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Removal of Concentrated PFOS and PFOA in Synthetic Industrial Wastewater by Powder Activated Carbon and Hydrotalcite

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ABSTRACT

Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA), mainly applied in industries, have silently contaminated the global water sources for many decades. Moreover, high persistent in environment and estrogenic effects on some aquatic animals have been reported in many studies. The failure of conventional wastewater treatment plant indicates need for development of the effective treatment technique for wastewater containing the compounds. However, the previous studies mostly developed treatment at lower compound concentration than industrial wastewater. In this study, compounds removal at the comparatively high concentration with the wastewater was preliminary investigated using six different adsorbents. Among tested adsorbents, Powder activated carbon (PAC) and hydrotalcite provided greater than 97% removal for both compounds and were selected for study of sorption behaviors. Their sorption equilibrium was achieved rapidly in all tests, especially the sorption of PFOS on PAC. For hydrotalcite, equilibrium was achieved within 1 hour. The kinetic study showed higher initial sorption rate (v_0) of PFOS than PFOA with both adsorbents. pH was found to affect only the initial sorption rate in all experiments. For isotherm study, Langmuir isotherm was effective in evaluating the sorption of both compounds on PAC. Freundlich isotherm was appropriate with hydrotalcite. The isotherm result clearly reveals different sorption behavior of PAC and hydrotalcite with concentrated compounds.

Keywords: PFOS; PFOA; sorption; kinetic study; isotherm

1. INTRODUCTION

The anthropogenic compounds, Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA), have attracted global concerns in recent years for their global distribution, persistence, strong bioaccumulation and toxicity. The main source of PFOS and PFOA are the perfluorinated compound-based industries involved in: compound production, semiconductor, fire fighting-foam, metal plating, etc. For example, the wastewater generated from photolithographic process in a semiconductor industry was reported to have PFOS and PFOA in the concentration of 1,650-3,000 mg/L and 1,000 mg/L, respectively (Lampert et al., 2007; Tang et al., 2006). The contamination of global environment; surface waters, groundwater, rain, oceans, snow, etc. with PFOS and PFOA has been reported (Kim and Kannan, 2007; Rostkowski et al., 2006; Ya-

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mashita et al., 2005; So et al., 2004). They have also been detected in tap water (Jin et al., 2009). The level of PFOS and PFOA in surface water near industrial zone varying in range of 0.1 – 5,700 ng/L and 0.7 – 19,200 ng/L, have been reported (Rostkowski et al., 2006; Yamashita et al., 2005; So et al., 2004). In addition, PFOS and PFOA in the traceable concentration (in ng/L) have been detected in many unpolluted fresh water sources such as at North Atlantic Ocean (Yamashita et al., 2005). Apart from their mere persistence in the environment, their harmful effects on animal and human have also been reported in many studies. Hence, PFOS has been added to the list of Persistence Organic Pollutants (POPs). Therefore, wastewater containing high concentration of PFOS and PFOA necessitates effective removal before it is discharged into the environment.

The development of effective techniques to remove PFOS and PFOA from industrial wastewater has become extremely essential for the above reasons. The conventional treatment techniques were not successful and feasible in removal of PFOS and PFOA in ambient environment due to their stable properties. For example, the conventional wastewater treatment by activated sludge process was ineffective in the removal of these compounds, instead it has increased the concentration of the compounds in the effluent through degradation of precursors (Loganathan et al., 2007; Lien, 2007; Boulanger et al., 2005). Adsorption was revealed to be a promising technique for treating highly polluted wastewater, as well as having high potential for compound recovery and their reuse in the processes requiring lower quality compounds.

Activated carbon adsorbent was proved to be effective for the removal of PFOS and PFOA in a concentration lower than that actually found in wastewater generated from the industrial process (Tanaka et al., 2007; Qiu, 2007; Yu et al., 2009; Ochoa-Herrer and Sierra-Alvarez, 2008 and Yu et al, 2008). Moreover, the concentration of PFOS and PFOA was reported to have effect on the removal by PAC. PFOS and PFOA are surfactants, their critical micelle concentration (CMC) values are 4,453 and 15,696 mg/L, respectively (Yu et al., 2009). The PFOS or PFOA mono-molecule could agglomerate and form hemi-micelle, when their concentrations are applied in range of 0.001–0.01 times of CMC. Therefore, their removal by particular adsorbents might be affected at high PFOS and PFOA concentrations applied.

This study was intended to determine effective sorption for removal of high PFOS and PFOA concentrations, which are comparable with those contained in wastewater from industrial process. The preliminary test was firstly conducted with six different adsorbents namely PAC, hydrotalcite, ZnO nanopowder, anionic resin, chitosan and alumina for the removal of PFOS and PFOA. Then kinetic and isotherm studies were further investigated with the most effective adsorbents found in preliminary study to study their sorption behaviors.

2. ADSORBENT SELECTIONS

This study was initiated with the potential adsorbents based on the reports of previous studies. Adsorbents such as activated carbon and anionic resin were reported to be effective in the removal of PFOS and PFOA at low concentration. Most frequently used adsorbents; granular activated carbon (GAC) and PAC (Yu et al., 2009; Ochoa-Herrer and Sierra-Alvarez, 2008; Tanaka et al., 2007; Qiu, 2007), were effective in the removal of both the compounds. Lampert et al. (2007) reported strong base resin to be good in removal of PFOS and PFOA in exception for taking longer time to reach equilibrium than other ions. Chitosan based polymer provided 0.258 mmol/g of sorption capacity (Yu et al., 2008). Similarly, chitosan is also expected to possess sorption capacity, which is yet to be investigated. Hydrotalcite or Layer Doubled Hydroxides (LDH), also known as anionic clay, $(Mg^{2+}_6\ Al^{3+}_2(OH)_{16})\ (CO^{2-}_3)_3.xH_2O$, is stack of layers, which consists of positively charged-mixed metals. It has exchangeable anions, intercalated between layers, to maintain neutrality. LDH has been reported to have better sorption capacity with anionic surfactants as compared to GAC, PAC, various types of anion resins and bentonite (Schouten et al., 2007). Moreover, Adak et al. (2005) revealed alumina (Al_2O_3), which is extensively used in drinking water production and wastewater treatment, to be effective in removal up to 94% of high concentration of anionic surfactant. Moreover, nanoparticles increasingly used for wastewater treatment especially, ZnO with its superior zeta potential might be effective for sorption with anionic compound. Based on the above information, six adsorbents namely PAC, hydrotalcite, anionic resin, chitosan, alumina and ZnO were selected for the study.

3. MATERIALS AND METHODS

3.1 Materials

PFOS $[CF_3(CF_2)_7SO_3^-]$ and PFOA $[CF_3(CF_2)_6COO^-]$ purchased from Wako Pure Chemical Industry, Ltd., Japan, were used in this study. The commercial adsorbents such as Hydrotalcites ($Mg_6Al_2\ (CO_3)\ (OH)_{16}.\ 4H_2O$), ZnO nanopowder and alumina (WN-3: neutral) were purchased from SIGMA-ALDRICH, Inc., St.Louis, USA; Chitosn from SIGMA- ALDRICH, Japan; PAC (Fluka: 72343) from SIGMA- ALDRICH, Netherland and anionic resin (IRA-458) from SUPLECO, Bellefonte, USA were used in this study.

3.2 Adsorbent pretreatment

All adsorbents used in this study were new. Hence, the contamination due to keeping condition might be neglect. However, some adsorbents were pre-treated to remove impurities. Hydrotalcite was pretreated in oven at 500 ºC for 2 hours to remove the contaminants. PAC was heated at 105°C for 48 hours to remove moisture before use. Other adsorbents were used as such received from the company.

3.3 Experimental procedure

The synthetic wastewater used in this study was diluted from PFOS or PFOA stock solution in the Milli-Q water, while the stock solution was prepared in an acetronitrile and ultrapure water (40/60, v/v) mixture. All the experiments were carried out in plastic wares to avoid PFOS and PFOA sorption with container. Moreover, to prevent sample contamination, all the containers were rinsed once with methanol and thrice with Milli-Q water, before use.

3.3.1 Preliminary test

This test was aimed to evaluate the adsorbents' efficiency. The effective adsorbents would then be selected to study their sorption behavior. 100 mL of synthetic wastewater containing 50 mg/L of each compound (PFOS and PFOA) was poured to 125 mL bottle and added with 0.1 g of adsorbent. While, in case of hydrotalcite and ZnO, the adsorbent was firstly dispersed in Milli-Q water using ultrasonic machine for 30 minutes for complete dispersion before spiking concentrated compound solution. Sample bottles were shaken at 140 rpm and 25 ºC. The shaking duration was 48 h to provide enough sorption time.

3.3.2 Kinetic study

1 g/L of selected adsorbents such as PAC and hydrotalcite were tested individually with 100 mL of sample containing 50 mg/L of each compound. Samples were prepared same as described in section 3.3.1 but initial pH was controlled in this study to minimize its effect on sorption kinetic. Sorption with PAC was controlled at initial pH 3 and 7 whereas that of hydrotalcite was controlled at initial pH 3 and 9. pH was controlled with 1 N NaOH and 1 N HCl and small volumes (< 1 mL) of these solutions were applied to control initial concentration of compound. Sample bottles were shaken under the same conditions for 72 hours. 1 mL of sample was collected at time: 0, 5, 10, 30 minutes, 1, 2, 4, 8, 12, 21, 32 and 72 hours. Sampling was done under well mixed condition to maintain ratio of adsorbent to adsorbate.

3.3.3 Isotherm study

1g/L of PAC and hydrotalcite were studied individually with 100 mL of PFOS or PFOA solution, of which concentrations were varied in range of 1-1,000 mg/L (1, 10, 100, 250, 500, 750 and 1000 mg/L). Samples were prepared same as described in section 3.3.1 then stirred under the same conditions for 48 hours. pH was not controlled in this study besides pH affected only initial sorption rate in kinetic study.

3.3.4 Sample pretreatment and analysis

After sorption was completed, aqueous samples were collected and centrifuged at 4,000 – 12,000 rpm for 10 minutes. The supernatant was then filtered with 0.22 μm PVDF filter before being diluted by a mixture of acetronitrile and ultrapure water (40/60, v/v) for LCMS measurement.

PFOS and PFOA concentrations were determined by LCMS (Agilent 1200 SL HPLC and Agilent 6400 triple quadrupole mass spectrometer, tandem mass analysis) using column (Eclipse Plus C18, 2.1X100 mm 0.18 μm) from Agilent Technologies, USA. The mixture of acetronitirle in ultrapure water (40/60, v/v) and 10 mM CH_3COONH_4 solution were used as mobile phase. The calibration curves with correlation coefficient R^2 larger than 0.995 were used for the study.

Moreover, Zeta potential (Z_p) of adsorbents were analyzed. Z_p of hydrotalcite and PAC were measured with Nano-Zetasizer at National Metal and Materials Technology Center (MTEC), Thailand. Zp of chitosan and alumina were measured by using Z_p analyzer, Model: MuTeK SZP 06. pH of solution were measured by pH indicator strip from Merck.

4. RESULTS AND DISCUSSION

4.1 Zp of adsorbents

Table 1 demonstrates Z_p of adsorbents at different pH. The results would be discussed in section 4.2.

4.2 Preliminary test

The removal efficiency of six different adsorbents and pH of solutions were demonstrated in Figure 1.

The results showed more than 97% removal of PFOS and PFOA with hydrotalcite, anionic resin and PAC. The acid dissociation constant (pK_a), for PFOA is 2.5 (USEPA, 2008) and PFOS is -3.27 (Yu et al., 2009). Therefore both compounds in this test, whose pH varied in the range of 5.0-8.5 (Figure 1), carried negative charges (pH of solution > pK_a). The positive charges provided by the metals composed in hydrotalcite and the amino group on anionic resin, supported by positive Z_p values

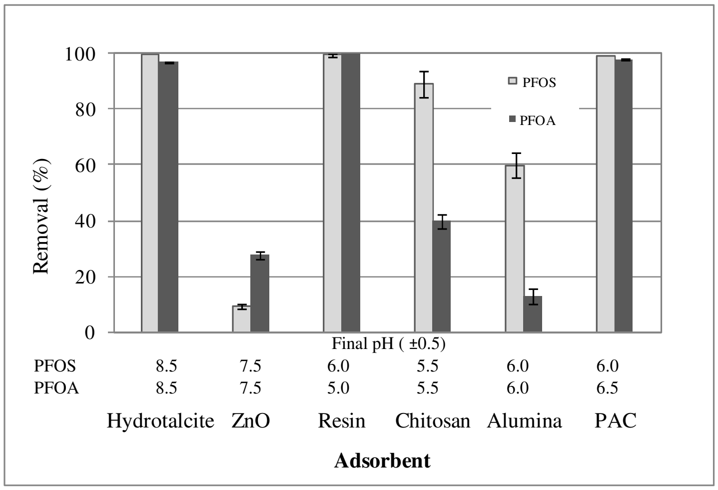


Figure 1 Removal efficiency of adsorbents in preliminary study

Table 1 Zp of adsorbents at different pH in this study

Adsorbent	pH (± 0.5)	Zp(mV)
PAC	3.0	17.17 ± 4.37
	7.0	-13.4 ± 5.89
Hydrotalcite	3.0	53.18 ± 5.98
	9.0	32.32 ± 4.07
Anion Resin	7.0	40 [a]
Chitosan	7.0	-2.87 ± 0.15
Alumina	7.0	-4.7 ± 0.46
ZnO	7.0	24[b]

Note: a is from Yoon et al., (2009), b is from Zhang et al., (2008).

in Table 1, could attract negatively charged por-tions of adsorbates that are SO_3^- of PFOS and COO^- of PFOA effectively. Even though, hydrotalcite and resin prossess moderate and low surface area, which has been reported to be around 200 (Parida and Das, 2000) and 0.1 (Symons et al., 1995) m^2/g respectively, they showed very high removals. On the other hand, PAC with less Z_p and larger surface area with typical range of around 500-2,000 m^2/g (Mohd Din et al., 2009), was found to sorb both of PFOS and PFOA effectively as well. In addition to negatively charged portion to bond with positive charge of PAC at slightly acidic condition (Table 1), both compounds also have fluorinated hydrophobic chain. Therefore PFOS and PFOA sorption on activated carbon, comparative hydrophobic material (Shi, 2005), possibly occurred through hydrophobic bond as well.

Chitosan and alumina were found to sorb PFOS and PFOA at moderate level, especially the PFOS. Zp of chitosan (pKa of amino group ≈ 6.5) and alumina (pH_{zpc} of the colloid = 7; pH at zero point of charge) should become slightly positive at tested pH of 5.5-6.0 (Table 1). Thus the sorption of PFOS and PFOA on chitosan and alumina could be achieved through electrostatic (chemical) sorption and some types of physical sorption.

The electrostatic attraction of chitosan occurred by its protonated amino group whereas protonated hydroxyl group might be a cause of attraction by alumina. Commercial ZnO nanopowder with Zp of 24+ mV (Zhang et al., 2008) showed lowest removal for both compounds. This might be resulted from the agglomeration of nanoparticles due to Van der Waals force during the experiment, which consequently decreased the actual Zp and surface area of the nanoparticles.

The preliminary test demonstrated that PAC, hydrotalcite and anionic resin are effective adsorbents for PFOS and PFOA removal. However, the same dry unit weight of adsorbents was used in the next experiment for comparison of sorption behavior of individual adsorbents. Hence, PAC and hydrotalcites were selected for further study of sorption behavior.

4.3 Kinetic study

To study of the sorption mechanisms, suitable contact time for sorption as well as effect of pH on sorption, the pseudo-second-order model was selected to fit the kinetic data, which assumes that the sorption at active site is only rate limiting step. This model fits for various adsorbates and adsorbents. The linear form of pseudo second order model used for the study is presented in Eq. (1).

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{t}{q_e} = \frac{1}{v_0} + \frac{t}{q_e} \tag{1}$$

where q_t and q_e is the amount of PFOS or PFOA adsorbed per gram of adsorbent (mmol/g) at time t and at equilibrium, K is sorption rate constant (g /(mmol h)), v_0 is the initial sorption rate (mmol/g h). All the pseudo second order model constants and correlation coefficient (R^2) were determined using linear regression, by plotting t/q_t vs. t.

Table 2 presents the adsorbent rate constants and correlation coefficient (R^2 values) obtained from the pseudo-second-order model.

The pseudo second order model with correlation coefficient ($R^2 \approx 1.00$) yielded the best fit for all experiments. Thus sorption at active site is only the rate limiting step. It should be resulted from the large amount of adsorbent (1 g/L) applied in this study. Hence, adsorbent has high chance to be in contact with compounds and other limiting steps on sorption including external diffusion and internal-pore diffusion of compounds were minimized. Moreover, there is no effect of pH on equilibrium sorption capacity of PFOS and PFOA (q_e) with both adsorbents. The amount of adsorbent might be large as compared to amount hydronium or hydroxide ions presenting in acid/base solutions used for initial pH adjustment. Thus q_e was not affected from pH in both adsorbents. However, pH was found to affect the initial sorption rate (v_0) (Table 2). v_0 of PAC was observed to be higher at pH 3 than at pH 7. At lower pH, faster PAC sorption at initial period should be resulted from more compound neutralization for hydrophobic attraction and/or more positive charges on PAC surface for electrostatic attraction. In the case of hydrotalcite, electrostatic attraction-based sorption was noticed because it had high Zp. At pH 3, even though negative charges of PFOS and PFOA were decreased but positive charges of hydrotalcite were increased as shown in Table 1. Therefore, v_0 of hydrotalcite was noticed to be higher at pH 3 than pH 9.

Figure 2(a) and (b) present the kinetic curves of PFOS and PFOA sorption on PAC and hydrotalcite, respectively. All kinetic curves reached equilibrium (constant sorption) rapidly and could not be observed clearly at initial period. It is resulted from too large amount of adsorbent applied as discussed in previous paragraph. From Figure 2(a), PFOS sorption on PAC was faster than PFOA, which showed desorption, especially at pH 7. The equilibrium of PFOA reached within 4 hours. But equilibrium of PFOS reached within 5 minutes and no desorption was observed at both pH values. In case of hydrotalcite [Figure 2(b)], 1 hour was required for achieving PFOS and PFOA equilibrium concentrations under all the pH values to be tested and no desorption was noticed. Normally, desorption of compound during sample shaking could be occurred if the sorption happened through weak bond. For example, the hydrophobic bond between PAC and PFOA, which has higher solubility and shorter length of C-chain (less hydrophobicity) than PFOS, should be weak type and desorption could be happened.

The adsorbent dose applied (1 g/L) showed too fast sorption for study of kinetics at the initial period but it provided > 95% removal within 5 minutes in all experiments. In a previous study, 4 hours time was reported for sorption at the same initial compound concentrations with lower dose of PAC as compared to this study (Yu et al., 2009). Thus 1 g/L of adsorbent applied in this study might be an effective dose in terms of removal efficiency and low contact time. Moreover, pH did not affect the sorption at this condition, hence chemical use for pH adjustment in treatment of pH-varying wastewater with this adsorbent amount (1 g/L) might be neglected.

4.4 Isotherm study

The kinetic study shows that there are no effects of pH and external and pore diffusions of compound on sorption between 1g/L of adsorbent and 50 mg/L of individual compounds. Therefore, isotherm study was further investigated with varying compound concentrations (1-1,000 mg/L) to determine the sorption capacity of adsorbents as well as understand the adsorbate–adsorbent interactions affected by compound concentration. Langmuir and Freundlich isotherms were applied in this study for correlating the sorption data of PAC and hydrotalcite with the selected isotherms. Langmuir isotherm is based on assumption that maximum compound uptake exists due to saturated monolayer of adsorbate on adsorbent surface. The sorption is energetically homogeneous and there is no interaction with neighboring adsorbed molecules. Freundlich isotherm assumes heterogeneous adsorption through multilayer sorption mechanisms. The Langmuir and Freundlich isotherms are expressed as Eq. (2) and Eq. (3).

Table 2 Kinetic parameters of the pseudo second order model for PFOS and PFOA sorptions on PAC and Hydrotalcite

Adsorbate	**Adsorbent**	**Initial pH**	**Pseudo second order parameter**		**R^2**
			q_e (mmol/g)	**v_0 (mmol/(g h))**	
PFOS	PAC	3	0.128	153.78	1.0000
		7	0.128	65.91	1.0000
	Hydrotalcite	3	0.132	307.23	1.0000
		9	0.132	276.19	1.0000
PFOA	PAC	3	0.171	9.44	0.9999
		7	0.166	4.08	0.9995
	Hydrotalcite	3	0.171	119.60	1.0000
		9	0.171	93.20	1.0000

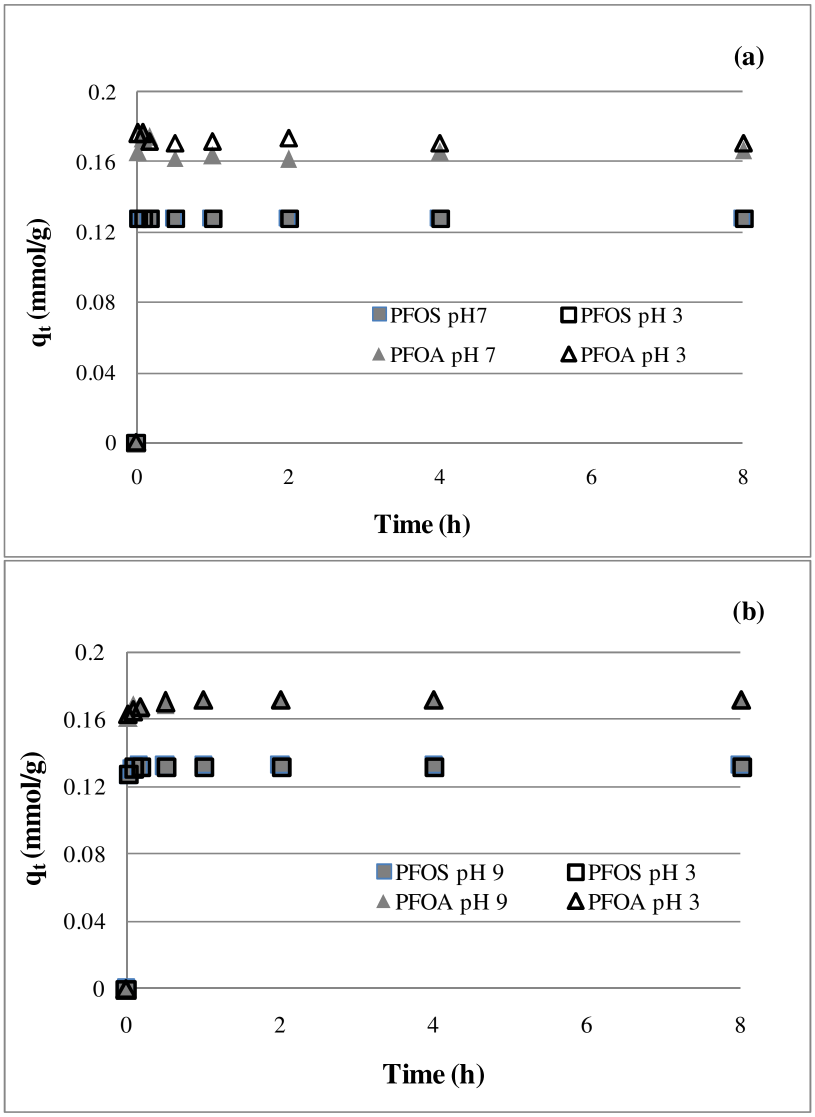


Figure 2 Kinetics of PFOS and PFOA sorptions on (a) PAC and (b) hydrotalcite

Langmuir adsorption isotherm equation

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (2)$$

Freundlich adsorption isotherm equation

$$q_e = K_F C_e^{1/n} \qquad (3)$$

where q_e is equilibrium sorption amount of PFOS or PFOA on adsorbents (mmol/g), q_m is maximum sorption capacity (mmol/g), C_e is equilibrium concentration in solution, K_F is a constant related to sorption capacity of the adsorbent ((mmol$^{1-1/n}$/g) L$^{1/n}$), b is Langmuir constant and n is Freundlich constant. The constants and R^2 of both the isotherms were determined using linear regression, by plotting, C_e/q_e vs. C_e for Langmuir isotherm and log q_e vs. log C_e for Freundlich isotherm.

As shown in Table 3 and Figure 3(a), Langmuir isotherm was more suitable than Freundlich isotherm, to describe the sorption mechanism of PFOS and PFOA on PAC. The maximum sorption capacity (q_m) of PFOS and PFOA with PAC was found to be 0.88 and

Table 3 Langmuir and Freundlich isotherm equilibrium constants for PFOS and PFOA sorption on PAC and hydrotalcite

Adsorbate	Adsorbent	Langmuir constants			Freundlich constants		
		q_m (mmol/g)	b (L/mmol)	R^2	K_F ($mmol^{(1-1/n)}/gL^{1/n}$)	n	R^2
PFOS	PAC	0.88	31.10	0.98	1.19	2.14	0.91
	Hydrotalcite	8.61	10.86	0.03	52.12	1.30	0.96
PFOA	PAC	1.03	20.80	0.99	1.35	2.10	0.96
	Hydrotalcite	6.20	6.75	0.14	27.04	1.06	0.98

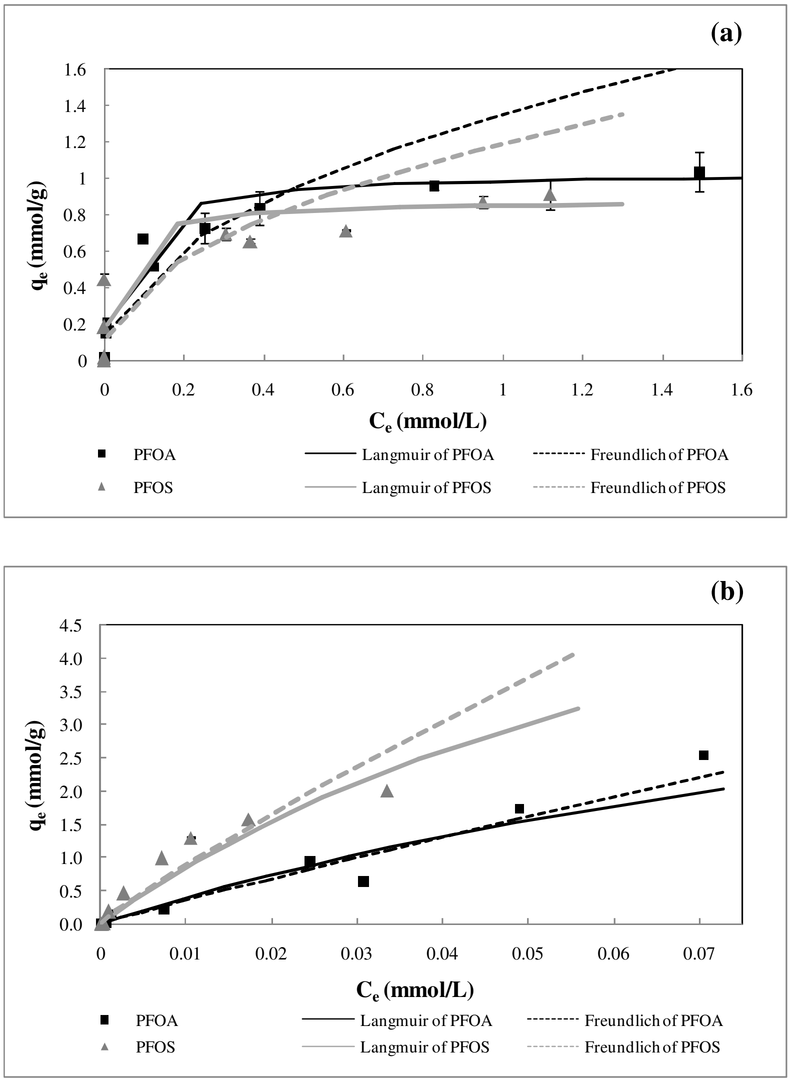


Figure 3 Sorption isotherms of PFOS and PFOA on (a) PAC and (b) hydrotalcite

1.03 mmol/g. However, at the initial concentration in the range of 20 – 250 mg/L, Yu et al. (2009) reported to have q_m of 1.04 and 0.67 mmol/g for PFOS and PFOA with PAC along with the possible formation of hemi-micelle. The higher sorption of PFOS on PAC than PFOA has also been reported by Ochoa-Herrera and Sierra-Alvarez (2008), in which initial concentration range of 15-150 mg/L was applied. At applied higher concentration in this study, q_m of PFOS was less than PFOA and less than the value reported by Yu et al., (2009). It might be resulted from at high compound concentration, PAC has demonstrated decreasing PFOS sorption as compared to PFOA.

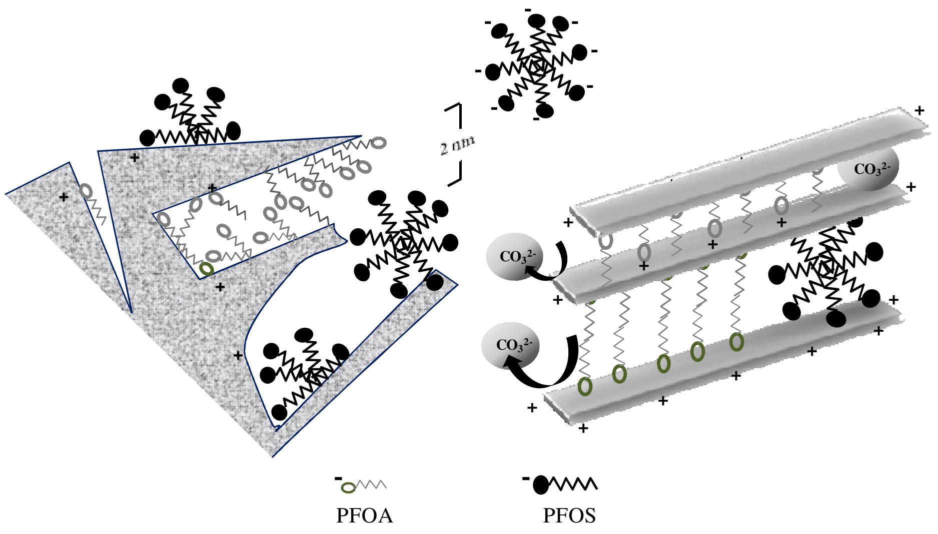
Moreover, sorption capacity of PAC in this study was higher than that of GAC, reported in the previous studies (Ochoa-Herrera and Sierra-Alvarez, 2008; Tanaka et al., 2007; Yu et al., 2007). This shows the high ability of PAC to be dispersed in solution and to be in contact with compounds.

The L-shaped curve generated [Figure 3(a)], demonstrates the difficulty of PAC to sorb PFOS and PFOA at high concentration. This was similar to the L-shaped curve generated in previous studies on sorption of PFOS/PFOA and some anionic surfactants with PAC (Yu et al., 2009; Schouten et al., 2007; Basar et al., 2004).

Mainly PAC has micro-pore of approximately 2 nm diameters [Figure 4(a)]. PFOS molecule was reported to have length of around 1 nm, calculated from combination of carbon-carbon distance (Erko and Erko, 2001). PFOA was estimated to have shorter length than PFOS because of less number of carbons in fluorinated chain. Thus, more PFOA molecules, of which some were possibly hemi-micelles, were sorbed as monolayer on surface of PAC micro-pore as compared to PFOS. Nevertheless, bigger hemi-micelle in the case of PFOS due to longer fluorinated C-chain, bigger functional group and much lower CMC than PFOA consequently limited the sorption by possibly blocking some micro-pores of PAC [Figure 4(a)]. Moreover, the hemi-micelles normally hide hydrophobic part of molecule and present polar part into the water [Figure 4(a)]. As discussed earlier, hydrophobic bond is a type of compound sorption on PAC. Thus the hiding of hydrophobic part of hemi-micelle might decrease PAC sorption as well.

In the case of hydrotalcites [Table 3 and Figure 3(b)], Freundlich isotherm was found to be effective in explaining the sorption behavior of both PFOS and PFOA. The very low R^2 value in Langmuir isotherm might be resulted from the concentration range of compounds applied in this study could not illustrate maximum sorption capacity of hydrotalcite. Hence, C-shaped curve (linear curve), which is implied for the constant availability of free site at high concentration, demonstrated [Figure 3(b)]. The multilayer of compound sorption might happen with hydrotalcite. The K_F of hydrotalcite was extremely higher than PAC, in which data more fitted with monolayer sorption (Langmuir isotherm).

Al^{3+} comprised in hydrotalcite mainly leads to residual positive charge in its layer, which requires anion to maintain neutrality [Figure 4(b)]. There is a number of researches reported that hydrotalcite sorbed anionic compounds in its interlayer through ion-exchange process. After sorption, the space of this interlayer increases based on size of sorbed compound (Bascialla and Regazzoni, 2008; Gasser et al., 2008; Pavlovic et al., 2005; Zhao and Nagy, 2004). Figure 4(b) presents the sorption mechanism of hydrotalcite showing interchanging of charged molecules, between anion in hydrotalcite (CO_3^{2-}) and compounds. The sorption on hydrotalcite was not decreased by hemi-micelle formation unlike in micro-porous PAC. There



(a) PAC (b) Hydrotalcite

Figure 4 Possible sorption mechanism of PFOS and PFOA at high concentration on (a) PAC and (b) hydrotalcite

is presence of charged portion of mono molecule or hemi-micelle playing an important role in hydrotalcite sorption. Thus sorption of PFOS was found to be better than PFOA on hydrotalcite, based on K_F values of 52.12 and 27.04 mmol$^{(1-1/n)}$/g L$^{1/n}$ for PFOS and PFOA, respectively. The low CMC of PFOS might lead its molecules to easily agglomeratetogether thus, increasing the sorption more than PFOA [Figure 4(b)] that was opposite to what happened in PAC sorption. Moreover, the very low R^2 in Langmuir isotherms for both compounds confirms that the monolayer sorption or limit of sorption was not observed in case of hydrotalcite.

CONCLUSIONS

From the preliminary study on six adsorbents, PAC and hydrotalcite were found to be effective adsorbents and were selected for kinetic and isotherm studies. The kinetic study showed faster sorption of PFOS than PFOA with both adsorbents. Most sorption processes occurred rapidly (5 minutes to 1 hour) with 1 g/L of adsorbent without pH effect. However, pH was found to affect the initial sorption rate. From isotherm study, PAC sorption was found to be limited at high compound concentration, especially for PFOS whereas hydrotalcite sorption was found to be constant for whole concentration range applied. Based on sorption behaviors and adsorbent/adsorbate properties, sorption of compounds with PAC happened through hydrophobic and electrostatic bonds whereas electrostatic bond mainly involved in hydrotalcite sorption. Moreover, the hemi-micelle formation at high compound concentration is highlighted to be a limiting factor of PAC sorption but it seems to enhance hydrotalcites sorption, especially with PFOS.

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NOMENCLATURE

b	Langmuir constant (L/mmol)
C_e	equilibrium concentration of compound in solution (mmol/L)
K	sorption rate constant of pseudo-second order model (g/(mmol h))
K_F	constant representing the sorption capacity (mmol^{1-1-n} /g $L^{1/n}$)
n	Freundlich constant
q_e	amount of compound sorbed on adsorbent at equilibrium (mmol/g)
q_m	maximum sorption capacity (mmol/g)
q_t	amount of compound sorbed on adsorbent at time t (mmol/g)
v_0	initial sorption rate (mmol/(g h))

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