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Adsorption of Perfluorocarbon Surfactant on Activated Carbon Adsorbents†

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The perfluorocarbon decontamination process using a dilute solution of a high molecular weight fluorinated surfactant in a perfluorocarbon liquid is very effective for the removal of micron sized hot particulate from surfaces in a hot cell. After the decontamination process, the removal of the fluorinated anionic surfactant within the perfluorocarbon solution through adsorption using a carbon adsorbent is needed for the reuse of spent perfluorocarbon. From the experimental results on the adsorption behaviour of a surfactant in a perfluorocarbon solution in terms of the structural and chemical properties of the activated carbon fiber and active carbon, it was found that the structural properties of the carbon adsorbent, particularly the surface area, have an important influence on the adsorption behaviour, rather than the chemical properties. A ACF-15 adsorbent with a large surface area has an excellent adsorption efficiency of 56 %, compared with other adsorbents such as ACF-7, AC-45X100 or AC-20X45.

Key Words: Perfluorocarbon, Surfactant, Adsorption, Activated carbon fiber, Active carbon.

INTRODUCTION

Highly radioactive particles adhered to the solid surfaces in a hot cell are a problem constraining the working condition and reuse of electronic equipment in a facility. The perfluorocarbon decontamination process using a dilute solution of a high molecular weight fluorinated surfactant in a perfluorocarbon liquid is very effective for the removal of micron-sized hot particulate from surfaces in a hot cell. In particular, the perfluorocarbon fluid facilitates the wetting and penetration into narrow holes and crevices[1,2].

The perfluorocarbon surfactant is relatively more superior in its surface activity than a saturated hydrocarbon surfactant, which has the same number of carbons. Its excellent surface activity can reduce the surface tension of both a pure organic substance and water. Therefore, when it is used together with a low molecular perfluorocarbon, it is expected to be effectively applied to the dry decontamination of highly radioactive particulate contaminants with an increased volatility, which is easy in the recovery of decontamination solution[3,4].

Spent fluorinated surfactant solutions can be recovered through filtration and distillation and the final step in the perfluorocarbon decontamination process is to rinse the processed parts with a surfactant-free perfluorocarbon to remove any radioactive contaminants that might have been trapped in the dried-out surfactant residue. This surfactant-free perfluorocarbon can be obtained by an adsorption process to remove the perfluorocarbon surfactant. Active carbon has been used mainly as an adsorbent using an adsorption process and more recently, there has been steady effort to develop and apply activated carbon fiber as a carbon adsorbent instead of active carbon. Unlike the existing particulate or powder active carbon, activated carbon fiber is composed of extremely small-sized micro-pore fillings that are all exposed to the surface, causing a superior adsorbability as a result of an excellent adsorption rate and an extremely large surface area.

Therefore, the purpose of this study is to compare the adsoption characteristics of existing active carbon with that of activated carbon fiber and to develop a selective adsorbent that can remove only the surfactant in a perfluorocarbon solution containing a surfactant.

EXPERIMENTAL

In this experiment, a solution mixed with perfluoroheptane (PFC-5070, 3M Co.) and fluorinated anionic surfactant (Krytox-157, Dupont Co.) was used.

After preparing 1 wt % of the solution by putting 1 mL of the ionic surfactant into 1 L of pure perfluorocarbon solution, 12 mL of the 1 wt % solution was mixed into 18 mL of the pure perfluorocarbon solution to generate 300 mL of a 0.4 wt %

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solution. The pitch-based activated carbon fiber with non-woven fabric (Osaka Gas Co., FN-200PS-15, FN-200PS-7) and active carbon (Dong Yang Carbon Co., AC-45X100, AC-20 X45) were used as an adsorbent. The FN-200PS-15 activated carbon fiber and FN-200Ps-7 activated carbon fiber is named as ACF-15 and ACF-7, respectively. Krytox (Dupont Co.) was used as a perfluorocarbon surfactant. The properties of the perfluorocarbon are summarized in Table-1.

TABLE-1
PROPERTY OF PERFLUOROCARBON

Density (g/cm^3)	1.72
Surface tension, dynes/cm	13
Boiling point (ºC)	80
Heat of vapourization (cal/g)	80
Formula	C_7F_{16}
Molecular weight	388

After preparing 1 wt % of the solution by putting an anionic surfactant of 10 mL into the pure perfluorocarbon solution, the experiment was conducted toward the samples selected at a constant interval by maintaining the temperature at 25 ºC, while preparing 300 mL of the 0.4 wt % solution by mixing 120 mL of the 1 wt % surfactant solution into 180 mL of the pure perfluorocarbon solution. We obtained the optimum adsorption experiment method through a batch experiment. In this experiment, various changes in the rotation speed from 300, 500, 700 and up to 1000 rpm were used to examine the optimum adsorption conditions and we examined the adsorbent appropriate for the surfactant adsorption experiment by changing the types of adsorbent. For this purpose, the removal efficiency of the surfactant was measured under a respective condition, by filling the carbon adsorbent into an Erlenmeyer flask and adjusting the type and amount of the adsorbent in the perfluorocarbon solution.

The FT-IR spectrometer (Model MB-102, Bomem Co.) was applied to establish the elements of the perfluorocarbon system surfactant and the structural properties of the adsorbent surface was analyzed by measuring the nitrogen adsorption isotherm in 77 K with a BET surface area measuring device (Quantachrome, Autosorb 1). As for the concentration of the surfactant within the perfluorocarbon solution, its absorbance was measured at a 210 nm wavelength using UV (Milton Roy Co., Spectronic 1201).

RESULTS AND DISCUSSION

The structural properties of activated carbon fiber and active carbon used as an adsorbent were analyzed from the nitrogen adsorption and desorption isotherm of the adsorbent. Table-2 shows the structural property values calculated from the nitrogen adsorption and desorption isotherm. In the results of an analysis on the active carbon and activated carbon fiber adsorption isotherm, it promptly makes adsorption of a considerable amount of nitrogen at a low relative pressure and subsequently, the adsorption amount is not increased further even when raising the relative pressure to achieve adsorption equilibrium. The low-pressure part in the early stage of the adsorption isotherm shows a micro-pore filling and the slope of the plateau shown in the high relative pressure part is known to be involved in the multi-layer adsorption occurring in the external surface of the adsorbent. Therefore, it was found that only micro-pore fillings were developed in the active carbon and activated carbon fiber.

TABLE-2
BET DATA OF CARBON ADSORBENTS

	ACF-7	ACF-15	AC (45 × 100)	AC (20 × 45)
S_{BET} (m_2/g)	870	1733	1077	1275
V_{tot} (cc/g)	0.41	0.83	0.53	0.63
V_{mic} (cc/g)	0.34	0.59	0.39	0.44

As shown in Table-2, the surface area shows the highest value of ACF-15 as 1733 m^2/g and then AC-20X45, AC-45X100 and ACF-7 in order. Looking on the results of the gas phase adsorption of active carbon and activated carbon fiber, the micro-pore filling accounts for 84 % of the total pore volume and the average radius of the pore is 15.12Å.

In IUPAC, the pore with less than 20Å in diameter is classified as a micro-pore. Considering this along with Fig. 1, it was found that most of the pores developed in the active carbon and activated carbon fiber were micro-pore fillings. A characteristic feature of an adsorption-desorption isotherm for mesoporous solids is its hysteresis loop on the adsorption and desorption curve, but the adsorbent applied in this experiment shows no hysteresis loop. Therefore the number of pores is ignorable compared with that of micro-pore filling. The adsorption process is importantly influenced by the chemical properties of the adsorbent surface as well as the structural properties such as the adsorbent pore size and surface area. The chemical properties of the adsorbent depend on the chemical properties of the functional group formed on the adsorbent surface.

In this study, the pH of the liquid was measured after soaking the carbon adsorbent in the solution and the surface functional group was then measured on a quantitative basis using Boehm's neutralization technique. As shown in Table-3, activated carbon adsorbents have larger surface acidities than activated carbon fibers.

TABLE-3
SURFACE ACIDITIES OF ADSORBENTS BY BOEHM'S NEUTRALIZATION METHOD

	Functional group (meq/g)			Total (meq/g)
	Carboxyl	Lactone	Phenol	
ACF-15	0.32	1.30	0.84	2.46
ACF-7	0.23	0.58	0.64	1.45
AC (45 × 100)	1.51	1.13	1.86	4.50
AC (20 × 45)	2.05	1.92	1.43	5.40

Fig. 1 shows the FT-IR spectra for the perfluorocarbon and the perfluorocarbon+ 2.0 vol % surfactant. In the spectrum (b), we can observe the carboxyl group at a wave number of 3300 cm^{-1}.

To examine the adsorption behaviour regarding the perfluorocarbon surfactant adsorption efficiency, the experiment was performed by changing the amount, stirring speed and types of adsorbent.

The pre-test on the adsorption efficiency for Krytox was performed by changing the amount of adsorbent in the range of 0.01-1 g after putting 20 mL of 0.4 wt % solution into the vial bottle at a constant stirring speed. As the adsorbent amount increases in the 48-h test-run, the adsorption amount also increases, but the adsorption efficiency is not considerably improved for the increased amount.

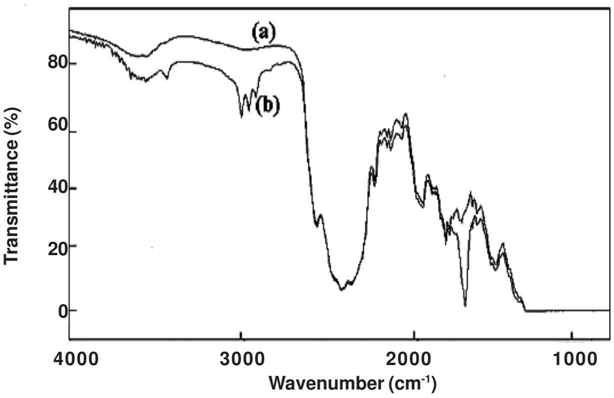

Fig. 1. FT-IR spectra, (a) pure perfluorocarbon, (b) perfluorocarbon + 2.0 vol % surfactant

To examine the adsorption behaviour of ACF-15 adsorbent for the surfactant according to the stirring speed, the experiment was performed by changing this speed within a range of 300-1000 rpm, the results of which are shown in Fig. 2. The result indicates that the adsorption is well achieved when increasing the stirring speed. Therefore, it was found that the stirring speed influences the performance capabilities of the transfer of foreign matters. Accordingly, in this study, the experiment was performed at a fastest flow rate of 700 rpm within the adjustable range enabling a smooth stirring speed.

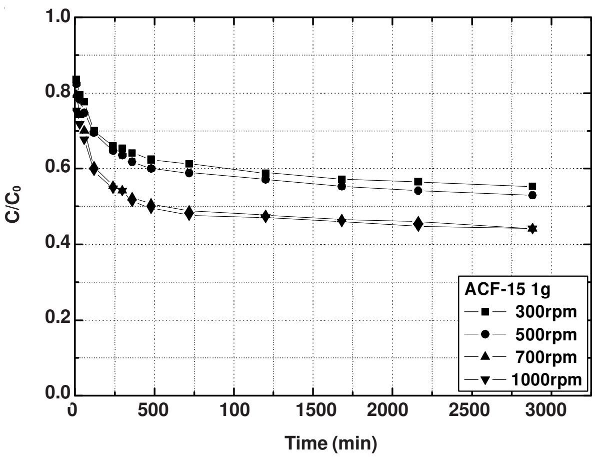

Fig. 2. Effect of stirring speed on the Krytox adsorption for batch system with ACF-15

For the four types of adsorbent prepared for this study, the adsorption efficiency was evaluated using a 0.4 wt % Krytox solution (Fig. 3). Among the four types of adsorbent, ACF-15 indicates the greatest performance showing 56 % adsorption efficiency for a 48-h reaction. Compared with this, ACF-7 shows a considerably low adsorption efficiency of 11 %; AC-45X100, 22 %; and AC-20X45, 31 %, respectively. It is found that ACF-15 has excellent adsorption efficiency compared with other adsorbents such as ACF-7, AC-45X100 or AC-20X45, which is evaluated as related to the physical properties such as the surface area of the adsorbent (Fig. 4).

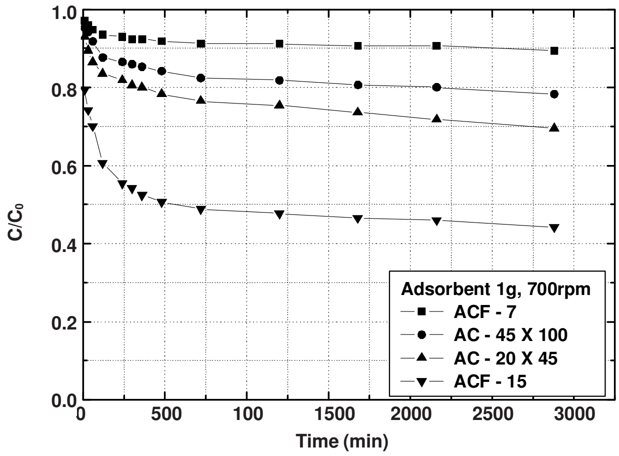

Fig. 3. Adsorption rate of carbon adsorbents for 0.4 % Krytox solution at a stirring speed of 700 rpm

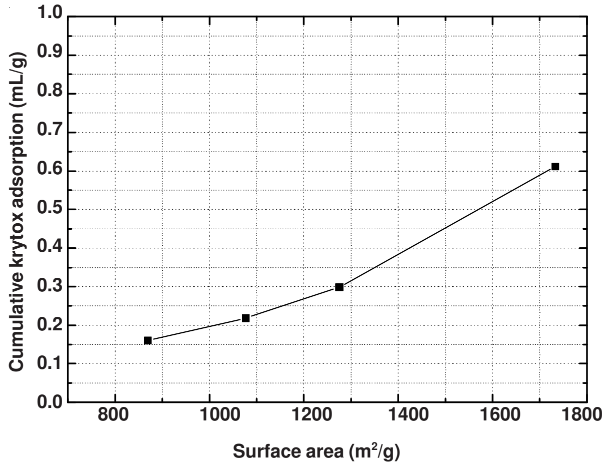

Fig. 4. Effect of specific surface area on the adsorption capacity of carbon adsorbents for Krytox

Conclusion

From the experimental results on adsorption behaviour of the surfactant in the perfluorocarbon solution the structural properties, particularly the surface area, have an important influence on the adsorption behaviour, rather than the chemical properties. It was found that ACF-15 with large surface area has excellent adsorption efficiency of 56 % compared with other adsorbents such as ACF-7, AC-45X100, or AC-20X45.

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