	PFHxA	Wako Pure Chemicals
Perfluoroheptanoic acid	PFHpA	Wako Pure Chemicals
Perfluorooctanoic acid	PFOA	Wako Pure Chemicals
Perfluorononanoic acid	PFNA	Wako Pure Chemicals
Perfluorodecanoic acid	PFDA	Wako Pure Chemicals
Perfluoroundecanoic acid	PFUnDA	Wako Pure Chemicals
Perfluorododecanoic acid	PFDoDA	Wako Pure Chemicals
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]hexanoic acid	MPFHxA	Wellington Laboratory Inc.
Perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>2</sub> ]octanoic acid	MPFOA	Wellington Laboratory Inc.
Perfluoro-n-[1,2- <sup>13</sup> C <sub>2</sub> ]decanoic acid	MPFDA	Wellington Laboratory Inc.
Sodium perfluoro-n-[1,2,3,4- <sup>13</sup> C <sub>2</sub> ]octanesulfonate	MPFOS	Wellington Laboratory Inc.

Table 3.2 Details of solvents, inorganic chemicals and cartridges

Type	Name	Abbreviation	Supplier
Solvent	Methanol (LC/MS grade)	MeOH	Wako Pure Chemicals
	Acetonitrile (LC/MS grade)	ACN	Wako Pure Chemicals
Inorganic chemicals	Sodium chloride	NaCl	Wako Pure Chemicals
	Sodium fluoride	NaF	Wako Pure Chemicals
	Sodium hydroxide	NaOH	Wako Pure Chemicals
	Sodium sulfate	Na <sub>2</sub> SO <sub>4</sub>	Wako Pure Chemicals
	Sodium nitrate	NaNO <sub>3</sub>	Wako Pure Chemicals
	Potassium chloride	KCl	Wako Pure Chemicals
	Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>	Wako Pure Chemicals
	Hydrogen chloride	HCl	Wako Pure Chemicals
	Calcium chloride	CaCl <sub>2</sub>	Wako Pure Chemicals
	Magnesium sulfate	Mg <sub>2</sub> SO <sub>4</sub>	Wako Pure Chemicals
Cartridge	Oasis®HLB	-	Waters Corporation
	PresepC-Agri (C18)	-	Wako Pure Chemicals
	ENVI-Carb	-	Supelco



## Cartridges

Oasis<sup>®</sup>HLB is a hydrophilic-lipophilic balance reversed phase sorbent for solid phase extraction. PresepC-Agri (C18) is using styrene divinylbenzene polymethacrylate resin as an adsorbing material. Oasis<sup>®</sup>HLB and PresepC-Agri (C18) cartridges were used to concentrate of PFCs while ENVI-Carb cartridge was used to clean up samples. Supplier of all cartridges is shown in **table 3.2**.

### 3.1.2 Adsorbent

GAC, non ion exchange polymers and anion exchange polymers were purchased from Calgon Mitsubishi Chemical, Sigma Aldrich and Purolite Company. **Table 3.3** shows properties of these adsorbents. The adsorbents were prepared and cleaned by the following steps.

#### GAC

Coal based activated carbon of Filtrasorb 400 was used in this study. 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 0.25 to 0.50 mm meshes. The fine particles or powder attached on the surface of crushed GAC during pulverization should be removed by washing with *Milli-Q* water. The cleaning process was repeated several times until the water over GAC was clean and clear. GAC was again dried in oven at 105°C for 48 hours and stored in air tight bottles.

GAC was necessary to remove air inside pores because they might adversely reduce adsorption rate and capacity (Cheremisinoff, 1993). GAC was put into PP tube and soaked with small amount of *Milli-Q* water to pre-wet inner pore and applied in a vacuum for 24 hours before using. The total pore volume was 0.61 cm<sup>3</sup>/g and the pore size distributions of macropores, mesopores and micropores were 0.04, 0.09 and 0.48 cm<sup>3</sup>/g, respectively.

Table 3.3 Properties of GAC, non ion exchange polymers and anion exchange polymers as given by manufacturers

Type of adsorbent	Name of adsorbent	Matrix	Functional group	Diameter (mm)	Exchange capacity (eq/kg)	Surface area (m <sup>2</sup> /g)
Granular activated carbon	GAC <sup>a</sup> (Filtrisorb 400, coal based)	Stacked layers of fused hexagonal ring of C atoms	-	0.25 to 0.5	-	900 to 1,100
Non ion exchange polymers	XAD4 <sup>b</sup>	Polystyrene crosslinked with divinylbenzene (Gel)	-	0.35 to 1.18	-	> 750
Strong base anion exchange polymers	PFA300 <sup>c</sup>	Polystyrene crosslinked with divinylbenzene (Gel)	R-(CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH)N <sup>+</sup> (Dimethylethanolammonium, Type II)	0.56	1.4	-
	PFA400 <sup>c</sup>		R-(CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup> (Trimethylbenzylammonium, Type I)	0.57	1.3	-
	A860 <sup>c</sup>	Polyacrylic (Macroporous)		0.3 to 1.2	0.8	-
Weak base anion exchange polymers	B-A103 <sup>c</sup>	Polystyrene crosslinked with divinylbenzene (Macroporous)	R-(CH <sub>3</sub> ) <sub>2</sub> N (Tertiary amine)	0.3 to 1.2	1.5	-
	MN102 <sup>c</sup>				0.3	1,000

Note: a. Calgon Mitsubishi Chemical ([www.calgoncarbon.com](http://www.calgoncarbon.com))

b. Sigma Aldrich Company ([www.sigmmaldrich.com](http://www.sigmmaldrich.com))

c. Purolite Company ([www.purolite.com](http://www.purolite.com))

### **Non ion and anion exchange polymers**

Commercial non ion and anion exchange polymers were selected for adsorption of PFHxA. Non ion exchange polymers, Amberlite®XAD4 (XAD4), it is hydrophobic cross linked polystyrene polymers. XAD4 is a macroreticular (Gel) porosity and large surface area. Senevirathna (2010) reported that XAD had higher adsorption of PFOS than the other type of non ion exchange polymers. Five anion exchange polymers with different polymer matrix, porosity and functional groups were evaluated PFHxA removal. There are two common types of polymeric matrix namely polystyrene and polyacrylic. Divinylbenzene (DVB) that was used to crosslink the polymer matrix. Porosity (gel or macroporous polymers) depends upon the degree of crosslinking within the polymeric backbone. Gel type polymers have about 4 to 10 % of DVB crosslinking while macroporous polymers have approximately 20 to 25 % DVB crosslinking. Strong base anion exchange polymers were classified as type I (Trimethylbenzylammonium) and type II (Dimethylethanolammonium) based on their functional groups. The functional group of weak base anion exchange polymers is tertiary amine group.

Non ion exchange polymers (XAD4), strong base anion exchange polymers (PFA300, PFA400 and A860) and weak base anion exchange polymers (BA103 and MN102) were prepared by the following steps before conducting experiments. The polymeric adsorbents were washed several times 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 for 48 hours. After that, the polymers were stored in a dry and moisture free place.

## **3.2 Measurements**

### **3.2.1 PFCs**

#### **Pretreatment and extraction**

Analytical procedure of PFCs in liquid and particulate phases is shown in **Fig 3.1**. Sampling bottles and laboratory equipment (Filtration equipment, syringe and syringe barrels, beakers, measuring flasks, measuring cylinders, test tubes, etc.) were rinsed with methanol before using. Teflon materials were avoided throughout the sample preparation.

Samples were filtered through dry GF/B filter papers (1  $\mu\text{m}$ , Whatman, Japan), which were washed with methanol and dried.

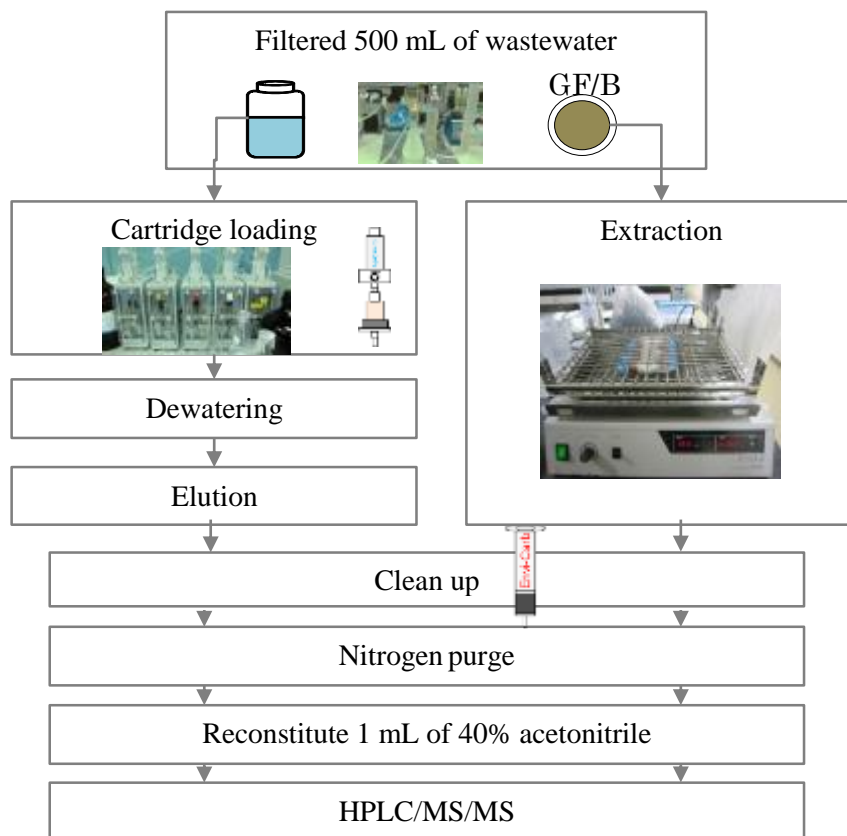


Figure 3.1 Analytical procedure of PFCs in liquid and particulate phase

Filtrated sample (liquid phase) was concentrated into two cartridges in order to enhance recovery of PFCs. The samples were passed through PresepC-Agri (C18) cartridge connected in line with Oasis®HLB. Both cartridges were pre-conditioned by 10 mL of methanol and 20 mL of ultrapure water, manually. The peristaltic pump was washed with methanol for 5 min at 5 mL/min followed by ultrapure water for 15 min at 10 mL/min before concentrating each sample. Filtrated samples were loaded into two cartridges at 5 mL/min. Cartridges were dried in a vacuum manifold (Water, USA) for two hours. PFCs in dried cartridges were eluted by 2 mL of methanol (LC/MS grade) followed by 2 mL of acetonitrile into PP tube. They were evaporated until dried by nitrogen gas (N<sub>2</sub>) and reconstituted with 1 mL of 40% acetonitrile in *Milli-Q* water (v/v), then analyzed by HPLC-MS/MS.

Suspended solid contained filter papers were used for PFCs analysis in particulate phase. Each filter paper was placed into 15 mL PP tube. Methanol (5 mL) was added into the PP tube and then it was shaken at 120 rpm for 30 minute. Extracted sample was separated into another PP tube and the extraction processes were conducted two times. Final extracted sample (10 mL) was passed through ENVI-Carb cartridge which was cleaned up by 4 mL of methanol in advance. Then, eluent solution was dried by nitrogen gas (N<sub>2</sub>) and reconstituted by 40% acetonitrile in ultrapure water (Suzuki *et al.*, 2011).

### HPLC electrospray tandem mass spectrometry

PFCs were measured using a high performance liquid chromatography mass spectrometer (HPLC/MS/MS). HPLC 1200SL and MS/MS 6410 Triple Quadrupole (Agilent, Japan) were used in this study. Operation conditions for the HPLC and MS/MS are shown in **Table 3.4**.

Table 3.4 HPLC-MS/MS operation condition

HPLC	1200SL, Agilent
Main column	Agilent Eclipse Plus C18 (2.1 x 100 mm, particle size 3.5 µm)
Guard column	Agilent Eclipse Plus C18 (2.1 x 20 mm, particle size 3.5 µm)
Mobile phase A	5 mM ammonium acetate in ultrapure water
Mobile phase B	Acetonitrile
Flow rate	0.25 mL/min
Injection volume	10 µL
MS/MS	6410 Triple Quadrupole, Agilent
Ion source	Electrospray ionization negative (ESI)
Mode	Multiple reaction monitoring (MRM)
Vaporizer temp.	150 °C
Gas temp.	300 °C
Gas flow rate	5 L/min
Nebuliser	60 psi
Charging voltage	2000 V

Ten µL of extracted sample was injected to a 2.1 x 100 mm (3.5 µm) Agilent Eclipse Plus C18 column. The HPLC mobile phase contained of 5 mM ammonium acetate in ultrapure water and acetonitrile. The initial mobile phase was 30% acetonitrile with a flow rate of 0.25 mL/min. The mobile phase gradient linearly ramped from 30 to 50% acetonitrile at 16.5 minutes, and then went to 70% acetonitrile at 16.6 minutes, held at 70% acetonitrile for 3.4 minutes. At 21 minutes, acetonitrile went up to 90%, held at 90% acetonitrile for 7 minutes, and then ramped down again to 30% over 6 minutes. The column temperature

was set at 40 °C with a capillary voltage of 0.5 kV. The mass spectrometer was operated in the electrospray ionization (ESI) negative mode. Analyse ions were monitored using multiple reactions monitoring (MRM) mode. **Table 3.5** shows analytical parameters of PFCs.

Table 3.5 Analytical parameters of analyzed PFCs by HPLC-MS/MS

Compounds	Parent ion ( <i>m/z</i> )	Daughter ion ( <i>m/z</i> )	<i>CE</i> ( <i>eV</i> )	Retention time (min)	<i>LOD</i> (ng/L)	<i>LOQ</i> (ng/L)
PFBuS	299	80	55	2.7	0.01	0.04
PFHS	399	80	55	7.9	0.01	0.04
PFOS	499	80	55	13.8	0.02	0.08
PFPeA	263	219	5	1.9	0.02	0.05
PFHxA	313	269	5	2.8	0.02	0.06
PFHpA	363	319	5	4.7	0.01	0.07
PFOA	413	369	5	7.2	0.01	0.04
PFNA	463	419	5	9.9	0.02	0.03
PFDA	513	469	5	12.7	0.01	0.06
PFUnDA	563	519	5	15.4	0.01	0.02
PFDoDA	613	569	5	18.0	0.01	0.03
MPFHxA	315	271	5	2.8	0.04	0.05
MPFOA	417	373	5	7.2	0.04	0.08
MPFDA	515	471	5	12.7	0.04	0.12
MPFOS	503	80	55	13.8	0.04	0.16

Note : *CE* = collision energy

*LOD* = limit of detection

*LOQ* = limit of quantification

Calibration curves for quantification consisted of six points ranging from 0.05 to 10 µg/L. All of the calibration curves showed high linearity ( $R^2 > 0.99$ ). The limit of detection (*LOD*) was empirically was defined as the injected amount producing a signal-to-noise ratio of 3, and the limit of quantification (*LOQ*) was defined as the injected amount producing a signal-to-noise ratio of 10.

### 3.2.2 Wastewater characteristics

#### Anions and cations

Analytical instruments in this study is shown in **table 3.6**. Anions including chloride, sulfate, and nitrate were analyzed using an ion chromatograph (IC, Dionex ICS-2000) as well as cations including sodium, potassium, calcium and magnesium were analyzed using an inductively coupled plasma (ICP, Agilent 700 Series Axial ICP-OES).

Table 3.6 Analytical instrument for wastewater parameter

Parameter	Analytical instrument
Chloride, sulfate, nitrate and fluoride	IC
Sodium, potassium, calcium and magnesium	ICP
DOC	TOC analyzer
pH	pH meter
Conductivity	Pocket conductivity meter
Temperature	Thermometer

### Dissolved organic carbon (DOC)

DOC was analyzed by total organic carbon analyzer (TOC-V<sub>CSN</sub>, Shimadzu). The potassium hydrogen phthalate is a standard chemical according to 5310 method for TOC. The standard calibration curves in analysis were more than 0.99 of correlation coefficient ( $R^2$ ).

### Molecular size distribution of dissolved organic carbon

Bench scale dead-end filtration tests were carried out to compare the molecular size distribution of dissolved organic carbon. There were two types of filtration equipment were used to filtration the samples. The first one was a vacuum filtration which Whatman GF/B Glass fiber filter and MF-Millipore membrane filters (pore size 0.22 and 0.45 $\mu$ m) were used to filtrate by this filtration (**Figure 3.2**). These filters/membranes were washed with *Milli-Q* water before filtration the samples.

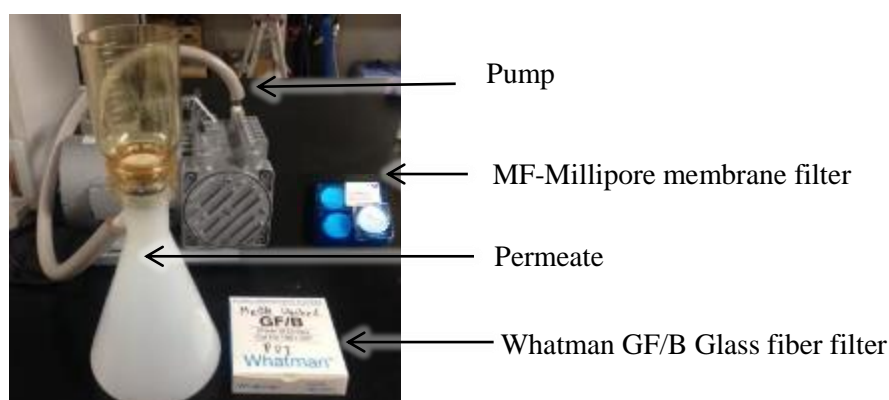


Figure 3.2 Vacuum filtration

Secondly, a commercially available dead-end filtration test cell (UHP-90K, Advantec Toyo, Tokyo, Japan) was used with polysulfone membrane. There are three sizes of

molecular weight cut-off (MWCO) membrane were used in this study which are 10, 50 and 200 kDa. The steps to filtrations are following.

1. Pretreatment membrane by washing with 20% ethanol and following by *Milli-Q* water.
2. Setup the ultrafiltration vessel as in **fig 3.3**.
3. Add 600 mL of samples into ultrafiltration vessel
4. Adjust the stirrer at 100 rpm
5. Control the pressure at 0.1 MPa
6. Collect 500 mL of permeate sample and stop supply the nitrogen gas
7. Measure DOC concentration in permeate and retentate

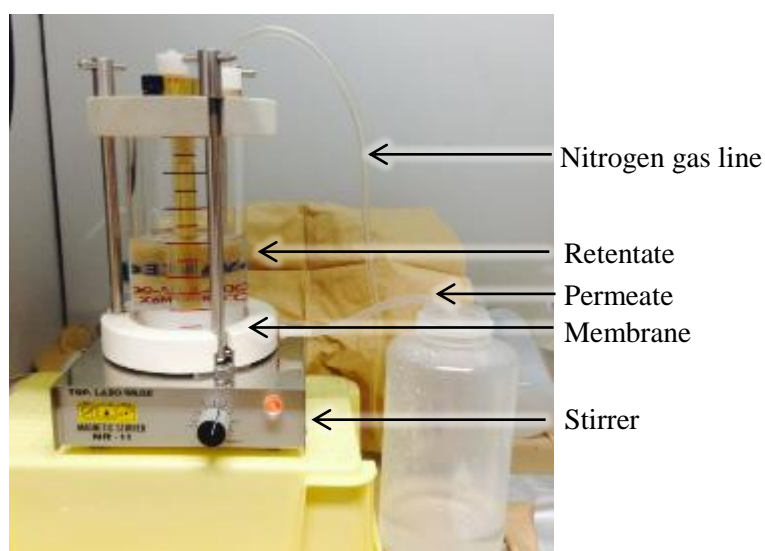


Figure 3.3 Ultrafiltration vessel driving by pressure (UHP 90, Advantec)

### **Conductivity, pH and temperature**

Conductivity and pH were measured by pH meter (Horiba D-51S) and pocket conductivity meter (Horiba B-173), respectively. Temperature were measured by mercury thermometer during surveys.



## **Chapter 4 PFCs contaminations and industrial wastewater characteristics in Thailand and Japan**

### **4.1 Introduction**

Occurrences of PFCs in industrial wastewater were investigated in Thailand and Japan (Kunacheva *et al.*, 2009; Shivakoti *et al.*, 2010; Chularueangaksorn *et al.*, 2013). These researchers found that concentrations of PFCs exceed several thousand ng/L in some WWTPs. PFOS, PFOA, and PFNA were mainly detected in WWTPs in Japan, while PFBuS, PFOA, and PFHxA were mainly detected in WWTPs of industrial areas in Thailand. They conducted survey during 2006 to 2010 and there were some regulations related to PFOS and PFOA during this period.

In 2006, voluntary commitments to reduce and/or restrict their manufacturing were implemented. PFOS and related substances were also listed in Annex B of the Stockholm Convention on POPs (Wang *et al.*, 2009). In 2010, manufacturers and suppliers of fluorochemicals reduced their use and emissions of PFOA, its precursors, and the higher homologues based on the United States Environmental Protection Agency 2010/15 PFOA Stewardship Program (USEPA, 2006).

Some industries switched to C6 PFCs such as PFHxA to replace C8 PFCs such as PFOS and PFOA. On the other hand, PFOS and PFOA related industries in developed countries might move to developing countries. The composition patterns of PFCs in industrial wastewater may change as a result of these modifications in production and application.

Biological treatment processes were ineffective to remove PFCs (Kunacheva *et al.*, 2009). The developments of effective target PFCs (PFHxA) removal techniques in industrial wastewater are required. Adsorption process was considered as a good candidate of technologies removing PFCs from wastewater. In general, inorganic ion as well as dissolved organic matter are present in industrial wastewater which might affect the adsorption capacity of absorbents on target PFCs. Therefore, wastewater characteristics had to be investigated to understand effects of interference on PFHxA adsorption in chapter 5.

## 4.2 Objectives

Specific objectives of this study are shown as follows.

1. To determine concentration and loading of PFCs in industrial wastewater in Thailand and Japan
2. To compare the PFCs concentration pattern with that reported in previous study
3. To investigate industrial wastewater characteristics

## 4.3 Methodology

### 4.3.1 Wastewater sampling sties

#### Thailand

Ten central WWTPs were selected from 40 central WWTPs in industrial areas, in Central and Eastern of Thailand. These industrial areas have a potential to discharged PFCs from production processes. There are many factories located in each industrial area. Each central WWTP area receives wastewater from various types of factory such as electronics, chemical, paper, plastic, glass, food packaging and automobile. Uses of PFCs in production processes have potential to discharge PFCs through wastewater. Activated sludge process was used in all central WWTPs. WWTP6 had activated sludge process with advance treatment including an ultrafiltration (UF) and a reverse osmosis (RO) for reuse the treated wastewater. The location of each industrial area and information are shown in **Fig. 4.1** and **Table 4.2**.

Field surveys were conducted from 13 December 2012 to 23 January 2013. Samples were collected at tap, influent, aeration tank, secondary clarifier, UF, RO and effluent from central WWTPs of each industrial area using grab sampling technique. PFCs in tap water was measured to know the background level of PFCs in each central WWTP. Many types of untreated wastewater from electronic, plastic, chemical, paint, paper, automobile, textile, metal and food areas were collected. Tap water sample (used in industrials production process) were collected to identify the background concentration of PFCs.

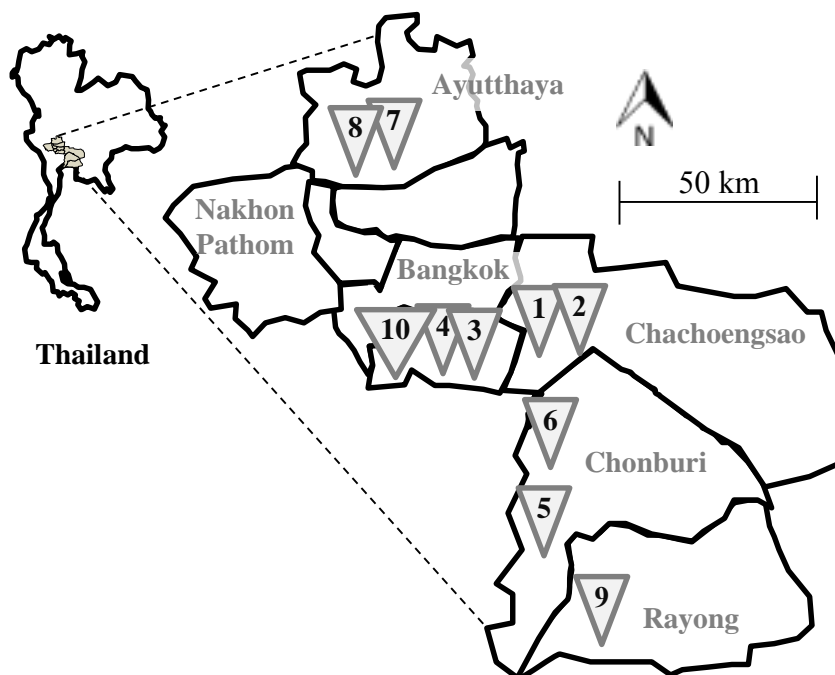


Figure 4.1 WWTPs sampling sites in Thailand

### Japan

In this study, wastewater samples were collected from the treated wastewater of a fluorochemical factory in Japan on 25 April 2013, 17 May 2013, 19 and 29 October 2014. These wastewater were treated by the coagulation process (using poly aluminium chloride as a coagulant) followed by the adsorption process (using GAC and anion exchange polymer as adsorbents). **Figure 4.2** shows the wastewater treatment process of a fluorochemical factory. The wastewater sample were collected from point A1 to A8 in **Fig. 4.2** using the grab sampling technique.

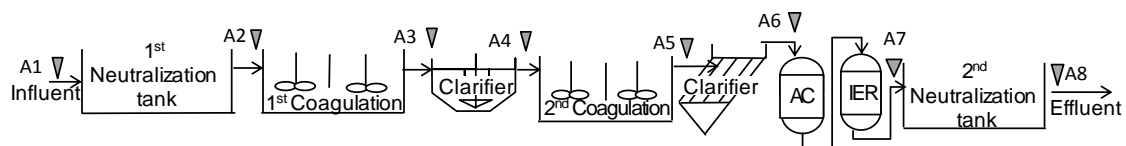


Figure 4.2 WWTP flow diagram of a fluorochemicals industry in Japan

Table 4.1 Location information of WWTPs and sampling details

No.	Capacity (m <sup>3</sup> /day)	Number of industry	Treatment process <sup>a</sup>	Main industrial types <sup>b</sup>	Sampling date	Sample point	Number of sample
WWTP1	8,400	118	Inf→PC→AS→SC→Eff	- Plastic (26%) - Automotive (21%) - Steel and metal (12%)	13/12/2012	Tap, Inf, AS, SC, Eff	10
WWTP2	9,200	42	Inf→PC→AS→SC→Eff	- Automotive (21%) - Plastic (19%) - Electronics (17%)	13/12/2012	Tap, Inf, AS, SC, Eff	10
WWTP3	21,000	320	Inf→PC→AS→SC→Eff	- Steel and metal (19%) - Plastic (16%) - Automotive (13%)	17/12/2012	Tap, Inf, AS, SC, Eff	10
WWTP4	26,000	550	Inf→PC→AS→SC→Eff	- Electronics (26%) - Automotive (22%) - Plastic (10%)	17/12/2012	Tap, Inf, AS, SC, Eff	10
WWTP5	14,000	200	Inf→PC→AS→SC→Eff	- Automotive (28%) - Electronics (18%) - Steel and metal (16%)	18/1/2013	Tap, Inf, AS, SC, Eff	10
WWTP6	24,000	484	Inf→PC→AS→SC→SF →UF→RO	- Automotive (32%) - Steel and metal (17%) - Electronics (14%)	18/1/2013	Tap, Inf, AS, SC, SF, UF feed, UF retentate, RO feed (UF permeate), RO retentate and RO permeate	40
WWTP7	12,000	316	Inf→PC→AS→SC→Eff	- Electronics (33%) - Automotive (14%) - Food (12%)	21/1/2013	Tap, Inf, AS, SC, Eff	10
WWTP8	16,000	244	Inf→PC→AS→SC→Eff	- Electronics (45%) - Plastic (20%) - Automotive (9%)	21/1/2013	Tap, Inf, AS, SC, Eff	10
WWTP9	11,200	213	Inf→PC→AS→SC→Eff	- Chemicals and related (55%) - Petroleum and energy (19%) - Plastic (7%)	23/1/2013	Tap, Inf, AS, SC, Eff	10
WWTP10	45,000	350	Inf→PC→AS→SC→Eff	- Steel and metal (15%) - Paper and printing (13%) - Chemicals and related (12%)	23/1/2013	Tap, Inf, AS, SC, Eff	10

Note: a. AS = activated sludge, Eff = effluent, Inf = influent, PC = primary clarifier, RO = reverse osmosis, SC = secondary clarifier, SF = sand filter, Tap = tap water and UF = ultrafiltration b. Data source (<http://ereport.ieat.go.th/index.php/main/default/factory/>)

#### 4.3.2 Wastewater sample collection

Wastewater samples were collected below the water surface using a stainless steel bucket. The 1.5 L narrow-neck polyethylene terephthalate (PET) bottles were rinsed with wastewater sample twice then the wastewater samples were transferred into those bottles. Conductivity, pH and temperature were measured on-site. The wastewater samples were storage at 4°C during transportation to the laboratory. All the wastewater samples were filtrated by GF/B. The filtrated samples were pretreatment and extraction to analyzed PFCs in liquid and particular phase. The wastewater samples were measured suspended solid (SS) and TOC on the sampling days. The wastewater characteristics such as anion, DOC and pH were also measured. Section 3.2 shows how to measure PFCs and wastewater characteristics.

A matrix spike recovery test was conducted by spiking PFCs standards and PFCs internal standard into 20% of sample number ( $n = 2$ ). For liquid phase samples, standards were spiked before loading into cartridges, while particulate samples were spiked standards before extraction process. PFCs in wastewater samples were also analyzed without spiking and the recovery rates for the matrix spike test were calculated by subtracting the amount of PFCs originally contained in the samples. The average absolute recovery rates in the matrix spike test ranged from 84% (PFPeA) to 106% (PFNA) in liquid phase samples and from 91% (PFBuS) to 120% (PFOS) in particulate phase samples. The absolute recovery rates in the matrix spike test of PFCs were determined from the samples as shown in **Table 4.2**.

Table 4.2 Analytical recoveries percentage based on spiked PFCs in liquid and particulate phases

Phase	Liquid (%)				Particulate (%)			
Compounds	Ave	Max	Min	SD	Ave	Max	Min	SD
PFBuS	94	118	80	10	91	101	71	8
PFHS	102	110	85	5	94	108	78	9
PFOS	101	115	89	8	96	120	80	10
PFPeA	82	92	71	6	97	109	87	7
PFHxA	94	113	80	8	93	106	81	6
PFHpA	91	107	82	7	93	107	80	7
PFOA	95	109	80	10	100	119	87	10
PFNA	106	120	90	9	94	119	75	12
PFDA	96	116	75	13	92	105	78	8
PFUnDA	93	123	74	15	99	116	78	8
PFDoDA	89	107	72	12	104	117	84	7
MPFHxA	92	99	81	7	91	111	71	8
MPFOA	96	107	84	7	94	108	78	9
MPFDA	104	117	97	6	96	111	80	9
MPFOS	103	115	91	8	97	109	87	7

\*Ave = Average, Max = Maximum, Min = Minimum and SD = Standard deviation

A sampling blank was conducted to check the contamination during transportation and analytical procedure. At the laboratory, 1.5 L of *Milli-Q* water was added to a washed PET bottle and carried out in the same manner with the wastewater samples. PFCs analyses in the sampling blank were less than the *LODs*.

## 4.4 Results and discussion

### 4.4.1 PFCs concentration in central WWTPs in Thailand

Effluents of each factory inside the industrial area were discharged to central WWTPs. Wastewater from different types of industries were combined by equalization tank before treating by biological processes. Each industrial area had different wastewater characteristics depend on sources of water supply and industrial production processes.

Wastewater samples were collect at influent, activated sludge, secondary clarifier and effluent.

PFCs concentration (ng/L) in ten central WWTPs is shown in **Appendix A**. PFBuS, PFOS, PFHxA and PFOA were found in all WWTPs. PFCs concentrations in each WWTP were constant during biological treatment process. It means that biological treatment processes were ineffective to remove PFCs.

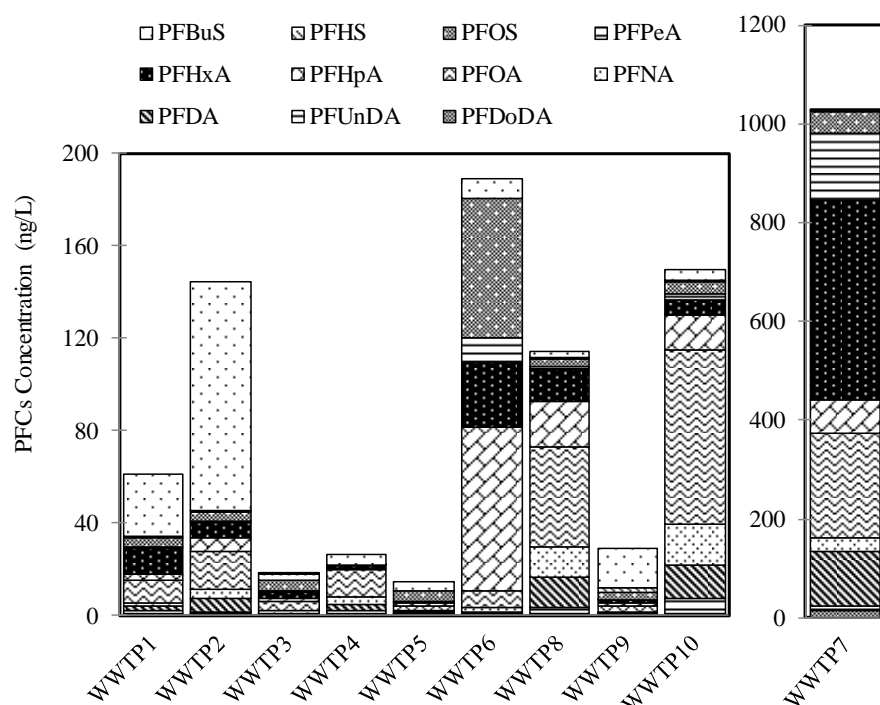


Figure 4.3 Total PFCs concentrations in effluent of central WWTPs

**Figure 4.3** shows profile of PFCs concentrations in effluent of ten central WWTPs. Total PFCs concentration in effluent ranged from 15 to 1,030 ng/L among which WWTP7 had the highest concentration of PFCs. The dominant of PFCs were PFHxA and PFOA which they contributed 39.3% and 20.4% of total PFCs concentration, respectively. Electronic and automotive industries were the major wastewater sources of WWTP7. PFOA was

dominant in WWTP8 and WWTP10. PFBS was dominant in WWTP1 and WWTP2. PFDoDA was rarely detected in wastewater. The result indicated that PFCs concentrations were different in each industrial area and number of industries or wastewater volume did not relate to PFCs concentrations. The specific types of industry that use PFCs in their production process might contribute the PFCs concentration in central WWTPs.

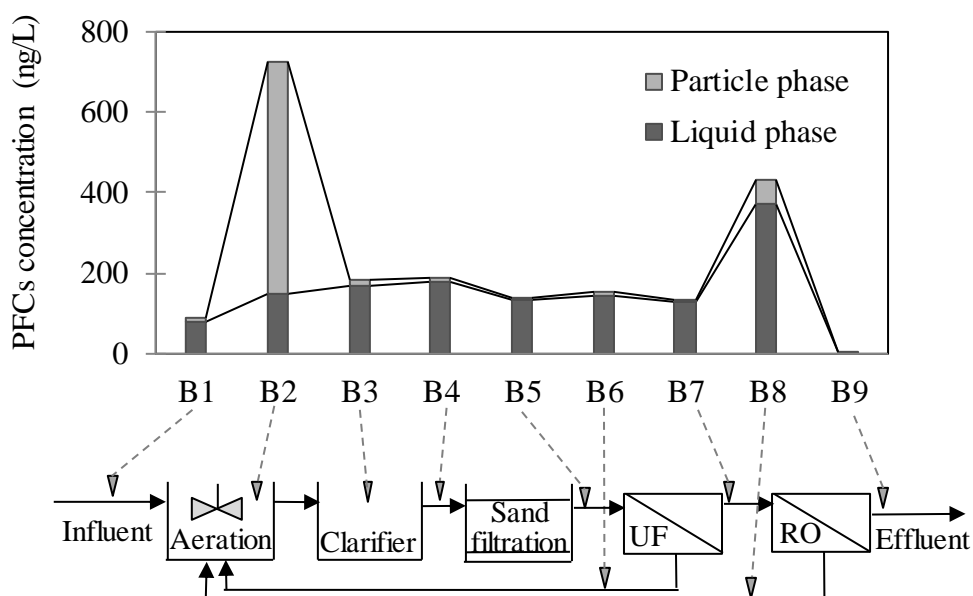


Figure 4.4 PFCs concentrations in WWTP6

WWTP6 had advanced wastewater treatment process (UF and RO) after treatment by activated sludge process. **Figure 4.4** shows total PFCs concentration in liquid and particulate phases in each wastewater treatment step. PFCs were removed by RO process. This is in accordance with the results of Tang *et al.* (2006). It was found that RO membrane could reject more than 99% of PFOS.



#### 4.4.2 PFCs loading from ten central WWTPs in Thailand

Total PFCs concentrations was calculated by assigning the concentration equal to 0 if it was less *LOD* and *LOQ*. Mass flow rates of PFCs were estimated through multiplying total PFCs concentration with the average flows rate of wastewater, which is supplied by the officials of each WWTPs in each industrial area. **Table 4.3** shows PFCs loading from ten central WWTPs. The ten WWTPs discharged 28.7 g/day of PFCs. PFOA, PFHxA and PFHpA were the dominant compounds in discharged wastewater. PFOA, PFHxA and PFHpA loadings were 7.46, 6.33 and 3.66 g/day, respectively. WWTP7 is the main sources of PFCs which it contributed 43% of total PFCs loading.

Table 4.3 PFCs loading from ten WWTPs (g/day)

WWTP	PFBuS	PFHS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	ΣPFCs
WWTP1	0.23	0.01	0.03	0.01	0.09	0.02	0.09	0.01	0.01	0.01	0.01	0.51
WWTP2	0.91	0.00	0.04	0.01	0.06	0.06	0.15	0.03	0.06	0.01	0.01	1.33
WWTP3	0.01	0.05	0.09	0.02	0.05	0.02	0.08	0.03	0.01	0.01	0.00	0.36
WWTP4	0.12	0.00	0.02	0.00	0.03	0.02	0.30	0.07	0.00	0.02	0.01	0.59
WWTP5	0.06	0.00	0.05	0.00	0.02	0.01	0.03	0.01	0.01	0.01	0.00	0.19
WWTP6	0.21	0.00	1.44	0.25	0.68	1.71	0.17	0.04	0.02	0.02	0.00	4.54
WWTP7	0.03	0.05	0.48	1.63	4.85	0.80	2.50	0.35	1.24	0.13	0.15	12.22
WWTP8	0.04	0.02	0.06	0.03	0.22	0.31	0.72	0.23	0.23	0.05	0.02	1.92
WWTP9	0.19	0.02	0.03	0.00	0.01	0.01	0.03	0.00	0.00	0.00	0.00	0.31
WWTP10	0.20	0.02	0.25	0.10	0.29	0.70	3.40	0.78	0.65	0.31	0.04	6.74
Total	1.99	0.18	2.49	2.05	6.30	3.66	7.46	1.56	2.23	0.56	0.23	28.70

Tap water is used for the industrial processes and daily-life activities of worker. The comparison between PFCs loadings in effluent and tap water is shown in **Fig. 4.5**. PFCs loading in tap water ranged from 0.02 to 0.29 g/day. PFCs loadings in effluent were higher than in tap water for most of the central WWTPs due to industrial processes. However, PFCs loading of WWTP9 in effluent was slightly higher than in tap water. It

indicated that industrial processes discharged a small amount of PFCs. Major factories discharging PFCs to WWTP9 were chemicals, petroleum and energy and plastic.

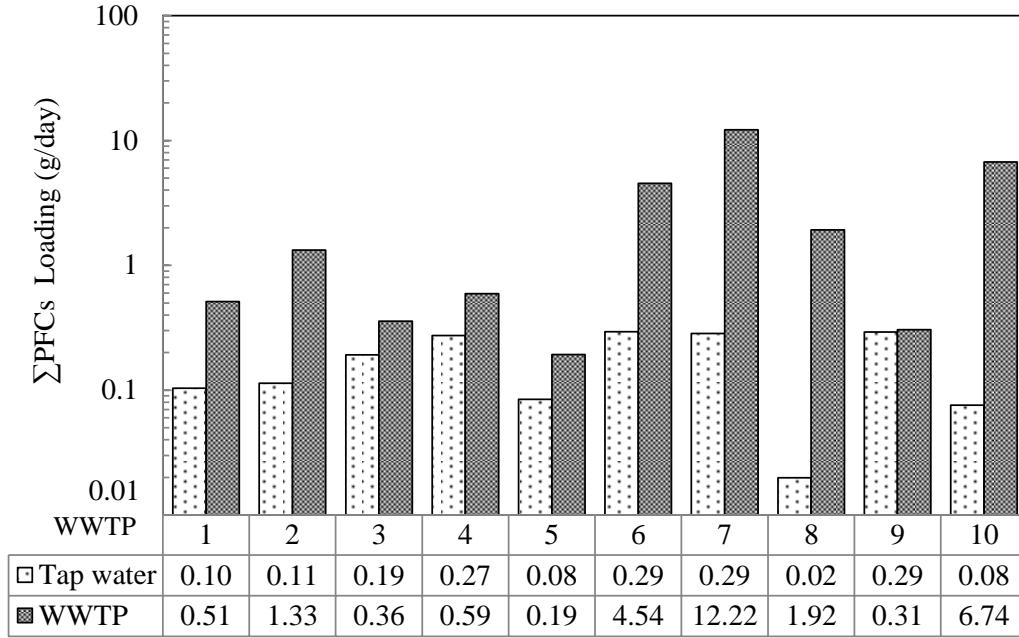


Figure 4.5 Comparison of PFCs loading in tap water and effluent

#### 4.4.3 Relationship between PFHxA and other PFC concentrations at effluent in Thailand

Comparison of PFHxA and other PFC concentration from ten central WWTPs were shown in **Fig 4.6**. The plots were below linear line 1:1 indicating that PFHxA concentration was higher than concentration of other PFC. The PFCs concentration data was calculated the ratio of geometric mean of PFC and PFHxA by the following equation.

$$\begin{aligned}
 R(PFC:PFHxA) &= \frac{\text{Geometric mean of PFC}}{\text{Geometric mean of PFHxA}} \\
 &= \sqrt[n]{\frac{PFC \text{ of WWTP1} \times PFC \text{ of WWTP 2} \times \dots \times PFC \text{ of WWTPn}}{PFHxA \text{ of WWTP1} \times PFHxA \text{ of WWTP 2} \times \dots \times PFHxA \text{ of WWTPn}}} \quad 4.1
 \end{aligned}$$

where  $R(PFC:PFHxA)$  = ratio of geometric mean of PFC and PFHxA concentration

PFC of WWTP  $n$  = PFC concentration of WWTP  $n$

PFHxA of WWTP  $n$  = PFHxA concentration of WWTP  $n$

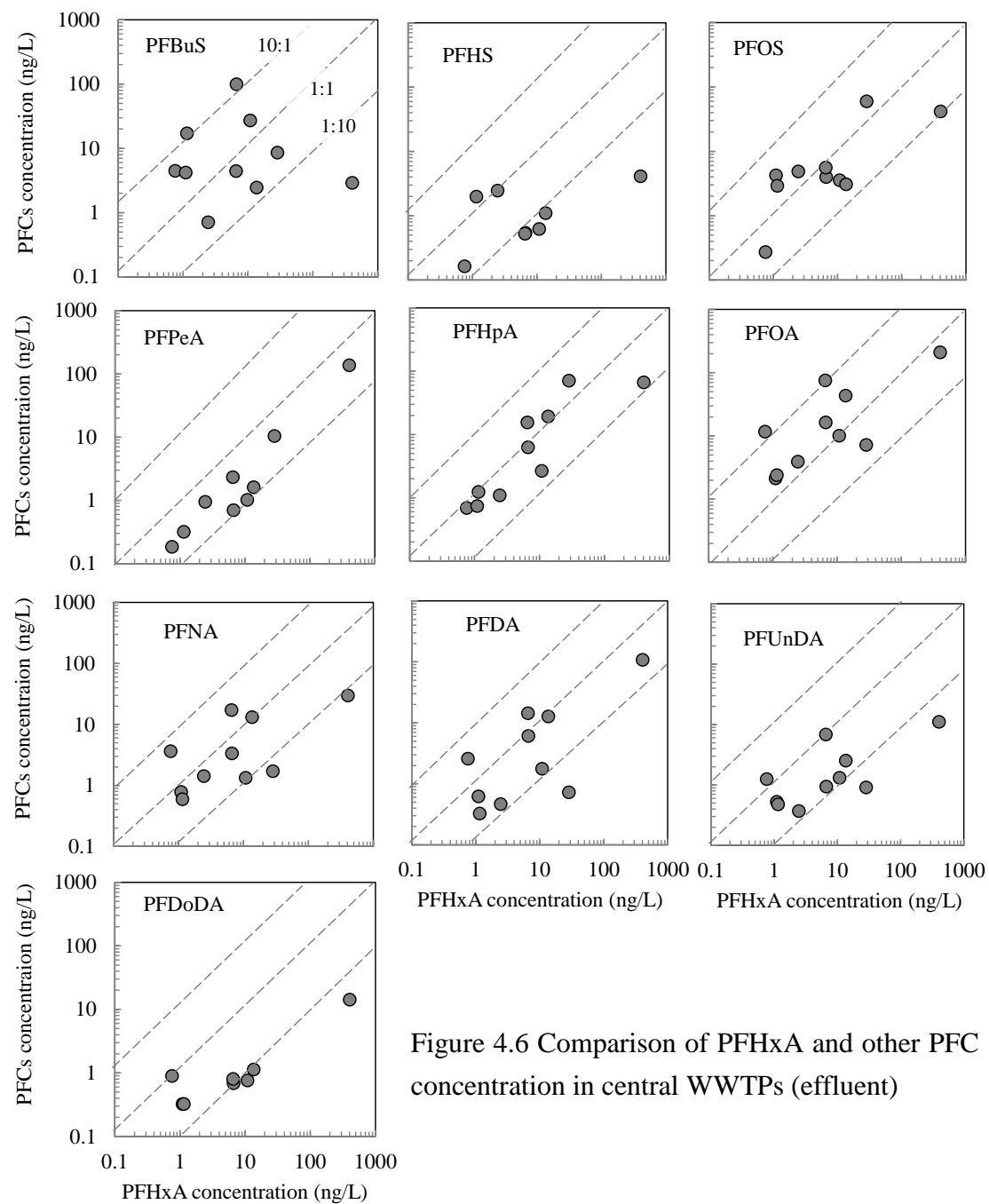


Figure 4.6 Comparison of PFHxA and other PFC concentration in central WWTPs (effluent)

Table 4.4 The ratio of geometric mean of PFC and PFHxA concentration in ten central WWTPs

PFC	PFBuS	PFHxS	PFOS	PFPeA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
<i>R</i> (PFC:PFHxA)	0.994	0.099	0.754	0.173	0.791	2.021	0.486	0.430	0.208	0.066

The geometric means of PFHxS, PFOS, PFPeA, PFHpA, PFNA, PFDA, PFUnDA and PFDoDA concentration were lower than geometric mean of PFHxA (**Table 4.4**). It was indicated that use of those PFC compounds in industrial production was less than use of PFHxA. The geometric means of PFBuS and PFHxA were similar. In 2011, Chularueangaksorn (2013) and Shivakoti (2010) reported that PFBuS was the dominant PFC in central WWTPs (Thailand). This result shows that some industries might apply PFBuS in their production processes due to PFOS regulations (Wang *et al.*, 2009). Only the geometric mean of PFOA concentration was higher than PFHxA. It means that PFOA was used in the industries in Thailand.

#### 4.4.4 Comparison of PFCs concentration with results in previous studies

PFCs concentration in WWTP1 and WWTP2 were measured by Chularueangaksorn (2013) in May 2011 and Kunacheva (2009) have been measured PFCs concentration in central WWTPs (WWTP3 to WWTP10) during June 2007 to October 2008. PFCs concentrations in previous studies were compared with the results in this study (**Fig. 4.7**). The PFC concentration data was calculated the ratio of geometric mean of PFC in previous study and this study by the following equation.

$$R(\text{pre: this}) = \frac{\text{Geometric mean of PFC concentration in previous study}}{\text{Geometric mean of PFC concentration in this study}} = \frac{n \sqrt[n]{PFC_{\text{pre of WWTP1}} \times PFC_{\text{pre of WWTP2}} \times \dots \times PFC_{\text{pre of WWTPn}}}}{\sqrt[n]{PFC_{\text{this of WWTP1}} \times PFC_{\text{this of WWTP2}} \times \dots \times PFC_{\text{this of WWTPn}}}} \quad 4.2$$

where  $R(\text{pre: this})$  = ratio of geometric mean of PFC concentration in previous study and this study

$PFC_{\text{pre of WWTP } n}$  = PFC concentration in previous study of WWTP  $n$

$PFC_{\text{this of WWTP } n}$  = PFHxA concentration in this study of WWTP  $n$

Table 4.5 The ratio of geometric mean of PFC concentration in previous study and this study

PFC	PFHxS	PFOS	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA
<i>R</i> (pre:this)	6.255	6.382	2.692	0.775	1.123	4.672	1.323	1.901	0.963

**Table 4.5** shows the ratio of geometric mean of PFC concentration in previous study and this study. Most of PFOS and PFHS concentrations reported in previous study were higher than the detected concentration in this survey. It was indicated that reduction of PFOS concentration in effluent might relate to countermeasure of PFOS under the Stockholm Convention (Stockholm Convention, 2012).

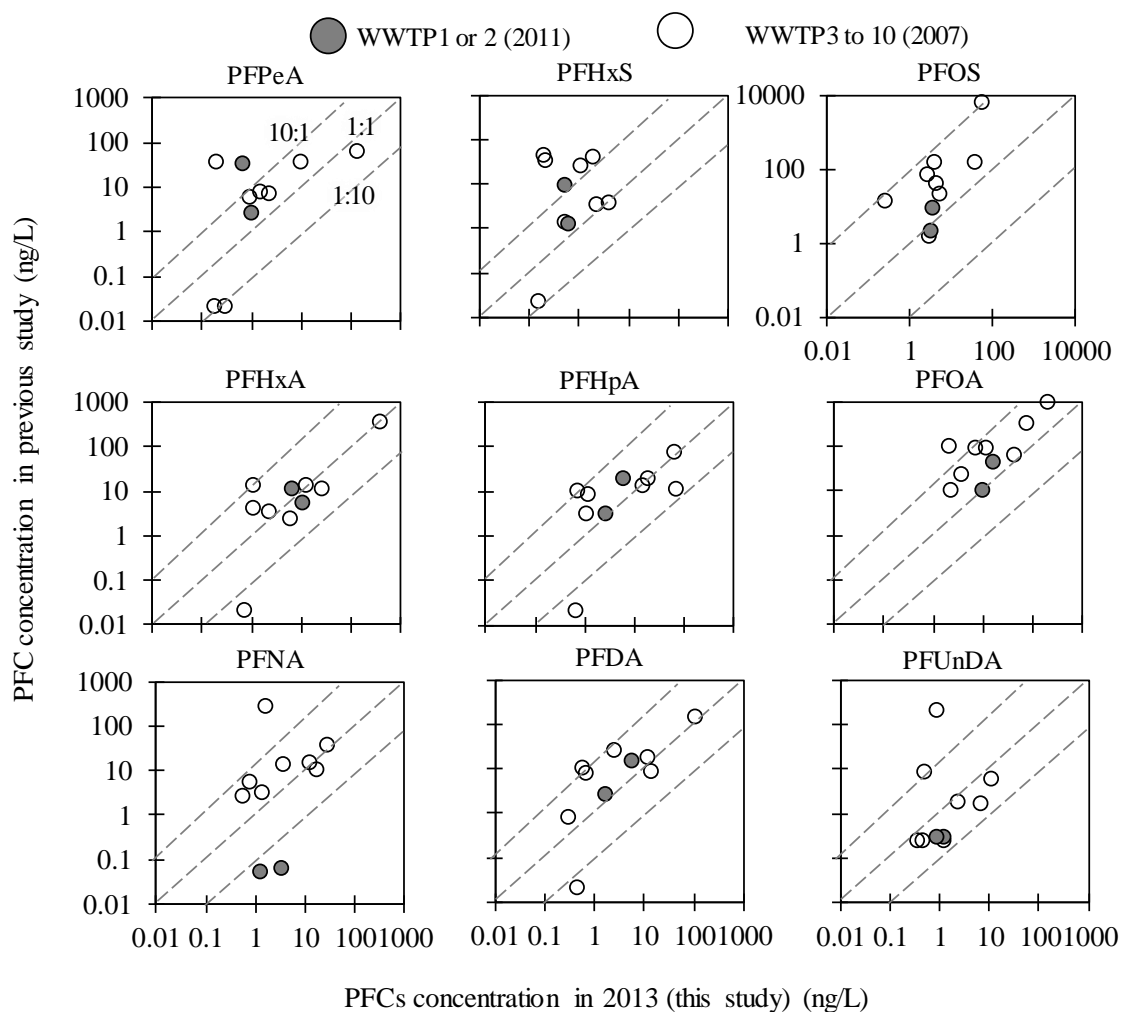


Figure 4.7 Comparison of PFC concentrations in effluent with that reported in previous study

For PFCAs group, concentrations in effluent of PFPeA, PFHpA, PFOA, PFNA, PFDA and PFUnDA in previous were higher than those concentrations in this study. On the other hand, concentrations of PFHxA and PFHpA in previous work were lower than the concentrations of this study. Manufacturers and suppliers of fluorochemicals in the industrial areas might reduce their use and emissions of PFOA, its precursors, and the higher homologues based on the United States Environmental Protection Agency 2010/15 PFOA Stewardship Program (USEPA, 2006). Some companies might switch to PFHxA to replace PFOA. The composition of PFCs in the environment may change as a result of these modifications in production and application patterns.

#### **4.4.5 PFCs concentrations from industries in industrial area**

Wastewater samples from 31 industries inside industrial areas were collected to investigate PFCs contaminations in different types of factories such as electronic, plastic, chemicals, paint, paper, automobile, textile, metals and food factory. Average PFCs concentrations in effluent of factories inside industrial areas are shown in **Fig 4.8**.

Total PFCs concentrations in effluent of each factory ranged from 1 to 881 ng/L. The highest and lowest total PFCs concentrations were detected in electronic and plastic industry, respectively. Kunacheva (2009) reported that the highest concentration was detected in electronic factory. The major factories discharging wastewater to WWTP7 were electronic factories, which might be related to the high PFCs concentration detected in WWTP7 (**Table 4.1**). The average concentrations of total PFCs in electronic, plastic, chemicals, paint, paper, automobile, textile, metal and food factories were 124, 13, 28, 108, 15, 10, 10, 136 and 37 ng/L. It is noted that short-chain PFCs were more frequently detected than long-chain PFCs. PFBuS, PFHxA and PFOA were detected in all types of factories.

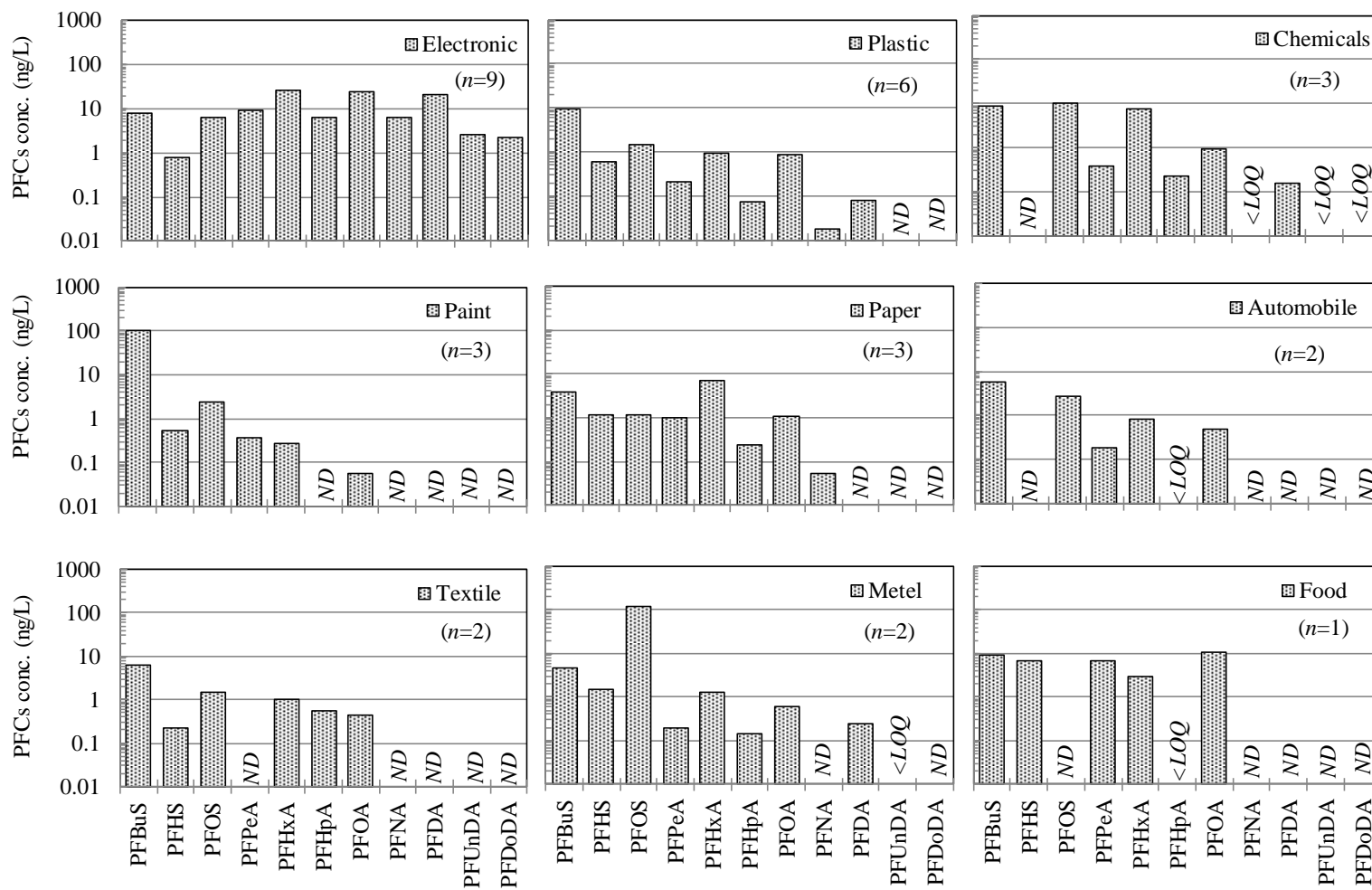


Figure 4.8 PFCs concentration in effluent of industries inside industrial areas

#### 4.4.6 Relationships among total PFCs and different parameters

Total concentrations of PFCs in influent of ten central WWTPs and wastewater from 31 factories were plotted versus DOC, conductivity, chloride and sulfate ion on log chart (**Fig. 4.9**). Correlations of PFCs and these parameters were explained below.

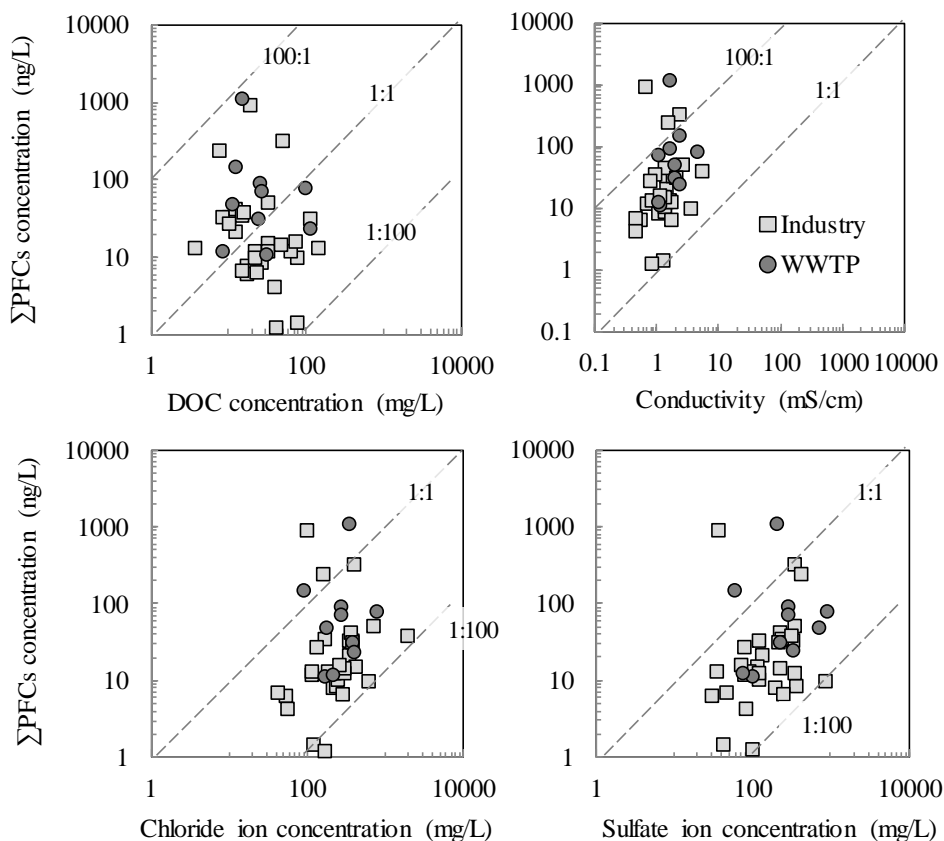


Figure 4.9 Total PFCs concentration with different parameters

**Total PFCs versus DOC:** DOC equivalent of PFCs was generally lower than DOC showing that carbon content of PFCs account for very small fraction of DOC. Most of samples had total PFCs concentration in the range 1 to 1,030 ng/L, while DOC concentration within 4 to 155 mg/L. PFCs concentration was ng/L unit but DOC concentration was mg/L unit. DOC concentrations in central WWTPs and wastewater from 31 factories were 1,000 to 100,000,000 times higher than PFCs concentration (in the same unit).

**Total PFCs versus conductivity:** Conductivity as a summation parameter is a measure of the level of ion concentration of a solution. The dissociation of salts, acids or bases



shows the greater the conductivity of the solution. Conductivity is mainly a matter of the ions of dissolved salts and is an index of the salt load in wastewater (Barros *et al.*, 2012). Conductivity values in WWTPs and industries ranged from 0.5 to 5.8  $\mu\text{S}/\text{cm}$  at 25 °C. Most of plots are in between linear line 100:1 and 1:1.

**Total PFCs versus chloride and sulfate ion:** Chloride and sulfate concentration ranged from 44 to 2,013 and 32 to 917 mg/L, respectively. Most of plots are in between linear line 1:1 and 1:100. Chloride and sulfate concentration were 1,000,000 to 100,000,000 times higher than total PFCs concentration (in the same unit) in most of plot. The profiles of total PFCs and chloride ion were also different from that of sulfate ion.

#### 4.4.7 PFHxA concentrations and wastewater characteristics in industrial wastewater in Japan

Wastewater samples were collected from the treated wastewater of a fluorochemical factory in Japan on 25 April 2013, 17 May 2013, 19 and 29 October 2014. **Appendix A.4** presents PFHxA concentrations and wastewater characteristics. **Figure 4.10** shows PFHxA concentrations in wastewater treatment process. The wastewater treatment processes consisted of influent, neutralization tank, coagulation, clarifier, adsorption (GAC and anion exchange polymers) and effluent.

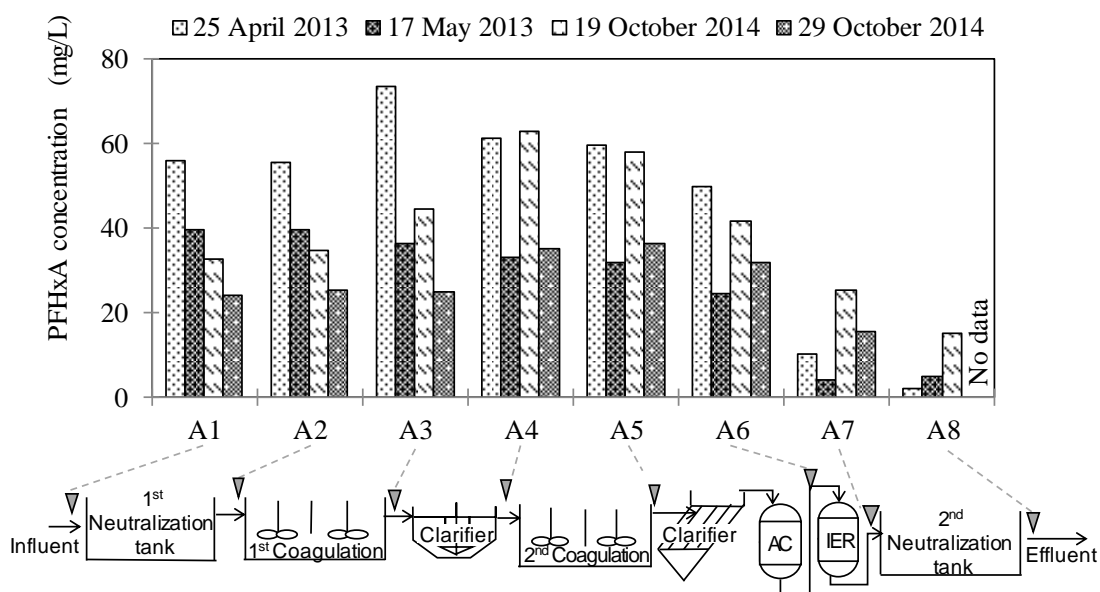


Figure 4.10 PFHxA concentrations in wastewater treatment plant in Japan

PFCs concentrations except PFHxA were not detectable due to limitation of PFCs analysis. PFHxA concentrations ranged from 4 to 73 mg/L through wastewater treatment process. The average concentration of PFHxA in influent was 39 mg/L, while PFHxA concentration in effluent was 6 mg/L. The removal efficiency of this treatment process was 85%. PFHxA concentration decreased after adsorption process by GAC and PFA400. The effluent PFHxA concentration was relatively high when compared with the effluent of WWTPs in Thailand or water environment (ng/L unit).

Not only PFHxA concentrations were investigated but also wastewater characteristics such as anion and DOC were studied. Chloride, sulfate and DOC concentrations in wastewater treatment plant in Japan shows in **Fig. 4.11**. DOC concentration ranged from 40 to 50 mg/L, and chloride and sulfate ranged from 134 to 345 mg/L and 206 to 417 mg/L, respectively. DOC concentrations were almost constant through this treatment process. It means that coagulation and adsorption were ineffective to remove DOC.

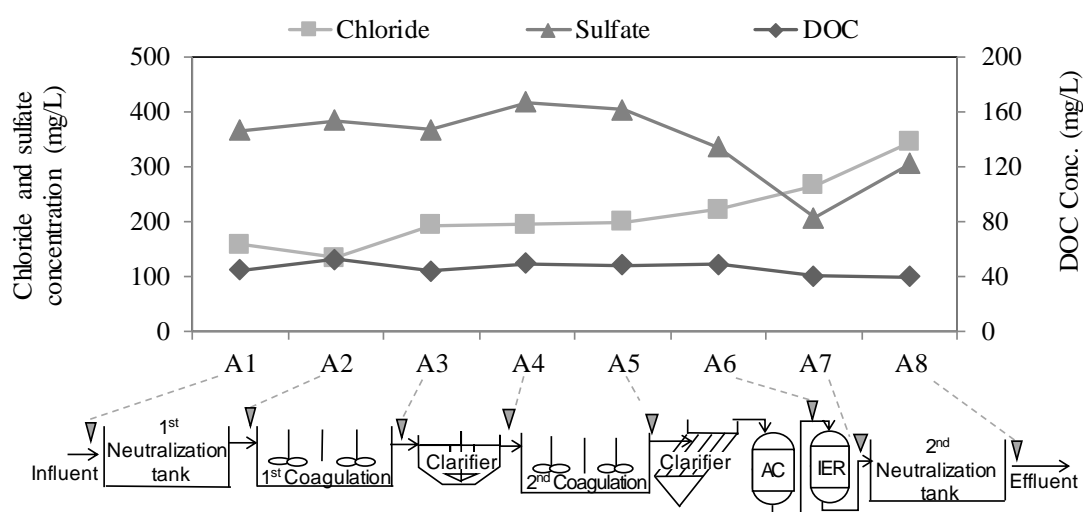


Figure 4.11 Chloride, sulfate and DOC concentration in wastewater treatment plant in Japan

Chloride concentration increased after coagulation because this wastewater treatment plant used polyaluminium chloride (PACL) as a coagulant. In addition, adjusting pH before coagulation or after adsorption (anion exchange polymers) by such as hydrogen chloride can cause increasing of chloride concentration. Sulfate concentration slightly decreased after adsorption by GAC then it rapidly decreased after anion exchange process.

A wastewater sample was collected again from a fluorochemical factory in Japan on June 17<sup>th</sup>, 2013. The sampling point is A6 in **Fig 4.2**. This wastewater was treated by the coagulation process (using polyaluminium chloride as a coagulant) followed by the adsorption process (using GAC as an adsorbent). This wastewater sample was used to analyze PFCs and wastewater characteristics (Anions, cations and molecular size distribution of dissolved organic carbon) because it was selected to conduct the adsorption experiment which was detailed in chapter 5 and 6. **Table 4.6** shows the wastewater characteristics of a fluorochemical

Table 4.6 Wastewater characteristics of a fluorochemical factory (A6)

Parameter		Unit	Value	Unit	Value	Total
PFHxA		mg/L	50.3	mmol/L	0.16	ions
Anion	Cl <sup>-</sup>	mg/L	243.0	meq/L	6.85	14.48
	SO <sub>4</sub> <sup>2-</sup>	mg/L	360.0	meq/L	7.50	
	F <sup>-</sup>	mg/L	1.0	meq/L	0.05	
	NO <sub>3</sub> <sup>-</sup>	mg/L	4.7	meq/L	0.08	
Cation	Na <sup>+</sup>	mg/L	185.2	meq/L	8.05	15.70
	K <sup>+</sup>	mg/L	37.1	meq/L	0.95	
	Mg <sup>2+</sup>	mg/L	6.9	meq/L	0.57	
	Ca <sup>2+</sup>	mg/L	122.6	meq/L	6.13	
DOC		mg/L	54.2			
Conductivity		mS/cm	1.6			
pH		-	7.2			

The concentration of PFHxA in wastewater was higher than ionic strength and DOC concentration. According to electro-neutrality, the summation of the positive ions (cations) must be equal to the summation of negative ions (anions) in solution (Equation 4.3).

$$\sum cations = \sum anions \quad 4.3$$

The percent difference is calculated with the equation 4.4:

$$\text{Percent difference (\%)} = 100 \left| \frac{\sum cations - \sum anion}{\sum cations + \sum anion} \right| \quad 4.4$$

where  $\sum cations$  and  $\sum anions$  are summation of cations and anions (meq/L), respectively. The percent difference of this wastewater was 4.0%. The DOC concentration was attributed by the PFHxA (equivalent to 11.6 mg/L of DOC), and other reaction by-products in wastewater may also have the contribution.

**Figure 4.12** shows the DOC concentrations in wastewater and DOC concentrations contributed by PFHxA in permeate of each membrane/filter. The DOC concentrations in permeate of larger effective pore size of membrane were higher than those of the tighter membrane (smaller pore size). The PFHxA concentrations were similar in all permeate samples. It means that PFHxA could not be removed by these membranes/filters.

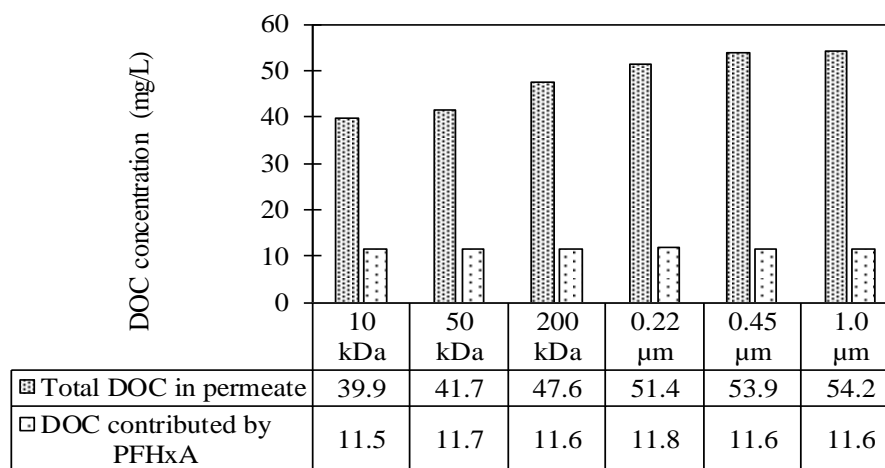


Figure 4.12 DOC concentrations in wastewater and DOC concentrations contributed by PFHxA in permeate of each membrane/filter

**Figure 4.12** could be interpreted that the percentage of DOC distribution of each range of molecular size in fluorochemical wastewater (**Fig. 4.13**) by the following calculation.

$$DOC \text{ distribution } (\%) = \frac{(DOC_1 - DOC_2)}{Total \text{ DOC}} \times 100\% \quad 4.5$$

where  $DOC_1$  = DOC concentration in permeate from membrane/filter A (mg/L)

$DOC_2$  = DOC concentration in tighter membrane/filter (mg/L)

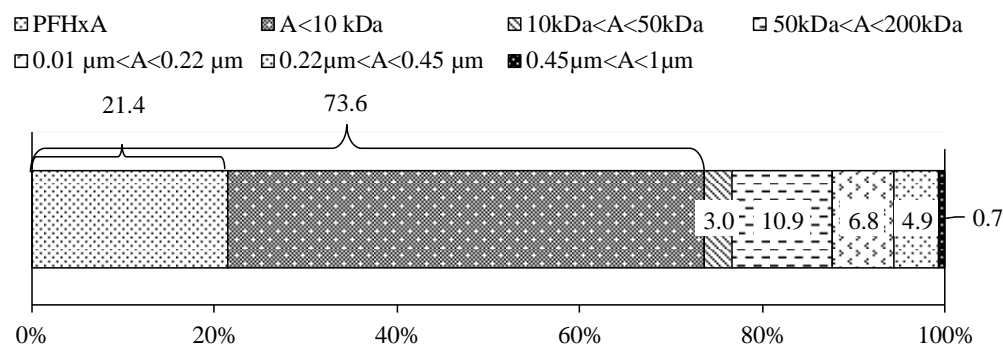


Figure 4.13 Percentage of DOC distribution of each range of molecular size in fluorochemical wastewater (A is size of DOC)

Most of the organic matters that contributes to the DOC in fluorochemical wastewater have a molecular size less than 10 kDa. Its percentage was as high as 73.6 % of total DOC in wastewater. This group of organic matter also includes PFHxA, whose content has contributed 21.4% of the total DOC.

#### 4.5 Summary

Wastewater samples were collected from ten central WWTPs, 31 industries inside industrial areas in Thailand and a fluorochemical factory in Japan in order to investigate PFCs concentrations and wastewater characteristics. Central WWTPs in Thailand used biological treatment process. Coagulation and adsorption processes were used in WWTP in Japan.

In Thailand, all PFCs were detected in most samples above *LOQ*. Total PFCs concentrations in tap water ranged from 1.2 to 26.1 ng/L. Total PFCs concentrations in influent and effluent from biological treatment process were similar because biological treatment process was ineffective to remove PFCs. Total PFCs concentrations in central WWTPs at effluent ranged from 15 to 1,030 ng/L. WWTP7 had elevated total PFCs concentration and its predominant of PFCs was PFHxA. Ten WWTPs discharged 28.7 g/day of PFCs. Total PFCs concentrations in effluent of each factory (e.g., electronic, plastic, chemicals and food industries) ranged from 1 to 881 ng/L. DOC concentration ranged from 4 to 155 mg/L. Chloride and sulfate concentration ranged from 44 to 2,013 and 32 to 917 mg/L, indicating that anion and DOC concentrations were higher than PFCs concentrations.

In Japan, PFHxA concentrations ranged from 4 to 73 mg/L in WWTP of a fluorochemical factory, while other PFCs could not be detected. PFHxA concentration decreased after adsorption process by GAC and PFA400. The effluent PFHxA concentration was very high when compared with the effluent of WWTPs in Thailand (ng/L unit). Wastewaters from different industrial processes had the different wastewater characteristics. Concentrations of ionic strength and DOC were higher than total PFCs concentration which these compounds affected to adsorption process. Thus, the effective PFHxA removal techniques are required to minimize adverse effects from this compound.

## Chapter 5 Adsorption of PFHxA onto GAC, non ion exchange polymers and anion exchange polymers

### 5.1 Introduction

According chapter 4, the biological treatment process was ineffective to remove PFCs in industrial wastewater. Adoption techniques has been promised to remove PFOS and PFOA from contaminated wastewater (Ochoa-Herrera and Sierra-Alvarez, 2008; Yu *et al.*, 2009; Deng *et al.*, 2010; Senevirathna, 2010; Rattanaoudom *et al.*, 2013 and Chularueangaksorn, 2013). The adsorbents including activated carbon, anion exchange polymers, non ion exchange polymers and mineral materials have been used as adsorbents to remove PFOS and PFOA. Up to now, a few researchers have studied on adsorption of PFHxA. Comparison of different adsorbents on adsorption rate and capacity of PFHxA onto GAC, non ion exchange polymers and anion exchange polymer have not studied yet.

Adsorption kinetics is affected by adsorbents and adsorbates. **Table 5.1** shows some popular kinetic models and theirs assumptions. There are numerous mathematical models have been proposed to describe adsorption data which are adsorption reaction models and adsorption diffusion models. Adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption. Adsorption diffusion models consisted of three consecutive steps (Lazaridis and Asouhidou, 2003) (1) diffusion across the liquid film surrounding the adsorbent particles (2) diffusion in the liquid contained in the pores which called internal diffusion or intraparticle diffusion and (3) adsorption and desorption between the adsorbate and active sites.

Isotherm data are useful to estimate capacity of adsorbents. Many model have been developed to interpret experimental isotherms (**Table 5.2**). Adsorption isotherms were classified into three categories including two parameter isotherms, three parameter isotherms and multilayer isotherms (Foo and Hameed, 2010). The adsorption isotherm is an invaluable curve describing the phenomenon governing the retention or mobility of a substance from the aqueous to a solid phase at a constant temperature and pH (Limousin *et al.*, 2007).

Table 5.1 Lists of adsorption kinetic models

Type	Name	Assumption	Differential equation	Description
Adsorption reaction models	<i>First-order reaction</i>	Rate depends on initial concentration of compound	$\frac{dC_t}{dt} = -k_1 C_t$	$C_t$ = concentration at time $t$ $k_1$ and $k_2$ = first and second order constant rate
	<i>Second-order reaction</i>		$\frac{dC_t}{dt} = -k_2 C_t^2$	
	<i>Pseudo-first-order reaction</i>	Rate depends on adsorption capacity comparing with equilibrium	$\frac{dq_t}{dt} = k_{p1}(q_e - q_t)$	$q_e$ and $q_t$ = adsorption capacity at equilibrium and time $t$ $k_{p1}$ and $k_{p2}$ = first and second pseudo-order constant rate
	<i>Pseudo-second-order reaction</i>		$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2$	
	<i>Elovich model</i>	Rate depends on adsorption capacity (decreasing exponentially with increasing of surface coverage)	$\frac{dq}{dt} = a e^{-\alpha q}$	$q$ = amount of compound adsorbed at time $t$ $a$ = desorption constant $\alpha$ = initial adsorption rate
Adsorption diffusion models	Intraparticle diffusion model	Rate depends on pore diffusion and surface diffusion of compound in porous adsorbent (Homogeneous solid diffusion model)	$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right)$	$D_s$ = intraparticle diffusion coefficient $r$ = radial position $q$ = adsorption quantity of solute in the solid varying with radial position at time $t$
	Liquid film diffusion model	Rate of solute accumulation in the solid phase is equal to that of solute transfer across the liquid film according to the mass balance law	$V_p \left( \frac{\partial q}{\partial t} \right) = k_f A_s (C - C_i)$	$V_p$ = volume of the particle $q$ = average solute concentration in the solid $k_f$ = film mass transfer coefficient $A_s$ = rate of solute transfer across the liquid film $C_i$ = concentration of solute at the particle/liquid interface $C$ = concentration of solute in the bulk of the liquid far from the surface

Source: Summarized from Soto *et al.*, 2011

Table 5.2 List of adsorption isotherm models

Type	Name	Comment	Equation	Description
Two parameter isotherms	<i>Freundlich</i>	<ul style="list-style-type: none"> <li>- Applied to multilayer adsorption with non-uniform distribution of adsorption</li> <li>- Heterogeneous surface of adsorbent</li> <li>- Wide range of adsorbate concentration is acceptable</li> </ul>	$q_e = K_f C_e^{1/n}$	$q_e$ = equilibrium adsorption capacity $C_e$ = equilibrium concentration $K_f$ = <i>Freundlich</i> constants $1/n$ = <i>Freundlich</i> exponent
	<i>Langmuir</i>	<ul style="list-style-type: none"> <li>- Homogeneous surface of adsorbent</li> <li>- Have equal adsorption affinity and one site does not affect adjacent site</li> <li>- Limit at low range of adsorbate concentration</li> <li>- Monolayer adsorption</li> </ul>	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_m$ = maximum monolayer adsorption capacity of the adsorbent $K_L$ = <i>Langmuir</i> adsorption constant related to the free energy adsorption
	<i>Dubinin–Radushkevich</i>	<ul style="list-style-type: none"> <li>- Empirical model initially conceived for the adsorption of subcritical vapor onto micropore solid following a pore filling mechanism</li> </ul>	$q_e = (q_s) \exp(-k_{ad} \varepsilon^2)$	$q_s$ = theoretical isotherm saturation capacity $\varepsilon$ = <i>Dubinin-Radushkevich</i> isotherm constant $k_{ad}$ = <i>Dubinin-Radushkevich</i> isotherm constant
Three parameter isotherms	<i>Redlich-Peterson</i>	<ul style="list-style-type: none"> <li>- Hybrid isotherm featuring both the <i>Freundlich</i> and the <i>Langmuir</i> isotherm</li> <li>- Applied either homogeneous or heterogeneous</li> </ul>	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	$K_R$ = <i>Redlich-Peterson</i> constants $a_R$ = <i>Redlich-Peterson</i> constants $\beta$ = <i>Redlich-Peterson</i> exponent
	<i>Toth</i>	<ul style="list-style-type: none"> <li>- Empirical equation develop to improve the <i>Langmuir</i> isotherm fitting (experimental data)</li> <li>- Useful to describe heterogeneous adsorption system which satisfying low and high concentration</li> </ul>	$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	$K_T$ = <i>Toth</i> constants $a_T$ = <i>Toth</i> constants $t$ = <i>Toth</i> constants exponent
Multilayer isotherms	<i>Brunauer–Emmett–Teller</i> (BET)	<ul style="list-style-type: none"> <li>- Extension of the <i>Langmuir</i> isotherm</li> <li>- Surface with adsorbate multilayers</li> </ul>	$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e)(1 + (C_{BET} - 1)(C_e/C_s))}$	$C_{BET}$ = BET adsorption isotherm $C_e$ = adsorbate monolayer saturation concentration $q_s$ = theoretical isotherm saturation capacity

Source: Summarized from Foo and Hameed, 2010



The aim of this chapter is to investigate adsorption rates and capacities of PFHxA onto GAC, non ion exchange polymer (XAD4), strong base anion exchange polymers (PFA300, PFA400 and A860) and weak base anion exchange polymers (BA103 and MN102) in synthetic wastewater and fluorochemical wastewater. The effects of properties of adsorbents on PFHxA adsorption were understood. Adsorption rates and capacities of PFHxA in different wastewater characteristics were compared.

## 5.2 Objectives

The overall objective of this chapter was to investigate adsorption properties of GAC, non ion exchange polymers and anion exchange polymers to removal PFHxA in synthetic wastewater and fluorochemical wastewater.

1. To investigate PFHxA adsorption kinetics and isotherms in synthetic wastewater onto different adsorbents
2. To examine PFHxA adsorption kinetics and isotherms in wastewater onto different adsorbents
3. To understand effects of adsorbent characteristics on PFHxA adsorption
4. To compare adsorption kinetics and isotherms between synthetic wastewater and fluorochemical wastewater

## 5.3 Methodology

### 5.3.1 A fluorochemical wastewater source and wastewater characteristics

In this study, a sample was collected from the treated wastewater of a fluorochemical factory in Japan on 17 June 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 GF/B and stored at 4°C. Wastewater samples were analyzed PFCs and wastewater characteristics by procedure in section 3.2. **Table 4.4** shows the wastewater characteristics in this study and **Fig. 4.13** shows percentage of DOC distribution of each range of molecular size in fluorochemical wastewater.

### 5.3.2 Adsorption kinetics and isotherms

Adsorption kinetics and isotherms experiments were conducted by using seven adsorbents (GAC, XAD4, PFA300, PFA400, A860, BA103 and MN102). Details of adsorbents were shown in section 3.1. **Table 5.3** shows the summary of experimental conditions of the adsorption kinetics and isotherm experiments.

Table 5.3 Summary of experimental conditions in this study

Experiment	Adsorbent amount <sup>a</sup> (mg)	PFHxA solution		Contact time <sup>b</sup> (hours)
		Concentration (mg/L)	Volume (mL)	
Adsorption kinetics (Synthetic wastewater)	2	5	100	1, 3, 6, 12, 18, 24, 48, 72 and 96
Adsorption kinetics (Fluorochemical wastewater)	50	50.3 (Wastewater)	100	1, 3, 6, 12, 18, 24, 48, 72 and 96
Adsorption isotherm (Synthetic wastewater)	1	0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2	100	96
Adsorption isotherm (Fluorochemical wastewater)	1, 2, 4, 6, 8, 10, 15, 20 and 25	50.3 (Wastewater)	50	96

Note : a. Adsorbents (GAC, XAD4, PFA300, PFA400, A860, BA103 and MN102)

b. Shaking condition 120 rpm and 25 °C

### Kinetics experiments

Adsorption kinetics experiments of PFHxA were conducted by using a bottles point technique in synthetic wastewater and fluorochemical wastewater. For adsorption kinetics in synthetic wastewater, adsorbents (2 mg) were placed into polypropylene (PP) bottles containing 100 mL of PFHxA solutions (5 mg/L). PFHxA solution was prepared by dissolved PFHxA in pure acetonitrile (LC/MS grade). It was diluted again to target concentration by *Milli-Q* water (5 mg/L of PFHxA).

For adsorption kinetics in fluorochemical wastewater, adsorbent (50 mg) was placed into 100 mL of the fluorochemical wastewater. Adsorbents were not added into bottles of PFHxA solutions and fluorochemical wastewater to check the possible removal of PFHxA by other mechanisms than adsorption. All samples were shaken at 120 rpm and 25 °C using a thermo shaker ( $n=2$ ). The samples were analyzed the remaining concentration of PFHxA at different contact times.

### Isotherms experiments

Adsorption isotherm experiments were also carried out in synthetic wastewater and fluorochemical wastewater. Adsorbents (1 mg) were added into PP bottles that contained 100 mL of PFHxA solution at various initial concentrations (0.01 mg/L to 2 mg/L). For isotherm experiments in fluorochemical wastewater, different amounts of each adsorbent (1 to 25 mg) were placed into 50 mL of fluorochemical wastewater (50.3 mg/L of PFHxA). 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% (v/v) acetonitrile in *Milli-Q* water before analyzing the remaining concentration of PFHxA.

### 5.3.3 Kinetics and isotherm equations

#### Kinetics equation

To understand the behavior of adsorption kinetics, the *pseudo-second-order* model was introduced to explain the adsorption rates. This equation assumes that the adsorption rate is controlled by chemical adsorption and the adsorption capacity is proportional to the number of active sites onto adsorbent (McKay and Ho, 1999). Base on the *pseudo-second-order* model, the adsorption rate can be expressed by

$$\frac{\delta q_t}{\delta t} \propto (q_e - q_t)^2 \quad 5.1$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad 5.2$$

where  $k_2$  (g/mg/h) is the rate constant of the *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  $t$ . Equation 5.2 was integrated by boundary conditions ( $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ ) and rearranged to liner form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} = \frac{1}{v_0} + \frac{t}{q_e} \quad 5.3$$

where  $v_0$  (mg/g/h) represents the initial adsorption rate. The constants ( $v_0$ ) can be determined by plotting  $t/q_t$  against  $t$ .

#### Adsorption equation

The *Freundlich* equation is an empirical relationship describing the adsorption of solute from a liquid to solid surface. The *Freundlich* isotherm is defined by

$$q_e = K_f \cdot C_e^{1/n} \quad 5.4$$

where  $q_e$  is the concentration of PFHxA in solid phase (mg/g) and  $C_e$  is the equilibrium concentration of PFHxA in solution (mg/L).  $K_f$  is the *Freundlich* adsorption constant related to adsorption capacity ((mg/g)/(mg/L)<sup>1/n</sup>).  $1/n$  is the *Freundlich* exponent. Parameters of  $K_f$  and  $1/n$  were obtained by least square fitting of experiment data on  $q_e$  and  $C_e$ . These parameters of adsorbent are specific for a given equilibrium concentration at a given temperature.

## 5.4 Results and discussion

### 5.4.1 Adsorption kinetics of PFHxA in synthetic wastewater

Adsorption kinetics experiment of PFHxA onto GAC, non ion exchange polymer (XAD4), strong base anion exchange polymers (PFA300, PFA400 and A860) and weak base anion exchange polymers (BA103 and MN102) in synthetic wastewater were performed and the results were presented in **Fig. 5.1**. It can be seen that initial adsorption of PFHxA was very quick, followed by a slow adsorption approaching equilibrium within 96 hours. Kinetics data for seven adsorbents in synthetic wastewater were fitted by the *pseudo-second-order* equation (**table 5.4**). High correlation coefficients ( $R^2 > 0.982$ ) indicated that uptake of PFHxA onto seven adsorbents can be approximated favorably by the *pseudo-second-order* equation.

Table 5.4 The *Pseudo-second-order* model kinetic parameters for the adsorption of PFHxA in synthetic wastewater and fluorochemical wastewater

Name of adsorbent	Synthetic wastewater				Fluorochemical wastewater			
	$q_e$ (mg/g)	$k_2$ (g/mg/h)	$v_0$ (mg/g/h)	$R^2$	$q_e$ (mg/g)	$k_2$ (g/mg/h)	$v_0$ (mg/g/h)	$R^2$
GAC (■)	37.7	0.0050	7.1	0.997	58.5	0.0057	19.4	0.985
XAD4 (△)	12.2	0.0289	4.3	0.982	9.8	0.0365	3.5	0.980
PFA300(◆)	248.7	0.0051	317.2	0.999	88.9	0.0103	81.3	0.997
PFA400 (×)	240.2	0.0030	171.6	0.999	85.3	0.0080	58.2	0.991
A860 (●)	246.5	0.0008	46.7	0.998	7.3	0.0101	0.5	0.914
BA103 (▲)	249.9	0.0051	320.8	0.999	96.7	0.0108	101.3	0.998
MN102 (+)	39.4	0.0017	2.6	0.984	23.3	0.0202	11.0	0.998

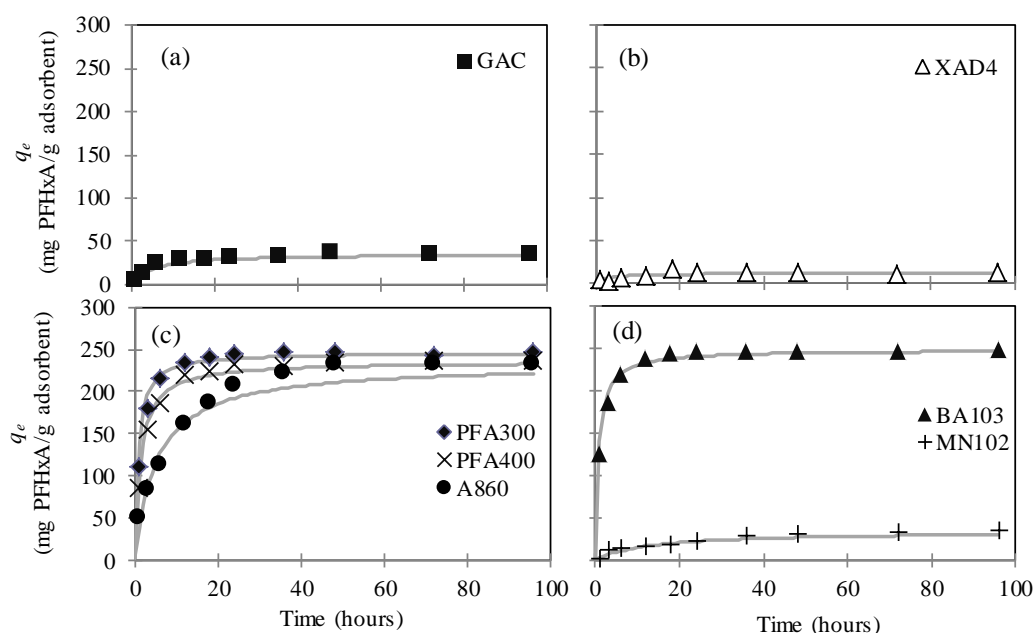


Figure 5.1 Adsorption kinetics of PFHxA in synthetic wastewater onto (a) GAC, (b) non ion exchange polymers, (c) strong base anion exchange polymers and (d) weak base anion exchange polymers

The values of  $q_e$  and  $v_0$  related to polymeric matrix, functional group and porosity of the adsorbents. BA103 had the highest values for the initial adsorption rate, followed by PFA300, PFA400, A860, GAC, XAD4 and MN102. The macroporous polymers of BA103 had a faster initial adsorption rate than the gel polymers (PFA300 and PFA400). PFA300 had a faster adsorption rate than PFA400 because the functional group of PFA300 (type II) has an ethanol group ( $-\text{C}_2\text{H}_4\text{OH}$ ). The ethanol group possesses more open structures than PFA400 (Bolto *et al.*, 2002). GAC had a slower initial adsorption rate than BA103, PFA300, PFA400 and A860 because it had a high proportion of micropores.

#### 5.4.2 Adsorption kinetics of PFHxA in fluorochemical wastewater

The adsorption kinetics in fluorochemical wastewater is important because it controls the process efficiency in applications. As depicted in **Fig. 5.2**, with the initial PFHxA concentration at 50.3 mg/L, the adsorption capacities onto adsorbents (GAC, PFA300, PFA400, BA103 and MN102) increased rapidly with increasing time until the equilibrium time and the adsorption of PFHxA reached the equilibrium time at 96 hours. The *pseudo-second-order* equation was applied to adsorption kinetics in fluorochemical wastewater. **Table 5.4** shows the kinetics data of all adsorbent fitted with the *pseudo-second-order*

model ( $R^2 = 0.914 - 0.998$ ). BA103 had the highest values for the initial adsorption rate, followed by PFA300, PFA400, GAC, MN102, XAD4 and A860. The initial adsorption rate values of XAD4 and A860 were lower than other adsorbents.

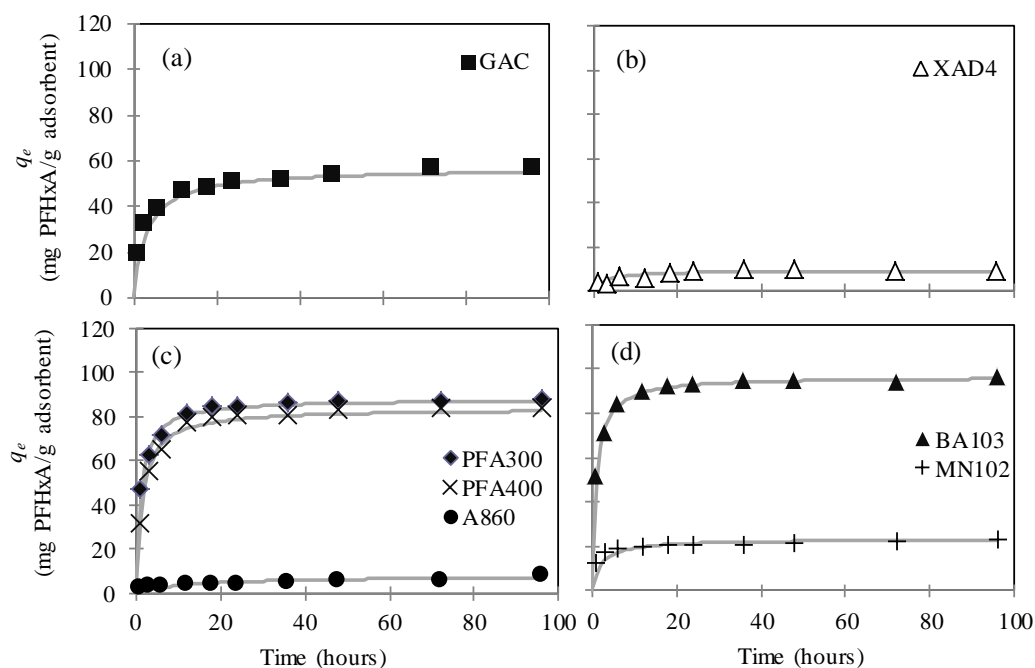


Figure 5.2 Adsorption kinetics of PFHxA in fluorochemical wastewater onto (a) GAC, (b) non ion exchange polymers, (c) strong base anion exchange polymers and (d) weak base anion exchange polymers

#### 5.4.3 Relationships between exchange capacities and initial adsorption rate in synthetic wastewater and fluorochemical wastewater

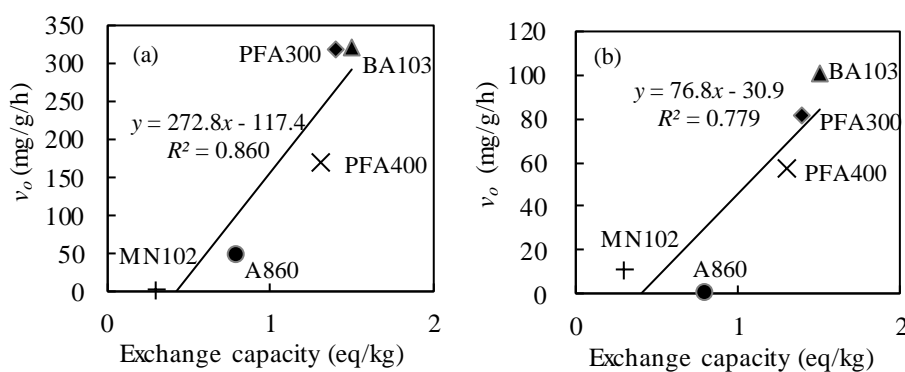


Figure 5.3 Relationships between exchange capacities of anion exchange polymers and initial adsorption rate ( $v_o$ ) of (a) synthetic wastewater and (b) fluorochemical wastewater

The relationships of exchange capacities of anion exchange polymers and initial adsorption rate in synthetic wastewater and fluorochemical wastewater were shown in **Fig. 5.3**. Anion exchange polymers with higher exchange capacities had higher values of  $v_o$ . This means that the higher exchange capacities of anion exchange polymers caused by faster initial adsorption rates.

#### 5.4.4 Adsorption isotherms in synthetic wastewater

According to the adsorption kinetics experiment, the shaking duration of the isotherm experiments was 96 hours to ensure that all adsorbents attained their equilibrium concentrations in synthetic wastewater and fluorochemical wastewater.

**Table 5.5** The *Freundlich* isotherm constants for adsorption of PFHxA in synthetic wastewater and fluorochemical wastewater

Name of adsorbent	Synthetic wastewater			Fluorochemical Wastewater		
	$K_f$ (mg/g)/(mg/L) <sup>1/n</sup>	1/n	$R^2$	$K_f$ (mg/g)/(mg/L) <sup>1/n</sup>	1/n	$R^2$
GAC (■)	16	0.59	0.950	1.66	0.92	0.860
XAD4 (△)	2	0.49	0.975	0.04	1.79	0.782
PFA300(◆)	304	0.93	0.988	36.33	0.52	0.980
PFA400 (×)	188	0.97	0.998	24.55	0.59	0.974
A860 (●)	195	1.00	0.973	0.05	1.68	0.881
BA103 (▲)	412	0.95	0.996	37.12	0.56	0.980
MN102 (+)	9	0.67	0.994	0.73	1.08	0.846

The *Freundlich* equation is widely used to describe the adsorption capacity of many compounds onto heterogeneous surface, including activated carbon, hydrotalcite, anion exchange polymers and silica (Senevirathna *et al.*, 2010, Deng *et al.*, 2010 and Rattanaoudom and Visvanathan, 2011). This model is based on the multilayer adsorption. Multilayer adsorption occurs at a higher equilibrium concentration due to the hydrophobicity of the C-F chains in PFHxA. **Figure 5.4** shows the adsorption isotherms of PFHxA onto different adsorbents using the *Freundlich* equation. The *Freundlich* isotherm constants of PFHxA adsorbed onto all adsorbents in this study are shown in **Table 5.5**. The *Freundlich* equation fitted all adsorbents with squared correlation coefficients ( $R^2$ ) ranging from 0.950 to 0.998.

In this study, the effect of the power  $1/n$  can be neglected when the equilibrium concentration ( $C_e$ ) is 1 mg/L. The amount of PFHxA adsorbed onto the adsorbents at this equilibrium concentration is  $K_f$  value. Anion exchange polymers had different types of polymeric matrix, functional group, ion exchange capacity, and porosity that affected their PFHxA adsorption capacities. BA103 had higher adsorption capacity of PFHxA than PFA300, PFA400, A860 and MN102. The adsorption capacities of PFHxA onto anion exchange polymers were related to their exchange capacities in **Table 3.3**. BA103 had the highest adsorption capacity of PFHxA (412 mg/g) because it had the highest exchange capacity (1.5 eq/kg). PFA300 had a higher adsorption capacity than A860 and PFA400 because type II polymers have a slightly higher adsorption capacity than type I polymers (Crittenden *et al.*, 2005). A860 exhibited slightly higher adsorption capacity than PFA400 which may be attributed to the macroporous structure of A860. Multilayer adsorption of PFHxA can occur via hydrophobic interaction after PFHxA was first adsorbed on the polymers through anion exchange.

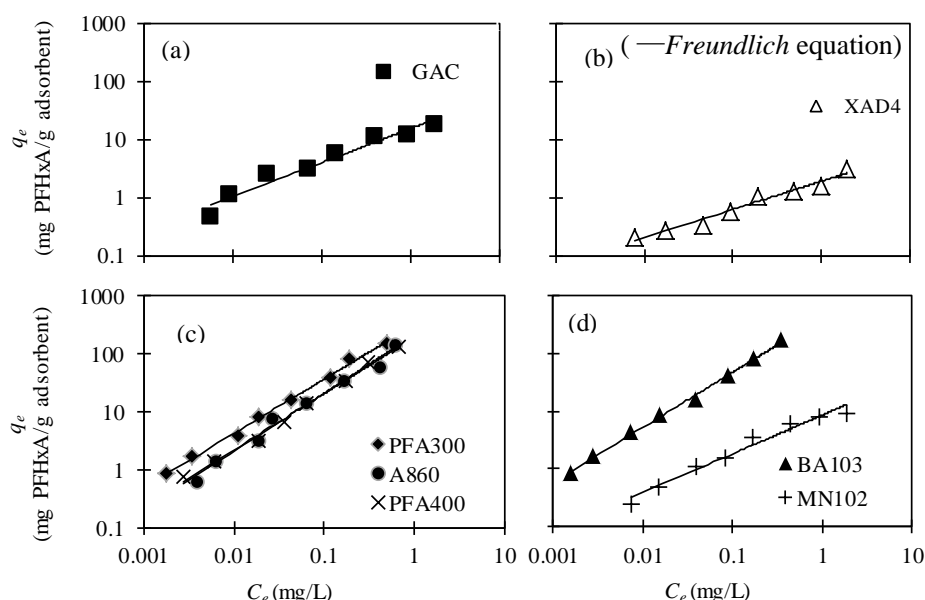


Figure 5.4 Adsorption isotherms of PFHxA in synthetic wastewater using the *Freundlich* equation onto (a) GAC, (b) non ion exchange polymers, (c) strong base anion exchange polymers and (d) weak base anion exchange polymers

XAD4 is white translucent beads characterized by a macroporous structure. The polystyrene matrix of XAD4 is highly hydrophobic. It means that XAD4 is difficult to contract with solution. As a result, XAD4 had small adsorption capacity of hydrophilic



organic compounds from solutions (Li *et al.*, 2013). XAD4 exhibited the lowest adsorption capacity of PFHxA (2 mg/g).

GAC was commonly used to remove organic compounds in water/wastewater. The GAC had lower PFHxA adsorption capacity than anion exchange polymers except MN102. On the other hand, the GAC had higher adsorption capacity than non ion exchange polymers (XAD4). It can be explained that the bonding forces between adsorbate and adsorbent of non ion exchange polymers were usually weaker than those of GAC (Busca *et al.*, 2008). The values of  $1/n$  were closer to one for anion exchange polymers (PFA300, PFA400, A860, BA103 and MN102) than XAD4 and GAC. It means that XAD4 and GAC had more nonlinearity than anion exchange polymers due to adsorption site heterogeneity and adsorbate-adsorbent interactions (Li *et al.*, 2013 and Cheung *et al.*, 2001).

#### 5.4.5 Comparison between adsorption isotherms of PFHxA and PFOA

The values of  $K_f$  and  $1/n$  of PFHxA were compared to those of PFOA because PFHxA and PFOA have some similar properties. The values of  $K_f$  and  $1/n$  of PFOA onto PFA300, XAD4 and GAC were reported in a previous study (Chularueangakorn *et al.*, 2013). **Figure 5.5** shows the relationships between the *Freundlich* isotherm constants ( $K_f$  and  $1/n$ ) of PFOA and PFHxA. Adsorption mechanism of PFCs (PFHxA and PFOA) onto anion exchange polymers (PFA300) was hypothesized to be mainly related to ion exchange. If ion exchange is the dominant mechanism in the adsorption process and all exchange sites are available for the adsorbate, the adsorption capacity of PFHxA and PFOA should be similar. However, the adsorption capacity of PFHxA was higher than those of PFOA onto PFA300 which is similar to the previous study. The adsorption capacity of PFBS was much higher than that of PFOS onto the anion exchange polymers (Deng *et al.*, 2010). It was explained that PFBS is more hydrophilic than PFOS, the higher adsorption capacity of PFBS than PFOS may also be related to the greater hydrophilicity of PFBS.

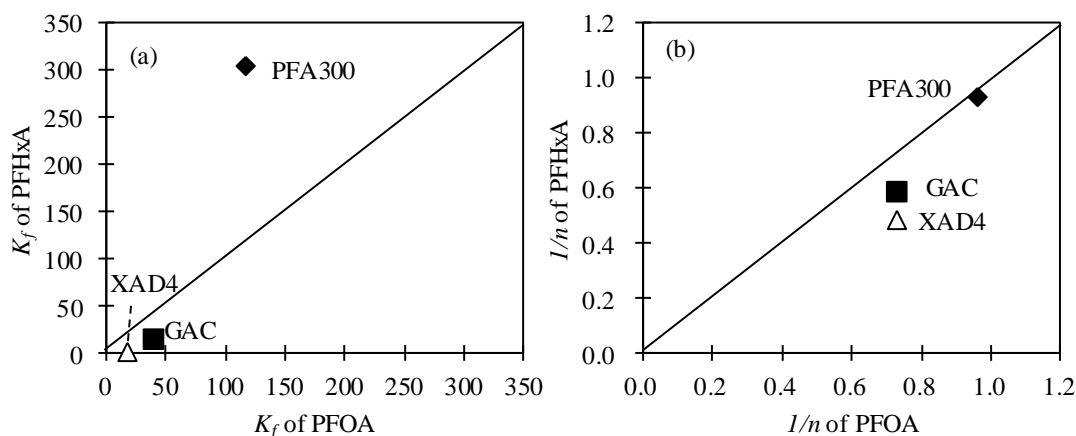


Figure 5.5 Relationships between the *Freundlich* isotherm constants  
(a)  $K_f$  and (b)  $1/n$  of PFOA and PFHxA

In contrast, the adsorption capacities of PFHxA were lower than those of PFOA onto XAD4 and GAC. PFOA has a long C-F chain (C8) which it was more hydrophobic than PFHxA (C6). Surfaces of activated carbon are generally non-polar with few functional groups and XAD4 also are non-polar adsorbent which they are suitable for removing hydrophobic pollutants. Thus, PFOA was easier to be adsorbed onto the surface of XAD4 and GAC by hydrophobic interaction.

The value of  $1/n$  of PFOA onto XAD4 ( $1/n = 0.73$ ) and GAC ( $1/n = 0.73$ ) had more nonlinearity than PFA300 ( $1/n = 0.96$ ) which similar to values of  $1/n$  of PFHxA. It means that adsorption of PFOA onto XAD4 and GAC had more nonlinearity than PFA300 due to adsorption site heterogeneity and adsorbate-adsorbent interactions (Li *et al.*, 2013 and Cheung *et al.*, 2001).

#### 5.4.6 Adsorption isotherms of PFHxA in fluorochemical wastewater

The adsorption isotherms of PFHxA on to seven adsorbents in fluorochemical wastewater are shown in **Fig. 5.6**. The *Freundlich* isotherm constants of PFHxA adsorbed onto seven adsorbents in fluorochemical wastewater are shown in **Table 5.5**. The *Freundlich* equation fitted all adsorbents with squared correlation coefficients ( $R^2$ ) ranging from 0.782 to 0.980.

The amounts of PFHxA adsorbed onto the adsorbents are  $K_f$  values at an equilibrium concentration ( $C_e = 1$  mg/L). 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 3.3**. BA103 had the highest adsorption capacity of PFHxA (37.12 mg/g) because it had the highest exchange capacity (1.5 eq/kg). PFA300 had higher adsorption capacity than PFA400 because type II polymers have a slightly higher adsorption capacity than types I polymers (Crittenden *et al.*, 2005).

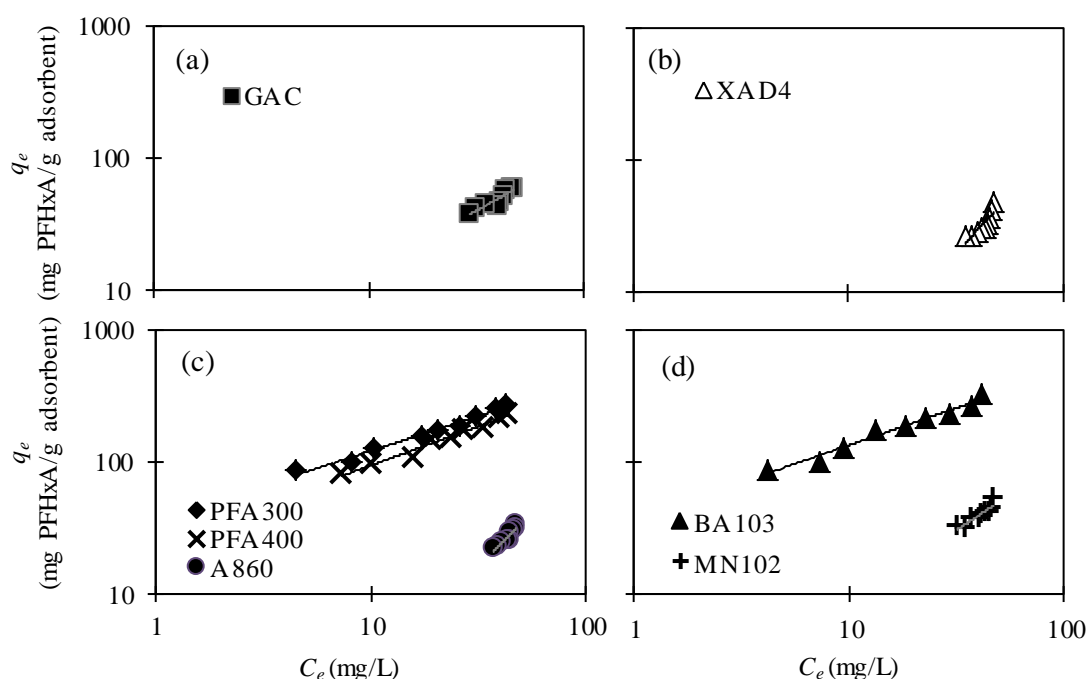


Figure 5.6 Adsorption isotherms of PFHxA in fluorochemical wastewater using the *Freundlich* equation onto (a) GAC, (b) non ion exchange polymers, (c) strong base anion exchange polymers and (d) weak base anion exchange polymers (*—Freundlich* equation)

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 solutions (Li *et al.*, 2013). 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 GAC (Busca *et al.*, 2008).

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 repulsion (Yu *et al.*, 2009).

#### 5.4.7 Relationship between exchange capacities and adsorption isotherms in synthetic wastewater and fluorochemical wastewater

The relationships of exchange capacities of anion exchange polymers and PFHxA adsorption capacities ( $K_f$ ) in synthetic wastewater and fluorochemical wastewater were shown in **Fig. 5.7**. Anion exchange polymers with higher exchange capacities had higher values  $K_f$ . This means that the higher exchange capacities of anion exchange polymers caused higher adsorption capacities.

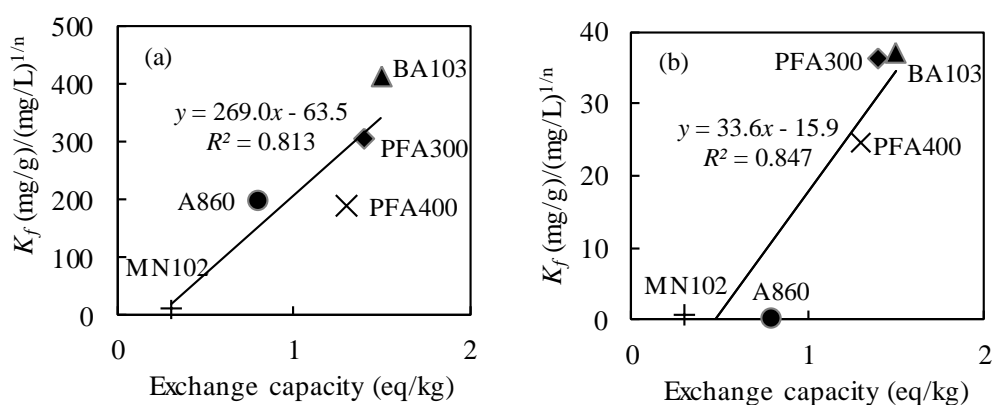


Figure 5.7 Relationship between exchange capacities of anion exchange polymers and PFHxA adsorption capacities ( $K_f$ ) in (a) synthetic wastewater and (b) fluorochemical wastewater

## 5.5 Summary

Adsorption kinetics and isotherms of PFHxA onto GAC, non ion exchange polymers as well as five anion exchange polymers in synthetic wastewater (*Milli-Q* water) and fluorochemical wastewater were investigated. All adsorption kinetics and isotherms data were fitted with the *pseudo-second-order* equation and the *Freundlich* equation, respectively.

BA103 had the highest values for the initial adsorption rate in synthetic wastewater, followed by PFA300, PFA400, A860, GAC, XAD4 and MN102. For fluorochemical wastewater, BA103 had the highest values for the initial adsorption rate, followed by PFA300, PFA400, GAC, MN102, XAD4 and A860. The initial adsorption rate of PFHxA onto BA103 in synthetic wastewater and fluorochemical wastewater were 320 mg/g/h and 101 mg/g/h, respectively.

Adsorption capacity of PFHxA on each adsorbent related to properties of adsorbent. BA103 showed the highest adsorption capacity in synthetic wastewater, followed by PFA300, A860, PFA400, GAC, MN102 and XAD4. The adsorption capacity ranking in fluorochemical wastewater were different from synthetic wastewater (BA103, PFA300, PFA400, GAC, MN102, A860 and XAD4). Adsorption capacities of BA103 were 412 and 37 mg/g in synthetic wastewater and fluorochemical wastewater, respectively.

PFHxA adsorption rate and capacity of anion exchange polymers in synthetic wastewater related to exchange capacity, polymeric matrix, functional group and porosity. Adsorption rates and capacities of PFHxA in synthetic wastewater were higher than in fluorochemical wastewater onto all adsorbents. Thus, effects of interferences in wastewater on PFHxA adsorption capacity were investigated in next chapter.

## Chapter 6 Factors affecting PFHxA adsorption in wastewater

### 6.1 Introduction

In general, inorganic anions and cations as well as dissolved organic matter are present in industrial wastewater. Chloride, sulfate and nitrate are common anions while sodium, calcium and potassium are cations in industrial wastewater. Deng *et al.* (2010) studied the effect of sulfate on the adsorption of PFOS on anion exchange polymer. They found that the adsorption capacity of PFOS decreased when sulfate concentration increased. On the other hand, Wang and Shih (2011) reported that the adsorption of both PFOS and PFOA onto alumina decreases with an increase in ionic strength of cations due to the compression of the electrical double layer.

Dissolved organic matter is highly heterogeneous, containing molecules of various molecular weights ranging from a simple compound to a complex compound. The composition of organic matter is a combination of natural organic matter (NOM), soluble microbial products and trace harmful chemicals (Shon *et al.*, 2006). It is recognized that NOM had adversely effects on adsorption of trace organic compounds, such as pesticides, onto activated carbons (Newcombe *et al.*, 2002) through two major competitive mechanisms: direct site competition and pore constriction/blockage (Li *et al.*, 2003). Yu *et al.* (2012) found that the presence of organic matter reduced adsorption capacities and sorption rates of PFOS.

Not only anions, cations and dissolved organic matter affect adsorption capacity but also adsorption condition such as pH and temperature. Deng *et al.* (2010) studied effect of pH on the adsorption of anion exchange polymers. It was found that the adsorption capacity decreased when pH was above 10 due to changing of mechanism in functional group. Effects of adsorption temperature on the adsorption of PFOS and PFOA onto magnetic mesoporous carbon nitride was examined by Yan *et al.* (2014). The adsorption amount

of PFOS and PFOA on magnetic mesoporous carbon nitride increased with increasing the adsorption temperatures.

To the best of our knowledge, factors affecting PFHxA adsorption capacity onto anion exchange polymers have not been widely studied yet. In this study, the influence of anions, cations, dissolved organic carbon (DOC), pH and temperature on PFHxA adsorption were studied.

## **6.2 Objectives**

The target of this study was to investigate effects of interferences containing in wastewater onto GAC, non ion exchange polymers and anion exchange polymers on PFHxA adsorption capacity.

1. To study effects of individual inorganic ion solution (NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, KCl, and CaCl<sub>2</sub>) in synthetic wastewater on adsorption of PFHxA
2. To study effects of mixture of inorganic ion solution in synthetic wastewater on adsorption of PFHxA
3. To investigate effects of DOC in humic acid solution and fluorochemical wastewater on adsorption of PFHxA
4. To investigate effects of adsorption conditions (pH and temperature) in synthetic wastewater on adsorption of PFHxA

## **6.3 Methodology**

Adsorption experiments in this chapter were conducted by using seven adsorbents (GAC, XAD4, PFA300, PFA400, A860, BA103 and MN102). Details of each adsorbent and chemical were shown in section 3.1. **Table 6.1** shows the summary of experimental conditions of factors affecting PFHxA adsorption in wastewater.

### **6.3.1 Fluorochemical wastewater source and wastewater characteristics**

In this study, a sample was collected from the treated wastewater of a fluorochemical factory. The details of industrial wastewater samples were shown in Section 5.3.1.

### 6.3.2 Effects of interferences on PFHxA adsorption

#### Effects of individual inorganic ions on PFHxA adsorption

Because high levels of PFHxA were detected in downstream of PFCs related industries, possible sources of pollution could be industrial wastewater. The concentration of PFHxA in the original wastewater generated from industrial process might be mg/L level. Chloride, sulfate and nitrate ions are common anions while sodium, potassium and calcium ions are common cations in industrial wastewater which their concentration also depends on industrial process. The effects of inorganic ions on PFHxA adsorption were investigated. The adsorbents (10 mg) were added to 100 mL of mixture solutions. The mixture solutions had 0.016 mmol/L of PFHxA and different ionic strengths (0 to 16.9 mmol/L) in *Milli-Q* water ( $n = 2$ ). The pH values of the solutions were adjusted to 7 with 0.1 M HCl or NaOH. The ionic solutions were prepared from NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, KCl, and CaCl<sub>2</sub>. All samples were shaken at 120 rpm and 25 °C for 96 hours using a thermo shaker. The adsorbents were immediately filtrated by GF/B glass filters after shaking. These filtrated samples were diluted with 40% (v/v) acetonitrile in *Milli-Q* water before analysing the concentration of PFHxA by HPLC-MS/MS.

#### Effects of mixed inorganic ions on PFHxA adsorption

Normally, there are more than one type of ions species in wastewater. The effects of mixed inorganic ions were investigated on PFHxA adsorption. In this experiment, 10 mg of adsorbent was added to 100 mL of mixture solutions ( $n = 2$ ). The mixture solutions were prepared through adding PFHxA into mixed inorganic ions (NaCl and Na<sub>2</sub>SO<sub>4</sub>; NaCl and NaNO<sub>3</sub>; Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>; NaCl, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>) into *Milli-Q* water. Concentration of PFHxA was controlled at 0.016 mmol/L, while the concentration of each inorganic ion was kept at 2 mmol/L. The pH values of the solutions were adjusted to 7 with 0.1 M HCl or NaOH. All samples were shaken and filtrated as similar step to previous experiment. These filtrated samples were diluted with 40% (v/v) acetonitrile in *Milli-Q* water before measuring the concentration of PFHxA by HPLC-MS/MS.



### Effects of DOC (Humic acid) on PFHxA adsorption

Humic acid was selected to represent organic compounds in this experiment. Humic acid solution was prepared by dissolving of 1 g humic acid (Wako Pure Chemical Industries, Ltd., Japan) to 100 mL of NaOH (0.1 M) and agitation during for 24 hours. After that the solution was filtrated with GF/B glass fiber filters after adjusting the pH to 7 using HCl (0.1 M) and diluting to 1.0 L. The TOC concentration of the filtrated sample was 401 mg/L. The adsorbents (10 mg) were added to 100 mL of mixture solution. The mixture contained 0.016 mmol/L of PFHxA and various concentration of DOC (0 to 60 mg/L) ( $n = 2$ ). Ion strength (NaCl) in all sample were controlled at 2 mmol/L. The samples were shaken at 120 rpm and 25 °C for 96 hours using a thermo shaker. The adsorbents were immediately filtrated by GF/B glass filters after shaking. These filtrated samples were diluted with 40% (v/v) acetonitrile in *Milli-Q* before the measurement of PFHxA and DOC by HPLC-MS/MS and TOC analyser, respectively.

### Effects of DOC (Wastewater) on PFHxA adsorption

Industrial wastewater contains specific organic compounds and their characteristics depend on production processes. Effects of DOC on PFHxA adsorption capacity in industrial wastewater could not be investigated directly due to unavailable chemical represented to organic compounds in industrial wastewater. The effects of DOC in wastewater were investigated by the following assumption. The difference of PFHxA adsorption capacity in *Milli-Q* water and those in fluorochemical wastewater causes by effects of DOC and inorganic ions. It means that if the effects of inorganic ions on PFHxA adsorption capacity were known, the effects of DOC in wastewater on PFHxA adsorption capacity could be estimated. Thus, the effects of inorganic ions in on PFHxA adsorption capacity were investigated.

The synthetic wastewater sample was prepared by adding inorganic strength (NaF, NaNO<sub>3</sub>, Mg<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaCl) and PFHxA which similar concentration in fluorochemical wastewater in **Table 4.4**. DOC and conductivity were measured after adjusting pH to 7.2 by 0.1 N of HCl and NaOH. It was found that DOC concentration was 11.6 mg/L and conductivity was 1.59 mS/cm. The DOC concentration

was quite different from that of fluorochemical wastewater (54.3 mg/L). The adsorbents (2 to 30 mg) were added to 50 mL of simulated inorganic strength solution. The samples were shaken at 120 rpm and 25 °C for 96 hours using a thermo shaker ( $n = 2$ ). The adsorbents were immediately filtrated by GF/B glass filters after shaking. These filtrated samples were diluted with 40% (v/v) acetonitrile before the measurement of PFHxA concentration by HPLC-MS/MS.

Adsorption isotherms in simulated inorganic strength solution of BA103 were compared with those in filtrated wastewater by MF membrane (10 kDa). The DOC concentration in this solution was 39.9 mg/L. The adsorbents (2 to 30 mg) were added to 50 mL of filtrated wastewater. The samples were shaken at 120 rpm and 25 °C for 96 hours using a thermo shaker ( $n = 2$ ). The adsorbents were immediately filtrated by GF/B glass filters after shaking. These filtrated samples were diluted with 40% (v/v) acetonitrile and analysed PFHxA.

#### **GAC adsorption followed by anion exchange polymer to remove PFHxA on PFHxA adsorption**

GAC was suspected to remove DOC in industrial wastewater. Thus, GAC was selected to pretreat industrial wastewater before adsorption by PFA300 and BA103. GAC (500 mg) was added to 1 L of industrial wastewater and the sample was shaken for 48 hours. The GAC was separated from wastewater by filtration with GF/B glass filters. The concentration of PFHxA in pretreated sample was adjusted to 0.16 mmol/L again for conducting the adsorption test by PFA300 and BA103. The different amounts of each adsorbent (2 to 30 mg) were placed into 50 mL of wastewater pretreated by GAC (0.16 mmol/L of PFHxA). All sample were shaken at 120 rpm and 25 °C for 96 hours using a thermo shaker ( $n = 2$ ). The samples were diluted with 40% (v/v) acetonitrile in *Milli-Q* water and analyzed using HPLC-MS/MS.

#### **Effects of pH on PFHxA adsorption**

Influence of pH was inspected by performing the experiment with varying pH from 2 to 12. The adsorbents (2 mg) were added to 100 mL of 0.032 mmol/L of PFHxA solution.

All samples were controlled pH at 2.4.6.8.10 by adding 0.1 M HCl or 0.1 M NaOH. During this step, the ionic strength was controlled at 2 mmol/L by 0.1 M NaCl. ( $n = 2$ ). All samples were shaken at 120 rpm and 25 °C for 96 hours using a thermo shaker ( $n = 2$ ). The adsorbents were immediately filtrated by GF/B glass filters after shaking. These filtrated samples were diluted before analyzing the concentration of PFHxA by HPLC-MS/MS.

### **Effects of temperature on PFHxA adsorption**

Temperature is an important parameter of adsorption performance. In order to know the effect of temperature on PFHxA adsorption performance, adsorption isotherm experiments were also carried out in synthetic wastewater at different temperature. Adsorbents (1 mg) were added into PP bottles that contained 100 mL of PFHxA solution at varying initial concentrations (0.02 to 2 mg/L). All sample were shaken at 120 rpm and 15, 25, 30, 35, 40 and 45 °C for 96 hours using a thermo shaker ( $n = 2$ ). The samples were diluted with 40% (v/v) acetonitrile in *Milli-Q* water before analyzing the concentration of PFHxA using HPLC-MS/MS.

### **Effects of PFHxS and PFOA on PFHxA adsorption**

Both PFHxA and PFHxS both have six fluorinated carbons but they have the different functional group, while PFHxA and PFOA have the same functional group but PFHxA have shorted fluorinated carbons than PFOA. To understand the effect of PFHxS and PFOA on PFHxA adsorption, the adsorption experiment were conducted in the solution containing these two compounds. The adsorbents (2 mg) were added to 100 mL of mixture solutions. The mixture solutions contained 0.016 mmol/L of PFHxA and various concentration of PFHxS and PFOA (0.002 to 0.030 mmol/L). The pH was measured in all samples and there samples were shaken at the same condition. The adsorbents were immediately separated by GF/B glass filters after shaking. These filtrated samples were diluted with 40% (v/v) acetonitrile in *Milli-Q* water before analyzing the concentration of PFHxA, PFHxS and PFOA.

Table 6.1 Summary of experiment condition in this study

Experiment	Adsorbent name <sup>a</sup>	Adsorbent amount (mg)	Solution			Initial pH	Shaking Temp. (°C)	Note
			PFHxA conc. (mmol/L)	Interference concentration (mmol/L)	Volume (mL)			
Effects of individual inorganic ions	All adsorbents	10	0.016	NaCl = 0 – 16.9, Na <sub>2</sub> SO <sub>4</sub> = 0 – 6.25, NaNO <sub>3</sub> = 0 – 9.6, KCl = 0 – 16.9, CaCl <sub>2</sub> = 0 – 16.9	100	7.0	25	Ionic solutions were prepared from NaCl, Na <sub>2</sub> SO <sub>4</sub> , NaNO <sub>3</sub> , KCl, and CaCl <sub>2</sub>
Effect of mixed inorganic ions	GAC, PFA300, PFA400 and BA103	10	0.016	NaCl and Na <sub>2</sub> SO <sub>4</sub> = 2 and 2, NaCl and NaNO <sub>3</sub> = 2 and 2, Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub> = 2 and 2, NaCl, Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub> = 2, 2 and 2	100	7.0	25	Ionic solutions were prepared from NaCl, Na <sub>2</sub> SO <sub>4</sub> , and NaOH
Effects of DOC (Humic acid)	All adsorbents	10	0.016	DOC = 0 – 60 mg/L	100	7.0	25	Ion strength 2 mmol/L
Effects of DOC (Wastewater)	GAC, PFA300, PFA400 and BA103	2, 10, 20 and 30	0.16 <sup>b</sup>	NaF = 0.05, NaNO <sub>3</sub> = 0.08, Mg <sub>2</sub> SO <sub>4</sub> =0.29, K <sub>2</sub> SO <sub>4</sub> =0.48, CaCl <sub>2</sub> =3.1, Na <sub>2</sub> SO <sub>4</sub> = 2.99 and NaCl =0.72	50	7.2	25	DOC = 11.6 mg/L Conductivity = 1.59 mS/cm Adjust pH
Pretreatment WW by GAC	PFA300, BA103	2, 10, 20 and 30	WW <sup>c</sup> (0.16)	Pretreated wastewater by GAC (After GAC, DOC= 28 mg/L)	50	7.2	25	Pretreatment WW was prepared by add 500 mg of GAC into 1 L of WW
Effects of pH	All adsorbents	2	0.032	-	100	2, 4, 6, 8, 10 and 12	25	Adjusted pH by 0.01 mmol/L of HCl and NaOH (Cl <sup>-</sup> )
Effect of temperature	GAC, PFA300, PFA400 and BA103	1	0.02-2 mg/L	-	100	6.9-7.0	15, 20, 25 35 and 40	-
PFHxS and PFOA	BA103	2	0.016	PFOA and PFHxS = 0.002, 0.010, 0.016, 0.020 and 0.030	100	6.9-7.0	25	-

Note: a. All adsorbents (GAC, XAD4, PFA300, PFA400, A860, BA103 and MN102), b. Simulated ionic strength and PFHxA concentration,

c. PFHxA concentration in fluorochemical wastewater

## 6.4 Results and discussion

### 6.4.1 Effects of inorganic ions on PFHxA adsorption capacity

Generally, inorganic anions (chloride, sulfate and nitrate) and inorganic cations (sodium, potassium and calcium) are present in industrial wastewater. Adsorption performances of PFHxA in NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, KCl, and CaCl<sub>2</sub> solutions were investigated. **Figure 6.1** shows the effects of inorganic ions on the adsorption of PFHxA onto GAC, non ion exchange polymers and anion exchange polymers.

Adsorption capacities of PFHxA onto GAC slightly decreased when inorganic ions concentration increased. The adsorption capacity of PFHxA in NaNO<sub>3</sub> solution was lower than other inorganic solutions. For monovalent ions, it could be explained that the adsorption process was favored by the higher hydration energy (Abou-Mesalam, 2003). The value of hydration energy of nitrate ( $\Delta G^o$ , -314 kJ/mol) was higher than those of chloride ( $\Delta G^o$ , -363 kJ/mol) (Gu *et al.*, 2004). Thus, NaNO<sub>3</sub> solution had more effects of PFHxA adsorption capacities onto GAC than sodium chloride.

Adsorption capacity of PFHxA in NaCl solution and KCl solution onto GAC were similar. It might be explained that monovalent cations species (Na<sup>+</sup> and K<sup>+</sup>) did not affected the adsorption of PFHxA. At the same ionic strength of CaCl<sub>2</sub> and NaCl in mmol/L unit, PFHxA adsorption capacity in CaCl<sub>2</sub> solution was lower than those in NaCl and KCl due to doubled concentration of Cl<sup>-</sup>. The divalent cation (calcium) might neutralize the surface charges of GAC and form bridges between negatively charge groups and PFHxA resulting in enhancing PFHxA removal efficiency (Kwadijk *et al.*, 2013). However, our results show that the adsorption capacity of PFHxA onto related to anions species rather than cations ones.

There were no significant effects of inorganic ions on PFHxA adsorption capacities onto XAD4 because XAD4 is non-polar (hydrophobic polymers). The binding of organic compounds onto XAD4 polymers was related with physical rather than chemical process (Paleos, 1969). Although the anions had no effects on adsorption of PFHxA

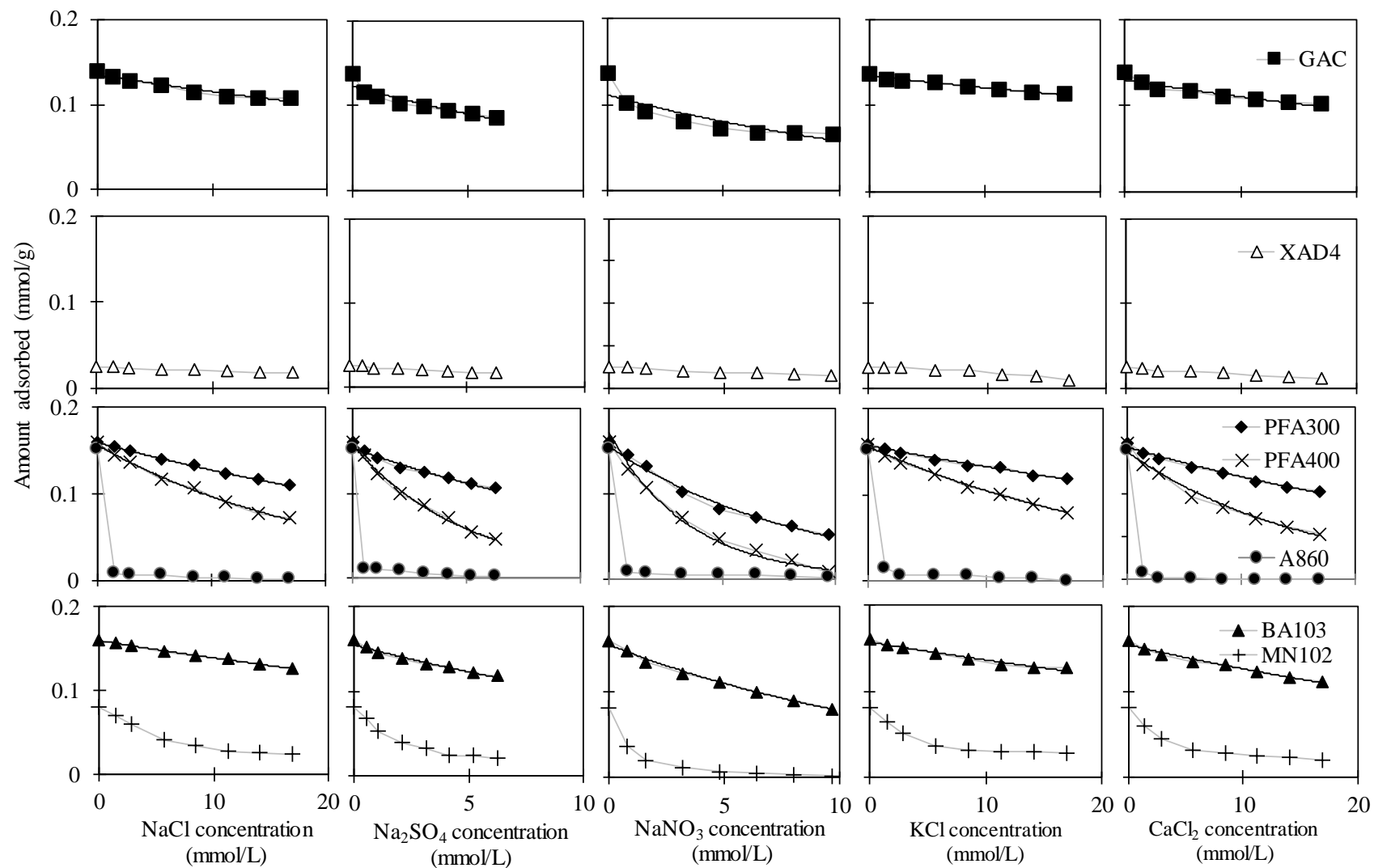


Figure 6.1 Effects of inorganic ions on PFHxA adsorption capacities (— Fitted equation for GAC, PFA300, PFA400 and BA103)

onto XAD4, it was not suitable to remove PFHxA due to its low adsorption capacity of PFHxA.

Adsorption capacities of PFHxA onto polystyrene polymers (PFA300, PFA400, BA103 and MN102) gradually decreased when ionic strength increased from 0 to 16.9 mmol/L. The increase of ionic strength results in the increasing competition between the PFHxA and anions, which may interact with the functional groups of the polymers. Adsorption capacities of PFHxA onto BA103 were higher than those of PFA300, PFA400 and MN102 at the same concentration of all ionic solutions. It also can be seen that NaNO<sub>3</sub> had more effects on the adsorption of PFHxA than the others ionic solutions. The mechanism of selective removal by anion exchange approach could be explained with the nature of ion (monovalent and divalent anion) and the hydration energy ( $\Delta G^o$ ) of the target ion. For monovalent ions, it could be explained that the adsorption process was favored by the higher hydration energy (Abou-Mesalam, 2003). Thus, this indicated that NaNO<sub>3</sub> solution had more effects of PFHxA adsorption capacities onto anion exchange than NaCl solution.

Adsorption capacities of PFHxA onto A860 (polyacrylic polymers) dramatically decreased when the inorganic ions were present in the solutions. The polyacrylic polymers were more hydrophilic, therefore, adsorbed more water in the solutions than styrene polymers (Parrish, 1977). The inorganic anions in the solutions might be easily exchanged (with mobile ions) instead of PFHxA on polyacrylic polymers. The PFHxA adsorption capacities reduced by 95% at 1 mmol/L of inorganic ions concentration. Therefore, A860 was not suitable to remove PFHxA in solutions containing inorganic ions.

Adsorption capacities of PFHxA solutions onto anion exchange polymers were similar in NaCl and KCl. It might be explained that monovalent cations (Na<sup>+</sup> and K<sup>+</sup>) did not affected the adsorption of PFHxA onto anion exchange polymers. PFHxA adsorption capacity in CaCl<sub>2</sub> solution was lower than those in NaCl and KCl solutions due to doubled concentration of chloride at the same ionic strength in mmol/L.

The adsorption data in ionic solution of GAC, PFA300, PFA400 and BA103 were fitted with the following equation.

$$y = Ae^{(-Bx)} \quad 6.1$$

where  $x$  = concentration of ionic strength (mmol/L)

$y$  = estimated adsorption capacity in ionic solution (mg/g)

$A$  = adsorption capacity in non ionic solution (mg/g)

$B$  = influence of ionic on PFHxA adsorption factor (L/mmol)

**Table 6.2** shows the estimation of adsorption capacity parameters in ionic solution. The parameters were fitted well with the exponential equation. The values of  $B$  were influence of ionic on PFHxA adsorption factor. A higher values of  $B$  showed a higher influence of ionic on PFHxA adsorption.

Table 6.2 Estimation of adsorption capacity parameters in ionic solution

Adsorbent	Parameter	Unit	Ionic				
			NaCl	Na <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	KCl	CaCl <sub>2</sub>
GAC	$A$	mg/g	0.135	0.123	0.111	0.135	0.130
	$B$	L/mmol	0.016	0.062	0.066	0.011	0.016
	$R^2$	-	0.933	0.868	0.808	0.963	0.893
PFA300	$A$	mg/g	0.160	0.157	0.155	0.157	0.154
	$B$	L/mmol	0.022	0.064	0.117	0.017	0.025
	$R^2$	-	0.999	0.976	0.990	0.982	0.985
PFA400	$A$	mg/g	0.156	0.157	0.172	0.156	0.149
	$B$	L/mmol	0.048	0.201	0.284	0.040	0.063
	$R^2$	-	0.994	0.995	0.973	0.995	0.987
BA103	$A$	mg/g	0.159	0.155	0.155	0.157	0.155
	$B$	L/mmol	0.014	0.046	0.068	0.014	0.020
	$R^2$	-	0.997	0.965	0.994	0.970	0.978

The influence of ionic on PFHxA adsorption factor ( $B$ ) were proposed to estimate the adsorption capacity in the mixed inorganic ions solution by the following equation in subsequent section.

$$y_{mix} = Ae^{(-B_1x_1 - B_2x_2 - B_3x_3 \dots - B_nx_n)} \quad 6.2$$

where  $x_n$  = concentration of ionic strength of  $n$  (mmol/L)

$y_{mix}$  = estimated adsorption capacity in mixed ionic solution (mg/g)

$B_n$  = influence of ionic of  $n$  on PFHxA adsorption factor (L/mmol)



#### 6.4.2 Effects of mixed inorganic ions solution on PFHxA adsorption capacity

This experiment aim to simulate the competition between mixed ions and PFHxA in solution on adsorption site. Mixed two types of ionic solution (NaCl and Na<sub>2</sub>SO<sub>4</sub>, NaCl and NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>) and three types of ionic solution (NaCl, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>) solution were mixed with PFHxA to understand effects of mixed ionic solution onto PFHxA adsorption capacity. **Figure 6.2** and **Figure 6.3** shows effects of mixed two and three types of ionic solution on PFHxA adsorption capacity, respectively.

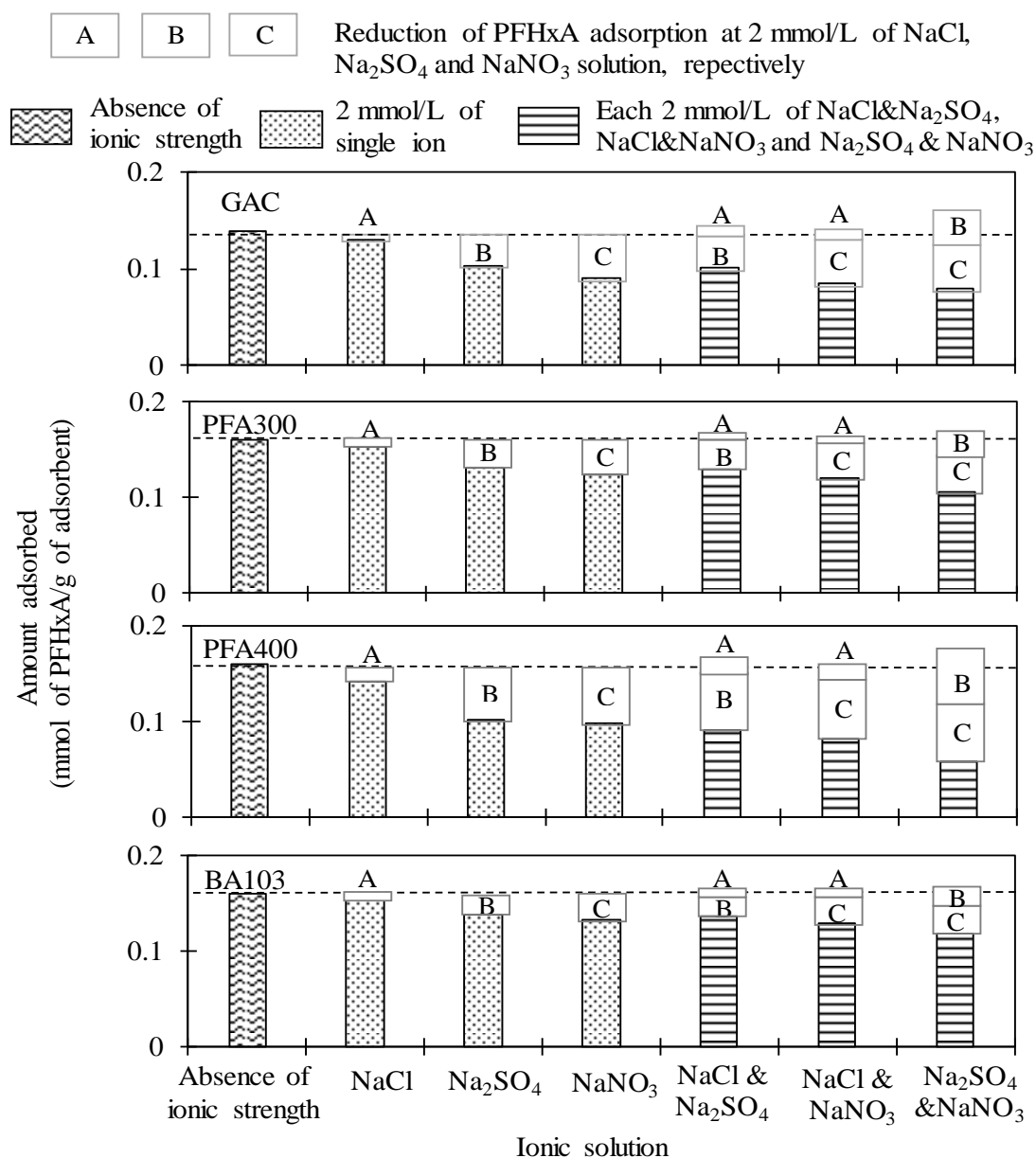


Figure 6.2 Effects of mixed ionic solution on PFHxA adsorption compare to single ionic solution

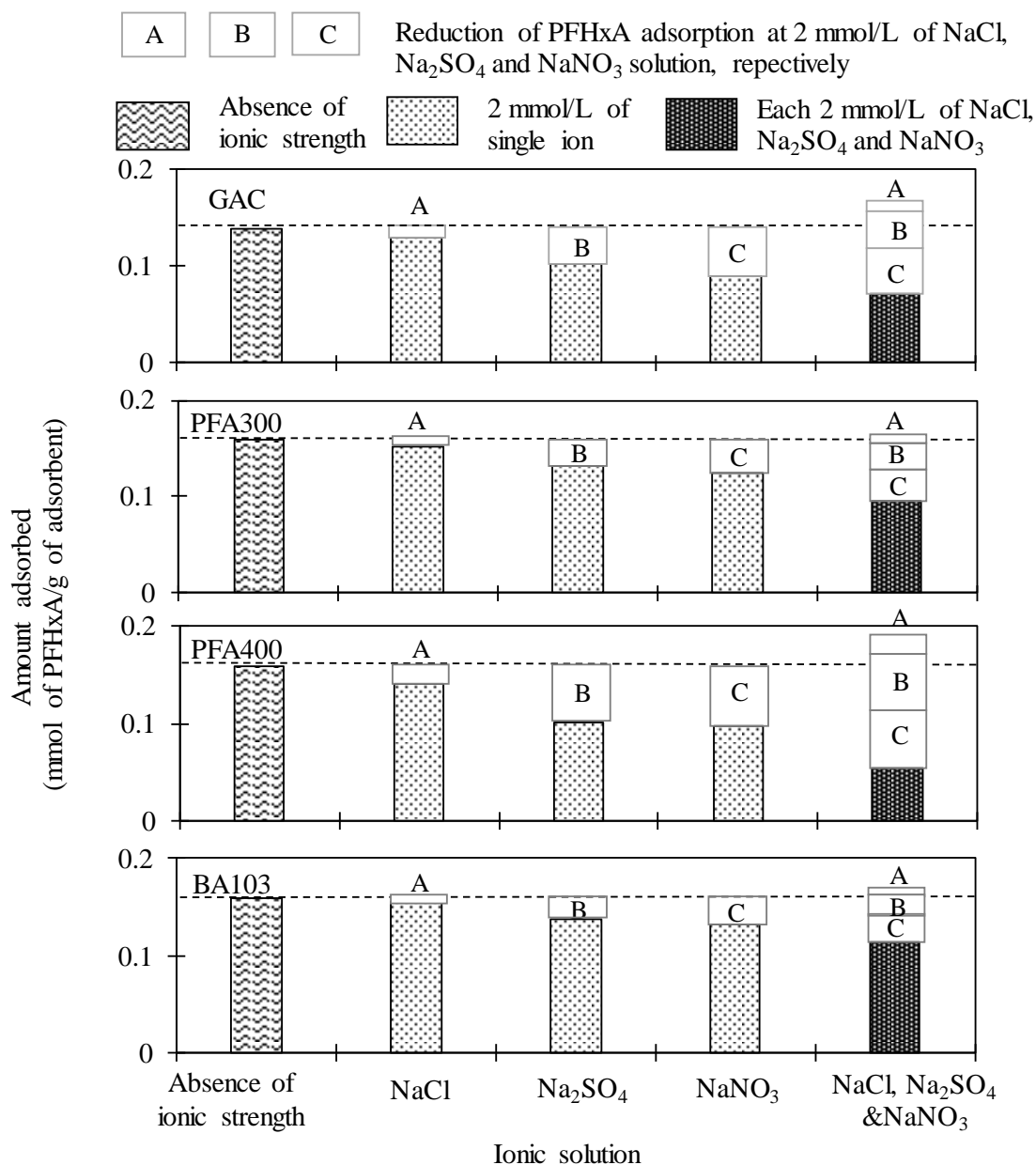


Figure 6.3 Effects of mixed inorganic ions on PFHxA adsorption compare to single inorganic ions

Both figures show the caparison of adsorption of capacity of PFHxA onto GAC, PFA300, PFA400 and BA103 in absence of ionic strength, single ionic solution and mixed ionic solution. A, B and C represented the reduction of PFHxA adsorption in 2 mmol/L of NaCl, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>, respectively. Adsorption capacities of PFHxA onto GAC and anion exchange polymers decreased when mixed ionic solutions existed. PFHxA adsorption capacities in mixed two ionic solution of NaCl and Na<sub>2</sub>SO<sub>4</sub> were higher than

those of others mixed ionic solution because the single inorganic ion of  $\text{NaNO}_3$  solution strongly affect to PFHxA adsorption. It is interesting that the reduction of adsorption capacity in mixed ionic solution was lower than combination of individual reduction of PFHxA in single ionic solution. Mixture of three types of ionic solution shows the lowest PFHxA adsorption capacity in all adsorbents due to the highest ionic strength.

The adsorption capacity of PFHxA in mixed ionic solution that obtained from experiment were compared with estimated adsorption capacity of PFHxA by Eq. 6.2 (Appendix B.1). The adsorption capacity in mixed ionic solution by estimation was higher than that in experiment onto GAC, PFA300, PFA400 and BA103. On the other words, there were synergistic effects in the mixed ionic solution. Thus, the adsorption capacity of PFHxA in single ionic solution was able to estimate by Eq. 6.1 but adsorption capacity of PFHxA in mixed ionic solution was not applicable by Eq. 6.2.

#### **6.4.3 Effects of humic acid solution on PFHxA adsorption capacity**

Humic acid is one of the major components of humic substances which arise by the microbial degradation of biomolecules. In this experiment, humic acid was used to represent organic compounds in wastewater to study the effect of dissolved organic carbon on adsorption capacity of PFHxA. In all experiments, DOC concentration contributed by humic acid ranges from 0 to 60 mg/L of DOC and PFHxA concentration was kept at 0.016 mmol/L. **Figure 6.4** shows the effects of humic acid on PFHxA adsorption.

Adsorption capacity of PFHxA onto GAC dramatically decreased when DOC concentration increased. At 60 mg/L of DOC, the adsorption capacities of PFHxA onto GAC reduced by 86.7% when compared with adsorption capacity in absence of humic acid. Humic acid in solution might affect the adsorption capacity of PFHxA by direct site competition and pore blockage (Li *et al.*, 2003). XAD4 was ineffective to remove PFHxA due to low adsorption capacity of XAD4. Thus, the effect of humic acid on PFHxA adsorption capacity onto XAD4 was unclear.

PFHxA adsorption capacity onto anion exchange polymers decreased when humic acid concentration increased from 0 to 60 mg/L of DOC. For strong base anion exchange polymers, PFHxA adsorption capacity onto polystyrene polymers (PFA300 and PFA400) reduced by 15.6 and 21.8 % at 60 mg/L of DOC when compared with adsorption capacity in absence of humic acid. A860 (polyacrylic polymers) had low adsorption capacity of PFHxA in humic acid solution. It means that polystyrene polymers had higher adsorption capacity than polyacrylic polymers had in humic acid solution. For weak base anion exchange polymers, PFHxA adsorption capacity onto BA103 and MN102 reduced by 27.7 and 85.7 % at 60 mg/L of DOC. The PFHxA adsorption capacity of PFA300 and PFA400 (gel polystyrene polymers) was higher than those of BA103 and MN102 (macroporous polystyrene polymers) in humic acid solutions.

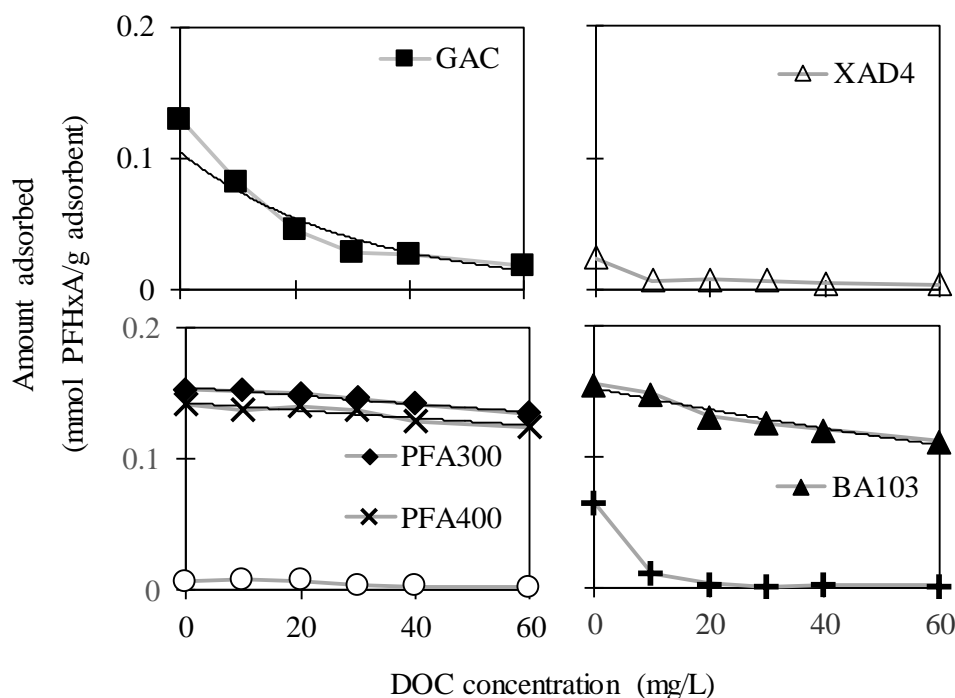


Figure 6.4 Effects of humic acid on PFHxA adsorption  
(— Fitted equation for GAC, PFA300, PFA400 and BA103)

The adsorption data in humic acid solution of GAC, PFA300, PFA400 and BA103 were fitted with the following equation.

$$y = Ae^{(-Cx)} \quad 6.3$$

where  $x$  = concentration of humic acid (mg/L)

$y$  = estimated adsorption capacity in humic acid (mg/g)

A = adsorption capacity in *Milli-Q* water (mg/g)

C= influence of humic acid on PFHxA adsorption factor (L/mg)

Table 6.3 Influence of humic acid on adsorption capacity of PFHxA

Adsorbent	Parameter	Unit	Humic acid
GAC	A	mg/g	0.105
	B	L/mg	0.033
	R <sup>2</sup>	-	0.913
PFA300	A	mg/g	0.155
	B	L/mg	0.002
	R <sup>2</sup>	-	0.952
PFA400	A	mg/g	0.143
	B	L/mg	0.002
	R <sup>2</sup>	-	0.836
BA103	A	mg/g	0.152
	B	L/mg	0.006
	R <sup>2</sup>	-	0.942

**Table 6.4** shows the influence of humic acid on adsorption capacity of PFHxA. The influence of humic acid on PFHxA adsorption factor onto GAC was 0.033 L/mmol and the influence of NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, KCl and CaCl<sub>2</sub> onto GAC were 0.016, 0.062, 0.066, 0.011 and 0.016 L/mmol, respectively. The influence of humic acid onto anion exchange polymers on PFHxA adsorption factors (PFA300, PFA400 and BA103) ranged from 0.002 to 0.006 L/mmol and the influences of five ionic solutions on PFHxA adsorption factors range from 0.014 to 0.284 L/mmol. It was obviously found that the influence of ionic on adsorption capacity of PFHxA onto anion exchange polymers was more than the influence of humic acid.

#### 6.4.4 Effects of DOC in wastewater on PFHxA adsorption capacity

Effects of DOC on PFHxA adsorption capacity in industrial wastewater could not be investigated directly due to unknown organic compounds in industrial wastewater. Thus, the effects of DOC on PFHxA adsorption were investigated through comparing the adsorption efficiency of PFHxA in solution with DOC (Fluorochemical wastewater) and without DOC. The solution without DOC was prepared by adding the equivalent amount of inorganic strength in fluorochemical wastewater into the *Milli-Q* water. Simulated

ionic strength solutions were prepared by adding PFHxA and inorganic ions such as NaF, NaNO<sub>3</sub>, Mg<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaCl which is similar to the concentration in fluorochemical wastewater (**Table 4.4**). The PFHxA concentration, ionic strength and pH in simulated ionic strength solutions were similar to fluorochemical wastewater except DOC concentration.

Adsorption isotherms of PFHxA onto GAC, PFA300 and PFA400 and BA103 were compared in *Milli-Q* water, simulated ionic strength solution and fluorochemical wastewater (**Fig. 6.5**). **Table 6.5** shows the *Freundlich* isotherm constants for adsorption of PFHxA in *Milli-Q* water, simulated ionic strength solution and fluorochemical wastewater. The adsorption capacity of PFHxA onto GAC in *Milli-Q* water were higher than those in simulated ionic strength and fluorochemical wastewater. PFHxA adsorption capacity in *Milli-Q* water, simulated ionic strength and fluorochemical wastewater were 22.88, 9.27 and 1.66 mg/g, respectively.

Table 6.4 The *Freundlich* isotherm constants for adsorption of PFHxA in *Milli-Q* water, simulated ionic strength solution and fluorochemical wastewater

Adsorbents	<i>Freundlich</i> isotherm <sup>a</sup>	<i>Milli-Q</i> water	Simulated ionic strength	Fluorochemical wastewater <sup>b</sup>
GAC	$K_f$	22.88	9.27	1.66
	$1/n$	0.51	0.55	0.92
	$R^2$	0.972	0.984	0.860
PFA300	$K_f$	156.00	38.29	36.33
	$1/n$	0.46	0.56	0.52
	$R^2$	0.994	0.981	0.980
PFA400	$K_f$	130.49	26.67	24.55
	$1/n$	0.41	0.58	0.59
	$R^2$	0.908	0.979	0.974
BA103	$K_f$	202.93	51.69	37.12
	$1/n$	0.43	0.53	0.56
	$R^2$	0.844	0.916	0.980

a. Unit of  $K_f$  is (mg/g)/(mg/L)<sup>1/n</sup> b. Filtrated by GF/B

Adsorption capacities of PFHxA in *Milli-Q* water were higher than those in simulated ionic strength solution and fluorochemical wastewater onto anion exchange polymers. Among three anion exchange polymers, BA103 had the highest adsorption capacities in *Milli-Q* water, simulated ionic strength solution as well as fluorochemical wastewater.

PFHxA adsorption capacity onto BA103 in these solutions were 202.93, 51.69 and 37.12 mg/g, respectively. The effects of inorganic ions and DOC on reduction of PFHxA adsorption capacity could be interpreted by the Eq. 6.4. These calculation is shown in Appendix B.2.

The adsorption capacity ( $K_f$ ) of PFHxA in simulated ionic strength and fluorochemical wastewater were estimated by the following equation.

$$K_f = K_{f \text{ in Milli-Q}} e^{((-B_{ion}X_{ion} - B_{DOC}X_{DOC}))} \quad 6.4$$

where  $K_f$  = estimation value of adsorption capacity ( $K_f$ ) in the solution (mmol/L)

$K_{f \text{ in Milli-Q}}$  = adsorption capacity ( $K_f$ ) in Milli-Q water (mg/g)

$B_{ion}$  = influence of ionic on PFHxA adsorption factor (L/mmol)

$X_{ion}$  = ionic strength (mmol/L)

$B_{DOC}$  = influence of ionic on PFHxA adsorption factor (L/mg)

$X_{DOC}$  = ionic strength (mg/L)

**Figure 6.6** shows influence of ions and DOC in wastewater on PFHxA removal onto BA103. The influence percentages of ion and DOC were calculated based on the  $B_{ion} X_{ion}$  and  $B_{DOC}X_{DOC}$ . The influence of ion in wastewater on adsorption capacity of PFHxA was 81% and the influence of DOC on adsorption capacity of PFHxA was 19%. Thus, ions in fluorochemical wastewater were the main factors which affecting the adsorption capacity of PFHxA.

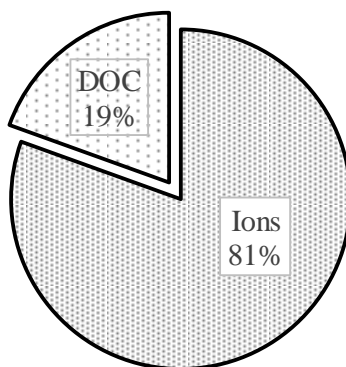


Figure 6.5 Influence of ions and DOC in wastewater on PFHxA removal onto BA103

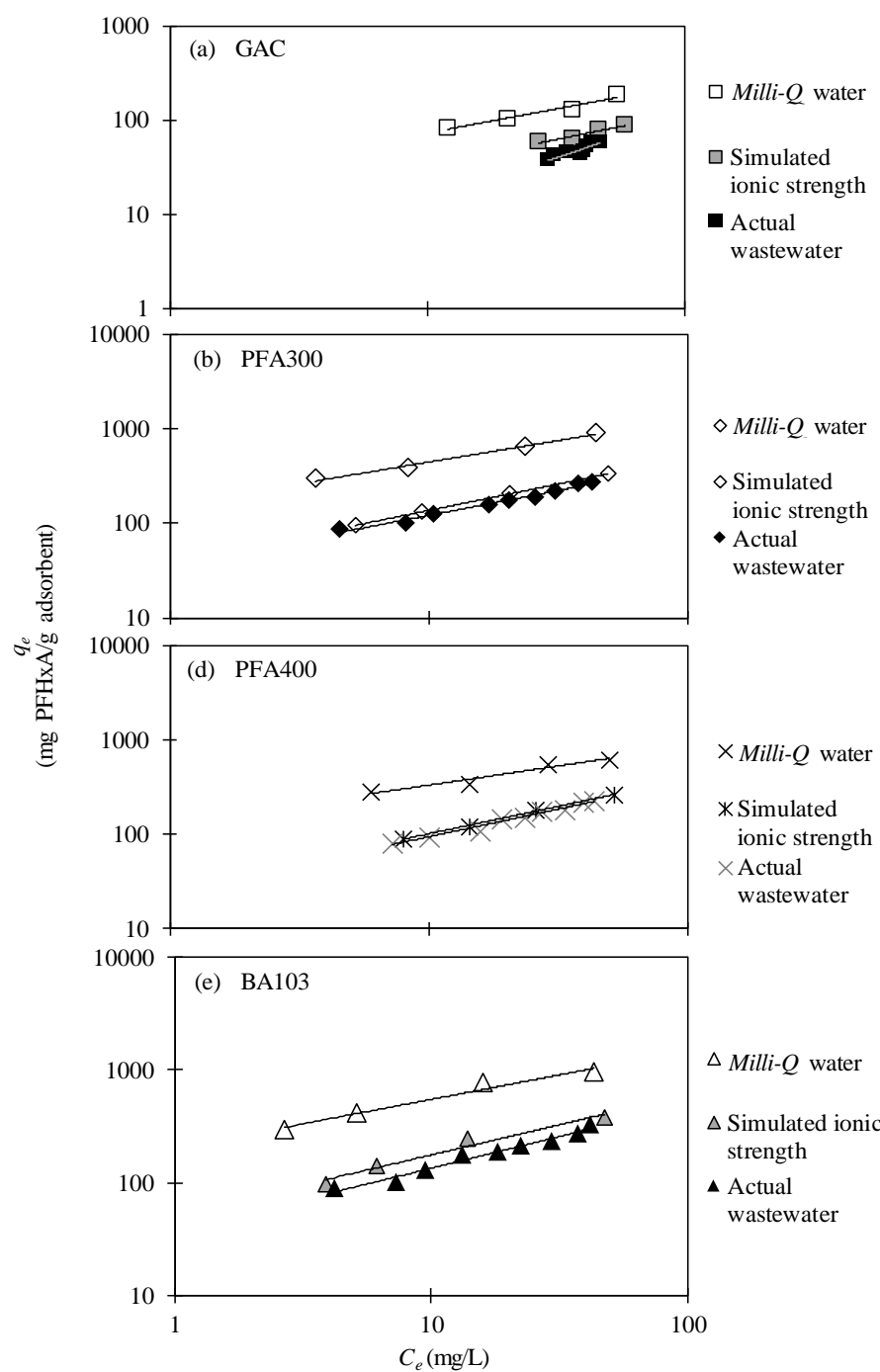


Figure 6.6 Comparison of adsorption isotherms of PFHxA in *Milli-Q* water, simulated ionic strength and fluorochemical wastewater onto GAC, PFA300 and PFA400 and



#### 6.4.5 GAC adsorption followed by anion exchange polymer to remove PFHxA

Mahmudov and Huang, (2011) found that GAC has potential to adsorb inorganic anions while Newcombe *et al.* (2002) revealed that GAC could adsorb organic matters such as NOM. Thus, GAC was also expected to improve adsorption efficiency of PFHxA in fluorochemical wastewater. This experiment was conducted by using GAC to adsorb a part of inorganic anion and DOC following by adsorption of anion exchange polymers (PFA300 and BA103). The initial concentrations of PFHxA and DOC in wastewater were 50.3 and 54.2 mg/L, respectively. After adsorption by GAC, PFHxA and DOC concentrations became 40.1 and 28.0 mg/L, respectively. The wastewater sample was adjusted PFHxA concentration to 50.3 mg/L (DOC concentration was 30.9 mg/L). **Figure 6.7** shows adsorption capacity of PFHxA in wastewater after pretreatment in comparison with that in wastewater without pretreatment onto PFA300 and BA103. The adsorption data were fit with the *Freundlich* equation. The *Freundlich* isotherms were elucidated by fitting equations.

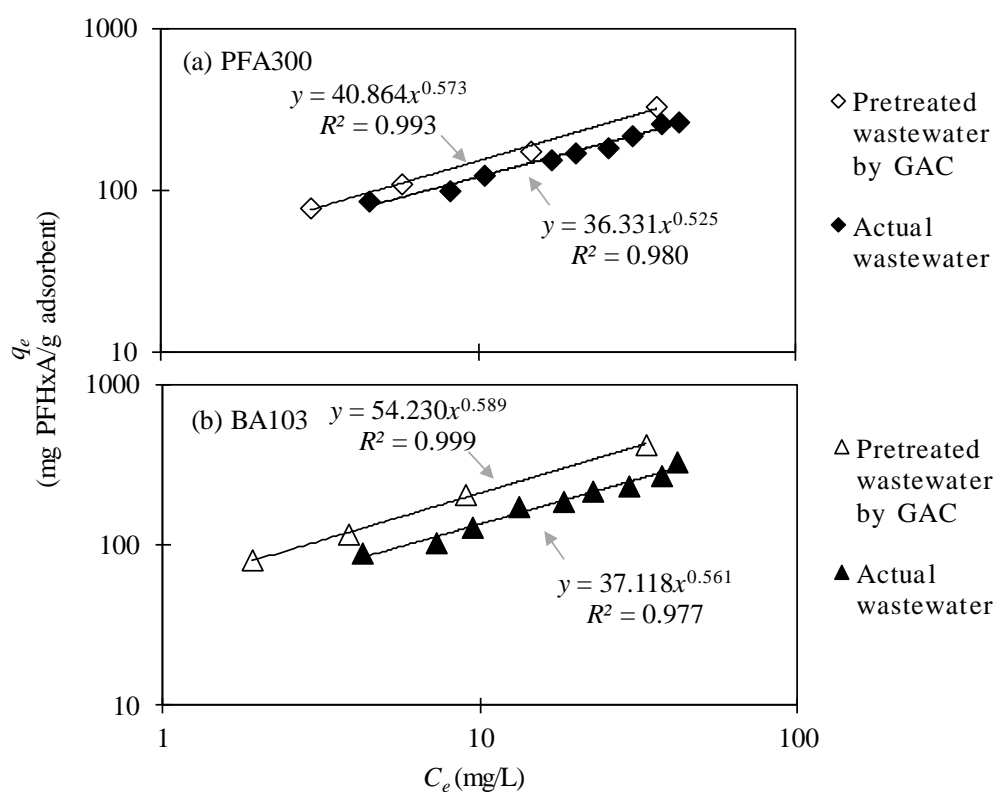


Figure 6.7 Adsorption capacity of PFHxA in pretreated wastewater by GAC compare to without pretreated onto PFA300 and BA103

After pretreatment, the adsorption capacity of PFHxA onto both PFA300 and BA103 were increased. The adsorption capacity of PFA300 was increased from 36.3 mg/g in fluorochemical wastewater to 40.86 mg/g in wastewater pretreated. The adsorption capacity of BA103 was higher than that of PFA300 and its adsorption capacity for PFHxA in wastewater with pretreatment has been increased to 54.2 mg/g. Thus, GAC could be used as an adsorbent to improve adsorption efficiency of PFHxA before adsorption by anion exchange polymers because it might be able to remove some interferences (inorganic anions and DOC) that inhibited the adsorption capacity of PFHxA onto anion exchange polymers.

#### **6.4.6 Effects of pH on PFHxA adsorption capacity**

The properties of both adsorbent and adsorbate may be changed by the effect of pH. In our experiment, adsorption capacities of PFHxA onto seven adsorbents were investigated at pH ranging from 2 to 12. Due to adjusting pH by 0.1 M of HCl and NaOH, the ion strength were different at each pH. Thus, NaCl was added into the samples after adjusting pH in order to keep the ionic strength of all samples at the same level. **Figure 6.8** shows effects of pH on PFHxA adsorption capacity onto GAC, non ion exchange polymers and anion exchange polymers.

Wastewater pH not only influences the properties of the adsorbent surface, but also affects the adsorbate (PFHxA) property in solution. The removal of PFHxA by GAC decreased gradually with increasing synthetic wastewater pH from 2 to 12 which is probably related to their speciation at different pH. The higher adsorption capacity were observed at lower pH. In consideration of the hydrophobic perfluorinated chain of PFHxA and the hydrophobic of activated carbons, the hydrophobic interaction should be also involved in the adsorption process. Wastewater pH 2 is very close to the  $pK_a$  value of PFHxA ( $pK_a = 0.74$ , Moroi *et al.*, 2001), some PFHxA may exist in the form of neutral molecules (Yu *et al.*, 2009). Thus, the hydrophobic interaction is also expected to occur between PFHxA and GAC. Adsorption capacity of PFHxA onto XAD4 is also expected to have higher adsorption capacity at lower pH but the result show that PFHxA adsorption capacity was constant at pH 2 to 12.

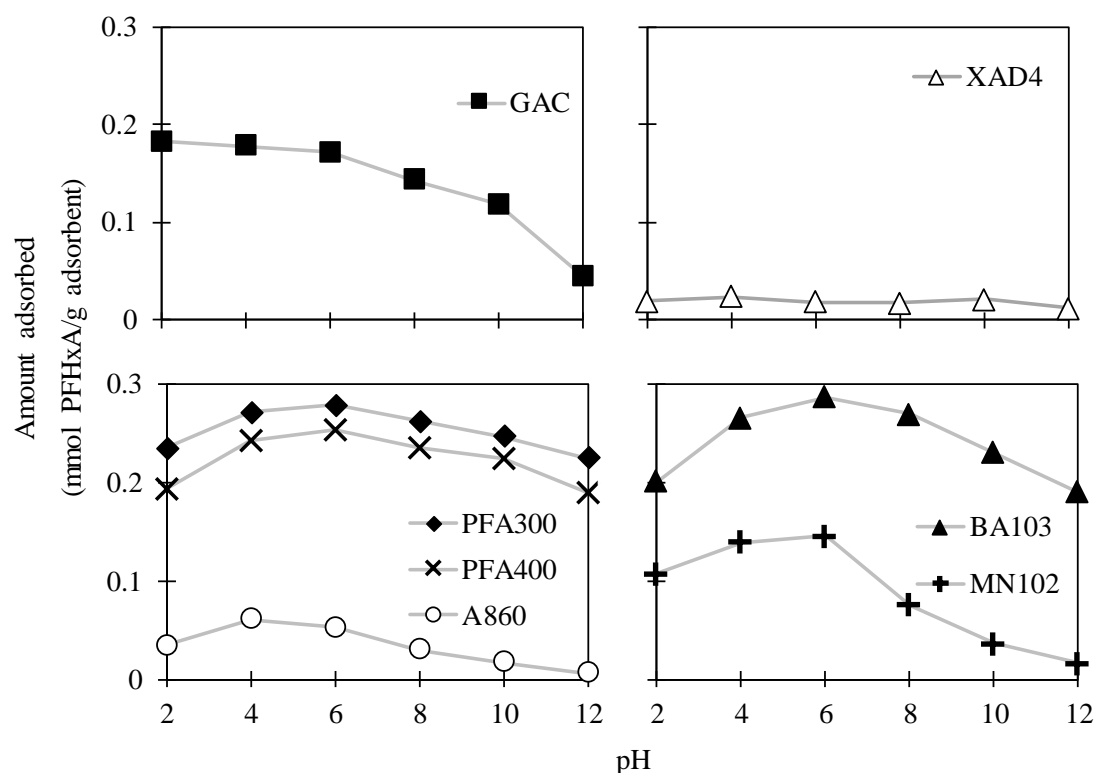


Figure 6.8 Effects of pH on PFHxA adsorption

Polystyrene with type I and II of function group (PFA300 and PFA400) could remove PFHxA effectively in all the pH ranges studied. The slight reduction in the PFHxA adsorption capacity onto PFA300 and PFA400 at higher pH region was because of competition of  $\text{OH}^-$  for ion the bonding sites. Polyacrylic polymers (A860) showed higher PFHxA adsorption capacity in acid range than alkaline range. However, polyacrylic polymers had much lower PFHxA adsorption capacity than those of polystyrene polymers.

Weak base anion exchange polymers (BA103 and MN102) had high adsorption capacity for PFHxA at natural pH. When wastewater pH was above 10, the adsorption capacity of PFHxA onto weak base anion exchange polymers due to the number of protonated sites decreased and lost ability of anion exchange (Deng *et al.*, 2010). An excess of  $\text{OH}^-$  can compete effectively with PFHxA for adsorption sites, resulting in lower adsorption capacity of PFHxA.

#### 6.4.7 Effects of temperature on PFHxA adsorption capacity

Effects of temperature on the adsorption of PFHxA were investigated at 15 to 45°C in synthetic wastewater. The initial concentration of PFHxA range from 0.02 to 2 mg/L in 100 mL with 1 mg of GAC, PFA300, PFA400 and BA103. The adsorption data were fit with the *Freundlich* equation. **Table 6.6** shows adsorption the *Freundlich* isotherm constants for adsorption of PFHxA in synthetic wastewater at different temperature while **Figure 6.9** shows adsorption isotherms of PFHxA in synthetic wastewater.

It was obvious that the *Freundlich* equation fitted well with adsorption data at 15, 25, 30, 35, 40 and 45°C ( $R^2 > 0.98$ ). The good fitness of linear sorption model demonstrated that the partitioning was the main adsorption mechanism in the PFHxA sorption as suggested by the *Freundlich* equation. Adsorption of PFHxA onto GAC increased with the increased of temperature and the adsorption capacity increased five times when temperature increased from 15°C to 45°C. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature. Thus, the mass transfer resistance of adsorbate in the boundary layer decreases (Fil *et al.*, 2012).

Table 6.5 The *Freundlich* isotherm constants for adsorption of PFHxA in synthetic wastewater at different temperature

Temperature	Constant*	GAC (■)	PFA300 (◆)	PFA400 (×)	BA103 (▲)
15°C	$K_f$	9	177	128	185
	$1/n$	0.65	1.06	1.01	0.94
	$R^2$	0.961	0.995	0.998	0.992
25°C	$K_f$	16	304	188	412
	$1/n$	0.59	0.93	0.970	0.95
	$R^2$	0.997	0.999	0.999	0.999
30°C	$K_f$	23	352	220	463
	$1/n$	0.56	0.90	0.98	0.94
	$R^2$	0.996	0.997	0.989	1.000
35°C	$K_f$	31	384	313	536
	$1/n$	0.55	0.85	0.94	0.91
	$R^2$	0.994	0.998	0.993	0.996
40°C	$K_f$	40	400	342	551
	$1/n$	0.56	0.86	1.07	0.95
	$R^2$	0.992	0.999	0.997	0.998
45°C	$K_f$	45	348	304	480
	$1/n$	0.56	0.89	1.06	0.94
	$R^2$	0.998	0.996	0.999	0.999

\* Unit of  $K_f$  is  $(\text{mg/g})/(\text{mg/L})^{1/n}$

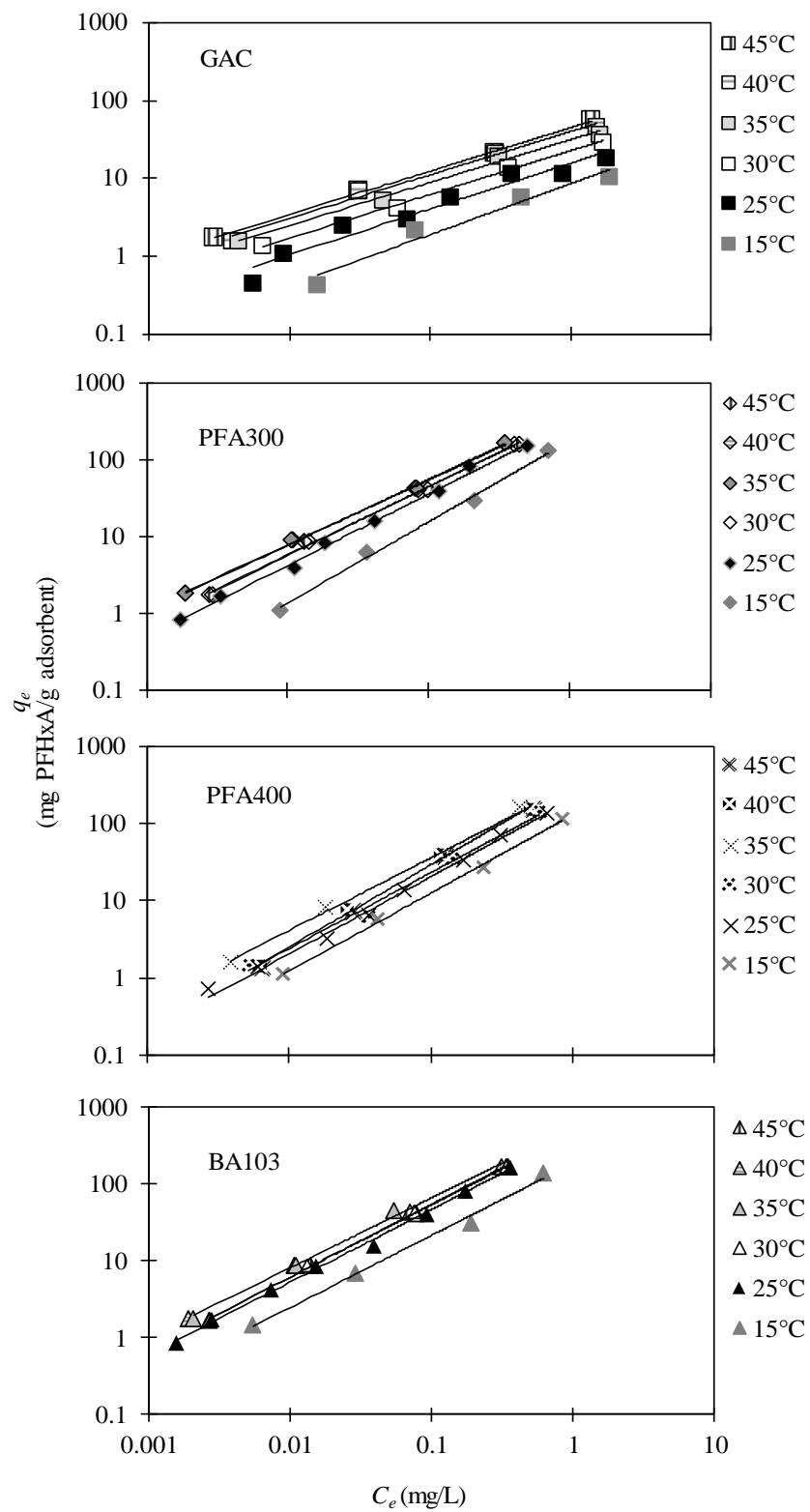


Figure 6.9 Adsorption isotherms of PFHxA in synthetic wastewater using the *Freundlich* equation onto GAC, PFA300, PFA400 and BA103 at different temperature

On the other hand, adsorption capacity of PFHxA onto anion exchange polymers (PFA300, PFA400 and BA103) increased when increased temperature from 15 to 40°C and the adsorption capacity of PFHxA slightly decreased at 45°C. The decreasing adsorption of PFHxA onto anion exchange polymers at 45°C is mainly due to two reasons. Firstly, the solubility of PFHxA increased with at higher temperature resulting in reduces hydrophobic interaction. Secondly, the degradation processes are accelerated at higher temperatures and the loss of total capacity becomes significant close to or above the maximum recommended operating temperatures (45°C) for the given resin type. (Purolite, 2009)

#### **6.4.8 Comparative adsorption of PFHxS and PFOA with PFHxA onto BA103**

Among seven adsorbents in this study, BA103 had higher performance to remove PFHxA than others adsorbents. PFHxA and PFHxS both have six fluorinated carbons but they have the different function group. While PFHxA and PFOA have the same functional group but PFHxA have shorted fluorinated carbons than PFOA. Thus, BA103 was selected as the adsorbent to investigate the effect of PFOA and PFHxS on the adsorption of PFHxA. PFOA and PFHxS were supposed to decrease the adsorption capacity of PFHxA through the competition attaching to the adsorption sites. In all experiments, PFHxA concentration was kept at 0.016 mmol/L, while the concentration of PFHxS and PFOA ranged from 0.002 to 0.030 mmol/L.

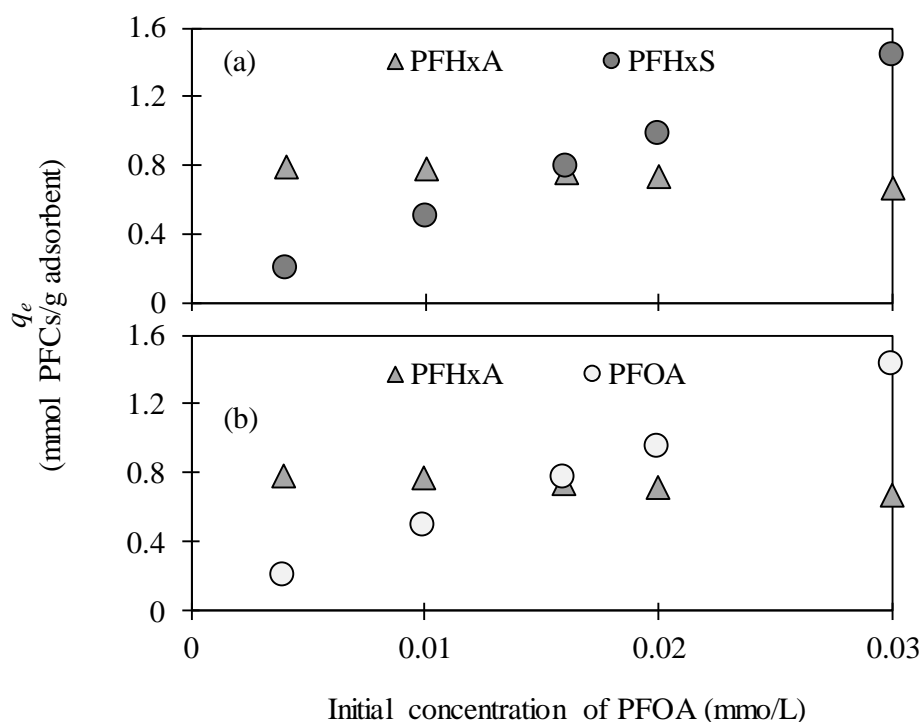


Figure 6.10 Comparative adsorption of PFHxS (a) and PFOA (b) on PFHxA adsorption capacity onto BA103

**Figure 6.10** show comparative adsorption of PFHxS and PFOA on PFHxA adsorption capacity onto BA103. PFHxA adsorption capacities decreased when PFHxS and PFOA concentrations increased. When PFHxA and PFHxS have the same initial concentration (0.016 mmol/L), their adsorption capacity onto BA103 were 0.79 and 0.75 mmol/L, respectively. It shows that the adsorption amount of sulfonate compound was higher than that of the corresponding carboxylic compound (Yu *et al.*, 2009). At the same initial concentration of PFOA and PFHxA, adsorption capacities onto BA103 were 0.77 and 0.74 mmol/L, respectively. It means that the adsorption amount increased regularly with increase of the chain length for the carboxylic compounds (Deng *et al.*, 2010).

## 6.5 Summary

Effects of interferences (ionic strength and DOC) and adsorption conditions (pH and temperature) on PFHxA adsorption capacities were identified onto GAC, non ion exchange polymers as well as five anion exchange polymers. Moreover, industrial wastewater samples were pretreated by adsorption of GAC before adsorption of anion exchange polymers (PFA300 and BA103) to improve adsorption efficiency. Comparative adsorption of PFHxS and PFOA with PFHxA onto BA103 were studied.

The inorganic ions ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{NO}_3$ ,  $\text{KCl}$ , and  $\text{CaCl}_2$ ) in wastewater affected adsorption capacities of PFHxA onto GAC and anion exchange polymers. The adsorption capacity of PFHxA onto GAC and anion exchange polymers decreased when increased inorganic ion concentrations. BA103 shows the better performance to remove PFHxA in wastewater containing inorganic ion than other adsorbents.

Adsorption capacity of PFHxA onto GAC and anion exchange polymers decreased when humic acid concentration increased in wastewater. The adsorption capacity of PFHxA in simulated inorganic strength slightly higher those in fluorochemical wastewater, indicating that influence of DOC is less significant than inorganic ion on PFHxA removal. The adsorption of GAC can be used as a pretreatment method for adsorption of inorganic ion and organic compound to improve PFHxA adsorption efficient of PFA300 and BA103.

PFHxA could be effectively adsorbed onto anion exchange polymers (polystyrene polymer) at pH ranging from 5 to 7 and temperature from 30 to 40 °C, while GAC has the effective adsorption performance at pH ranging from 2 to 4 and temperature of 45°C. The adsorption capacity of non ion exchange polymers (XAD4) keeps at a low level at all pH and temperature conditions tested. Moreover, PFHxS and PFOA could reduce the adsorption capacity of PFHxA through competition on adsorption sites with PFHxA.



## **Chapter 7 Evaluation of PFHxA regeneration efficiency of spent adsorbents**

### **7.1 Introduction**

Activated carbon have been adopted to remove PFCs (Yu *et al.*, 2009 and Senevirathna, 2010). The most common techniques for regeneration of organic compounds onto spent activated carbon are thermal regeneration (Torrents *et al.*, 1997) and chemical regeneration (Deng *et al.*, 2010). The main drawbacks of thermal regeneration method are following: the requirement of high temperature of the order of 300 to 500°C and excessive burnout of the carbon, resulting in capacity losses of 5 to 15% (Grant and King, 1990). The spent activated carbon was not easily regenerated by methanol or ethanol (Punyapalakul *et al.*, 2013). Thus, safe disposal of spent activated carbon is required.

In the previous study, the spent non ion exchange polymers with PFOS and PFOA can be fully regenerated by methanol (Senevirathna, 2010). Although non ion exchange polymers were able to be regenerated, they had a much lower adsorption capacity of PFCs than anion exchange polymers. The anion exchange polymers were selected to study the reusability performance because of two reason. Firstly, anion exchange polymers had a higher adsorption capacity than the GAC and non ion exchange polymers. Secondly, the anion exchange polymers are considerably expensive. Therefore, the effective regeneration of anion exchange polymers is required in order to minimize the cost of treatment.

Deng *et al.* (2010) reported that single salt solution or methanol was inefficient to regenerate PFOS but the mixture of salt solution and methanol was effective. This may be explained that these PFOS have very low solubility in the concentrated NaOH and NaCl regenerants (Carter and Farrell, 2010). However, the regeneration efficiency of PFHxA onto anion exchange polymers has not been studied yet.

This chapter applied various types of regenerant (various type of salt solution, various concentration of salt solution and several ratios of methanol and salt solution) to

regenerate spent anion exchange polymers. The effective regenerant was selected for reusability with industrial wastewater.

## 7.2 Objectives

The target of this study was to investigate regeneration efficiency of the selected adsorbent.

1. To determine the suitable regenerant of spent adsorbent after adsorption of PFHxA in synthetic wastewater
2. To study the regeneration rate of the spent adsorbent after adsorption of PFHxA in synthetic wastewater
3. To investigate the reusability of the spent adsorbent after adsorption of PFHxA in fluorochemical wastewater

## 7.3 Methodology

According to chapter 5, BA103 performed the fastest adsorption rate and highest adsorption capacity. It was selected to apply the regeneration experiment. Properties of BA103 were shown in section 3.1. Experiments are divided into three parts (Selection of suitable regenerant, determination of regeneration rate and reusability of spent adsorbent). The summary of regeneration experiments is shown in **table 7.1**.

### 7.3.1 Selection of suitable regenerant

#### Preparation of spent adsorbent

Adsorbent (BA103) was added into PP tube containing 10 mL of 50 mg/L of PFHxA in *Milli-Q* water and shaken for 96 hours by thermo shaker at 120 rpm 25°C ( $n=2$ ). The PFHxA solution was adjusted the initial pH to 7 by 0.1 M HCl or NaOH. The adsorbent was immediately filtrated by GF/B glass filter after shaking. These filtrated samples were diluted before analysing PFHxA concentration by HPLC-MS/MS. The adsorbent on GF/B glass filter was took into another PP tube. It was washed with 5 mL of *Milli-Q* water (two times), 5 mL of methanol (two times) and 5 mL of *Milli-Q* water (two times) to remove the unadsorbed PFHxA.

Table 7.1 Summary of experiment condition in this study

Experiment	Adsorbent	Preparation of spent adsorbent			Regeneration of spent adsorbent		
		PFHxA solution (mg/L)	Sample volume (mL)	Contact time (hour)	Regenerant	Sample volume (mL)	Contact time (hour)
Selection of suitable regnerant	10 mg of BA103	50	10	96	- Methanol (MeOH)	10	96
					- 5 % NaOH in <i>Milli-Q</i> water		
					- 5 % NaCl in <i>Milli-Q</i> water		
					- 1% NaOH in MeOH: <i>Milli-Q</i> water (3:7)		
					- 5% NaOH in MeOH: <i>Milli-Q</i> water (3:7)		
					- 1% NaCl in MeOH: <i>Milli-Q</i> water (3:7)		
					- 5% NaCl in MeOH: <i>Milli-Q</i> water (3:7)		
					- 1% NaOH in MeOH: <i>Milli-Q</i> water (7:3)		
					- 5% NaOH in MeOH: <i>Milli-Q</i> water (7:3)		
					- 1% NaCl in MeOH: <i>Milli-Q</i> water (7:3)		
					- 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3)		
Determination of regeneration rate	10 mg of BA103	50	10	96	- 1% NaOH in MeOH: <i>Milli-Q</i> water (7:3) - 5% NaOH in MeOH: <i>Milli-Q</i> water (7:3) - 1% NaCl in MeOH: <i>Milli-Q</i> water (7:3) - 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3)	10	0.5, 1, 2, 6, 24 and 48
Reusability of spent adsorbent (Ten cycles)	10 mg of BA103	50.3 <sup>a</sup>	10	96	- 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3)	10	24

Note: a. PFHxA concentration in wastewater (**Table 4.4**)

### Regeneration of spent adsorbent

Concentrated salt solutions (NaCl or NaOH) are the common regenerant of spent anion exchange polymers. Due to a low solubility of PFHxA in the concentrated salt solutions, the using of a solvent, such as methanol in the regenerant may increase regeneration efficiency. The concentrated salt solution, the solvent and the mixture of those solutions were used to desorb PFHxA onto adsorbent. The spent adsorbent was regeneration by 10 mL of regenerant in **table 7.1**. The sample was shaken for 96 hours by thermo shaker at 120 rpm 25°C before analyzing the PFHxA concentration.

### 7.3.2 Determination of regeneration rate

#### Preparation of spent adsorbent

Procedure of preparation of spent adsorbent is exactly same with previous section.

#### Regeneration of spent adsorbent

Regenerants with regeneration efficiency more than 90% were selected to determine the regeneration rate. The spent adsorbents were regenerated by 10 mL of the regenerants with different contact time (0.5, 1, 2, 6, 24 and 48 hours) as shown in **table 7.1**. After shaking, all samples were diluted into 40% (v/v) acetonitrile in *Milli-Q* water. PFHxA concentration were measured by HPLC-MS/MS.

### 7.3.2 Reusability of spent adsorbent (Fluorochemical wastewater)

#### Preparation of spent adsorbent

BA103 was added into PP tube containing 10 mL of fluorochemical wastewater containing 50.3 mg/L of PFHxA. The fluorochemical wastewater was adjusted initial pH to 7 by 0.1 M HCl or NaOH. **Table 4.4** shows the wastewater characteristics in this experiment. The sample shaken for 96 hours by thermo shaker at 120 rpm 25°C ( $n=2$ ). The adsorbent was immediately filtrated by GF/B glass filter after shaking. These filtrated samples were analysed the remaining PFHxA concentration by procedure in section 3.2. The adsorbent on GF/B glass filter was took into another PP tube. It was washed with 5 mL of *Milli-Q* water (two times), 5 mL of methanol (two times) and 5 mL of *Milli-Q* water (two times) to remove the unadsorbed PFHxA.

## Regeneration of spent adsorbent

The regenerant of 5% NaCl in MeOH:Milli-Q water (7:3) showed the fastest regeneration rate was used to study the reusability (Considered from the result in regeneration rate experiment). The spent adsorbent was regenerated by 10 mL of regenerant (5% NaCl in MeOH:Milli-Q water (7:3)). The sample was shaken for 24 hours by thermo shaker at 120 rpm 25°C. The remaining PFHxA concentration were measured by HPLC-MS/MS. The efficiencies of spent adsorbent was checked up to ten cycles

### 7.3.4 Calculation of regeneration efficiency

Data of PFHxA concentration was obtained and calculated the regeneration efficiency by Eq. 7.1.

$$\text{Regeneration efficiency (\%)} = \frac{C_{\text{desorption}}}{C_{\text{initial}} - C_{\text{remaining}}} \times 100 \quad 7.1$$

Where  $C_{\text{regeneration}}$  = Concentration of PFHxA in regenerant

$C_{\text{initial}}$  = Initial concentration of PFHxA (Preparation of spent adsorbent)

$C_{\text{remaining}}$  = Remaining concentration of PFHxA (Preparation of spent adsorbent)

## 7.4 Results and discussion

### 7.4.1 Selection of suitable regenerant

Because anion exchange polymers are expensive, spent anion exchange polymers need to be reused to minimize the treatment cost. The chemical regeneration such as salt solutions (NaOH or NaCl), organic solvent (Methanol) and the mixture of the salt solutions and the organic solvent. The advantages of chemical regeneration are convenient and ability to performed on-site. Regeneration of anion exchange polymers occurred by ion exchange process. To recovery the adsorbents, the adsorbed PFHxA on adsorbents was taken place by anion in regenerant. BA103 was selected to regeneration due to the fastest adsorption rate and the highest adsorption capacity of PFHxA.

Regeneration efficiencies of spent BA103 with various types of the regenerant are shown in Fig. 7.1. Methanol was unable to regenerate the spent BA103, indicating that the adsorbed PFHxA required anions in regenerant to replace PFHxA onto adsorbent. NaCl

and NaOH in *Milli-Q* water were also ineffective to regenerate the spent BA103 because these regenerants are low water solubility (Kim *et al.*, 2015). Deng *et al.*, 2010 found that weak base anion exchange polymers (IRA67) could be regenerated by NaOH solution due to desorption of amine groups. However, our results shows that weak base anion exchange polymers (BA103) cannot be desorbed by NaOH solution.

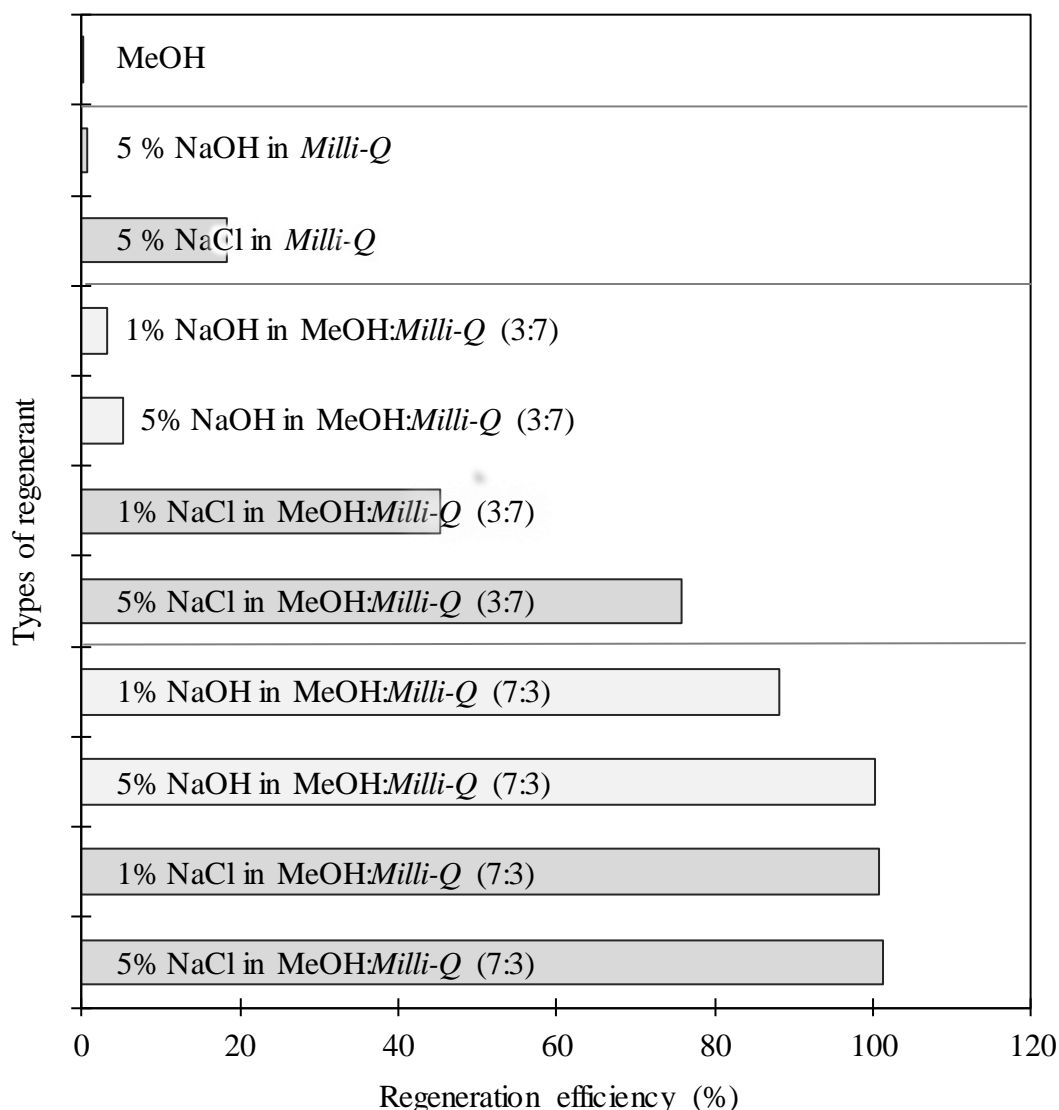


Figure 7.1 Regeneration efficiency of BA103 by various types of regenerant

The regenerant of 1% NaOH in MeOH:*Milli-Q* water (3:7) had a lower regeneration efficiency than the regenerant of 5% NaOH in MeOH:*Milli-Q* water (3:7) due to lower OH<sup>-</sup> concentration in the solution. Similarly, the regenerant of 1% NaCl in MeOH:*Milli-Q* water (3:7) had a lower regeneration efficiency than the regenerant of 5% NaCl in

MeOH:*Milli-Q* water (3:7). The regeneration efficiency of 5% NaOH in MeOH:*Milli-Q* water (3:7) was lower than that of 5% NaCl in MeOH:*Milli-Q* water (3:7) because the chloride ion has a higher ion selectivity than the hydroxide.

The regeneration efficiency increased from 3.2 to 88.3% when increased methanol concentration from 30 to 70% at presence of 1% NaOH. It is interesting that sodium salt in MeOH:*Milli-Q* water (7:3) except 1% NaOH in MeOH:*Milli-Q* water (7:3) could desorb PFHxA onto BA103 more than 98%. Thus, it can be concluded that the regeneration efficiency of BA103 related to the solubility of PFHxA in regenerant and salt concentration in regenerant.

PFHxA in wastewater can be recycled by anion exchange polymers. The spent adsorbents was able to reuse by sodium salt in mixed methanol and *Milli-Q* water, resulting in regenerant waste was produced. The further study is to management of regenerant waste. Our research work found the procedure to decomposed PFHxA in regenerant waste by UV after distillation of methanol (Ono, 2015). Fluoride ions were by product of UV decomposition which they are possible to be recovery fluoride ions by precipitation of calcium ( $\text{CaF}_2$ ).

#### 7.4.2 Determination of regeneration rate

The regeneration rate of spent BA103 with effective regenerants were determined. **Figure 7.2** and **Figure 7.3** show regeneration efficiencies of the spent BA103 with NaOH and NaCl in MeOH:*Milli-Q* water (7:3), respectively.

Regeneration reaction of 1 and 5% NaOH in MeOH:*Milli-Q* water (7:3) reached the equilibrium concentration within two hours. At 30<sup>th</sup> minute of regeneration contact time, regeneration efficiency of 1% NaOH in MeOH:*Milli-Q* water (7:3) was 71% while that of 5% NaOH in MeOH:*Milli-Q* water (7:3) was 81%. The regeneration rate increased when the NaOH concentration in MeOH:*Milli-Q* water (7:3) increased from 1 to 5% due to more anions in regenerants.

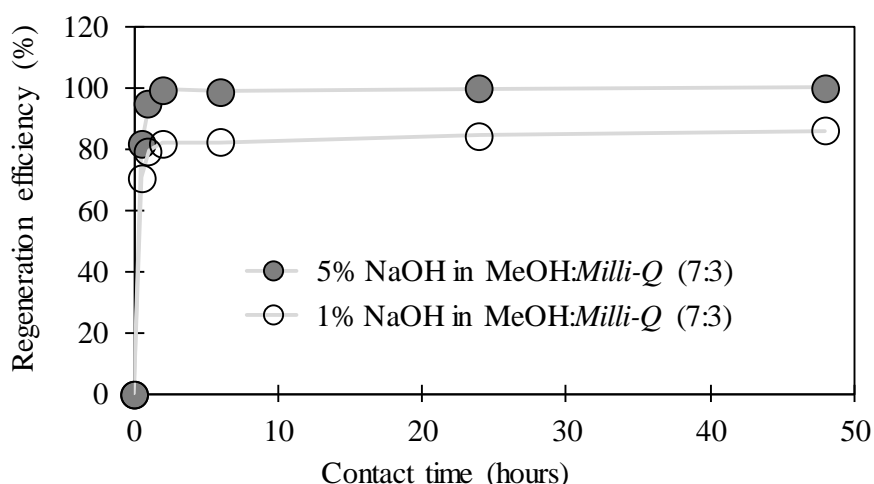


Figure 7.2 Regeneration rate of the spent BA103 with NaOH in MeOH:Milli-Q water

Similarly, the regeneration reaction of 1 and 5% NaCl in MeOH:Milli-Q water (7:3) reached the equilibrium concentration within a few hours. The regeneration efficiency of 1% NaCl in MeOH:Milli-Q water (7:3) was 87% and that of 5% NaCl MeOH:Milli-Q water (7:3) was 91% after 30 minute of regeneration contact time. The higher NaCl concentration in MeOH:Milli-Q water (7:3) had a faster regeneration rate. In conclusion, the sodium salt in MeOH:Milli-Q water (7:3) solutions except 1% NaOH in MeOH:Milli-Q water (7:3) show more than 99% of regeneration efficiency after two hours. It can be note that NaCl in MeOH:Milli-Q water (7:3) solutions performed faster regeneration rate than NaOH in those solutions due to a higher selectivity of NaCl than that of NaOH (Chularuengaksorn *et al.*, 2013).

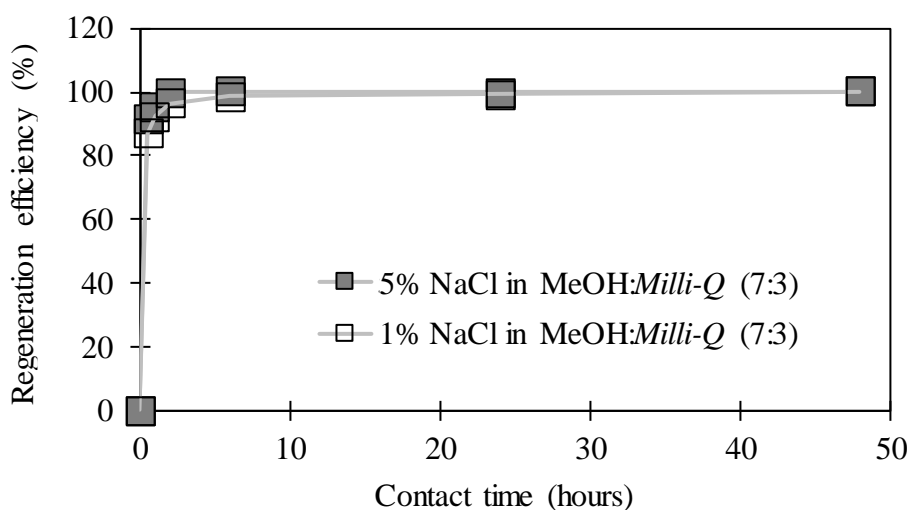


Figure 7.3 Regeneration rate of the spent BA103 with NaCl in MeOH:Milli-Q water



### 7.4.3 Reusability of spent adsorbent in fluorochemical wastewater

In the previous experiment (section 7.4.1 and 7.4.2), the spent BA103 adsorbed the PFHxA in *Milli-Q* water. For this experiment, the reusability of the spent BA103 in fluorochemical wastewater was investigated. The regenerant of 5% NaCl in MeOH:*Milli-Q* water (3:7) was selected to regenerate the spent BA103 because this solution had a higher regeneration efficiency and a faster regeneration rate than others regenerant. The reusability of spent BA103 with fluorochemical wastewater were perform for ten cycles. **Figure 7.4** shows the PFHxA adsorption amount and PFHxA regeneration amount of regenerant (5% NaCl in MeOH:*Milli-Q* water (7:3)).

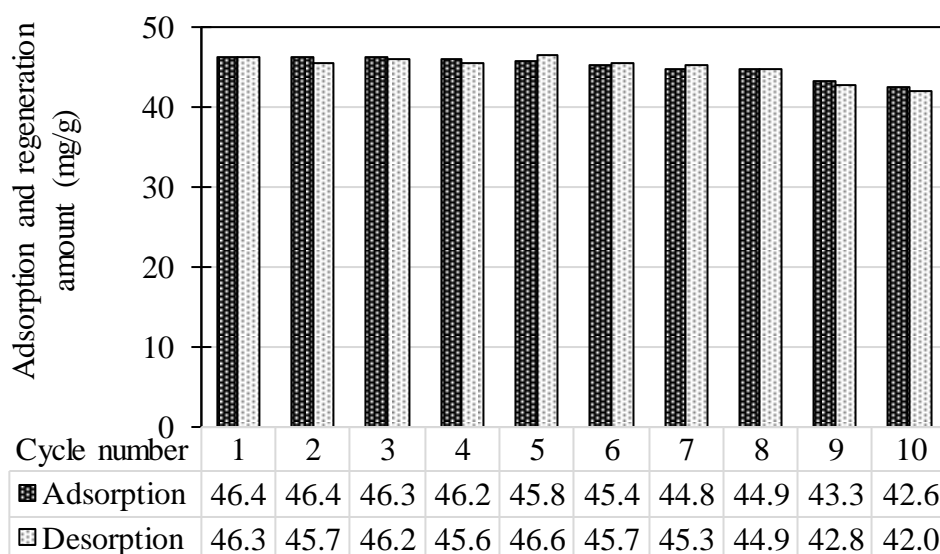


Figure 7.4 PFHxA adsorption amount and PFHxA regeneration amount of regenerant (5% NaCl in MeOH:*Milli-Q* water (7:3))

The adsorption amount of PFHxA in wastewater at the first cycle of regeneration was 46.4 mg/g and regeneration amount of PFHxA was 46.3 mg/g, showing 99.7% of regeneration efficiency. The adsorption and regeneration amount of PFHxA gradually decreased after the first cycle that may cause by interferences in wastewater. The adsorption amounts of PFHxA at the fifth, sixth and seventh were lower than those of regeneration amounts. It might be explained that the adsorbed PFHxA onto BA103 from the previous cycle was desorbed in the following cycle. At the tenth cycle of regeneration,

the adsorption amount of PFHxA was 42.6 mg/g. The remaining of adsorption amount of PFHxA after tenth cycle was 91.8 %. Thus, BA103 was able to reuse in fluorochemical wastewater.

## 7.5 Summary

The spent BA103 was used to regenerate by various types of regenerant such as methanol, salt solution and mixture of methanol and salt solution. The effective regenerants were selected to determine regeneration rate in synthetic wastewater and reusability in fluorochemical wastewater.

The methanol and salt solutions (5% of NaOH and NaCl in *Milli-Q* water) were unable to regenerate the adsorbed PFHxA onto BA103. On the other hand, the regeneration efficiencies of the mixture of methanol and salt solution were better than those of single solutions. A higher NaOH or NaCl concentration in MeOH:*Milli-Q* water (3:7) had a higher regeneration efficiency. Moreover, the regeneration efficiency of regenerant of MeOH:*Milli-Q* water (3:7) was lower than those of MeOH:*Milli-Q* water (7:3). The regenerant of 5% NaCl in MeOH:*Milli-Q* water (7:3) could desorb PFHxA onto BA103 more than 98%. It means that salt concentrations and ratios of methanol in *Milli-Q* water were important for regeneration.

The regenerant of 5% NaCl in MeOH:*Milli-Q* water (3:7) was selected to regenerate the spent BA103. The PFHxA adsorption and regeneration amount gradually decreased after first cycle that may cause from interferences in wastewater. The remaining of adsorption amount after ten cycles was 91.8 %. Thus, the BA103 was a reusable adsorbent. The effective regenerants were applied in the experiments of Chapter 8.

## **Chapter 8 Adsorption and regeneration of PFHxA in continuous modes**

### **8.1 Introduction**

As industrial wastewater is the major contributor to PFHxA in aquatic environment, the effective removal technique should be applied to minimize adverse effects of PFHxA. Fundamental studies of adsorption and regeneration of PFHxA (adsorption rates and capacities) were investigated by batch experiments in chapter 4 and 6. Although fundamental studies as mentioned above have been performed in batch experiment, it is necessary to conduct the adsorption of PFHxA in column experiments in order to determine breakthrough curves for column design parameters. Continuous adsorption experiments of PFHxA were conducted in synthetic wastewater and fluorochemical wastewater for comparison of breakthrough curves. According to chapter 4, the PFHxA was detected in the effluents of industrial wastewater treatment plant in Japan and Thailand. These wastewater samples were used in the column experiments.

In this chapter, adsorption and regeneration of PFHxA were performed by column experiments in synthetic wastewater and fluorochemical wastewater in Japan and Thailand in order to remove PFHxA for practical application. Moreover, column adsorption also studied in different parameters such as types of adsorbent, bed volume and initial concentration of PFHxA in wastewater.

### **8.2 Objectives**

The aim of this study was to investigate adsorption and regeneration of PFHxA by continuous experiments in synthetic wastewater and fluorochemical wastewater.

1. To study continuous removal of PFHxA in different conditions of synthetic wastewater (PFHxA in tap water containing PFHxA)
2. To apply the continuous adsorption and regeneration to industrial wastewater in Japan
  - 2.1 To examine the suitable adsorbent for removal PFHxA
  - 2.2 To study the effects of bed volumes on PFHxA adsorption efficiencies onto selected adsorbent

- 2.3 To investigate regeneration efficiencies of spent adsorbent in column mode
3. To apply adsorption and regeneration techniques to remove PFCs in wastewater from central WWTP in Thailand

## 8.3 Methodology

### 8.3.1 Apparatus: column

The continuous experiments to remove PFHxA were performed by the fixed-bed columns. The fixed-bed column configuration is shown in **Fig 8.1**. The main columns is made from polypropylene (PP). The inner diameter and length of column were 2 cm and 30 cm, respectively. Meshes were inserted between column and rubber seal at the top and bottom to prevent adsorbent loss. All equipments such as column, mesh and rubber seal were rinsed with methanol and *Milli-Q* water to avoid contamination. Peristaltic pumps were used to feed wastewater samples from feeding tank to influent tube of each column.

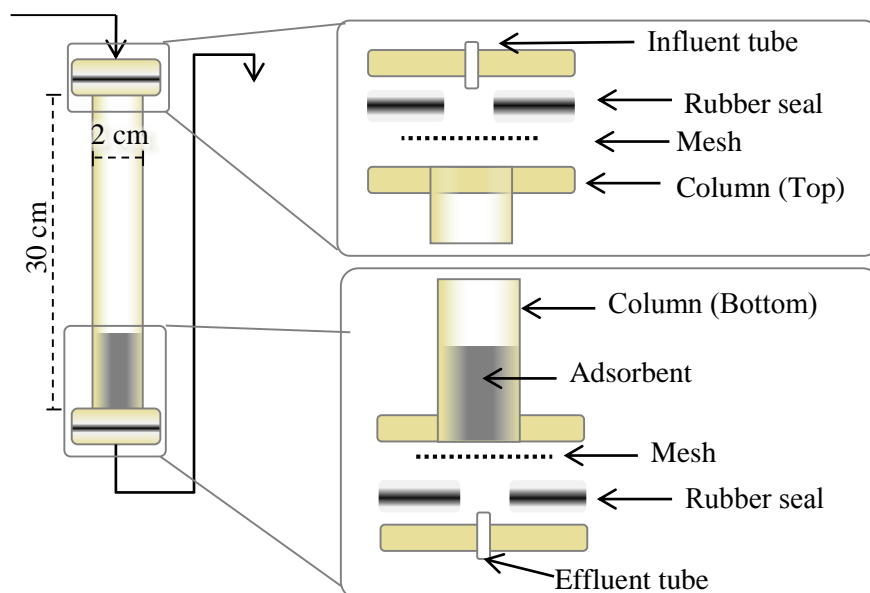


Figure 8.1 Configuration of column

PharMed<sup>®</sup>BPT tubes were used in the peristaltic pumps. Before start the column experiment, column containing adsorbent was feed 2 mL/min of *Milli-Q* water for 24 hours to eliminate air bubbles in the adsorbent. The effluent from control column was recycled to feeding tank. On the other hand, effluent samples from column containing adsorbent were treated with GAC again before discharge to protect water environment.

### 8.3.2 Adsorption and regeneration of PFHxA in synthetic wastewater

**Table 8.1** shows summary of the experiment condition in this chapter. Experimental setup of various adsorbents for removal of PFHxA in synthetic wastewater is shown in **Fig 8.2**. Adsorption experiments of PFHxA in synthetic wastewater were conducted by the following steps. GAC, XAD4, BA103, MN102, PFA300, PFA400 and A860 (20 cm<sup>3</sup>) were added into each column. Adsorbent was not added into control column. Tap water containing PFHxA concentration of 10 µg/L fed into each column with a flow rate 10 mL/min. The temperature of synthetic wastewater in feeding tank was 35°C due to higher adsorption capacity than lower temperature. Treated samples were collected every two days for measure remaining PFHxA concentration. Column experiments were terminated when PFHxA removal efficiencies of all columns dropped to 90%. The total operation days were 60 days.

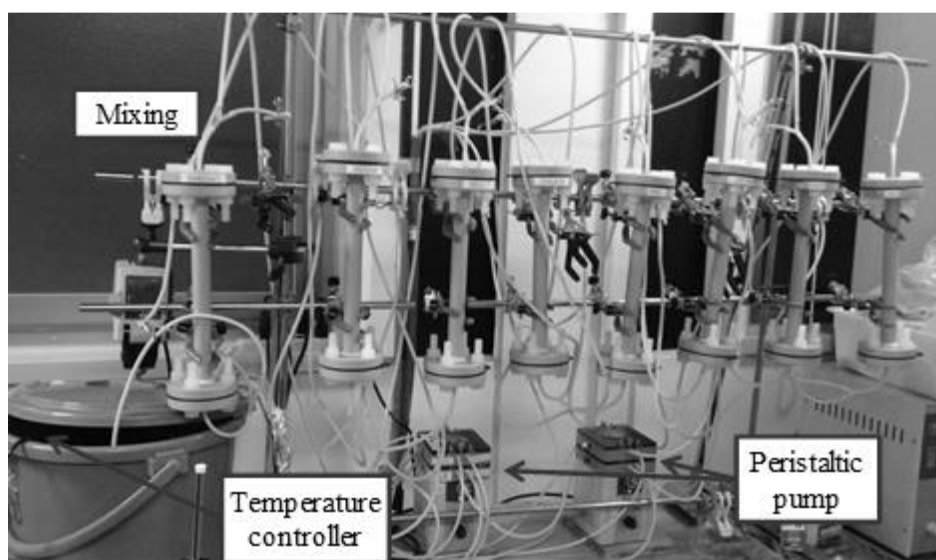
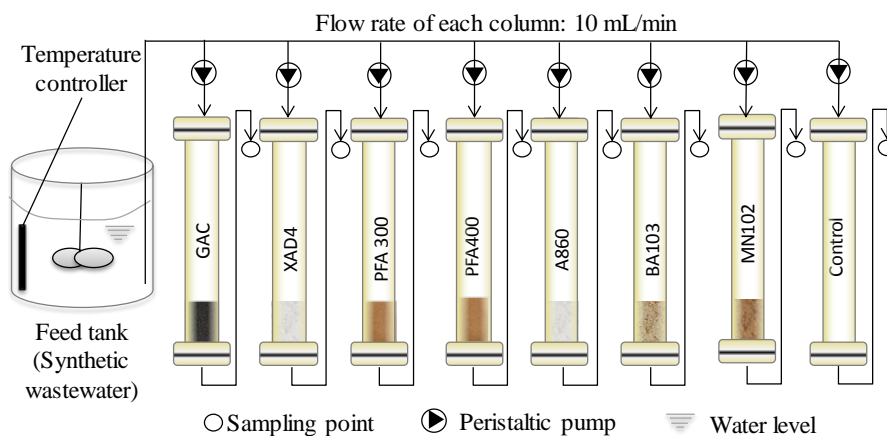


Figure 8.2 Experimental setup of various adsorbents to remove PFHxA in wastewater

Table 8.1 Summary of experiment condition in this study

Experiment	Adsorbent	Adsorption <sup>a</sup>			Regeneration <sup>a</sup>	
		Bed volume (cm <sup>3</sup> )	PFCs solution	Flow rate (mL/min)	Regenerant	Flow rate (mL/min)
Adsorption in synthetic wastewater	GAC, XAD4, PFA300, PFA400, A860, BA103 and MN102	20	10 µg/L of PFHxA in tap water	10	- MeOH for GAC and XAD4 - 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3) for PFA300, PFA400, A860, BA103 and MN102	2.5
Selection of suitable adsorbent	GAC, PFA300, PFA400 and BA103	20	36.0 mg/L of PFHxA (Sampling date 22 Sep 2014 <sup>c</sup> )	5	- MeOH for GAC - 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3) for PFA300, PFA400 and BA103	2
Examination of the effects of bed volumes on PFHxA removal	BA103 and used BA103 <sup>b</sup>	10, 20, 30 and 40	53.7 mg/L of PFHxA (Sampling date 2 Oct 2014 <sup>c</sup> )	5	- 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3)	2
Adsorption in wastewater (WWTP7)	BA103	20 x 2 <sup>d</sup>	617 ng/L of PFPeA, 904 ng/L of PFHxA 233 ng/L of PFHpA (Average value)	10	- 5% NaCl in MeOH: <i>Milli-Q</i> water (7:3)	2.5

Note: a. Control temperature of adsorption and regeneration experiment were 35°C and 25°C  
b. Bed volume of was 20 cm<sup>3</sup> of used BA103  
c. Fluorochemical wastewater (Sampling point A6)  
d. Consecutive column

After removal efficiency of columns dropped to 90%, they were regenerated by selected regenerant (MeOH or 5% NaCl in MeOH:*Milli-Q* water (7:3)). Experiment setup of regeneration experiment is shown in **Fig. 8.3**. GAC and XAD4 column were washed with *Milli-Q* water with flow rate 10 mL/min for three hours (up-flow). Regeneration experiment was performed by a solvent washing technique. GAC and XAD4 column were eluted by feeding a pure methanol from bottom of column at 2.5 mL/min. Eluted samples were collected every 50 mL in PP tubes and then they were diluted with 40% (v/v) acetonitrile. PFHxA concentrations in diluted samples were analyzed by HPLC-MS/MS.

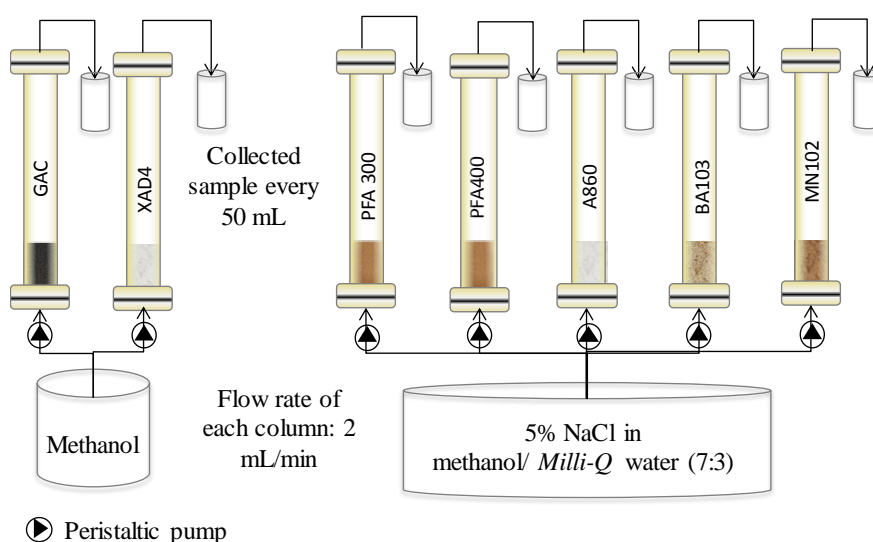


Figure 8.3 Experimental setup of regeneration of different adsorbents

The regenerations of anion exchange polymer columns (PFA300, PFA400, A860, BA103 and MN102) were different from GAC and XAD4 columns. Anion exchange polymers columns were back wash with *Milli-Q* water (10 mL/min for one hours), methanol (10 mL/min for one hours) and again with *Milli-Q* water (10 mL/min for one hours). These columns were eluted by regenerant of 5% NaCl in methanol/ *Milli-Q* water (7:3). Eluted samples were done in the similar way as regeneration of GAC and XAD4.

### 8.3.3 Continuous adsorption and regeneration of PFHxA in industrial wastewater (Japan)

#### Industrial wastewater in Japan

According to Chapter 4, elevated PFHxA concentration was detected in WWTP of a fluorochemical factory. **Figure 4.2** shows WWTP process of a fluorochemical factory. The wastewater samples after adsorption by GAC (A6) were selected to remove PFHxA. PFHxA concentrations at A6 ranged from 25 to 58 mg/L during four sampling times (25 April 2013, 17 May 2013, 19 and 29 October 2014). Wastewater samples at A6 were collected again on 22 September 2014 and 2 October 2014 for conducting column experiment. Wastewater samples were kept at 4°C during transportation to laboratory in Kyoto University. The wastewater samples were filtered by GF/B filter paper (1 µm) before feeding into column. Wastewater characteristics of a fluorochemical in Japan are shown in **table 8.2**.

Table 8.2 Wastewater characteristics of a fluorochemical factory (A6)

Parameter		Unit	Average value	
			22 September 2014	2 October 2014
PFCs	PFHxA	mg/L	36.0	53.7
Anion	Cl <sup>-</sup>	mg/L	243	238
	SO <sub>4</sub> <sup>2-</sup>	mg/L	312	355
	F <sup>-</sup>	mg/L	1	1
	NO <sub>3</sub> <sup>-</sup>	mg/L	2	1
	Cation	Na <sup>+</sup>	mg/L	155
K <sup>+</sup>		mg/L	43	49
Mg <sup>2+</sup>		mg/L	4	5
Ca <sup>2+</sup>		mg/L	124	149
DOC		mg/L	55	79
Conductivity		mS/cm	1.6	1.9
pH		-	7.2	7.1



### Selection of suitable adsorbent to remove PFHxA in wastewater

**Table 8.1** shows experiment condition in this study. The experimental setup is shown in **Fig. 8.4**. GAC, PFA300, PFA400 and BA103 were used in this study. Bed volumes of each column were 20 cm<sup>3</sup>. Adsorbent was not added into control column. The five columns (including control column) were fed filtrated wastewater at 5 mL/min. The temperature of wastewater in feeding tank was 35°C. Samples were collected every 24 hours and experiments were continued unit adsorbents saturated. The total operation time was 240 hours.

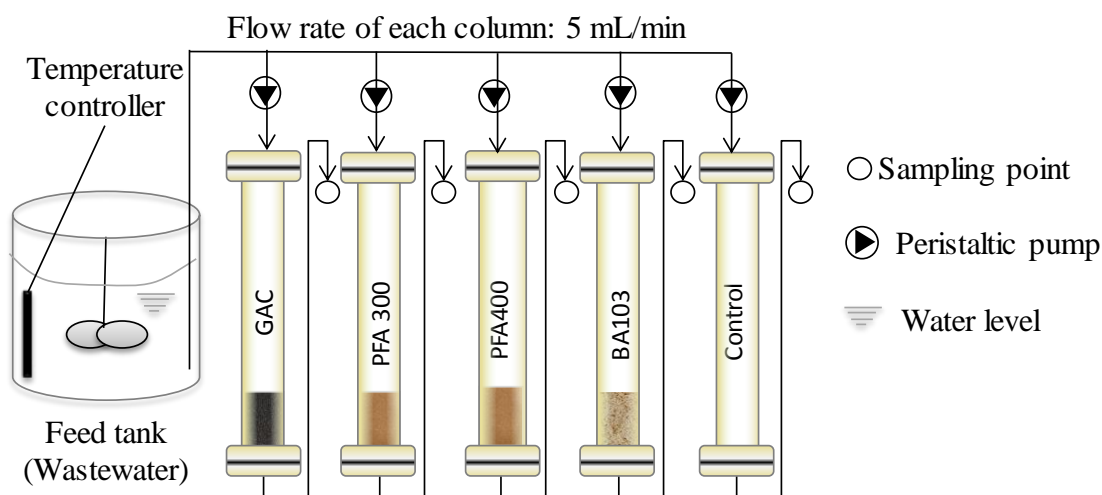


Figure 8.4 Experimental setup of different adsorbents for removal of PFHxA in wastewater

After all adsorbents saturated, they were prepared for regeneration experiments. This experimental setup was similar to Section 8.3.2. All adsorbents were washed and desorbed by proper regenerant. GAC was desorbed by methanol and anion (PFA300, PFA 400 and BA103) were desorbed by 5% NaCl in methanol/ *Milli-Q* (7:3). Regeneration experiments were conducted at room temperature (25°C). The regenerated BA103 was reused in the following section.

### Effects of bed volumes on PFHxA removal efficiencies in wastewater

BA103 was selected to study the effects of bed volumes on PFHxA removal efficiencies in wastewater in Japan. **Table 8.1** shows experiment condition in this study. Experimental setup of different bed volumes for removal of PFHxA in wastewater is shown in **Fig 8.5**. Adsorbents were added into column with different bed volumes (10, 20 30 and 40 cm<sup>3</sup>). Moreover, used BA103 for previous experiment was investigated the reusability. Wastewater sample was fed at 5 mL/min into each column and the temperature value in feed tank was controlled at 35°C. Samples were collected every 24 hours and experiments were continued unit adsorbents saturated. The total operation time was 240 hours. After all adsorbent saturated, they were prepared for regeneration experiments. This experimental setup was similar to Section 8.3.2. BA103 was desorbed by 5% NaCl in methanol/ *Milli-Q* (7:3) waster.

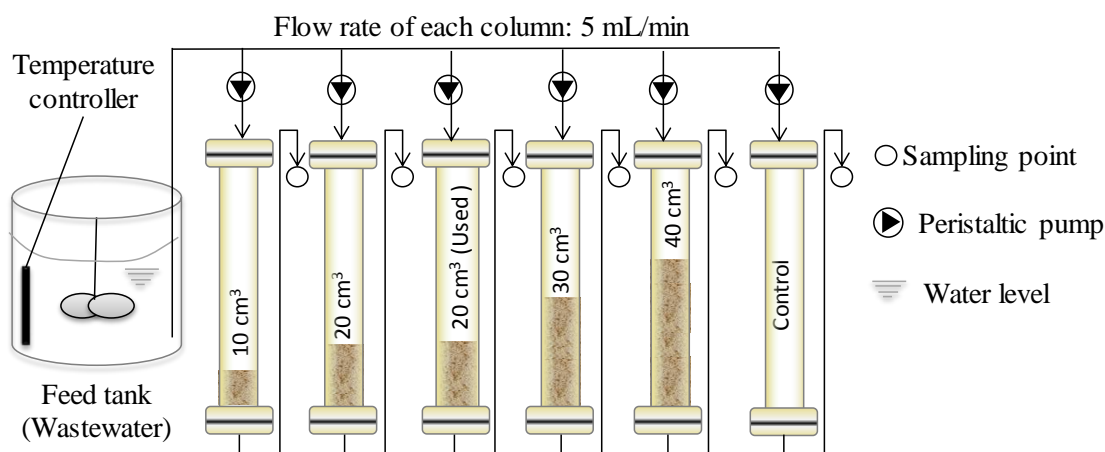


Figure 8.5 Experimental setup of different bed volumes for removal of PFHxA in wastewater

### 8.3.4 Continuous adsorption and regeneration of PFCs in central WWTP (Thailand)

#### Industrial wastewater in Thailand

Wastewater from central WWTP 7 was selected to remove PFCs because it had the highest PFHxA concentration among ten central WWTPs in Thailand (Chapter 4). Effluent wastewater samples at WWTP 7 were collected again to conduct continuous experiments on 20 December 2013 and 15 January 2014. The major PFCs were PFPeA, PFHxA and PFOA. Wastewater samples were kept at 4 °C during transportation to laboratory in Mahidol University. They were filtered by 1 µm GF/B filter paper. Wastewater characteristics of central WWTP 7 in Thailand are shown in **table 8.3**.

Table 8.3 Wastewater characteristic in effluent of central WWTP 7 in Thailand

Parameter		Unit	Average value	
			20 December 2013	15 January 2014
PFCs	PFPeA	ng/L	621	614
	PFHxA	ng/L	911	897
	PFOA	ng/L	238	229
Anion	Cl <sup>-</sup>	mg/L	243	225
	SO <sub>4</sub> <sup>2-</sup>	mg/L	470	452
	F <sup>-</sup>	mg/L	0.6	0.6
	NO <sub>3</sub> <sup>-</sup>	mg/L	1.1	0.9
Cation	Na <sup>+</sup>	mg/L	334	322
	K <sup>+</sup>	mg/L	14	11
	Mg <sup>2+</sup>	mg/L	10	10
	Ca <sup>2+</sup>	mg/L	51	50
DOC		mg/L	26.2	24.8
Conductivity		mS/cm	1.7	1.7
pH		-	7.2	7.2

#### Adsorption of PFCs in central WWTP 7 by consecutive column

For enhancing the removal efficiency of PFCs, the connecting of two similar columns were used to remove PFCs. The filtrated wastewater samples at effluent of WWTP 7 were used in this study. The major PFCs in effluent of WWTP 7 were PFHxA, PFPeA and PFOA (**Table 8.3**). **Figure 8.6** shows experimental setup of consecutive column.

BA103 (20 cm<sup>3</sup>) was added into both column. Wastewater in feeding tank was fed at 10 mL/min and controlled at 35°C. Samples of each column were collected every day for 35 operation days. After collecting samples, they were pretreated to analyze PFCs in Thailand by the procedure in **section 3.2.1**. The pretreated samples (cartridges) were kept at 4°C. Then, cartridges were brought back to Japan for analyzed PFCs.

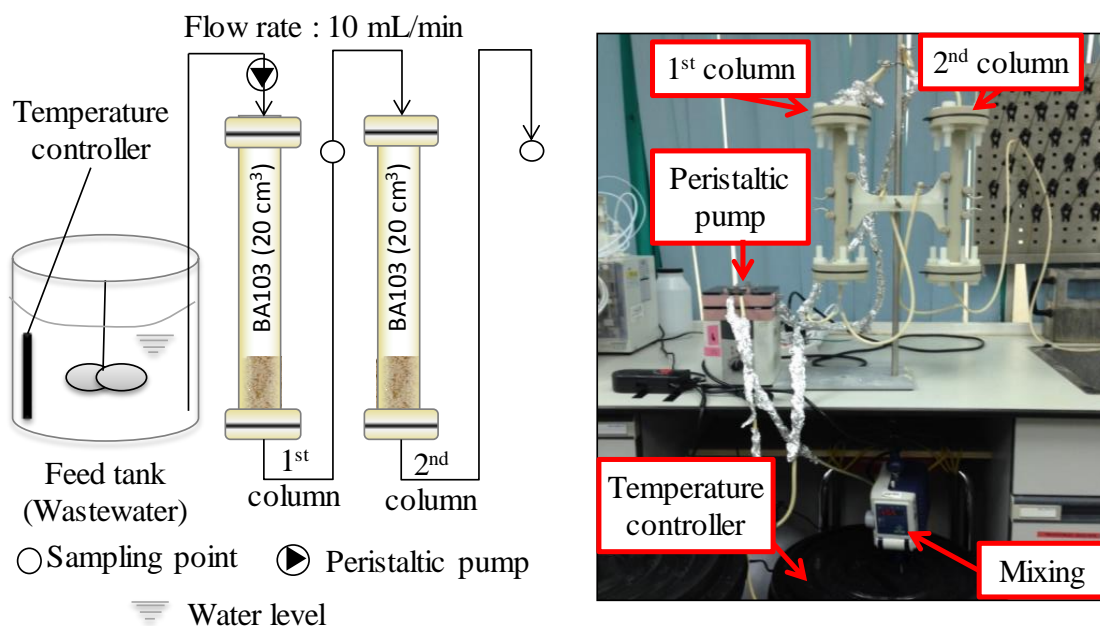


Figure 8.6 Experimental setup of consecutive column

After 35 operation days, both column were back washed separately by *Milli-Q* water, methanol and *Milli-Q* water with 10 mL/min (one hour). After that each column was filled with *Milli-Q* water and kept at 25±2°C during transportation to Japan. *Milli-Q* water was taken out from column before feeding the regenerant (5% NaCl in methanol/ *Milli-Q* (7:3)) into column with flow rate 2.5 mL/min (up-flow). Eluted samples were collected every 50 mL in PP tubes and then they were diluted with 40% (v/v) acetonitrile. PFHxA concentrations in the diluted samples were analyzed by HPLC-MS/MS.

### 8.3.5 Column data analysis

#### Adsorption amount

Adsorption capacities are important performance indicator in column test. Normally, breakthrough curve shows the performance of adsorbent in the fixed-bed column (Suh *et al.*, 2008). Breakthrough curve is expressed in term of  $C_t/C_0$  versus volume of the effluent for a given condition, where  $C_t$  is the concentration of effluent and  $C_0$  is the initial concentration. The adsorption capacity of adsorbent could be calculated from breakthrough curve. Breakthrough point is the time that effluent concentration reaches 10% of the initial concentration. The corresponding time is called breakthrough time. The exhaustion time is the time that the effluent concentration equal to initial concentration. The total mass of adsorbates adsorbed onto adsorbents could be calculated by the following Eq. 8.1.

$$q_{total} = \int_{V=0}^{V=V} (C_0 - C_t) dV \quad 8.1$$

where  $q_{total}$  = PFHxA adsorbed amount (mg)

$V$  = treated volume (L)

$C_0$  = initial concentration

$C_t$  = effluent concentration (mg/L)

Maximum capacity of the column or equilibrium PFHxA uptake per mass of adsorbent,  $q_{exp}$  (mg/g), is calculated as following Eq. 8.2

$$q_{exp} = \frac{q_{total}}{M} \quad 8.2$$

#### Regeneration efficiency

Regeneration efficiencies were calculated by the following Eq. 8.3.

$$\text{Regeneration efficiency (\%)} = \frac{q_{amount}}{q_{total}} \times 100\% \quad 8.3$$

where  $q_{amount}$  = PFHxA desorbed amount (mg)

### **Thomas model**

The *Thomas* model is a widely used theoretical method to describe the column performance which assumes plug flow behavior in the bed (Thomas, 1944). This model assumes that adsorption process follows the *Langmuir* kinetics of adsorption-desorption and also obeys the *second order* reversible reaction kinetics. This model can be used well when internal and external diffusion limitation were absent. It was applied to the data to predicting breakthrough curves and to determine the characteristics parameters. The linearized form of the *Thomas* model can be expressed as Eq. 8.4.

$$\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{K_{th} q_0 m}{Q} - k_{th} C_0 t \quad 8.4$$

where  $K_{th}$  = the *Thomas* model constant (L/hr.mg)

$q_0$  = adsorption capacity (mg/g)

The values of  $K_{th}$  and  $q_0$  can be determined from the liner plot of  $\ln[(C_0/C_t)-1]$  against  $t$ .

### **Empty bed contact time (EBCT)**

The empty bed contact time (EBCT) in the column is described as Eq. 8.5.

$$\text{EBCT (min)} = \frac{\text{bed volume (mL)}}{\text{flowrate (mL/min)}} \quad 8.5$$

## **8.4 Results and discussion**

### **8.4.1 Adsorption and regeneration of PFHxA in synthetic wastewater**

#### **Adsorption of PFHxA in synthetic wastewater**

GAC, XAD4, BA103, MN102, PFA300, PFA400 and A860 (20 cm<sup>3</sup>) in column were investigated the performance to remove PFHxA in tap water. The flow rate of synthetic wastewater that applied to each column was 10 mL/min, resulting in contact time was 1.3

minutes. Initial concentration of PFHxA in tap water was 10 µg/L. The breakthrough point was set at  $C_t/C_0$  equal to 0.1 (removal efficiency 90%). Breakthrough curves of PFHxA adsorption by column experiments of different adsorbents is shown in **Fig 8.7**.

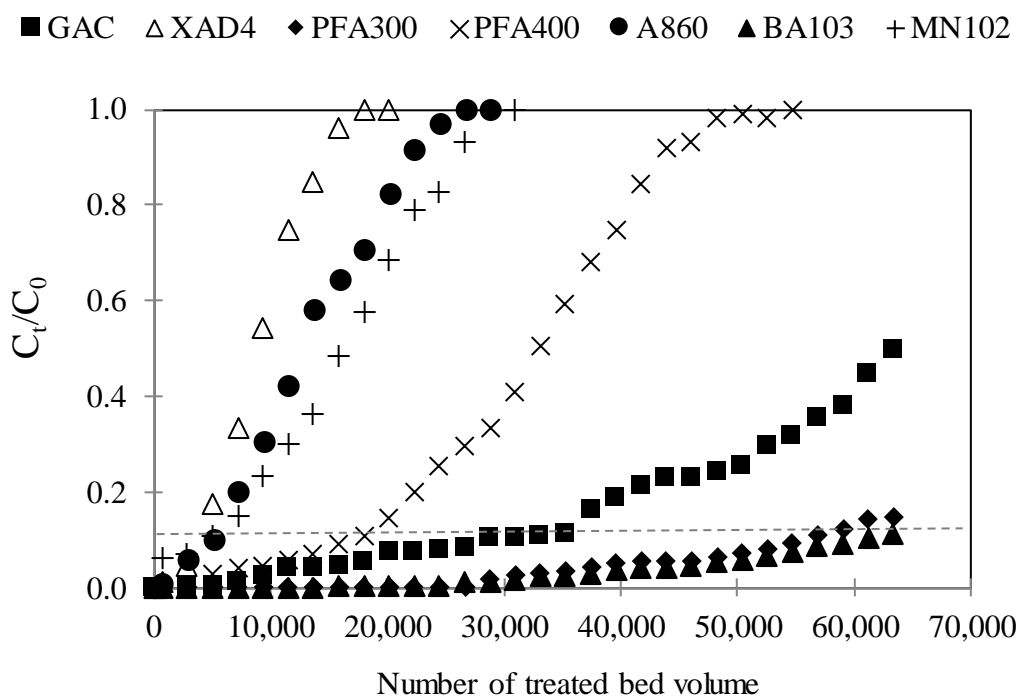


Figure 8.7 Breakthrough curves of PFHxA adsorption by column experiments of different adsorbents

Removal efficiencies were more than 90% for BA103 for 61,200 bed volume, PFA300 for 55,800 bed volumes, GAC for 27,720 bed volumes, PFA400 for 16,920 bed volumes, MN102 for 5,040 bed volumes, A860 for 5,000 bed volumes and XAD4 for 3,960 bed volumes. BA103 showed the best performance to remove PFHxA in tap water followed by PFA300, GAC, PFA400, MN102, A860 and XAD4. Generally, the properties of anion exchange polymers mainly differ in three aspects which are polymeric, function groups and porosity. These properties influence adsorption capacity and adsorption rate. It is interesting that GAC was more effectively remove PFHxA than PFA400 and A860 in the column test, even PFA400 and A860 has higher adsorption capacity in batch test. It might

be explained that batch test was conducted in *Milli-Q* water while column test was performed in tap water. DOC concentration ranged from 0.8 to 2.4 mg/L, chloride concentration ranged from 12 to 14 mg/L and sulfate concentration ranged from 8 to 10 mg/L in tap water tap water containing PFHxA. Ionic and DOC might affect adsorption efficiencies in column test. XAD4, MN102 and A860 were ineffective to remove PFHxA resulting in short exhausted time.

### Regeneration of PFHxA in synthetic wastewater

All adsorbents in column were regenerated by methanol or 5% NaCl in methanol/ *Milli-Q* water (7:3) after they were exhausted. **Figure 8.8** shows regeneration efficiency of spent adsorbent by column mode.

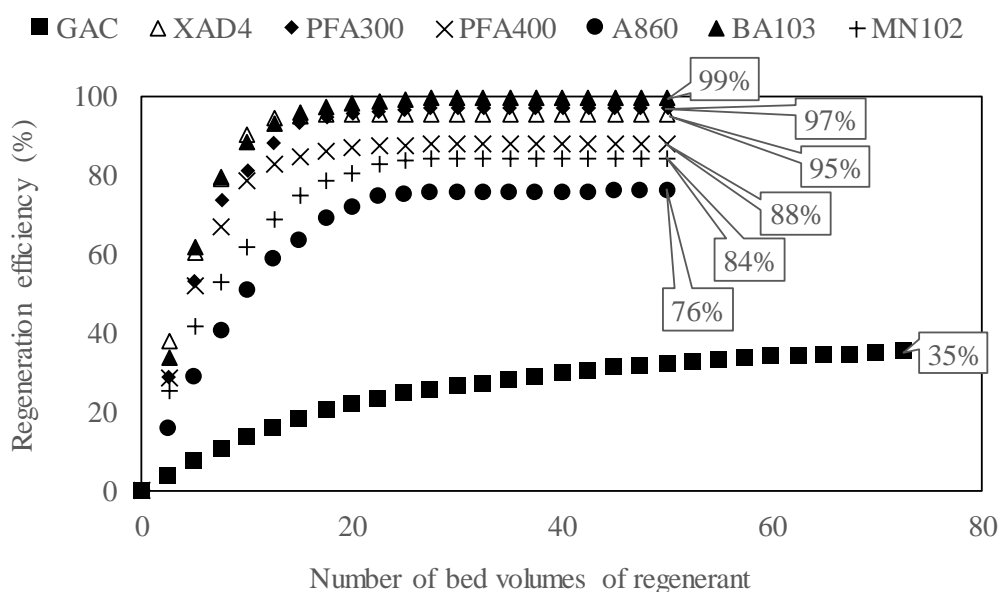


Figure 8.8 Relationship between regeneration efficiency and number of bed volumes of regenerant

At the beginning of regeneration, a regeneration rate of XAD4 was faster than BA103, PFA300, PFA400, MN102, A860 and GAC. Only XAD4 and BA103 reached 90% regeneration efficiency within 10 bed volumes. XAD4 and BA103 are non ion exchange



polymers and weak base anion exchange polymers which both of them are easily desorbed PFHxA. There were three adsorbents (XAD4, PFA300 and PFA400) that achieved 90% of regeneration efficiency.

Regeneration efficiencies of all adsorbents except GAC almost were constant after 20<sup>th</sup> bed volumes of regenerant. GAC shows the lowest regeneration efficiency due to the interaction force between adsorbate and adsorbent. Interactions of PFHxA onto GAC surface was stronger than interaction of PFHxA onto anion exchange polymers in regenerant. Moreover, adsorption rate of PFHxA onto GAC was slower than anion exchange polymers. PFHxA might adsorbed into the micropore of GAC resulting long regeneration time. Thus, weak base anion exchange polymers (BA103) is suitable adsorbent to remove PFHxA in aqueous solution.

#### **8.4.2 Suitable adsorbents for adsorption and regeneration of PFHxA in wastewater**

##### **Adsorption of PFHxA in wastewater**

The elevated PFHxA concentration were detected in the industrial wastewater in Japan (Chapter 4). Wastewater samples after adsorption by GAC were selected to remove PFHxA by column experiments. **Table 8.2** shows the wastewater characteristics in this experiments. The initial average PFHxA concentration was 36.1 mg/L. Adsorbents (GAC, PFA300, PFA400 and BA103) were used to remove PFHxA in wastewater samples until the adsorbents exhausted. Breakthrough curves of PFHxA adsorption by column experiments of those columns is shown in **Fig.8.9**.

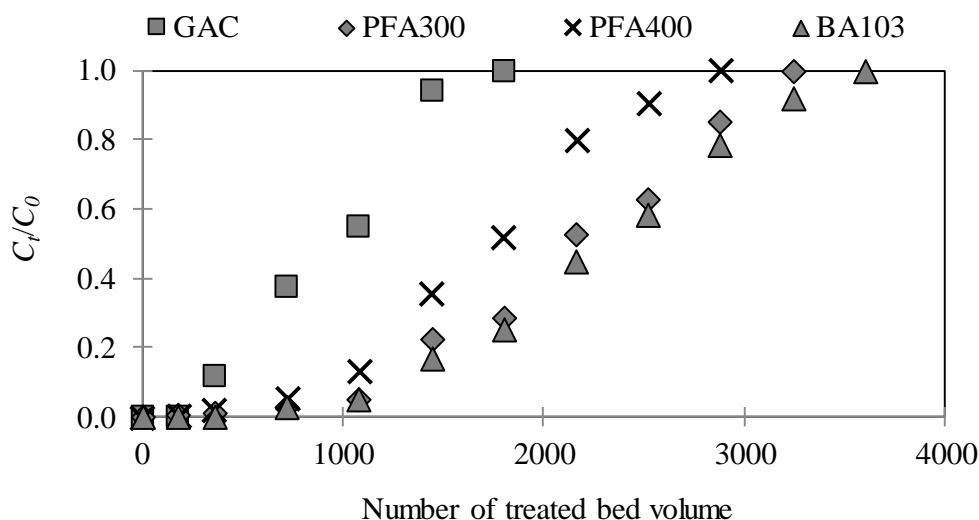


Figure 8.9 Breakthrough curves of PFHxA adsorption by column experiments of GAC,

As industrial wastewater flow into each column continuously, the point on the S-shaped curve gradually approached its exhaustion value. The exhaustion time of GAC, PFA300, PFA400 and BA103 occurred at 1,800, 2,880, 3,240 and 3,600 treated bed volumes, respectively. The column adsorption capacity data were calculated and presented in **table 8.4**. All adsorption capacities of anion exchange polymers were higher than those of GAC. Adsorption capacity ( $q_{cap}$ ) of BA103 column was 270 mg/g and it showed the highest adsorption capacity in this study.

Table 8.4 *Thomas* fitting parameters for the adsorption of PFHxA

Adsorbent	Experiment			Thomas parameter		
	$q_{total}$ (mg)	$M$ (g)	$q_{exp}$ (mg/g)	$K_{th}$ (L/hr.mg)	$q_0$ (mg/g)	$R^2$
GAC	652	8.9	73	0.0017	70	0.943
PFA300	1,235	7.9	194	0.0011	198	0.986
PFA400	1,537	6.8	183	0.0012	183	0.997
BA103	1,624	6.0	270	0.0010	272	0.992

The column data for PFHxA adsorption were fitted to linearized form of *Thomas* model. Linear fitting lines were shown in **Fig 8.10**. The parameters of  $K_{th}$  and  $q_0$  can be calculated from the intercept and slope of the liner plot of  $\ln[(C_0/C_t)-1]$  against  $t$ . The *Thomas* parameters ( $K_{th}$  and  $q_0$ ) as well as correlation coefficient ( $R^2$ ) for experimental breakthrough curves were presented in **table 8.4**. Analysis of the correlation coefficient indicated that linear from of *Thomas* model could be fitted well with experimental data ( $R^2 > 0.94$ ). Values of  $q_0$  calculated from linear from of *Thomas* model were very close to the experimental values of  $q_{exp}$ . Thus, the *Thomas* model was suitable for the adsorption process, which indicated that the external and internal diffusions were not the limiting steps (Thomas, 1944).

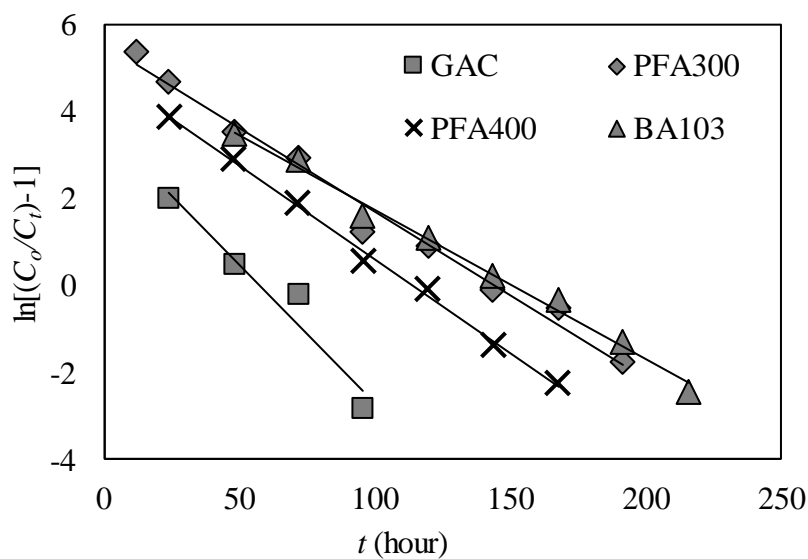


Figure 8.10 The linear fitting of  $\ln[(C_0/C_t)-1]$  against  $t$  of *Thomas* model for adsorption

### Regeneration of PFHxA in wastewater

After all columns were exhasuated, GAC column were suddenly regenerated by methanol while other columns were regenerated by 5% NaCl in methanol:*Milli-Q* (7:3). Regenerants were fed with the up-flow direction with flow rate 2.5 mL/min. **Figure 8.11** shows the regeneration efficiency of spent adsorbents from column experiement. BA103

had the highest regeneration efficiency, followed by PFA300, PFA400 and GAC. BA103 showed the fastest regeneration above 80% at tenth bed volumes of regenerant and reached 95% at 20<sup>th</sup> bed volumes of regeneration solution. The regeneration efficiency of PFA300 was higher than PFA400 related to their functional groups. Functional group of PFA300 (Dimethylethanolammonium) had a slightly greater regeneration efficiency than functional group of PFA400 (Trimethylbenzylammonium) (Crittenden *et al.*, 2005).

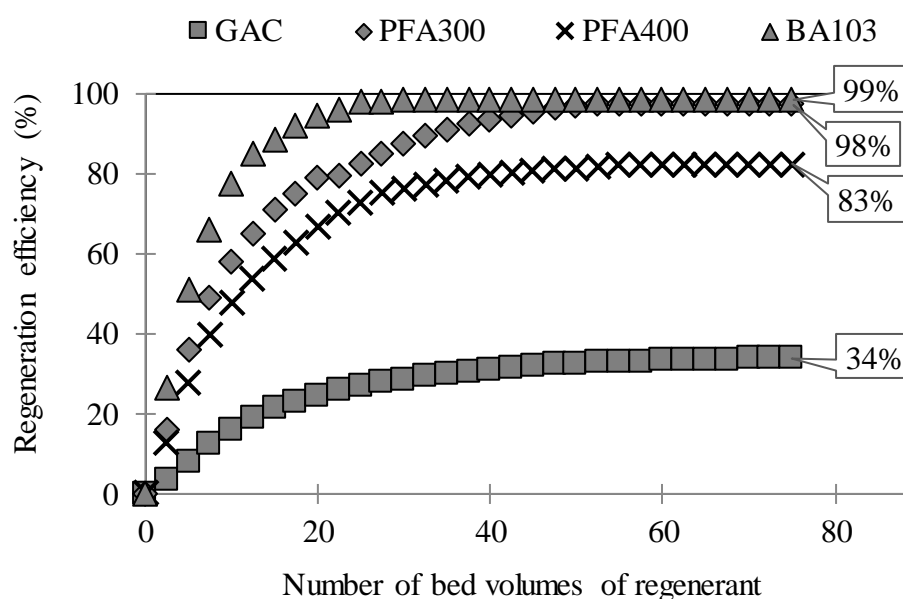


Figure 8.11 Regeneration efficiency of different spent adsorbents

#### 8.4.3 Effects of bed volumes for adsorption and regeneration on removal of PFHxA in wastewater

##### Adsorption of PFHxA in wastewater at different bed volumes

According to the previous section, BA103 showed the best performance to adsorb and desorb PFHxA by column experiment. It was selected to treat PFHxA from wastewater with three different bed volumes (10, 20, 30 and 40 cm<sup>3</sup>). At the same feeding flow rate, the higher bed volume had the higher empty bed contact time. The empty bed contact

times were 2, 4, 6 and 8 minutes for 10, 20, 30 and 40 cm<sup>3</sup> of bed volumes, respectively. Moreover, the used BA103 column from the previous experiment were reused to compare PFHxA adsorption efficiency. Average PFHxA concentration in wastewater in this experiment was 53.7 mg/L while PFHxA concentration in previous experiment was 36.1 mg/L. **Figure 8.12** shows PFHxA removal efficiencies of different bed volumes.

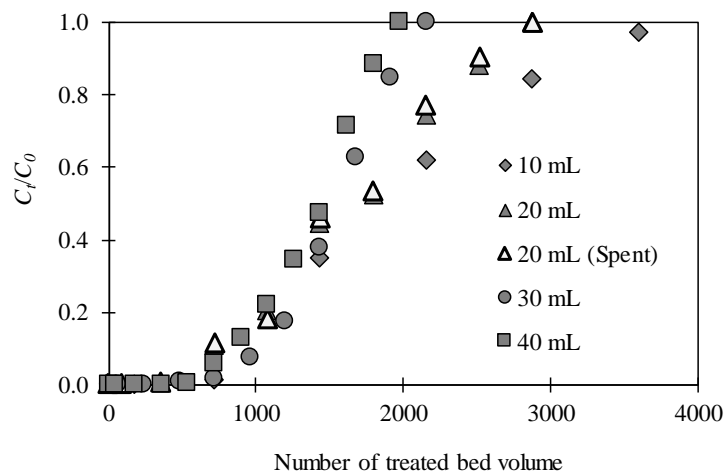


Figure 8.12 Breakthrough curves of PFHxA adsorption by column experiments of BA103 with different bed volumes

Wastewater containing PFHxA continuously flowed into column, the point on the S-shaped curve gradually approached its exhaustion value, and the breakthrough time increased with increased the bed volume. The breakthrough curves of the longer bed tended to be more gradual. It means that a larger sized of bed volume was more difficult to be completely exhausted. As show in **table 8.5**, the adsorption of PFHxA by different bed (10, 20, 30 and 40 cm<sup>3</sup>) volumes were 296, 279, 270 and 249 mg/g, respectively. It was interesting to observe that adsorption capacity decreased at a larger bed volume. The empty bed contact time increased from 2 to 8 minutes with the bed depth increasing from 10 to 40 cm<sup>3</sup>. Although an increasing of bed volume (increasing of contact time), it was not useful to increase the column adsorption capacity

Table 8.5 The *Thomas* fitting parameters for the adsorption of PFHxA

Bed volume of BA103 (cm <sup>3</sup> )	Experiment			<i>Thomas</i> parameter		
	$q_{total}$ (mg)	$M$ (g)	$q_{exp}$ (mg/g)	$K_{th}$ (L/hr.mg)	$q_0$ (mg/g)	$R^2$
10	889	3	296	0.0011	296	0.998
20	1,678	6	279	0.0007	281	0.988
20 (Spent)	1,652	6	275	0.0007	275	0.982
30	2,431	9	270	0.0009	266	0.994
40	2,947	12	249	0.0008	246	0.985

According to section 8.4.2, BA103 can be desorbed well by regenerant. The spent BA103 column was washed with *Milli-Q* water before reuse. The comparison of PFHxA adsorption efficiencies by column experiment of spent BA103 and fresh BA103 were shown in **Fig 8.12**. Spent BA103 shows the similar breakthrough curve as fresh BA103. It means that BA103 can be reused after regeneration. The adsorption capacity from experiment ( $q_{exp}$ ) of spent BA103 (20 cm<sup>3</sup>) was 275 mg/g while those of fresh BA103 was 279 mg/g. The adsorption capacity of second cycle onto BA103 reduced only 1.5%.

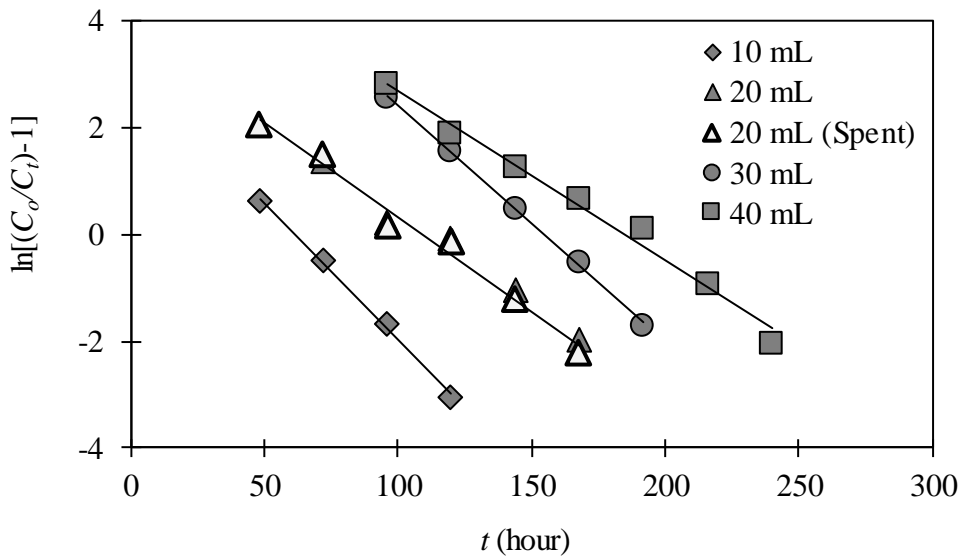


Figure 8.13 The linear fitting of  $\ln[(C_0/C_t)-1]$  against  $t$  of the *Thomas* model for adsorption of PFHxA onto BA103 with different bed depth

The column data for PFHxA adsorption were fitted to the linearized form of the *Thomas* model in **Fig.8.13**. The *Thomas* parameters ( $K_{th}$  and  $q_0$ ) and the correlation coefficient for experimental breakthrough curves were presented in **table 8.5**. The value of  $K_{th}$  and  $q_0$  both decreased as increase of the bed volume. Analysis of the correlation coefficient showed that the regressed lines fit well with the experimental data which  $R^2$  values ranged from 0.982 to 0.998. The values of  $q_0$  of all sizes of bed volume which calculated from the *Thomas* equation were close to the experimental data. This experimental data obey the *Thomas* equation indicating that the external and internal diffusions were not the limiting step.

#### Regeneration of PFHxA in wastewater at different bed volumes

To understand the required bed volumes of regenerant to regeneration BA103, regenerants were fed to saturated BA103 with different bed volumes (10, 20, 30 and 40 cm<sup>3</sup>) at the same flow rate. After BA103 in each column was saturated, it was immediately regenerated by effective regenerant (5% NaCl in MeOH: *Milli-Q* water (7:3)).

**Figure 8.14** shows regeneration efficiency of saturated BA103.

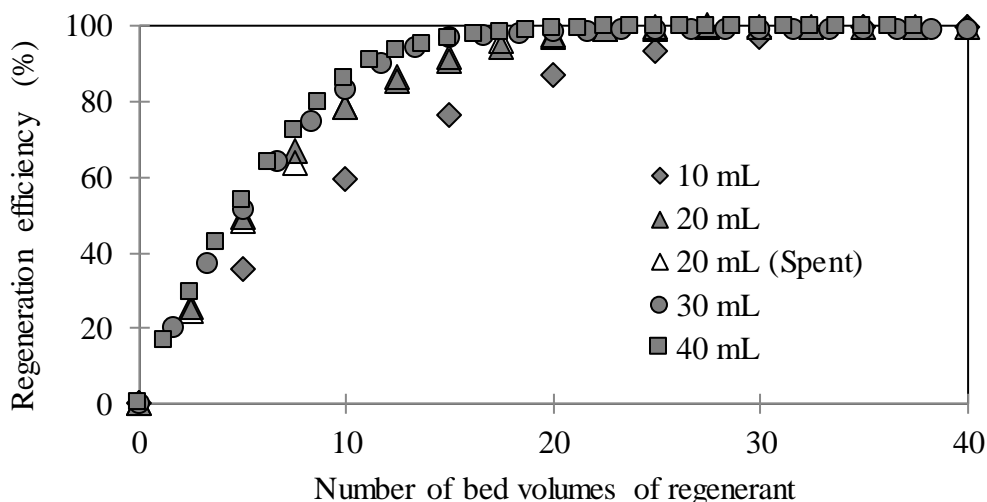


Figure 8.14 Regeneration efficiency of different bed volumes of BA103

At the tenth bed volumes of regenerant, the regeneration efficiencies of 10, 20, 30 and 40 cm<sup>3</sup> of bed volumes were 59, 78, 83 and 86%. It means that a larger bed volume required a less than amount of regenerant. The different sizes of bed volumes did not affect the maximum regeneration percentage, the regeneration percentage of all columns were more than 99 % at 35<sup>th</sup> bed volumes of regenerant. It can be noted that the spent BA103 (second cycles) required the similar amount of spent BA103 (first cycle). The regeneration percentage of spent BA103 was more than 99%.

#### **8.4.4 Adsorption and regeneration of PFCs in wastewater (Thailand) with connected columns**

##### **Adsorption of PFCs in wastewater (Thailand)**

According to **section 8.4.1** and **8.4.2**, BA103 was the best adsorbent in to remove PFHxA in synthetic wastewater and industrial wastewater (Japan). BA103 was selected to apply to remove PFHxA and other PFCs with effluent of WWTP 7 because the WWTP 7 had the highest PFCs concentration among ten WWTPs (Chapter 4). Wastewater samples were collected again on 20 December 2013 and 15 January 2014. The wastewater characteristics shows in **table 8.3**. Predominate PFCs in wastewater were PFPeA, PFHxA and PFOA, average concentrations of those PFCs were 618, 904 and 233 ng/L. Two similar column containing BA103 (20 cm<sup>3</sup>) were connected to remove those PFCs.

**Figure 8.15** shows removal efficiencies of PFPeA, PFHxA and PFOA onto BA103 in industrial wastewater of first and second column. Removal efficiencies of PFPeA, PFHxA and PFOA gradually decreased with operation time in both column. At the same operation time, removal efficiencies of three PFCAs by BA103 in both column decreased



in the order of PFOA > PFHxA > PFPeA. It means that longer chain of PFCAs can be easier to adsorb by BA103 rather than shorter chain ones. BA103 may adsorb the long-chain PFCAs onto anion exchange polymers through the formation of micelles (Du *et al.*, 2015). The second column showed better performance to remove PFCs than first column. At 80% of PFPeA, PFHxA and PFOA removal efficiency, it could be observed at 4<sup>th</sup>, 5<sup>th</sup> and 19<sup>th</sup> operational days in the first column. At the same removal efficiency, it also could be observed at 11<sup>th</sup>, 14<sup>th</sup> and 29<sup>th</sup> operational days in the second column.

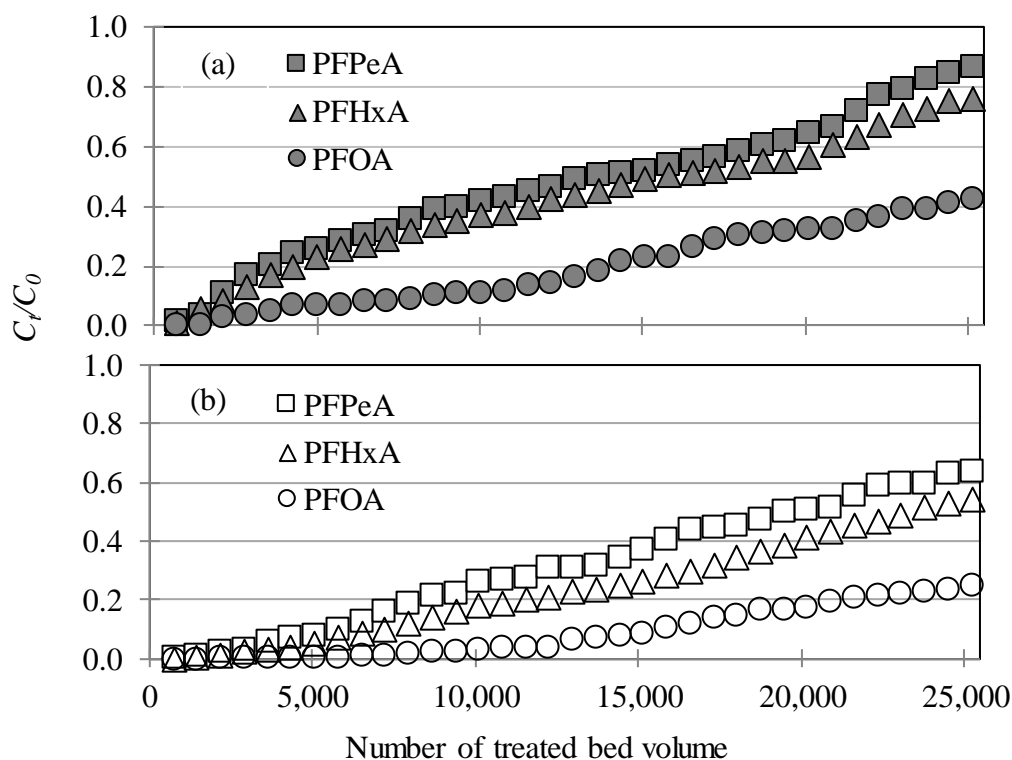


Figure 8.15 Breakthrough curves of PFPeA, PFHxA and PFOA onto BA103 in industrial wastewater of (a) first column (b) second column

### Regeneration of spent BA103 with wastewater (Thailand)

After two connected columns operated for 35 days, they were regenerated in the column to simulate the on-site regeneration. Both column were prepared for regeneration by washing with *Milli-Q* water and methanol. Spent BA103 in column were regenerated by

5% NaCl in MeOH:Milli-Q water (7:3). **Figure 8.15** shows regeneration efficiency of PFPeA, PFHxA and PFOA onto BA103 in industrial wastewater of first and second column.

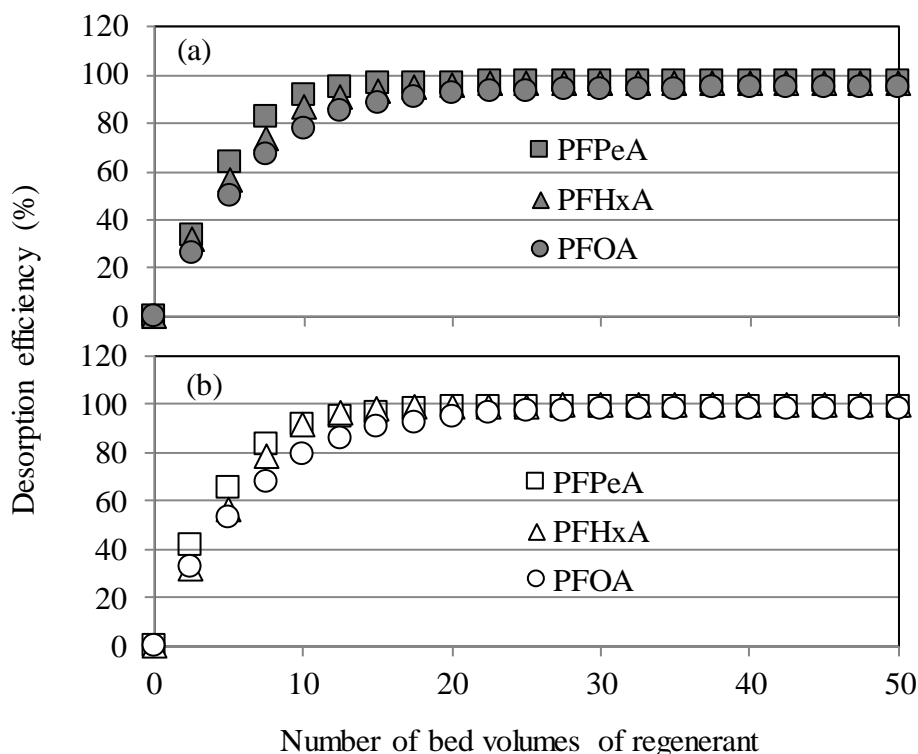


Figure 8.16 Regeneration efficiency of PFPeA, PFHxA and PFOA onto BA103 in industrial wastewater of (a) first column (b) second column

Regeneration efficiencies of three PFCAs onto spent BA103 increased at first bed volume of regenerant and then they were constant after 20<sup>th</sup> bed volumes of regenerant in both column. At the beginning, it was found that PFPeA could be desorbed faster than PFHxA and PFOA due to shorter chain. At 50<sup>th</sup> bed volumes of regenerant, regeneration efficiencies of PFPeA, PFHxA and PFOA were 97, 97 and 95% in the first column, while regeneration efficiencies in second column of those PFCAs were 99, 99 and 98%, respectively. It is interesting that regeneration efficiency of second column was higher than first column, they might be explained by the following reason. The first column

might adsorbed more interferences such as organic compounds which they might be difficult to desorbed by 5% NaCl in MeOH:*Milli-Q* water (7:3).

## 8.5 Summary

Continuous adsorption and regeneration of PFHxA were investigated in synthetic wastewater (tap water containing PFHxA) and industrial wastewater in Japan and Thailand. The adsorption and regeneration experiments in this chapter are summarized below. Breakthrough curves of PFHxA by column experiment of each adsorbent were different. BA103 and PFA300 showed higher PFHxA adsorption performance than the other adsorbents (GAC, MN102, A860 and XAD4) in synthetic wastewater. PFHxA removal efficiency of BA103 was more than 90% until 61,200 bed volumes in tap water. There were three adsorbents (XAD4, PFA300 and PFA400) that achieved 90% of regeneration efficiency.

Elevated concentration of PFHxA in wastewater in Japan were treated by GAC, PFA300, PFA400 and BA103. The column data of PFHxA adsorption onto four adsorbents was fitted to the linearized form of the *Thomas* model. BA103 shows the highest adsorption capacity ( $q_{exp} = 275$  mg/g). Breakthrough curves of BA103 with different bed volumes were observed, a higher bed volume of BA103 could treat a larger amount of wastewater. Exhausted BA103 was regenerated by 5% NaCl in methanol/*Milli-Q* water (7:3), the regeneration efficiency was more than 99%. Connected columns of BA103 were removed PFCs (mainly PFPeA, PFHxA and PFOA) in effluent of central wastewater in Thailand. The second column showed the better performance to remove PFCs than the first one. Thus, column adsorption of BA103 could be applied to remove PFHxA in wastewater.

## Chapter 9 Conclusions and recommendations

### 9.1 Conclusions

PFHxA is widely used in industrial products because of its surfactant properties. Because industrial WWTPs are not sufficient to treat PFHxA, it is discharged to water environments. The main objective of this study is to investigate the effects of interferences in industrial wastewater on removal efficiencies of PFHxA by adsorption. The main results of this study were shown in **Fig 9.1**.

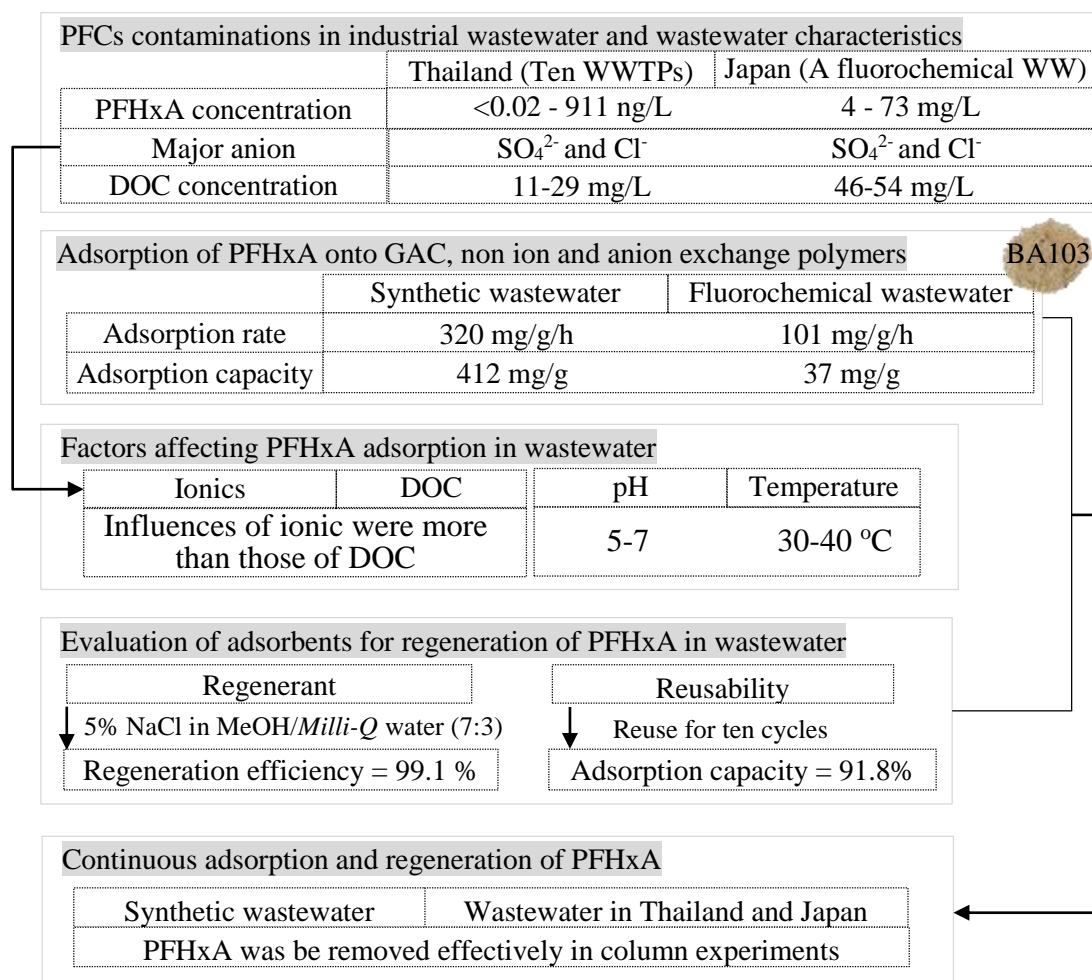


Figure 9.1 Illustration of main results of this study

PFCs contaminations and wastewater characteristics were surveyed in ten central WWTPs in Thailand and a WWTP of a fluorochemical factory in Japan. Eleven PFCs, anions, cations, as well as DOC were measured in each wastewater treatment unit. PFHxA could be detected at all central WWTPs in Thailand. Total PFCs concentrations at effluent ranged from 15 to 1,030 ng/L. In Japan, PFHxA concentrations ranged from 4 to 73 mg/L in wastewater treatment process, while the other PFCs were not detected. The characteristics of wastewater in each industrial process were different. Ionic strength and DOC concentrations were higher than that total PFCs concentration and they showed a significant impact on the adsorption process.

GAC, non ion exchange polymers and five anion exchange polymers were used to investigate adsorption kinetics and isotherms of PFHxA in both synthetic and fluorochemical wastewater. PFHxA adsorption rate and capacity onto anion exchange polymers in synthetic wastewater related to exchange capacity, polymeric matrix, functional group and porosity. The *pseudo-second-order* equation and the *Freundlich* equation fitted well with adsorption rate and capacity data, respectively. Among seven adsorbents in this study, BA103 exhibited the fastest initial adsorption rate in synthetic (320 mg/g/h), and fluorochemical wastewater (101 mg/g/h). Adsorption capacities of BA103 were 412 and 37 mg/g in synthetic and fluorochemical wastewater, respectively. It is remarkable that adsorption performances of PFHxA in synthetic wastewater were higher than those in wastewater onto all adsorbents.

The effects of interferences (inorganic ions and DOC) and adsorption conditions (pH and temperature) on PFHxA adsorption capacities were identified onto all adsorbents.

Adsorption capacities of PFHxA onto GAC and anion exchange polymers had decreased after increase of inorganic ions in wastewater. The DOC of humic acid and DOC in fluorochemical wastewater could reduce the adsorption capacities of PFHxA. In addition, the impact of inorganic ions on PFHxA adsorption in fluorochemical wastewater was more significant than that of DOC. BA103 shows the best performance to remove PFHxA in wastewater containing inorganic ion and DOC. Moreover, the adsorption of GAC can be used as a pretreatment to adsorb inorganic ion and DOC to improve PFHxA adsorption efficient of PFA300 and BA103. When the pH of wastewater ranged from 5 to 7 and 30 to 40°C, PFHxA in wastewater could be adsorbed by anion exchange polymers (polystyrene polymer).

Spent BA103 was effectively regenerated by 5% NaOH or NaCl in MeOH:*Milli-Q* water (7:3). However, the regeneration rate of 5% NaCl was faster than that of 5% of NaOH in MeOH:*Milli-Q* water (3:7). The 5% NaCl in MeOH:*Milli-Q* water (3:7) was used to regenerate BA103 in fluorochemical wastewater for ten cycles, the remaining of adsorption capacity after tenth cycle was 91.8 %. Regenerants were applied to continuous adsorption and regeneration experiments.

Continuous adsorption and regeneration of PFHxA were conducted with synthetic wastewater and fluorochemical wastewater in Japan and Thailand. Breakthrough curves of PFHxA by column experiment of each adsorbent were different. BA103 showed a higher PFHxA adsorption performance than the other adsorbents in synthetic wastewater. PFHxA removal efficiency of BA103 was more than 90% until 61,200 bed volumes in synthetic wastewater. Elevated concentration of PFHxA in wastewater in Japan were treated by GAC, PFA300, PFA400 and BA103. The column data for PFHxA adsorption

of four adsorbents were fitted to the linearized form of the *Thomas* model. BA103 shows the highest adsorption capacity ( $q_{exp} = 275$  mg/g). Moreover, a higher bed volume of BA103 could treat a larger amount of wastewater. Exhausted BA103 was regenerated by 5% NaCl in methanol/*Milli-Q* water (7:3), the regeneration efficiency was more than 99%. Connected columns of BA103 were removed PFCs (mainly PFPeA, PFHxA and PFOA) in effluent of central wastewater in Thailand. The second column showed the better performance to remove PFCs than the first column. This study found that many factors could affect the adsorption process of PFHxA such as (polymeric matrix, functional group and porosity), wastewater characteristics (inorganic ions and DOC), adsorption condition (pH and temperature) and contact time.

## 9.2 Recommendations

Based on the results from this research, following suggestions are recommended for further research:

- Modified adsorbents (AC, polymers and mineral materials and biomaterials) for improving PFHxA selectivity and increasing efficiency of regeneration and reused ability are recommended for further study.
- In this study, only the size distribution of DOC in a fluorochemical wastewater samples was determined. As molecular size distribution had a significant impact on the adsorption efficiency of PFHxA in industrial wastewater. Therefore, the molecular size distribution of DOC in wastewater from various industrial process should also be well determined.

- The adsorbents such as BA103 and PFA300 could be regenerated and reused via regenerant. Regenerant waste requires further treatments. Fuhrer *et al.* (2010) reported a method for recovering fluorinated surfactants in regenerant waste. Thus, the techniques on how to recover PFHxA from regenerant waste are also highly recommended to do in order to reduce the cost.
- As the interferences in wastewater could impact the adsorption efficiency of PFHxA onto adsorbents negatively, the pretreatment methods for industrial wastewater should be developed to increase the adsorption efficiency.
- This study found that the adsorption capacities of PFHxA in industrial wastewater decreased after reuse for ten cycles. The countermeasures to maintain the reusability performance of adsorbents should be well studied.



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## Appendix A

### A.1. Average PFCs concentration in liquid phase and wastewater characteristics

WWTP	Sampling point	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDODA (ng/L)	pH	Cond. (mS/cm)	DOC (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)
1	Inf	15.57	1.40	2.48	0.32	3.71	0.79	3.55	0.51	0.15	0.15	ND	8.5	2.0	26	414	234
	AS	23.74	0.45	2.45	2.45	8.22	2.59	6.47	0.93	1.24	0.76	<LOQ	8.3	2.0	70	399	268
	SC	24.34	0.52	1.41	0.33	7.37	2.37	7.35	0.88	0.73	0.28	<LOQ	7.8	2.0	10	401	268
	Eff	26.98	0.62	2.41	1.01	10.84	2.57	9.61	0.81	0.81	0.42	ND	8.3	2.0	12	410	267
	Tap	1.93	<LOQ	2.00	0.33	6.43	0.47	1.02	0.74	0.26	<LOQ	ND	-	-	-	-	-
2	Inf	20.24	0.57	1.82	1.10	8.25	2.05	5.18	1.42	ND	<LOQ	ND	9.5	2.4	13	97	60
	AS	104.94	0.62	8.14	3.34	4.09	1.26	13.06	ND	1.00	ND	ND	8.9	2.3	11	816	307
	SC	92.09	0.99	3.62	0.67	5.13	5.13	17.20	3.54	6.23	0.97	<LOQ	8.4	2.6	9	821	302
	Eff	98.67	0.54	3.56	0.70	6.65	6.18	15.95	2.91	5.31	0.57	<LOQ	8.7	2.9	10	974	318
	Tap	2.01	<LOQ	0.97	0.53	5.89	0.37	1.03	0.52	0.16	<LOQ	ND	-	-	-	-	-
3	Inf	0.15	1.61	2.44	0.94	0.84	0.16	1.10	0.55	0.00	0.13	ND	8.9	1.2	33	178	105
	AS	1.12	3.03	4.55	0.39	2.68	0.88	4.25	1.60	0.34	0.19	ND	9.0	1.1	16	212	143
	SC	0.96	3.66	6.34	3.61	1.41	1.03	5.01	1.63	0.49	0.28	ND	9.1	1.3	6	212	136
	Eff	0.71	2.45	3.67	0.94	2.13	0.91	3.53	1.11	0.26	0.19	ND	9.1	1.3	17	211	134
	Tap	ND	ND	0.41	1.08	6.09	0.17	0.84	0.23	0.33	ND	ND	-	-	-	-	-
4	Inf	3.84	ND	<LOQ	0.16	0.62	0.80	7.13	2.61	0.33	0.60	0.23	7.6	2.5	118	416	335
	AS	14.02	0.26	2.23	0.62	3.03	2.16	19.46	10.02	17.13	1.23	<LOQ	8.3	2.3	9	444	403
	SC	13.53	0.09	1.79	2.34	2.79	1.68	17.10	7.44	12.61	1.29	0.28	8.6	2.2	23	453	409
	Eff	4.46	0.16	<LOQ	0.18	0.76	0.60	11.13	2.56	0.00	0.66	0.24	8.3	2.2	23	433	390
	Tap	0.23	ND	0.46	0.47	5.70	0.67	1.21	0.57	0.99	0.22	ND	-	-	-	-	-

WWTP	Sampling point	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	pH	Cond. (mS/cm)	DOC (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)
5	Inf	4.57	ND	1.24	ND	0.95	0.33	1.42	0.35	0.16	<LOQ	<LOQ	8.1	1.1	9	227	79
	AS	4.82	0.21	1.73	0.18	1.25	0.63	2.52	0.61	0.54	0.13	<LOQ	7.5	1.0	8	230	72
	SC	4.29	0.07	3.54	ND	1.06	0.65	1.93	0.50	0.34	<LOQ	<LOQ	7.7	1.1	7	233	73
	Eff	4.20	<LOQ	2.98	ND	1.10	0.74	1.94	0.48	0.31	0.14	<LOQ	7.9	1.0	7	222	62
	Tap	2.62	ND	0.64	ND	0.44	0.46	1.23	0.51	0.13	<LOQ	ND	-	-	-	-	-
6	Inf	7.13	ND	20.21	1.03	12.05	30.05	4.56	1.57	0.39	0.70	<LOQ	8.5	1.7	27	283	298
	AS	7.96	ND	20.61	16.63	31.45	64.37	5.67	1.47	0.31	0.43	<LOQ	7.8	1.9	14	270	446
	SC	9.31	ND	44.38	8.55	27.30	67.85	6.27	1.11	0.37	0.38	<LOQ	7.8	2.0	16	247	404
	Eff	8.55	ND	53.50	10.36	27.83	70.48	6.97	1.47	0.50	0.59	<LOQ	8.2	2.0	16	289	516
	UF feed	9.22	0.50	49.43	8.37	19.67	35.74	5.28	1.48	0.36	0.49	<LOQ	8.4	2.0	17	294	515
	UF reject	8.52	0.49	24.65	6.86	30.17	65.96	7.39	1.47	0.33	0.47	<LOQ	8.2	2.0	19	300	540
	RO feed	8.36	ND	48.45	9.39	20.37	34.46	4.85	1.41	<LOQ	<LOQ	<LOQ	8.3	2.0	16	291	509
	RO pro	ND	ND	0.18	0.39	1.19	0.75	<LOQ	0.62	ND	ND	ND	8.8	0.3	-	17	16
	RO reject	33.77	0.75	68.39	15.23	71.91	154.62	21.07	4.50	0.00	0.66	<LOQ	8.7	5.8	77	907	1702
	Tap	5.37	0.17	1.81	0.00	0.52	0.98	2.22	0.80	0.35	0.00	0.00	-	-	-	-	-
7	Inf	1.51	2.69	32.88	132.03	426.05	64.34	233.01	31.30	109.90	11.65	11.25	7.7	1.7	16	215	368
	AS	2.28	2.93	42.68	145.35	499.13	83.26	235.05	33.03	119.39	9.54	9.57	7.5	1.7	10	197	399
	SC	1.94	2.64	30.55	95.56	381.86	63.18	217.17	28.18	87.58	8.35	8.99	7.8	1.8	16	193	410
	Eff	2.91	4.11	38.38	135.10	403.06	66.24	206.71	28.81	99.20	10.13	11.46	7.6	1.8	15	203	410
	Tap	0.25	0.07	3.03	0.71	4.57	1.95	8.58	1.80	2.80	<LOQ	ND	-	-	-	-	-

WWTP	Sampling point	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	pH	Cond. (mS/cm)	DOC (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)
8	Inf	3.28	0.94	2.54	0.95	5.32	2.65	30.39	8.59	7.97	4.01	1.14	8.2	1.1	29	283	295
	AS	1.50	0.88	2.03	2.44	23.95	23.21	41.10	12.53	18.49	4.57	1.38	7.7	2.0	15	259	462
	SC	1.52	0.86	1.88	2.67	24.79	25.21	44.36	13.88	16.49	3.57	1.21	7.9	2.0	13	289	539
	Eff	2.45	1.09	2.04	1.60	12.88	18.96	40.19	10.17	8.84	1.65	0.76	9.2	1.5	12	228	331
	Tap	ND	ND	0.41	ND	<LOQ	<LOQ	0.69	<LOQ	0.15	ND	ND	-	-	-	-	-
9	Inf	19.80	4.39	6.62	1.19	2.14	3.49	5.18	1.63	0.46	0.17	ND	7.7	2.0	12	185	717
	AS	15.79	1.65	0.68	0.85	1.38	1.68	2.06	0.53	0.00	0.11	<LOQ	7.7	2.2	11	230	800
	SC	14.80	1.67	1.18	0.33	1.19	1.27	2.22	0.39	0.20	0.12	ND	7.6	2.1	10	249	808
	Eff	17.03	1.97	2.17	0.32	1.15	1.24	2.40	0.35	0.16	0.19	ND	7.9	2.0	9	251	737
	Tap	18.36	1.01	3.18	ND	0.49	1.24	1.19	0.54	0.14	ND	ND	-	-	-	-	-
10	Inf	1.80	0.26	2.36	2.55	1.35	9.32	32.83	9.50	4.83	1.98	0.52	8.9	4.6	104	811	917
	AS	4.02	0.32	2.63	2.16	8.78	15.75	75.39	14.94	13.66	6.32	<LOQ	8.0	4.6	16	782	886
	SC	4.57	0.45	4.01	0.42	7.68	16.34	76.85	15.72	13.87	5.75	<LOQ	8.5	4.5	17	853	923
	Eff	4.44	0.52	5.26	2.31	6.54	15.41	74.07	16.39	12.95	6.01	0.48	8.7	4.6	18	838	891
	Tap	0.95	ND	<LOQ	ND	ND	<LOQ	0.18	0.56	ND	<LOQ	ND	-	-	-	-	-

Note: Inf = influent, AS = activated sludge, SC = secondary clarifier, Eff = effluent, SF = sand filter, UF = ultrafiltration and RO = reverse osmosis



## A.2. Average PFCs concentration in particulate phase and suspended solid (SS)

WWTP	Sampling point	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	SS (mg/L)
1	Inf	ND	ND	0.46	ND	ND	ND	<LOQ	ND	0.34	0.28	0.33	98
	AS	0.48	ND	12.07	0.21	0.33	0.28	2.28	0.45	5.16	8.99	6.67	8885
	SC	ND	ND	0.53	ND	ND	ND	<LOQ	ND	0.26	0.29	0.31	19
	Eff	ND	ND	1.54	ND	ND	0.10	0.70	0.49	0.83	0.67	0.49	31
2	Inf	ND	ND	1.40	ND	<LOQ	0.11	0.46	0.36	0.41	0.23	0.25	145
	AS	3.47	ND	13.13	0.57	4.32	0.71	7.14	3.36	33.48	12.38	82.60	3068
	SC	ND	ND	1.41	ND	0.26	0.14	1.10	0.30	2.09	0.49	1.51	40
	Eff	ND	ND	0.50	ND	ND	0.11	0.46	0.44	0.89	0.35	0.66	15
3	Inf	ND	ND	0.41	0.46	1.53	0.41	0.33	0.63	0.26	0.37	<LOQ	33
	AS	ND	ND	2.17	ND	0.18	0.08	0.86	0.68	0.45	0.33	0.31	175
	SC	ND	ND	0.89	ND	<LOQ	ND	0.22	0.18	0.19	0.18	<LOQ	23
	Eff	ND	ND	1.25	ND	0.32	0.18	0.36	0.30	0.14	0.15	<LOQ	13
4	Inf	ND	ND	0.56	ND	0.21	0.08	0.47	1.35	2.63	0.36	0.73	228
	AS	ND	ND	14.64	ND	0.90	0.44	5.11	9.05	86.24	41.82	20.34	8416
	SC	ND	ND	0.46	ND	0.43	0.10	1.50	1.70	5.82	0.84	0.43	9
	Eff	ND	ND	0.24	ND	<LOQ	0.09	0.64	1.13	2.40	0.52	0.60	59
5	Inf	ND	ND	1.45	ND	<LOQ	ND	0.30	0.51	0.30	0.38	0.21	171
	AS	ND	ND	1.75	ND	0.43	ND	0.33	0.34	0.34	0.29	0.42	388
	SC	ND	ND	0.98	ND	ND	ND	<LOQ	0.37	0.13	<LOQ	<LOQ	13
	Eff	ND	ND	1.18	ND	<LOQ	<LOQ	0.18	0.31	0.29	0.32	0.25	15

WWTP	Sampling point	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	SS (mg/L)
6	Inf	ND	ND	3.32	<LOQ	2.54	2.30	0.31	0.48	0.25	0.79	0.21	112
	AS	ND	ND	349.54	32.31	63.41	53.87	6.41	5.08	7.54	51.43	10.23	3468
	SC	ND	ND	10.87	<LOQ	0.96	0.60	0.26	0.50	0.33	0.58	0.22	7
	Eff	ND	ND	4.67	<LOQ	0.57	0.55	0.27	0.15	0.19	0.29	<LOQ	6
	UF feed	ND	ND	7.55	<LOQ	0.42	0.60	0.27	0.40	0.24	0.39	0.21	10
	UF reject	ND	ND	5.75	<LOQ	0.30	0.43	0.20	0.31	0.22	0.30	<LOQ	10
	RO feed	ND	ND	4.01	<LOQ	0.38	0.61	0.35	0.36	0.21	0.36	<LOQ	4
	RO reject	ND	ND	42.04	0.35	1.61	4.20	1.75	1.90	0.90	0.92	0.21	29
7	Inf	ND	ND	1.53	1.54	2.67	0.45	2.70	0.79	5.06	1.26	6.05	38
	AS	ND	ND	94.78	0.70	1.60	1.85	16.77	6.66	90.14	32.40	181.92	124
	SC	ND	ND	4.56	1.10	2.14	0.33	2.82	0.93	11.08	1.51	4.78	16
	Eff	ND	ND	3.43	1.03	1.92	0.46	3.63	0.98	8.81	0.99	2.78	18
8	Inf	ND	ND	0.32	ND	0.31	ND	<LOQ	ND	0.21	0.28	0.50	55
	AS	ND	ND	0.72	0.69	2.94	1.57	2.50	ND	1.95	2.37	3.06	633
	SC	ND	ND	0.29	ND	0.72	0.19	1.08	0.47	2.33	0.80	0.45	24
	Eff	ND	ND	1.03	ND	0.79	0.46	4.11	3.06	4.07	0.80	0.35	62
9	Inf	ND	ND	0.32	ND	<LOQ	<LOQ	0.16	0.20	0.15	0.19	0.22	21
	AS	ND	ND	23.10	ND	<LOQ	<LOQ	0.15	0.15	0.15	0.18	0.21	19
	SC	ND	ND	0.17	ND	<LOQ	<LOQ	0.15	0.16	0.15	0.20	0.24	170
	Eff	ND	ND	0.76	ND	<LOQ	<LOQ	<LOQ	0.30	0.17	0.29	0.33	15
10	Inf	ND	ND	0.88	ND	<LOQ	0.09	0.99	0.60	1.85	3.66	1.49	65
	AS	ND	ND	9.34	0.49	<LOQ	0.42	7.41	5.96	37.51	97.51	45.16	1309
	SC	ND	ND	0.23	ND	ND	ND	0.39	0.25	1.02	1.24	0.36	13
	Eff	ND	ND	0.32	ND	ND	0.09	1.62	0.92	1.33	0.63	0.32	11

Note: Inf = influent, AS = activated sludge, SC = secondary clarifier, Eff = effluent, SF = sand filter, UF = ultrafiltration, RO = reverse osmosis

### A.3. Average PFCs concentration and wastewater characteristics in industrial wastewater

Sample	L/P	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDODA (ng/L)	pH	Cond. (mS/cm)	DOC (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SS
Electronic1	L	15.77	0.21	0.98	0.47	1.45	0.45	1.78	ND	ND	ND	ND	8.1	1.47	13	369	141	-
	P	ND	ND	0.47	<LOQ	<LOQ	ND	ND	ND	ND	ND	ND	-	-	-	-	-	11
Electronic2	L	11.20	0.32	2.76	0.24	1.24	1.70	9.93	ND	3.46	ND	0.38	7.6	1.52	11	399	123	-
	P	ND	ND	0.29	ND	ND	ND	0.24	ND	0.33	ND	<LOQ	-	-	-	-	-	9
Electronic3	L	4.14	0.18	3.06	0.52	1.09	ND	0.35	ND	ND	ND	ND	7.3	0.73	23	120	83	-
	P	ND	ND	1.37	ND	ND	ND	ND	ND	ND	0.15	0.23	-	-	-	-	-	18
Electronic4	L	20.53	1.31	2.05	0.82	1.59	0.84	2.81	ND	ND	ND	ND	7.6	1.88	9	372	350	-
	P	ND	ND	1.20	<LOQ	0.37	0.09	0.33	0.19	0.18	<LOQ	0.23	-	-	-	-	-	33
Electronic5	L	1.08	3.03	27.54	78.23	218.06	50.10	159.31	45.91	104.75	11.55	4.10	7.6	0.7	20	108	39	-
	P	ND	ND	2.98	5.52	15.53	2.66	35.29	10.11	62.77	12.41	15.69	-	-	-	-	-	22
Electronic6	L	<LOQ	0.66	ND	ND	ND	ND	0.43	ND	ND	ND	ND	7.9	1.36	83	126	45	-
	P	ND	0.36	ND	ND	ND	ND	<LOQ	ND	ND	ND	ND	-	-	-	-	-	61
Electronic7	L	2.27	0.24	2.18	ND	ND	ND	ND	ND	ND	ND	ND	8.5	1.13	18	223	202	-
	P	ND	ND	2.39	<LOQ	<LOQ	ND	ND	ND	ND	ND	ND	-	-	-	-	-	57
Electronic8	L	1.21	0.15	1.16	0.15	0.25	<LOQ	2.00	ND	ND	ND	0.21	7.9	0.56	18	57	32	-
	P	ND	ND	0.14	ND	ND	ND	ND	ND	ND	<LOQ	<LOQ	-	-	-	-	-	191
Electronic9	L	20.00	0.34	3.60	0.35	4.05	1.63	5.98	ND	0.35	ND	<LOQ	7.7	1.4	13	378	236	-
	P	ND	ND	1.28	ND	<LOQ	ND	0.74	ND	0.69	0.13	0.58	-	-	-	-	-	11

Sample	L/P	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	pH	Cond. (mS/cm)	DOC (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SS
Plastic1	L	7.00	0.25	0.29	0.48	0.82	ND	<LOQ	ND	ND	ND	ND	7.4	3.8	81	658	878	-
	P	ND	0.29	0.33	<LOQ	0.20	ND	ND	ND	ND	ND	ND	-	-	-	-	-	61
Plastic2	L	20.91	1.93	2.92	<LOQ	0.86	0.25	0.88	ND	ND	ND	ND	8.1	0.96	16	182	245	-
	P	1.01	ND	0.73	<LOQ	1.48	0.25	3.03	ND	0.42	ND	ND	-	-	-	-	-	15
Plastic3	L	6.34	0.24	ND	0.34	0.19	ND	ND	ND	ND	ND	ND	7.7	1.4	28	254	368	-
	P	ND	ND	0.36	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-	-	44
Plastic4	L	12.40	0.48	ND	0.18	0.31	ND	ND	ND	ND	ND	ND	7.5	1.31	34	456	121	-
	P	ND	ND	<LOQ	ND	0.84	ND	ND	ND	ND	ND	ND	-	-	-	-	-	11
Plastic5	L	6.19	ND	2.82	0.32	0.63	<LOQ	1.04	ND	ND	ND	ND	8	0.86	4	125	96	-
	P	ND	ND	0.82	<LOQ	0.19	ND	ND	0.10	ND	ND	ND	-	-	-	-	-	5
Plastic6	L	0.84	0.35	ND	ND	ND	ND	ND	ND	ND	ND	ND	8	0.87	44	178	102	-
	P	ND	ND	<LOQ	ND	ND	ND	ND	ND	ND	<LOQ	<LOQ	-	-	-	-	-	42
Chemicals1	L	20.44	ND	19.49	<LOQ	0.25	0.54	0.93	ND	ND	ND	ND	7.8	2.7	35	750	362	-
	P	ND	ND	13.44	ND	ND	ND	ND	ND	0.28	<LOQ	<LOQ	-	-	-	-	-	23
Chemicals2	L	4.33	ND	0.67	ND	1.86	ND	0.53	ND	ND	ND	ND	8.9	1.38	23	264	125	-
	P	ND	ND	1.43	<LOQ	ND	ND	<LOQ	ND	ND	<LOQ	ND	-	-	-	-	-	34
Chemicals3	L	1.32	ND	0.21	1.29	21.12	0.11	1.23	ND	ND	ND	ND	7.4	0.84	11	140	83	-
	P	ND	ND	0.18	ND	0.45	ND	0.17	ND	0.16	<LOQ	<LOQ	-	-	-	-	-	11

Sample	L/P	PFBuS (ng/L)	PFHS (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	PFUnDA (ng/L)	PFDoDA (ng/L)	pH	Cond. (mS/cm)	DOC (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SS
Paint1	L	1.47	0.17	0.20	0.84	0.84	ND	ND	ND	ND	ND	ND	7.8	1.8	25	310	254	-
	P	ND	ND	2.40	<LOQ	<LOQ	ND	0.17	ND	ND	ND	ND	-	-	-	-	-	362
Paint2	L	289.18	0.63	ND	0.18	ND	ND	ND	ND	ND	ND	ND	8	2.5	53	420	362	-
	P	18.48	0.39	2.58	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-	-	58
Paint3	L	8.30	0.12	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.7	1.54	34	236	358	-
	P	ND	ND	3.06	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-	-	23
Paper1	L	5.19	ND	1.11	ND	18.91	0.76	ND	ND	ND	ND	ND	7.8	2.1	119	412	222	-
	P	ND	ND	1.40	0.15	0.17	ND	ND	0.16	ND	ND	ND	-	-	-	-	-	9
Paper2	L	2.60	1.88	ND	2.68	0.53	<LOQ	2.24	ND	ND	ND	ND	7.7	1.72	155	197	36	-
	P	1.18	0.88	ND	<LOQ	ND	<LOQ	0.88	ND	ND	ND	ND	-	-	-	-	-	131
Paper3	L	2.13	0.85	ND	ND	ND	ND	ND	ND	ND	ND	ND	8	1.78	69	325	123	-
	P	ND	ND	<LOQ	0.15	0.28	ND	ND	ND	ND	ND	ND	-	-	-	-	-	77
Automobile1	L	3.71	ND	0.48	0.43	1.26	ND	1.03	ND	ND	ND	ND	7.8	0.47	16	44	49	-
	P	ND	ND	0.33	ND	<LOQ	ND	ND	ND	ND	<LOQ	<LOQ	-	-	-	-	-	25
Automobile2	L	8.22	ND	0.54	ND	0.45	ND	ND	ND	ND	ND	ND	8.5	1.45	50	323	235	-
	P	ND	ND	4.24	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-	-	60
Textile1	L	2.25	0.39	0.56	ND	ND	ND	ND	ND	ND	ND	ND	7.6	0.49	42	59	84	-
	P	ND	ND	0.69	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-	-	-	18
Textile2	L	8.61	ND	ND	ND	1.59	0.66	0.40	ND	ND	ND	ND	7.7	1.19	79	274	73	-
	P	1.24	0.10	1.53	ND	0.44	0.26	0.51	ND	<LOQ	<LOQ	<LOQ	-	-	-	-	-	80
Metal1	L	3.76	3.14	150.1	0.26	0.77	0.30	0.52	ND	ND	<LOQ	ND	9.6	1.62	8	169	426	-
	P	ND	ND	72.69	ND	0.35	ND	0.20	ND	0.19	<LOQ	<LOQ	-	-	-	-	-	191
Metal1	L	7.22	0.83	0.44	<LOQ	0.36	ND	ND	ND	ND	ND	ND	7.3	1.22	54	247	178	-
	P	ND	0.45	0.68	0.18	0.42	ND	ND	ND	ND	ND	ND	-	-	-	-	-	67
Food1	L	6.60	4.88	ND	4.68	2.53	<LOQ	9.24	ND	ND	ND	ND	7.3	5.8	17	2103	321	-
	P	2.60	1.88	ND	2.68	0.53	<LOQ	2.24	ND	ND	ND	ND	-	-	-	-	-	736

Note: L = liquid phase and P = particulate phase

## Appendix B

### Appendix B.1. Comparison of PFHxA adsorption between experiment and estimation

Adsorbent	Adsorption capacity of PFHxA in experiment (mg/g)			
	NaCl and Na <sub>2</sub> SO <sub>4</sub>	NaCl and NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub>	NaCl, Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub>
GAC	0.1008	0.0850	0.0795	0.0710
PFA300	0.1296	0.1168	0.1066	0.0948
PFA400	0.0916	0.0725	0.0539	0.0442
BA103	0.1358	0.1292	0.1183	0.1048
Adsorbent	Adsorption capacity of PFHxA by estimation (mg/g)			
	NaCl and Na <sub>2</sub> SO <sub>4</sub>	NaCl and NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub>	NaCl, Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub>
GAC	0.1084	0.1076	0.0981	0.0950
PFA300	0.1319	0.1186	0.1091	0.1044
PFA400	0.0960	0.0813	0.0599	0.0544
BA103	0.1385	0.1325	0.1243	0.1209
Adsorbent	Ratio of adsorption capacity of PFHxA by estimation and experiment			
	NaCl and Na <sub>2</sub> SO <sub>4</sub>	NaCl and NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub>	NaCl, Na <sub>2</sub> SO <sub>4</sub> and NaNO <sub>3</sub>
GAC	1.0758	1.2648	1.2336	1.3385
PFA300	1.0180	1.0156	1.0228	1.1009
PFA400	1.0476	1.1207	1.1106	1.2301
BA103	1.0199	1.0255	1.0511	1.1533

## Appendix B.2 Calculation of influence of ionic and DOC on adsorption capacity of PFHxA onto GAC

Given:

The adsorption capacity of PFHxA ( $K_f$ ) in simulated ionic strength was 51.69 mg/g.

The adsorption capacity of PFHxA ( $K_f$ ) in *Milli-Q* water was 202.93 mg/g.

From Eq. 6.4

$$K_f = K_{f \text{ in Milli-Q}} e^{((-B_{ion}X_{ion} - B_{DOC}X_{DOC}))}$$

Determination:

$B_{ion}$  = influence of ionic on PFHxA adsorption factor (L/mmol)

$X_{ion}$  = ionic strength (mg/L)

From Eq. 6.4  $K_f = K_{f \text{ in Milli-Q}} e^{((-B_{ion}X_{ion} - B_{DOC}X_{DOC}))}$

$$51.69 = 202.93 e^{((-B_{ion}X_{ion} - B_{DOC}(0))}$$

$$B_{ion}X_{ion} = 1.3675$$

Assumption:

The simulated ionic strength wastewater contain the following ionic (NaF = 0.05, NaNO<sub>3</sub> = 0.08, Mg<sub>2</sub>SO<sub>4</sub>=0.29, K<sub>2</sub>SO<sub>4</sub> =0.48, CaCl<sub>2</sub> =3.1, Na<sub>2</sub>SO<sub>4</sub> = 2.99 and NaCl =0.72 (mmol/L)). Influence of ionic factor ( $B_{ion}$ ) (such as NaF, Mg<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>) were unavailable. For the calculation of influence of each ionic, the simulated ionic strength wastewater contain the following ionic (Na<sub>2</sub>SO<sub>4</sub> =3.75, NaNO<sub>3</sub> = 0.08, KCl =0.72 and CaCl<sub>2</sub> =3.1 (mmol/L))

Given:

$B_{Na_2SO_4}$  = influence of Na<sub>2</sub>SO<sub>4</sub> on PFHxA adsorption factor (L/mmol) (0.046)

$B_{NaNO_3}$  = influence of NaNO<sub>3</sub> on PFHxA adsorption factor (L/mmol) (0.068)

$B_{KCl}$  = influence of KCl on PFHxA adsorption factor (L/mmol) (0.014)

$B_{CaCl_2}$  = influence of CaCl<sub>2</sub> on PFHxA adsorption factor (L/mmol) (0.020)

$$B_{ion}X_{ion} = 1.3675$$

$$B_{Na_2SO_4}X_{Na_2SO_4} + B_{NaNO_3}X_{NaNO_3} + B_{KCl}X_{KCl} + B_{CaCl_2}X_{CaCl_2} = 1.3675$$

$$(0.046 \times 3.75) + (0.068 \times 0.08) + (0.014 \times 0.72) + (0.020 \times 3.1) = 1.3675$$

$$0.2500 = 1.3675$$

Given:

The adsorption capacity of PFHxA ( $K_f$ ) in fluorochemical wastewater was 37.12 mg/g.

The adsorption capacity of PFHxA ( $K_f$ ) in *Milli-Q* water was 202.93 mg/g.

Determination:

$B_{DOC}$  = influence of ionic on PFHxA adsorption factor (L/mmol)

$X_{DOC}$  = ionic strength (mg/L)

From Eq. 6.4  $K_f = K_{fin Milli-Q} e^{((-B_{ion}X_{ion} - B_{DOC}X_{DOC}))}$

$$37.12 = 202.93 e^{((-1.3675 - B_{DOC}X_{DOC}))}$$

$$B_{DOC}X_{DOC} = 0.3312$$

Given:

The DOC concentration in fluorochemical wastewater (except DOC equivalent of PFHxA) was  $54.2 - 11.6 = 42.6$  mg/L

$$B_{DOC}(42.6) = 0.3312$$

$$B_{DOC} = 0.0078$$



## Appendix C

### C.1 Removal of PFHxA in synthetic wastewater (Tap water containing PFHxA)

Day	Influent concentration of PFHxA (µg/L)	Effluent concentration of PFHxA (µg/L)						
		GAC	XAD4	PFA300	PFA400	A860	BA103	MN102
0.5	10	0.00	0.12	0.01	0.00	0.01	0.00	0.60
1	10	0.00	0.12	0.01	0.01	0.09	0.00	0.60
3	10	0.00	0.47	0.00	0.04	0.59	0.00	0.69
5	10	0.04	1.72	0.00	0.28	1.02	0.00	1.09
7	10	0.12	3.32	0.00	0.40	2.00	0.00	1.50
9	10	0.25	5.42	0.00	0.47	3.08	0.00	2.33
11	10	0.42	7.49	0.00	0.59	4.24	0.00	2.99
13	10	0.45	8.49	0.00	0.72	5.81	0.01	3.64
15	10	0.46	9.61	0.00	0.91	6.44	0.01	4.82
17	10	0.57	10.00	0.00	1.09	7.09	0.01	5.75
19	10	0.75	10.00	0.00	1.45	8.26	0.03	6.86
21	10	0.77	10.00	0.00	1.99	9.18	0.04	7.90
23	10	0.80	10.00	0.00	2.55	9.70	0.04	8.25
25	10	0.85	10.00	0.02	2.95	10.00	0.10	9.32
27	10	1.07	10.00	0.16	3.33	10.00	0.13	10.00
29	10	1.08	10.00	0.25	4.08	10.00	0.18	10.00
31	10	1.08	10.00	0.29	5.05	10.00	0.23	10.00
33	10	1.15	10.00	0.35	5.95	10.00	0.23	10.00
35	10	1.65	10.00	0.42	6.78	10.00	0.29	10.00
37	10	1.90	10.00	0.53	7.48	10.00	0.36	10.00
39	10	2.14	10.00	0.55	8.45	10.00	0.39	10.00
41	10	2.29	10.00	0.56	9.18	10.00	0.42	10.00
43	10	2.31	10.00	0.57	9.32	10.00	0.44	10.00
45	10	2.44	10.00	0.62	9.83	10.00	0.54	10.00
47	10	2.57	10.00	0.71	9.91	10.00	0.57	10.00
49	10	2.98	10.00	0.80	9.83	10.00	0.65	10.00
51	10	3.17	10.00	0.95	10.00	10.00	0.75	10.00
53	10	3.56	10.00	1.09	10.00	10.00	0.86	10.00
55	10	3.80	10.00	1.21	10.00	10.00	0.92	10.00
57	10	4.50	10.00	1.43	10.00	10.00	1.04	10.00
59	10	4.97	10.00	1.49	10.00	10.00	1.13	10.00
Total adsorption amount (µg)		10591	1589	12153	6079	2415	12266	2937

C.2 Regeneration amount of PFHxA in synthetic wastewater (Tap water containing PFHxA)

Number of bed volumes of regenerant	Accumulated regenerant (mL)	Amount of PFHxA from regenerant (μg)						
		GAC	XAD4	PFA300	PFA400	A860	BA103	MN102
2.5	50	365	602	3520	1744	376	4134	742
5.0	100	387	360	2949	1425	320	3420	475
7.5	150	368	292	2459	899	279	2209	341
10.0	200	275	181	901	699	247	1051	251
12.5	250	257	66	876	268	191	591	208
15.0	300	249	7	641	113	113	376	183
17.5	350	234	5	147	85	137	147	113
20.0	400	192	2	113	48	71	113	57
22.5	450	134	1	87	32	73	87	68
25.0	500	129	1	41	15	9	41	28
27.5	550	109	0	23	8	6	23	8
30.0	600	80	0	6	5	1	6	3
32.5	650	85	0	0	4	0	0	1
35.0	700	91	0	0	0	0	0	0
37.5	750	99	0	1	1	1	1	0
40.0	800	73	0	1	0	1	1	0
42.5	850	72	0	2	0	2	2	0
45.0	900	97	0	4	0	4	0	0
47.5	950	65	0	5	0	5	0	0
50.0	1000	47	0	1	0	1	1	0
52.5	1050	47	-	-	-	-	-	-
55.0	1100	47	-	-	-	-	-	-
57.5	1150	42	-	-	-	-	-	-
60.0	1200	37	-	-	-	-	-	-
62.5	1250	27	-	-	-	-	-	-
65.0	1300	27	-	-	-	-	-	-
67.5	1350	27	-	-	-	-	-	-
70.0	1400	27	-	-	-	-	-	-
72.5	1450	25	-	-	-	-	-	-
Total adsorption amount (μg)		3717	1517	11776	5349	1836	12203	2475

### C.7 PFCs concentration in central WWTP 7 by consecutive column (ng/L)

Day	Influent concentration (ng/L)			Effluent concentration from 1 <sup>st</sup> column (ng/L)			Effluent concentration from 2 <sup>nd</sup> column (ng/L)		
	PFPeA	PFHxA	PFOA	PFPeA	PFHxA	PFOA	PFPeA	PFHxA	PFOA
1	621	911	238	10	11	0	1	1	0
2	621	911	238	22	52	1	5	6	0
3	621	911	238	68	74	7	15	13	1
4	621	911	238	108	121	9	22	22	1
5	621	911	238	127	153	11	35	30	1
6	621	911	238	150	178	17	47	38	2
7	621	911	238	161	213	17	48	49	2
8	621	911	238	176	237	17	63	65	2
9	621	911	238	189	248	21	78	77	2
10	621	911	238	196	265	21	100	91	3
11	621	911	238	223	288	21	119	109	4
12	621	911	238	244	307	24	133	128	6
13	621	911	238	250	322	26	140	150	7
14	621	911	238	260	336	27	166	166	8
15	614	897	229	269	343	28	169	172	9
16	614	897	229	280	366	32	173	182	9
17	614	897	229	291	387	34	192	190	9
18	614	897	229	306	397	39	195	208	16
19	614	897	229	313	410	44	197	218	18
20	614	897	229	320	428	52	213	228	19
21	614	897	229	324	448	54	232	240	20
22	614	897	229	337	464	55	253	261	25
23	614	897	229	342	466	63	273	274	29
24	614	897	229	353	476	70	280	292	33
25	614	897	229	364	486	72	283	317	35
26	614	897	229	377	503	74	294	333	41
27	614	897	229	387	505	76	311	352	41
28	614	897	229	403	518	77	318	379	41
29	614	897	229	416	554	77	323	396	47
30	614	897	229	448	576	84	347	417	49
31	614	897	229	481	615	87	367	430	52
32	614	897	229	492	644	93	371	443	53
33	614	897	229	514	664	94	372	467	55
34	614	897	229	528	687	98	393	480	56
35	614	897	229	538	696	102	398	493	59

### C.8 PFCs regeneration amount in consecutive column (WWTP 7)

Number of bed volumes of regenerant	Accumulated regenerant (mL)	Amount of PFHxA from 1 <sup>st</sup> column (mg)			Amount of PFHxA from 2 <sup>nd</sup> column (mg)		
		PFPeA	PFHxA	PFOA	PFHxA	PFPeA	PFOA
2.5	50	54.96	83.34	24.26	20.11	26.15	4.03
5.0	100	49.05	63.89	22.40	11.46	20.05	2.53
7.5	150	30.23	44.62	15.98	8.40	18.32	1.83
10.0	200	14.57	34.24	10.40	4.05	10.89	1.38
12.5	250	5.55	11.66	6.26	1.46	3.66	0.83
15.0	300	2.89	6.44	3.30	0.94	1.84	0.62
17.5	350	0.31	3.27	2.30	0.77	0.39	0.28
20.0	400	0.14	2.05	1.46	0.29	0.24	0.27
22.5	450	0.11	1.35	0.80	0.06	0.10	0.19
25.0	500	0.04	0.65	0.46	0.02	0.05	0.11
27.5	550	0.03	0.51	0.37	0.02	0.02	0.04
30.0	600	0.01	0.18	0.21	0.01	0.00	0.02
32.5	650	0.00	0.11	0.11	0.00	0.00	0.00
35.0	700	0.00	0.07	0.07	0.00	0.00	0.00
37.5	750	0.00	0.04	0.05	0.00	0.00	0.00
40.0	800	0.00	0.03	0.04	0.00	0.00	0.00
42.5	850	0.00	0.04	0.03	0.00	0.00	0.00
45.0	900	0.00	0.03	0.03	0.00	0.00	0.00
47.5	950	0.00	0.03	0.04	0.00	0.00	0.00
50.0	1000	0.00	0.01	0.02	0.00	0.00	0.00
Summation (µg)		158	253	89	48	82	12
Regeneration efficiency (%)		97	97	95	100	99	99

