

Preparation of Fluoroalkyl End-Capped Oligomer/Cyclodextrin Polymer Composites: Development of Fluorinated Composite Material Having a Higher Adsorption Ability toward Organic Molecules

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Abstract

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer

$[R_F-(CH_2CHSi(OMe)_3)_n-R_F]$; $R_F = CF(CF_3)OCF_7$, $n = 2, 3$; $R_F-(VM)_n-R_F]$ was applied to the preparation of fluoroalkyl end-capped vinyltrimethoxysilane oligomer/ α -, β -, γ -cyclodextrin polymers (α -, β -, γ -CDPs) composites

$[R_F-(VM-SiO_2)_n-R_F/\alpha$ -, β -, γ -CDPs] by the sol-gel reaction of the corresponding oligomer in the presence of the α -, β -, γ -CDPs under alkaline conditions. The $R_F-(VM-SiO_2)_n-R_F/\alpha$ -, β -, γ -CDPs composites thus obtained were found to give a good dispersibility toward the traditional organic media except for water, and were applied to the surface modification of glass to provide a superoleophilic/superhydrophobic characteristic on the modified surface, although the corresponding $R_F-(VM-SiO_2)_n-R_F$ nanocomposites can give a usual oleophobic/superhydrophobic property on the surface. These composite powders were also found to be applicable to the packing material for the column chromatography to separate the mixture of oil/water and the water in oil (W/O) emulsions. More interestingly, these composite powders were found to have a higher adsorption ability toward not only low-molecular weight aromatic compounds such as bisphenol A and bisphenol AF but also volatile organic compounds, compared to that of the pristine α -, β -, γ -CDPs.

Keywords

Fluorinated Oligomeric Composite, Cyclodextrin Polymer, Surface

1. Introduction

There has been a great interest in cyclodextrins which consist of a hydrophilic exterior and a hydrophobic interior capable of binding small hydrophobic structures, due to their ability to form inclusion complexes with a wide variety of water-insoluble compounds [1] [2] [3] [4]. Cyclodextrins have been predominantly used for the stabilization, solubilization and formulation of drugs, and for the separation of the isomers and analogs in analytical chemistry [5] [6]. However, cyclodextrins possess a solubility toward water, limiting its reusability as the adsorbent for these compounds. Therefore, it is deeply desirable to develop the water-insoluble cyclodextrin polymers. In fact, there have been numerous reports on the synthesis of the water-insoluble cyclodextrin polymers by the use of epichlorohydrin and diisocyanates as the crosslinking agents, so far [7] [8] [9] [10] [11]. These water-insoluble cyclodextrin polymers thus obtained have been applied to the adsorbents for the organic pollutants such as phenol, *p*-nitrophenol, benzoic acid, *p*-nitrobenzoic acid, 4-*t*-butylbenzoic acid, and bisphenol A [12] [13] [14]. Hitherto, we have been comprehensively studying on the synthesis and applications of two fluoroalkyl end-capped oligomers $[R_F-(M)_n-R_F]$; R_F = fluoroalkyl group, M = radical polymerizable monomer] by the use of fluoroalkanoyl peroxide $[R_F-C(=O)-OO-(O=)C-R_F]$ as a key intermediate [15] [16] [17] [18] [19]. In these two fluoroalkyl end-capped oligomers, especially, two fluoroalkyl end-capped vinyltrimethoxysilane oligomers $[R_F-(CH_2CHSi(OMe)_3)_n-R_F]$; R_F = $CF(CF_3)OC_3F_7$] have been already applied to the composite reactions with not only talc fine particles in the presence of low-molecular weight organic molecules but also organic polymers such as poly (tetrafluoroethylene) fine particles to afford the corresponding fluorinated oligomeric silica nanocomposites encapsulated these guest molecules [20] [21] [22]. It was also demonstrated that these fluorinated nanocomposites can exhibit a superoleophilic/superhydrophobic characteristic toward the modified surface, although the corresponding original fluorinated oligomeric silica nanoparticles $[R_F-(CH_2CHSiO_2)_n-R_F]$ can give a usual oleophobic/superhydrophobic property on their modified surface [20]. In addition, these fluorinated nanocomposites are applicable to the packing materials for the column chromatography to separate the mixture of oil and water [21] [22]. From the developmental viewpoint of the cyclodextrin polymer derivatives possessing a higher adsorption ability toward a variety of organic molecules in aqueous media than that of the pristine cyclodextrin polymers, it is of particular interest to explore the cyclodextrin polymer derivatives possessing a superoleophilic/superhydrophobic characteristic; however, such studies have been heretofore very limited. Here we report that two fluoroalkyl end-capped vinyltrimethoxysilane oligomers can be applicable to the sol-gel reaction in the presence of

α -, β -, γ -cyclodextrin polymers (α -, β -, γ -CDPs) under alkaline conditions to afford the corresponding fluorinated oligomeric silica/ α -, β -, γ -CDPs composites. Interestingly, these fluorinated composites thus obtained were found to provide a higher adsorption ability toward low-molecular weight aromatic compounds such as bisphenol A and bisphenol AF in the aqueous solutions than that of the pristine α -, β -, γ -CDPs. More interestingly, a higher adsorption behavior toward the volatile organic compounds such as toluene, xylenes, trichloroethylene and tetrachloroethylene was also observed by using these fluorinated composites. These results will be described in this article.

2. Experimental

2.1. Measurements

Dynamic light scattering (DLS) measurements were measured by using Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Micrometer size-controlled composite particles were measured by using laser diffraction particle size analyzer: Shimadzu SALD-200 V (Kyoto, Japan). Field emission scanning electron micrographs (FE-SEM) were obtained using JEOL JSM-7000F (Tokyo, Japan). Thermal analyses were recorded on NETZSCH JAPAN TG-DTA2010SE α differential thermobalance (Kanagawa, Japan). Contact angles were measured using a Kyowa Interface Science Drop Master 300 (Saitama, Japan). Dynamic force microscopy (DFM) was recorded by using SII Nano Technology Inc. E-sweep (Chiba, Japan). HPLC (high performance liquid chromatography) analyses were conducted on a Shimadzu LC10A (Kyoto, Japan). GC-Mass spectra were recorded on a JEOL JMS-Q1000GC K9 (Tokyo, Japan).

2.2. Materials

α -, β - and γ -cyclodextrin polymers (α -, β -, γ -CDPs) were received from Kankyo Kogaku (Hirosaki, Japan). Fluoroalkyl end-capped vinyltrimethoxysilane oligomer [R_F -(CH₂CHSi(OMe)₃)_{*n*}-R_F: *n* = 2, 3; R_F = CF(CF₃)OC₃F₇; R_F-(VM)_{*n*}-R_F] was synthesized according to our previously reported method. [23] Glass plate (borosilicate glass) [micro cover glass: 18 mm × 18 mm] was purchased from Matsunami glass Ind. Ltd. (Osaka, Japan) and was used after washing well with 1,2-dichloromethane. Bisphenol A and bisphenol AF were purchased from Tokyo Chemical Industrial Co. (Tokyo, Japan).

1) Preparation of fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica/ α -CDP composites [R_F -(VM-SiO₂)_{*n*}-R_F/ α -CDP]

A typical procedure for the preparation of R_F -(VM-SiO₂)_{*n*}-R_F/ α -CDP composites is as follows: To methanol solution (5 ml) containing fluoroalkyl end-capped vinyltrimethoxysilane oligomer [R_F -(VM)_{*n*}-R_F] (300 mg) was added α -CDP (10 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 10 min. 25% aqueous ammonia solution (1.0 ml) was added to the methanol solution, and was successively stirred at room temperature for 5 hrs. After the solvent was evaporated off, methanol was added to the obtained

crude products. The methanol suspension thus obtained was stirred with magnetic stirring bar at room temperature for 1 day, and then was centrifuged for 30 min. The expected fluorinated oligomeric silica/ α -CDP composites were easily separated from the methanol solution, and were successively washed several times with methanol. After centrifugal separation of this solution, the obtained product was dried under vacuum at 50°C for 1 day to produce the purified fluorinated composite white colored powders (190 mg). Other fluorinated composites were prepared under similar conditions.

2) Surface modification of glass treated with the R_F -(VM-SiO₂)_n- R_F / α -CDP composites

To methanol solution (5 ml) containing R_F -(VM)_n- R_F oligomer (300 mg) was added α -CDP (10 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 10 min. 25% aqueous ammonia solution (1.0 ml) was added to the methanol solution, and was successively stirred at room temperature for 5 hrs. The glass plate was dipped into this methanol solution at room temperature and left for 1 min. These glass plates were lifted from the solutions at a constant rate of 0.5 mm/min and subjected to the treatment for 1 day at room temperature; finally, these were dried under vacuum for 1 day at room temperature. After drying, the contact angles of dodecane and water were measured by the deposit of each droplet (2 μ l) on the modified glasses.

3) Preparation of the surfactant-stabilized water in oil (toluene) emulsion

The surfactant (span 80:30 mg) was added into the mixture of water (0.05 ml) and toluene (5.0 ml). The expected white-colored W/O emulsion was easily prepared through the ultrasonic irradiation of the obtained mixture for 5 min at room temperature. Other W/O (oil: 1,2-dichloroethane) emulsion was also prepared under similar conditions.

4) Adsorption of bisphenol A in the aqueous solution by using the R_F -(CH₂CHSiO₂)_n- R_F / β -CDPs composites

Solid-phase extraction cartridge connected with the polyethylene frit containing the R_F -(CH₂CHSiO₂)_n- R_F / β -CDPs composite powders (20 mg; Run 20 in **Table 1**) was used for the adsorption of bisphenol A. 5 ml of aqueous methanol solution (concentration of methanol: 6%) containing bisphenol A (0.1 mmol/dm³) was applied to the cartridge, and the obtained eluent was analyzed by HPLC [Shimadzu LC10A; column: RP-18PA^{TR} (4.6 mm I.D. = 150 mm); injection volume: 10 ml; mobile phase: methanol/water/phosphoric acid (70.0/29.9/0.1 (vol/vol/vol); detection wavelength: 278 nm] to detect the residual bisphenol A. Schematic process for analyzing the residual bisphenol A was illustrated in **Scheme 2**, and the residual bisphenol AF was also analyzed under similar conditions. In addition, Schematic illustration for the adsorption and desorption of BPA through the recycling process by using the R_F -(CH₂CHSiO₂)_n- R_F / β -CDPs composite powders as the packing material is shown in **Scheme 3**.

5) Adsorption of volatile organic compounds (VOCs) in the aqueous solutions by using the R_F -(CH₂CHSiO₂)_n- R_F /CDPs composites

Table 1. Preparation of $R_F-(VM-SiO_2)_n-R_F/\alpha-, \beta-, \gamma$ -CDPs composites.

Run	CDPs (mg)	$R_F-(VM)_n-R_F$ (ml)	MeOH (ml)	<i>aq.</i> NH ₃ (ml)	Yield ^{a)} (%)	Size of the composites ^{b)} (μ m)
1	α -CDP (10)	300	5	1	38	5.2 \pm 0.4
2	β -CDP (10)	300	5	1	56	2.8 \pm 0.2
3	γ -CDP (10)	300	5	1	40	4.9 \pm 0.3
4	α -CDP (25)	300	5	1	61	6.7 \pm 0.4
5	β -CDP (25)	300	5	1	53	4.1 \pm 0.2
6	γ -CDP (25)	300	5	1	58	6.9 \pm 0.3
7	α -CDP (50)	300	5	1	62	10.9 \pm 0.4
8	β -CDP (50)	300	5	1	55	4.3 \pm 0.3
9	γ -CDP (50)	300	5	1	58	6.6 \pm 0.4
10	α -CDP (100)	300	5	1	63	16.7 \pm 0.4
11	β -CDP (100)	300	5	1	64	10.1 \pm 0.3
12	γ -CDP (100)	300	5	1	61	9.6 \pm 0.4
13	α -CDP (200)	300	5	1	70	10.1 \pm 0.3
14	β -CDP (200)	300	5	1	66	11.2 \pm 0.3
15	γ -CDP (200)	300	5	1	62	12.5 \pm 0.3
16	α -CDP (300)	300	5	1	67	12.6 \pm 0.3
17	β -CDP (300)	300	5	1	71	8.4 \pm 0.3
18	γ -CDP (300)	300	5	1	72	11.9 \pm 0.3
19	α -CDP (200)	200	5	1	78	20.5 \pm 0.4
20	β -CDP (200)	200	5	1	69	7.3 \pm 0.3
21	γ -CDP (200)	200	5	1	67	11.7 \pm 0.5
22	α -CDP (200)	100	5	1	77	20.4 \pm 0.4
Original $R_F-(VM-SiO_2)_n-R_F$ nanoparticle						27.7 \pm 6.7 nm ^{c)}
Original α -CDP						15.8 \pm 0.2 μ m ^{b)}
β -CDP						16.6 \pm 0.3 μ m ^{b)}
γ -CDP						17.1 \pm 0.4 μ m ^{b)}

a) Yields are based on $R_F-(VM-SiO_2)_n-R_F$ oligomer and CDPs; b) Determined by laser diffraction particle size analyzer in methanol; c) Determined by dynamic light scattering (DLS) measurements in methanol.

5 ml of 0.1% methanol solution containing VOCs (concentration of each VOC: 100 μ g/dm³) was poured into the solid-phase extraction cartridge connected with the polyethylene frit containing the $R_F-(CH_2CHSiO_2)_n-R_F$ /CDPs composite powders (20 mg), and the eluent thus obtained was added into the head space vial. Head space operating conditions were 30 min for sample equilibration at a temperature of 60 °C, and successively subjected to analysis by head space gas chromatography/mass spectrometer (conditions: capillary column: Aquatic^{TR}; 0.25 mm I.D. = 60 m df = 1.4 μ m; inlet temperature: 200 °C; injection

volume: 2 ml; carrier gas: Helium; column oven temperature: from 40°C to 200°C (programming rate: 10°C/min); ion source temperature: 200°C; ionization energy: 70 eV). The adsorption ratios (%) of VOCs were determined based on the calibration curve created by using the corresponding pristine VOCs having known concentrations. Schematic outline for the analytical measurements of the adsorption ratios of the VOCs is illustrated in **Scheme 4**.

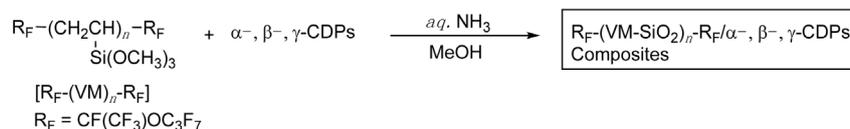
3. Results and Discussion

1) Preparation of R_F -(VM-SiO₂)_n-R_F/α-, β-, γ-CDPs composites

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer [R_F -(CH₂CHSi(OMe)₃)_n-R_F: $n = 2, 3$; $R_F = CF(CF_3)OC_3F_7$; R_F -(VM)_n-R_F] was found to cause the sol-gel reaction under alkaline conditions in the presence of α-, β-, γ-CDPs at room temperature to provide the corresponding fluorinated oligomeric silica/α-, β-, γ-CDPs composites. The results are shown in **Scheme 1** and **Table 1**.

As shown in **Scheme 1** and **Table 1**, the expected composites [R_F -(VM-SiO₂)_n-R_F/α-, β-, γ-CDPs] were obtained as 38% - 78% isolated yields through the sol-gel reaction of the R_F -(VM)_n-R_F oligomer in the presence of CDPs under alkaline conditions. **Table 1** shows that the yields of the composites are sensitive to the feed ratios of CDPs and R_F -(VM)_n-R_F oligomer employed, increasing with greater feed ratios of CDPs in the oligomer-CDPs. In addition, the size of the composites was found to increase with the increase of the feed ratios of CDPs. These findings would be due to the presence of micrometer-size controlled CDPs particles.

The pristine CDPs have no solubility toward both water and fluorinated aliphatic solvents [1:1 mixed solvents (AK-225^{TR}) of 1, 1-dichloro-2, 2, 3, 3, 3-pentafluoropropane and 1, 3-dichloro-1, 2, 2, 3, 3-pentafluoropropane]; however, the CDPs have a dispersibility toward not only water but also some organic solvents such as dimethyl sulfoxide (DMSO), 1,2-dichloroethane and *N,N*-dimethylformamide (DMF). On the other hand, the fluorinated composites in **Table 1** were found to give an extremely poor dispersibility in water; however, these composites afforded good dispersibility and stability in traditional organic media such as tetrahydrofuran, DMSO, 1,2-dichloroethane, DMF, methanol, and 2-propanol including fluorinated aliphatic solvents: AK-225^{TR}. Such dispersibility toward the fluorinated composites; that is, no dispersibility toward water and a good dispersibility toward fluorinated aliphatic solvents, quite different from the pristine CDPs, would be due to the presence of the fluoroalkyl segments in the composites illustrated in **Scheme 1**.



Scheme 1. Preparation of R_F -(VM-SiO₂)_n-R_F/α-, β-, γ-CDPs composites.

The sizes of the composites in methanol were measured by laser diffraction particle analyzer at 25 °C (**Table 1**). Each size of these fluorinated composites is micrometer size-controlled fine particles: 3 - 17 μm as shown in **Table 1**, on the contrary, the size of the pristine CDPs is 16 - 17 μm levels. The decrease of the size of the obtained composites, compared to that of the pristine CDPs would be due to the agglomeration and aggregation of the pristine CDPs.

In order to clarify the morphology of the obtained composites, FE-SEM photograph of the $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F\text{/CDPs}$ composite powders (Runs 16, 17 and 18 in **Table 1**) was recorded. The FE-SEM measurements of pristine CDPs particle powders and $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ oligomeric nanoparticle powders, which were prepared under alkaline conditions, were also measured under similar conditions, for comparison. The results are shown in **Figures 1-3**.

Figure 1 shows that the pristine α -, β -, γ -CDPs particles are irregular in size, and FE-SEM picture of the $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ oligomeric particle powders shows the formation of nanometer size-controlled fine particles (see **Figure 2**).

In contrast, electron micrographs of our present $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F/\alpha\text{-CDP}$, $\beta\text{-CDP}$, and $\gamma\text{-CDP}$ composites show that the $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ oligomeric nanoparticles are uniformly coated on each CDP particle surface to provide the corresponding fluorinated oligomeric silica/CDPs composites.

In order to verify the presence of the $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ oligomeric nanoparticles in the composites, thermal stability of the fluorinated composites in **Table 1** was studied by thermogravimetric analyses, in which the weight loss of these composites was measured by raising the temperature around 800 °C (the heating rate: 10 °C min^{-1}) in air atmosphere, and the results were shown in **Figures 4-6**.

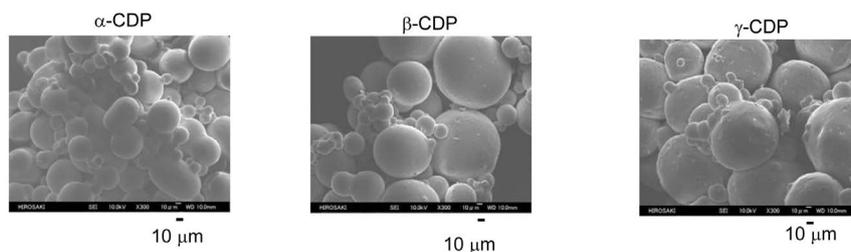


Figure 1. Field emission scanning electron microscopy (FE-SEM) image of pristine α -CDP, β -CDP and γ -CDP powders.

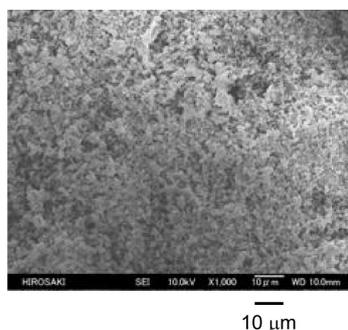


Figure 2. FE-SEM image of the pristine $\text{R}_F\text{-(VM-SiO}_2)_n\text{-R}_F$ nanoparticle powders.

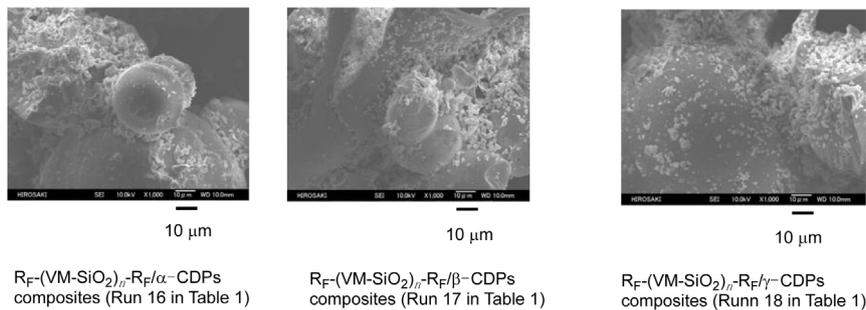


Figure 3. FE-SEM images of $R_F-(VM-SiO_2)_n-R_F/\alpha-, \beta-, \gamma$ -CDPs composite powders.

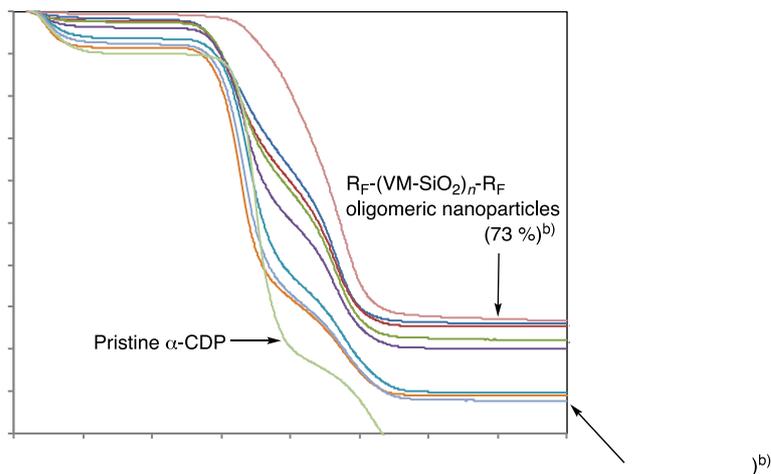


Figure 4. Thermogravimetric analyses of $R_F-(VM-SiO_2)_n-R_F/\alpha$ -CDP composites. a) Run No corresponds to that of **Table 1**; b) Weight loss (%) at 800 °C.

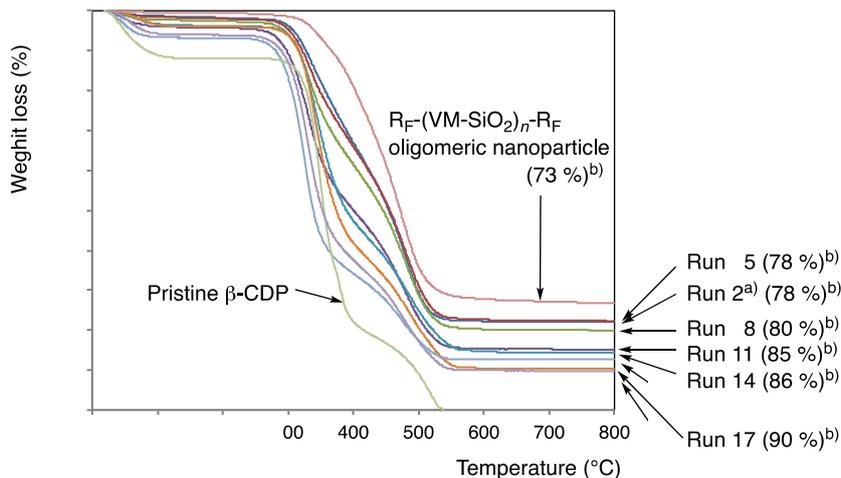


Figure 5. Thermogravimetric analyses of $R_F-(VM-SiO_2)_n-R_F/\beta$ -CDP composites. a) Run No corresponds to that of **Table 1**; b) Weight loss (%) at 800 °C.

As shown in **Figure 4**, the pristine $R_F-(VM-SiO_2)_n-R_F$ oligomeric nanoparticles, which were prepared by the sol-gel reaction of $R_F-(VM)_n-R_F$ oligomer under

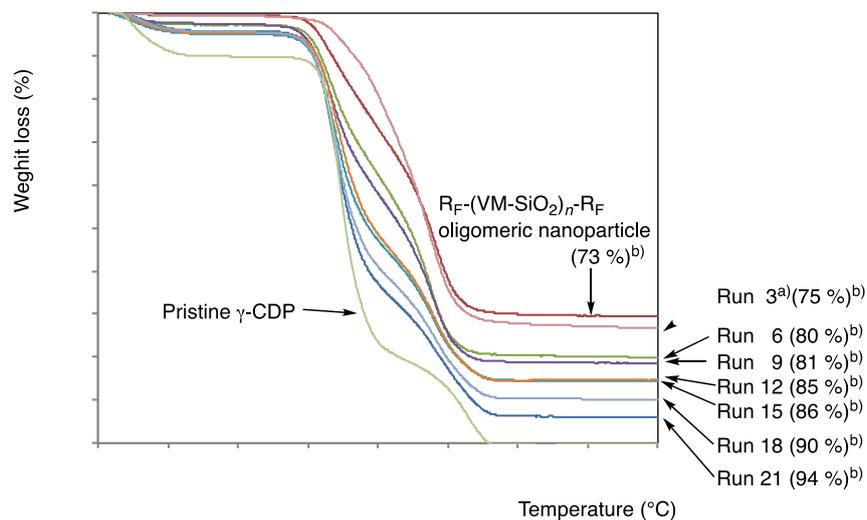


Figure 6. Thermogravimetric analyses of $R_F-(VM-SiO_2)_n-R_F/\gamma$ -CDP composites. a) Run No corresponds to that of **Table 1**; b) Weight loss (%) at 800 °C.

alkaline conditions in **Scheme 1**, afforded the 73% weight loss around at 530 °C, owing to the partial formation of silica gel during the calcination process. Pristine α -CDP afforded a perfect weight loss at around 540 °C. In contrast, the $R_F-(VM-SiO_2)_n-R_F/\alpha$ -CDP composites (Runs 1, 4, 7, 10, 13 and 16 in **Table 1**) were found to provide the weight loss behavior in proportion to the contents of the $R_F-(VM-SiO_2)_n-R_F$ oligomeric nanoparticles in the composites after calcination at 800 °C, and the contents of α -CDP in the composites were estimated to be from 1% to 19%. Similar TGA curves for the $R_F-(VM-SiO_2)_n-R_F/\beta$ -CDP and γ -CDP composites were observed, and the contents of β -CDP and γ -CDP in the $R_F-(VM-SiO_2)_n-R_F$ composites were also estimated under similar conditions. The results are as follows:

Contents (%) of CDPs in the composites:								
α -CDP	Run 1	Run 4	Run 7	Run 10	Run 13	Run 16	Run 19	
	1	2	5	7	17	18	19	
β -CDP	Run 2	Run 5	Run 8	Run 11	Run 14	Run 17	Run 20	Run 22
	5	5	7	12	13	17	17	14
γ -CDP	Run 3	Run 6	Run 9	Run 12	Run 15	Run 18	Run 21	
	2	7	8	12	13	17	21	

The contents of CDPs in the obtained composites were found to increase from 1% - 5% to 17% - 18% with increasing the feed ratios of CDPs in the CDPs-oligomer (300 mg) from 10 to 300 mg in the composites reactions (illustrated in **Scheme 1**).

2) Surface property of $R_F-(VM-SiO_2)_n-R_F/CDPs$ composites

In order to clarify the surface active characteristics of the present composites in **Table 1**, these fluorinated composites have been applied to the surface mod-

ification of glass, and we have measured the dodecane and water contact angle values on these modified glass surfaces. The results are shown in **Table 2**.

It is well known that $R_F-(CH_2CHSi(OMe)_3)_n-R_F$ oligomer can undergo the sol-gel reaction to afford the corresponding fluoroalkyl end-capped oligomeric silica nanoparticles $[R_F-(CH_2CHSiO_2)_n-R_F]$ [20]. $R_F-(CH_2CHSiO_2)_n-R_F$ oligomeric nanoparticles thus obtained were also applied to the surface modification to provide an oleophobic/superhydrophobic characteristic on the modified glass surface [20]. In fact, as shown in **Table 2**, the dodecane and water contact angle values on the modified glass surface treated with the $R_F-(CH_2CHSiO_2)_n-R_F$ oligomeric nanoparticles are 48 and 180 degrees to exhibit the oleophobic and superhydrophobic characteristic. However, interestingly, it was demonstrated that the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites illustrated in **Table 2** can afford a superoleophilic/superhydrophobic characteristic; because the dodecane and water contact angle values are 0 and 180 degrees in each case, although each composite contains the longer fluoroalkyl groups possessing a good oleophobic property.

There have been heretofore a variety of reports on the creation of the superoleophilic/superhydrophobic surface through the architecture of the roughness surface by using a variety of methods, such as a porous film formation composed of poly (tetrafluoroethylene) nanoparticles [24], spray coating with hydrophobic silica nanoparticles suspension [25], the treatment with a mixture of hydrophobic silica nanoparticles and polystyrene solution in toluene [26]. Especially, the introduction of a proper rough surface microstructure should make a flat hydrophobic surface superhydrophobic, owing to the introduction of an air cushion beneath the water droplet; in contrast, a flat oleophilic surface should become superoleophilic through the capillary effect [27]-[35]. Thus, in order to verify such unique surface wettability, we tried to study on the surface roughness of the modified glass surface by the treatments of the $R_F-(CH_2CHSiO_2)_n-R_F/\alpha$ -CDP composites (Run 16 in **Table 1**) by FE-SEM measurements and dynamic force microscopy (DFM) measurements. The modified glass surface treated with the

Table 2. Contact angles of dodecane and water on the modified glasses treated with the $R_F-(VM-SiO_2)_n-R_F/CDPs$ composites.

	Dodecane (degree)	Water(degree)
$R_F-(VM-SiO_2)_n-R_F/\alpha$ -CDP composites (Runs 1, 4, 7, 10, 13, 16 and 19)*	0	180
$R_F-(VM-SiO_2)_n-R_F/\beta$ -CDP composites (Runs 2, 5, 8, 11, 14, 17, 20 and 22)	0	180
$R_F-(VM-SiO_2)_n-R_F/\gamma$ -CDP composites (Runs 3, 6, 9, 12, 15, 18 and 21)	0	180
$R_F-(VM-SiO_2)_n-R_F$ oligomeric nanoparticles	48	180

*) Each Run No. corresponds to that of **Table 1**.

$R_F-(CH_2CHSiO_2)_n-R_F$ oligomeric nanoparticles were also studied under similar conditions, for comparison. The results are shown in **Figure 7**.

As shown in **Figure 7(a)**, we have observed the architecture of the effective roughness surface on the modified glass surface, compared with that (**Figure 7(b)**) of the modified glass surface treated with the $R_F-(CH_2CHSiO_2)_n-R_F$ oligomeric nanoparticles. Especially, the topographical image of the modified surface treated with the $R_F-(CH_2CHSiO_2)_n-R_F/\alpha$ -CDP composites afforded an effective roughness characteristic, and we can observe a higher roughness average values: R_a : 111 nm than that (R_a : 7 nm) of the pristine $R_F-(CH_2CHSiO_2)_n-R_F$ oligomeric nanoparticles. Such higher roughness value is due to the presence of micrometer size-controlled α -CDP particles in the composites, providing a superoleophilic/superhydrophobic characteristic on the modified surface. Similar higher roughness values (R_a): 135 nm and 82 nm were obtained on the modified glass surfaces treated with the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites (Run 17 in **Table 1**) and the $R_F-(CH_2CHSiO_2)_n-R_F/\gamma$ -CDP composites (Run 18 in **Table 1**), respectively (data not shown). Such higher roughness surfaces would interact with oil (dodecane) possessing the lower surface tension than that of water to

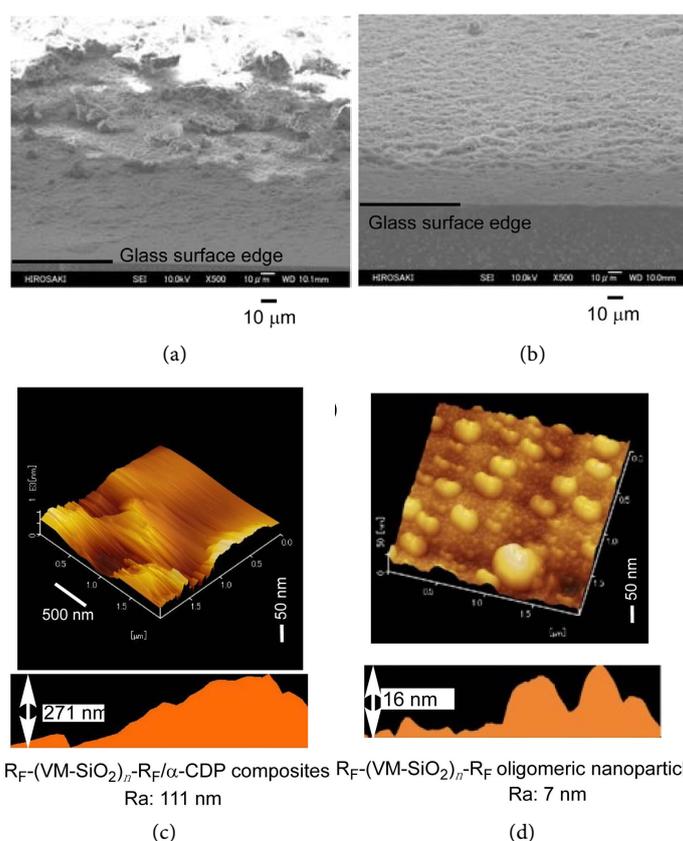


Figure 7. FE-SEM (Field Emission Scanning Electron Microscopy) images of the modified glass surface treated with the $R_F-(VM-SiO_2)_n-R_F/\alpha$ -CDP composites (a), the $R_F-(VM-SiO_2)_n-R_F$ nanoparticles (b); and DFM (Dynamic Force Microscopy) topographic images of the modified glass surface treated with the $R_F-(VM-SiO_2)_n-R_F/\alpha$ -CDP composites (c); the $R_F-(VM-SiO_2)_n-R_F$ nanoparticles (d).

give the superoleophilic characteristic, because an oil droplet could easily penetrate the very small orifice between the microsize-controlled composites particles. In contrast, the fluoroalkyl segments in the composites can be arranged on the modified roughness surface to afford the superhydrophobic characteristic.

3) Application of $R_F-(VM-SiO_2)_n-R_F/CDPs$ composites to the separation of the mixture of oil and water

In this way, it was demonstrated that our present fluorinated composites can provide a superoleophilic/superhydrophobic property. The superoleophilic surface possesses in general a strong affinity toward oils. Therefore, the surfaces having the superoleophilic/superhydrophobic characteristic can simultaneously repels water and strongly absorbs oils, of whose behavior should be applicable to the separation of oil and water [36] [37] [38] [39]. Thus, we tried to separate three kinds of mixtures of oil and water such as the O/W emulsions (oils: 1,2-dichloroethane and toluene) and the mixture of water [5 ml: water was colored with $CuSO_4 \cdot 5H_2O$ (200 mg)] and 1,2-dichloroethane (5 ml). The traditional silica-gel (Wakogel^{TR} C-500HG: average particle size: 21 μm) was not effective for the packing material for column chromatography to separate these mixtures under reduced pressure. However, interestingly, we can isolate the only transparent colorless oils under similar conditions by using the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composite powders as the packing materials for column chromatography. The recovery ratios (w/w_0) (w : weight of the isolated transparent colorless oil; w_0 : weight of the used oil) of the isolated transparent colorless oils from the mixtures of oil and water are shown in **Table 3**.

As shown in **Table 3**, the $R_F-(CH_2CHSiO_2)_n-R_F/\alpha$ -, β -, γ -CDPs composites (Runs 1, 2 and 3), which were prepared under the feed ratios of CDPs/oligomer: 10/300, were found to provide a similarly good recovery ratios to those of the

Table 3. Recovery ratios of oils from the mixtures of oils and water by using the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites as the packing materials for column chromatography.

Composites	Recovery ratio (%)		
	Mixture of 1,2-dichloroethane and water	W/O emulsion	
		oil: 1,2-dichloroethane	oil: toluene
	$R_F-(CH_2CHSiO_2)_n-R_F/\alpha$ -CDP composites		
Run 1*	80	82	82
Run 16	73	75	79
	$R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites		
Run 2	67	78	76
Run 17	70	81	81
	$R_F-(CH_2CHSiO_2)_n-R_F/\gamma$ -CDP composites		
Run 3	77	78	77
Run 18	77	82	83

*) Each Run No. corresponds to that of **Table 1**.

other fluorinated composites, which were prepared under the feed ratios of CDPs/oligomer: 300/300. This finding would be due to the superoleophilic/superhydrophobic characteristic in each composite illustrated in **Table 2**, and the composites possessing such wettability can strongly interact with oils in the aqueous solutions to isolate only oils from the mixtures.

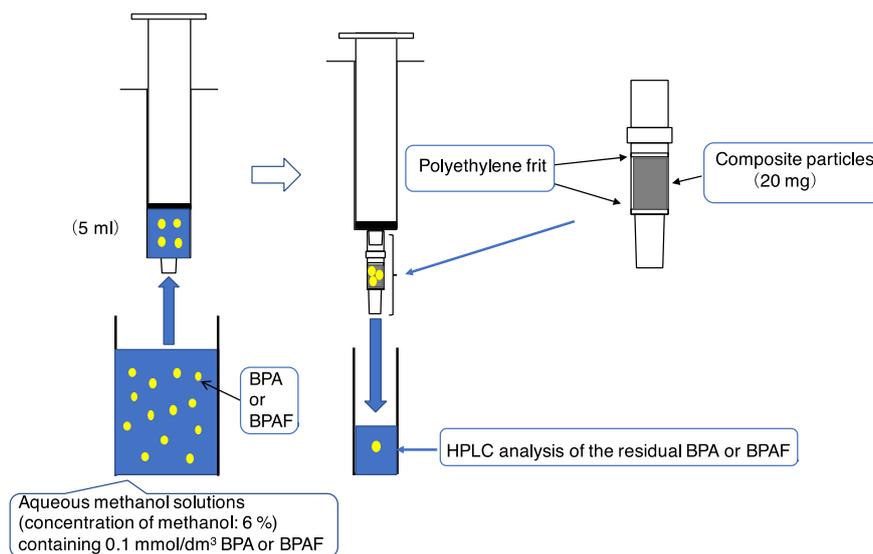
4) Adsorption of organic molecules by using the $R_F-(CH_2CHSiO_2)_n-R_F$ /CDPs composites

The traditional organic dyes in many industries such as plastics, textile and cosmetics are in general common water pollutants and we can detect trace quantities in industrial wastewater. Thus, it is very important to develop new technologies to eliminate them [40]. Hitherto, water-insoluble cyclodextrin polymers (CDPs) have been applied for the removal of various organic dyes from aqueous solutions [40]-[46]. From this point of view, it is deeply desirable to develop new CDP derivatives possessing a higher adsorption ability, compared to that of the pristine CDPs. Here our present $R_F-(CH_2CHSiO_2)_n-R_F$ /CDPs composites were investigated for adsorption of aromatic compounds such as bisphenol A and bisphenol AF in their aqueous methanol solutions. Schematic illustration for the adsorption process of bisphenol A (BPA) or bisphenol AF (BPAF) by using the solid-phase extraction cartridge connected with the polyethylene frit packed with the $R_F-(CH_2CHSiO_2)_n-R_F$ /CDPs composite powders is illustrated in **Scheme 2**. We have also investigated the adsorption ability of BPA and BPAF by using the pristine CDPs (20 mg), and the $R_F-(CH_2CHSiO_2)_n-R_F$ /PTFE (polytetrafluoroethylene) composites (20 mg) possessing a superoleophilic/superhydrophobic property [22] under similar conditions, for comparison. These results are shown in **Table 4**.

Table 4. Adsorption ratio (%) of BPA and BPAF using the $R_F-(CH_2CHSiO_2)_n-R_F$ /CDPs composites.

CDPs in the composites	Adsorption ratio (%)	
	BPA	BPAF
Run*		
	α -CDP	
19	47	52
10	-	34
	β -CDP	
20	100	93
11	-	94
	γ -CDP	
21	58	69
12	-	54
Pristine α -CDP	48	61
β -CDP	75	73
γ -CDP	59	64
$R_F-(CH_2CHSiO_2)_n-R_F$ /PTFE**	-	5

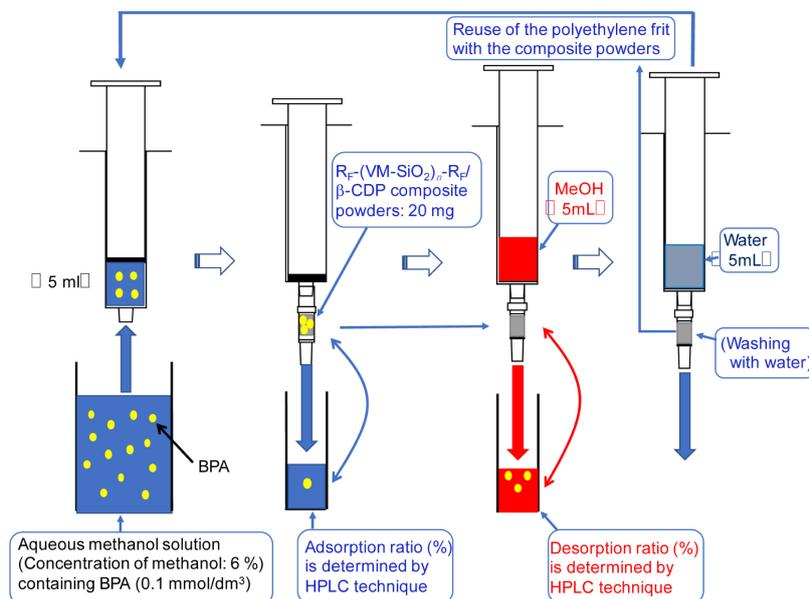
*Each Run No. corresponds to that of **Table 1**; **Preparative feed ratio of PTFE/oligomer (mg/mg): 100/300.



Scheme 2. Schematic outline for the analysis of the adsorption ratios of bisphenol A (BPA) or bisphenol AF (BPAF) by using the solid-phase extraction cartridge connected with the polyethylene frit packed with the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composite powders.

As shown in **Table 4**, the adsorption ability of BPA and BPAF is sensitive to the structures of CDPs in the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites, and the highest adsorption ability of BPA or BPAF was observed by the use of the β -CDP in the composites, respectively. It was also demonstrated that the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites can enhance the adsorption ability of BPA and BPAF, effectively than that of the pristine β -CDP under similar conditions, indicating that since the present $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites can exhibit a superoleophilic characteristic with a superhydrophobic property, such superoleophilic characteristic should interact strongly with oleophilic organic molecules in the aqueous solutions to give a higher adsorption ability; although the pristine β -CDP cannot possess such higher oleophilic property. Especially, the size-fitness of the interior cavity of β -CDP (not α - and γ -CDPs) in the composites toward BPA or BPAF can provide a higher adsorption ability to form the inclusion derivatives with such aromatic compounds. From this finding, it is suggested that the higher adsorption ratios of BPA or BPAF should be much related to the presence of CDPs in the composites. In fact, the $R_F-(CH_2CHSiO_2)_n-R_F/PTFE$ composites [22], which can exhibit a similar superoleophilic/superhydrophobic characteristic, were unable to provide the adsorption ability as shown in **Table 4**.

We tried to study on the reusability of the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composite powders (20 mg; Run 22 in **Table 1**) as the packing material for the solid-phase extraction cartridge for the adsorption and desorption of BPA. The Schematic outline for the recycling process for the adsorption and desorption of BPA by using the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composite powders as the packing material is shown in **Scheme 3**.



Scheme 3. Schematic outline for the recycling process for the adsorption and desorption of BPA by using the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composite powders as the packing material.

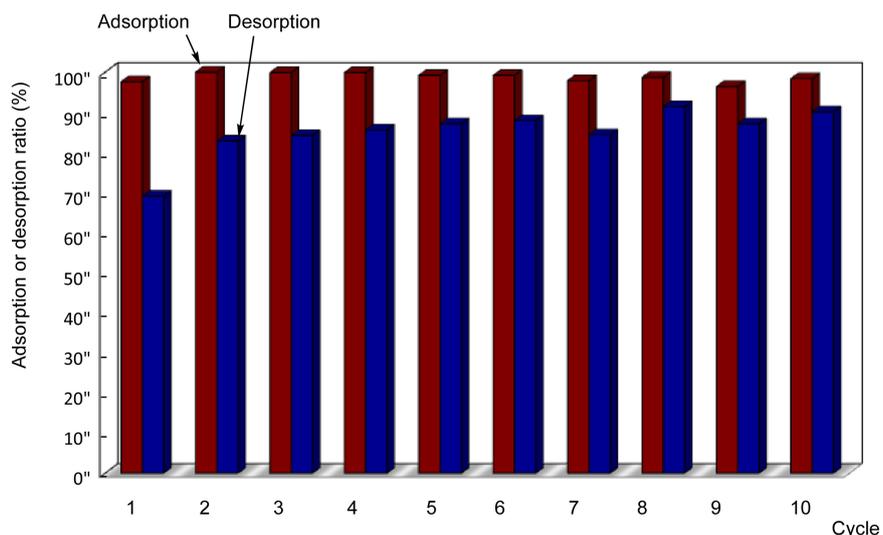
As shown in **Scheme 3** and **Figure 8**, a good recyclability was observed for the use of the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composite powders as the packing material for the adsorption and desorption of the BPA even after 10 cycle, and the adsorption and desorption ratios in each cycle are 98% - 100% and 69% - 91%, respectively. In this way, the present $R_F-(CH_2CHSiO_2)_n-R_F/CDP$ composites may be developed as the new adsorbent toward the aromatic molecules in their aqueous solutions, especially, the trace amounts of toxic aromatic compounds in industrial wastewater.

Recently, there is a serious problem in increasing environmental pollution, such as the discharge of the industrial wastewater including volatile organic compounds (VOC) [47] [48]. From this point of view, it is suggested that our present $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites would have high potential for the application of novel adsorbent toward not only aromatic compounds such as BPA but also a variety of VOCs. Thus, the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites (Runs19, 20 and 21 in **Table 1**) have been applied to the packing materials for the adsorption of VOCs such as benzene, toluene, xylenes, trichloroethylene, tetrachloroethylene, chloroform, and tetrachlorometane by using the head space-gas chromatograph/mass spectrometer (GC/MS) measurements (the analytical measurement outline: see **Scheme 4**). The adsorption ability of the VOCs was also studied by using the pristine CDPs under similar conditions, for comparison. The results are shown in **Table 5**.

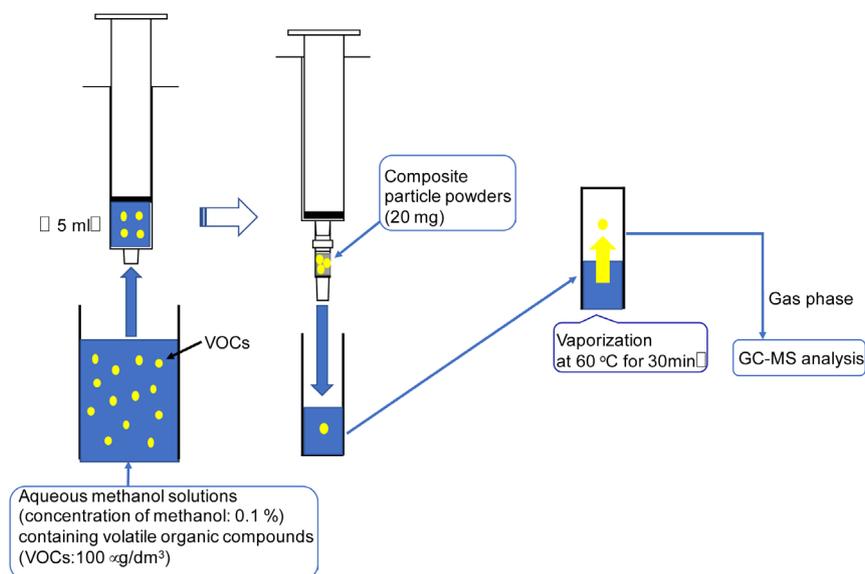
As shown in **Table 4**, the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites were found to exhibit a higher adsorption ability for VOCs, compared to that of the pristine CDPs. $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites can possess a higher adsorption ability, quite similar to that of BPA and BPAF illustrated in **Table 4**.

Table 5. Adsorption ratios of VOCs by the use of $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites (Run 20 in Table 1).

VOC	Adsorption ratio (%)					
	CDPs in the composites			Pristine CDPs		
	α -CDP	β -CDP	γ -CDP	α -CDP	β -CDP	γ -CDP
PhH	27	47	25	14	17	4
PhMe	67	73	69	18	15	6
<i>o</i> -Xylene	89	92	93	13	20	19
<i>m</i> - and <i>p</i> -Xylenes	94	95	95	24	21	18
CH ₂ = CHCl	3	0	6	13	4	3
Cl ₂ C = CH ₂	25	2	16	21	6	6
CHCl = CHCl (<i>cis</i>)	28	11	12	21	8	0
Cl ₂ C = CHCl	48	47	40	22	17	11
Cl ₂ C = CCl ₂	86	92	91	7	24	20
ClCH ₂ CH = CHCl (<i>cis</i>)	52	32	19	29	6	0
ClCH ₂ CH = CHCl (<i>trans</i>)	55	32	19	31	0	0
Cl ₂ CH ₂	15	1	6	14	1	0
CHCl ₃	23	35	15	15	12	0
CCl ₄	59	86	67	13	32	15

**Figure 8.** Relationship between the recyclability of the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites (Run 22 in Table 1) as the packing material, and the adsorption and desorption ratios of BPA in each cycle

In the adsorption of the mono and di-chlorinated VOCs such as CH₂ = CHCl, Cl₂C = CH₂, CHCl = CHCl, and Cl₂CH₂, the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites afforded a similar adsorption behavior to that of the pristine CDPs. However, in the cases of the tri- and tetra-chlorinated VOCs such as Cl₂C = CHCl, Cl₂C = CCl₂, CHCl₃, and CCl₄, interestingly, these VOCs can be easily adsorbed by the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites, especially by the



Scheme 4. Schematic outline for the analysis of the adsorption ratios of the VOCs by the head space-GC/MS measurements.

$R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites. These findings would be due to the increase of the oleophilicity of VOCs by introducing the additional chlorine atoms into VOCs; because the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites can possess a superoleophilic property to interact with more oleophilic organic molecules. On the other hand, dichlorinated VOCs such as $ClCH_2CH=CHCl$ (*cis* and *trans*) can give a higher adsorption ability than the pristine CDPs, quite different from the similar dichlorinated VOCs such as $CH_2=CHCl$ and $Cl_2C=CH_2$. This finding would be due to the longer carbon chains (three carbon chains) to give more oleophilic property.

In the cases of aromatic VOCs such as benzene, toluene, *o*-, *m*-, and *p*-xylenes, these aromatic VOCs are likely to interact with the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites to afford higher adsorption ratios than the pristine CDPs. Interestingly, higher adsorption ratios from 25% to 95% were obtained with the increase of the oleophobicity of the VOCs as following:

benzene < toluene < *o*-, *m*- and *p*-xylenes

More interestingly, the highest adsorption ability toward these VOCs was observed by using the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites. This finding is due to the size-fitness of the interior cavity of β -CDP toward these aromatic VOCs.

4. Conclusion

We have succeeded in preparing fluoroalkyl end-capped vinyltrimethoxysilane oligomer silica/ α -, β -, γ -cyclodextrin polymers (CDPs) composites [$R_F-(CH_2CHSiO_2)_n-R_F/CDPs$] by the sol-gel reactions of the corresponding oligomer in the presence of CDPs under alkaline conditions. These obtained fluorinated composites were found to exhibit a superoleophilic/superhydrophobic characteristic on the modified surface, although the corresponding fluoroalkyl

end-capped oligomeric silica nanoparticles can give an oleophobic/superhydrophobic property on the modified surface. The $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites possessing a superoleophilic/superhydrophobic characteristic have been applied to the packing material for the column chromatography to separate the mixture of oil/water and the W/O emulsions to isolate the transparent colorless oils. In addition, the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites have been also applied to the packing material for the solid-phase extraction cartridge to absorb the aromatic compounds such as BPA and BPAF in their aqueous solutions, and the highest adsorption behavior for these compounds was observed in the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDP composites. In addition to the adsorption of the aromatic compounds, the $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites have been also applied to the adsorption of the VOCs by the head-space-GC/MS technique. In a wide variety of VOCs, more oleophilic aromatic VOCs can afford a higher adsorption ability toward the present $R_F-(CH_2CHSiO_2)_n-R_F/CDPs$ composites, especially, the $R_F-(CH_2CHSiO_2)_n-R_F/\beta$ -CDPs composites, compared to that of the pristine CDPs. In the cases of chlorinated aliphatic VOCs, tri- and tetra-chlorinated VOCs can provide a higher adsorption ability toward the fluorinated CDPs composites, especially fluorinated β -CDP composites. These findings would be due to the effective oleophilic-oleophilic interaction between the oleophilic VOCs and the fluorinated CDPs composites possessing a superoleophilic property. In this way, our present fluorinated CDPs composites would have high potential for the development of not only the practical oil/water separation materials but also the new sorbents to remove the organic pollutants in the industrial wastewater.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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