Adsorption of benzene, aniline and benzoic acid in water by fullerene (C_{60}) and fullerene nanowhiskers

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Abstract.   Most aromatic hydrocarbons and their derivatives are harmful organic molecules. Despite their low solubility, trace amounts of aromatic hydrocarbons can be present in water. If water is contaminated by aromatic hydrocarbons, it is very difficult to remove these from water. Through contaminated water, these compounds can exert deleterious effects in plants and animals, as well as on human health. Fullerenes and their derivatives typically exhibit hydrophobic characteristics, and are therefore considered as good adsorbents for the removal of aromatic hydrocarbons. Herein, the removal of benzene, aniline and benzoic acid by fullerene and fullerene nanowhiskers was evaluated. While benzene was removed satisfactorily from water, aniline and benzoic acid were not, owing to the presence of ionized functional groups. However, adjustment of the solution pH to values where the functional groups of aniline or benzoic acid do not have any charge, resulted in an increase in their adsorption. High pH values were found to have a positive effect on the removal of aniline, while low pH values were beneficial for the adsorption of benzoic acid. Fullerenes and fullerene nanowhiskers were thus found to be promising adsorbents for the removal of aromatic hydrocarbons.

Keywords.   Adsorption; aromatic hydrocarbon; fullerene; fullerene nanowhiskers.

1. Introduction

Most aromatic hydrocarbons are harmful organic materials. Contact with them should be avoided as they can enter the body *via* the skin through osmotic pressure effects. It is believed that aromatic hydrocarbons damage genes, with the corresponding risks involving the development of cancer and other hereditary diseases [1–3]. Aromatic hydrocarbons are readily formed by incomplete combustion, either from household or natural forest fires. Although most aromatic hydrocarbons are barely soluble in water, they may still be present in aqueous bodies in very small amounts. Moreover, they can be readily transported by rain and snow, or in dust and volcanic ash. In addition, if pollutants such as aromatic hydrocarbons contaminate the rivers and oceans, animals and plants might endure unfavourable environments. Additionally, human beings may also be at risk by the consumption of products obtained from rivers and oceans, which are contaminated with these pollutants. Therefore, herein, the removal of aromatic hydrocarbons from water is investigated. In particular, aromatic hydrocarbons must be removed to provide acceptable drinking water, as even small amounts of solubilized aromatic hydrocarbons can have detrimental effects on our health.

The removal of aromatic hydrocarbons from water has been previously investigated using adsorbents made of clay

minerals and carbon materials [4–14]. A mesoporous material, folding silicate material (FSM)-16, was developed as an adsorbent to remove benzene, benzoic acid, toluene and phenol from aqueous media [4]. Mesoporous materials such as FSM-16 present a very wide surface area, and thus are expected to be excellent adsorbents for aromatic hydrocarbons [15]. However, the aforementioned aromatic hydrocarbons are barely adsorbed by FSM-16. In particular, most of benzene and toluene remain in water. FSM-16 is composed of silicate layers with hydroxide groups on its surface; therefore, the surface is more likely to interact preferentially with water molecules than aromatic hydrocarbons. Owing to this reason, very low amounts of benzene and toluene are adsorbed on the surface of FSM-16. However, benzoic acid was adsorbed more readily than benzene and toluene. It is likely that its carboxyl group favours its adsorption on FSM-16. The removal of aromatic hydrocarbons in water by clay minerals was also studied by Hashizume [5,6]. Talc and pyrophyllite are hydrophobic clays that are able to efficiently adsorb benzene and toluene. However, pyrophyllite did not effectively adsorb benzoic acid and aniline [6]. Although the authors did not investigate the adsorptive relationship between talc and benzoic acid or aniline, it is likely that talc is not able to adsorb aromatic hydrocarbons with hydrophilic functional groups. The removal of aromatic hydrocarbons has also been investigated using activated

carbons, carbon nanotubes (CNTs) and untreated wood skins [16–20]. de Souza *et al* [16] demonstrated the removal of benzene, toluene and *o*-xylene by activated carbon obtained from coconut shells. Such activated carbon was a good material for the removal of aromatic hydrocarbons, with the exception of hydrophilic aromatic hydrocarbons. Moreover, active carbons and other fruit-skin coals have been reported to exhibit similar behaviour to that of coconut-skin coal [21].

Fullerene is a nanomaterial discovered by Kroto *et al* [22]. Its hollow spherical structure is composed of 60 or 70 carbon atoms. The application of these fullerenes has been anticipated in fuel cells, conductors, solar cells and other areas [23–25]. In this context, Miyazawa *et al* [26] further developed fullerene nanowhiskers, which have also been applied in various devices such as field-effect transistors and solar cells.

Herein, we report the adsorption of aromatic hydrocarbons by fullerene (C_{60}) and fullerene nanowhiskers. The adsorption isotherms at different pH values were obtained for aniline and benzoic acid because their functional groups are charged depending on the pH of the solution. It is demonstrated that fullerene and fullerene nanowhiskers are promising materials for the removal of aromatic hydrocarbons (benzene, aniline and benzoic acid) from water.

2. Experimental

The aromatic hydrocarbons used in this study were benzene, aniline and benzoic acid. Benzene was purchased from Kanto Chemical Co. Inc., and aniline and benzoic acid from Wako Pure Chemical Industries Ltd. Deionized water was used in all the experiments. A benzene aqueous solution was prepared by stirring 100 cm^3 of benzene and 100 cm^3 of water in a 300 cm^3 flask with a stopper for 10 h. After stirring, the mixed solution was transferred to a separatory funnel and left to stand overnight, after which the benzene and aqueous solution was separated. The bottom layer, i.e., the benzene aqueous solution, in the funnel was isolated. In addition, 10 mmol dm^{-3} of aniline and benzoic acid solutions were prepared. The three solutions were diluted with water and the original and diluted solutions were used in adsorption experiments.

Fullerene (C_{60}) was purchased from MTR Ltd. and was used for adsorption experiments without any further treatment. The scanning electron microscopy (SEM: JEOL, JSM-6700FT) image of fullerene is shown in figure 1a, exhibiting a particle size smaller than 10 μm. The shape of fullerene granules is disordered. Fullerene nanowhiskers were prepared according to the method reported by Miyazawa *et al* [27]. The diameter of the fullerene nanowhiskers was ∼500 nm with a length of ∼20 μm (figure 1b).

For the adsorption experiments, 30 mg of fullerene or fullerene nanowhiskers and 6 cm^3 each of the aromatic hydrocarbon solutions were placed into a bottle with a stopper. The bottle was sealed tightly and shaken for 3 h. The solutions with the adsorbent were filtered using 0.2 μm disposal filters.
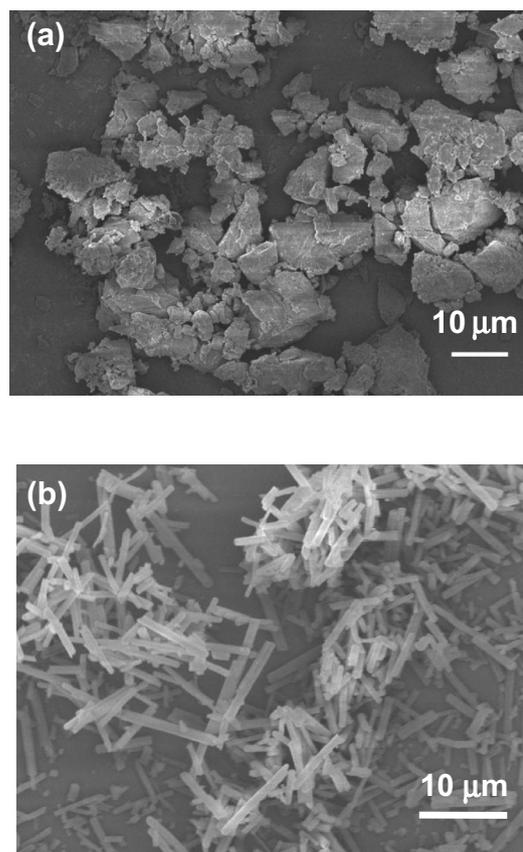

Figure 1. SEM images of: (**a**) fullerene and (**b**) fullerene nanowhiskers.

The filtered solutions were analysed using a total organic carbon analyser (Shimadzu, TOC-5000A). The carbon contents of the filtered and initial solutions were measured eight times, where six of the eight analytical values were used to obtain the mean concentration of carbon in the solutions. The six analytical values for which the coefficient of variation (CV) values (= standard deviation/mean value) were the lowest and were selected from the total eight values. The concentration of aromatic hydrocarbons was determined from the carbon content in the initial and treated solutions. The adsorption equation used is represented as $A = V(C_0 - C)/W$, where A (mol g^{-1}) is the extent of adsorption, V (dm^3) is the volume of the solution, C_0 (mol dm^{-3}) is the concentration of the initial solution, C (mol dm^{-3}) is the concentration of the filtered solution and W (g) is the mass of the adsorbent.

The time dependence of the adsorption with fullerene was evaluated. The stirring times were 10, 30, 60 and 180 min. In addition, an experiment at ca. 0 min was performed. For this test, 30 mg of fullerene was placed in a 10 cm^3 syringe with a 0.2 μm membrane filter. Next, 6 cm^3 of the benzene aqueous solution was poured into the syringe and, immediately, the solution was filtered by pushing the piston. The analytical method used was similar to that described above.

The functional groups of aniline and benzoic acid bear a charge depending on the pH value of the solution. Therefore, the pH values of the solutions for aniline adsorption were adjusted to 2.5, 5 and 8.5, while those of the benzoic acid samples were adjusted to 2, 4 and 11 using a 0.01 mol dm^{-3} solution of either HCl or NaOH.

3. Results

3.1 *Adsorption of benzene*

The variation in the adsorption with time is shown in figure 2. The adsorption extent after 180 min was similar to those after 30 and 60 min. Stirring for 180 min was thus sufficient to attain the adsorption equilibrium. The adsorption process likely proceeds immediately once fullerene comes into contact with the
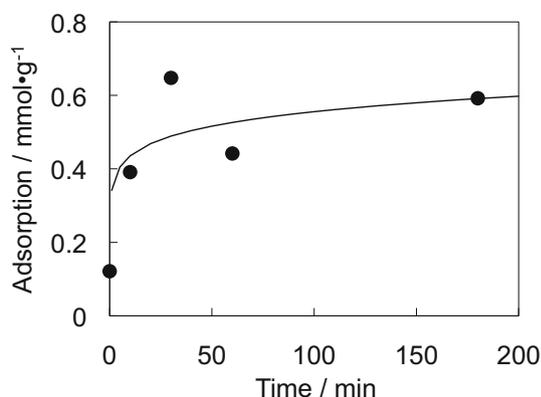
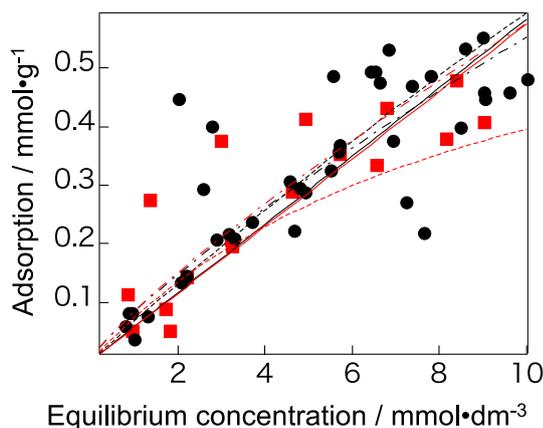**Figure 2.** Relationship between the adsorption of benzene by fullerene and the reaction time.

Figure 3. Isotherms for the adsorption of benzene by fullerene and fullerene nanowhiskers. The solid black circles and solid red squares refer to fullerene and fullerene nanowhiskers, respectively. The solid, dotted and dash-dotted lines show the Henry, Langmuir and Freundlich models, respectively. The black and red lines correspond to fullerene and fullerene nanowhiskers, respectively.

benzene aqueous solution, as half of the total amount adsorbed at equilibrium (180 min) is already removed in the experiment at ∼0 min.

Figure 3 shows the isotherms for the adsorption of benzene on fullerene and fullerene nanowhiskers. The extent of benzene adsorption increases linearly with the concentration of benzene. The behaviour with fullerene is very similar to that with fullerene nanowhiskers. Adsorption saturation was not attained with the concentration of benzene used in this study.

3.2 *Adsorption of aniline*

The isotherms for the adsorption of aniline by fullerene and fullerene nanowhiskers at pH 2, 5 and 8.5 and without pH adjustment (denoted as pH x) are shown in figure 4. The adsorption increases at high pH values. Fullerene nanowhiskers effectively adsorb aniline at pH 5 and 8.5, compared to the solutions at pH 2 and with no pH adjustment. Similarly, fullerene more effectively adsorbs aniline at pH 5 than at pH 2, 8.5 and the initial pH x. The adsorption with fullerene is negligible at pH x, while poor adsorption is observed at pH 2 and 8.5. At pH 5, the adsorption is better than that at other three pH values. The adsorption of fullerene shows linearity with the concentration of the solution. The adsorption extent is approximately 0.05, 0.03, 0.01 and 0 mmol g^{-1} at pH 5, 8.5, 2 and x at approximately 12 mmol dm^{-3} of the equilibrium concentration in figure 4, respectively.

For fullerene nanowhiskers, the adsorption at pH 5 was close to saturation, with a value of 0.2 mmol g^{-1} at an equilibrium concentration of 9 mmol dm^{-3} as shown in figure 4c. At pH 8.5, a plateau is observed in the isotherm at 0.15 mmol g^{-1}, at an equilibrium concentration of 5 mmol dm^{-3} and above. Without adjusting the pH (pH x), the adsorption isotherm linearly increases with the equilibrium concentration under the experimental conditions. At pH 2, the adsorption isotherm is very close to the horizontal axis, that is, aniline is barely adsorbed on the fullerene nanowhiskers. The extent of adsorption by fullerene is smaller than that by fullerene nanowhiskers at the same pH.

The changes in the adsorption isotherms at different pH values can be explained by the dissociation constant of aniline, pK = 4.87. At pH values below pH 4.87, aniline is positively charged; therefore, at pH 2, aniline becomes more hydrophilic. Contrarily, fullerene and fullerene nanowhiskers are hydrophobic. Therefore, adsorption does not occur between aniline and fullerene or fullerene nanowhiskers. At pH 5, some aniline molecules have a positive charge but most of them do not have any charge, while at pH 8.5, most aniline molecules are neutral. Fullerene nanowhiskers and fullerene can only adsorb aniline in a neutral state; therefore, aniline is more effectively adsorbed at pH 8.5 than at low pH values. The adsorption extent at pH 5 by fullerene nanowhiskers is almost the same as that at pH 8.5, indicating that saturation has likely been attained at pH 5 and 8.5.
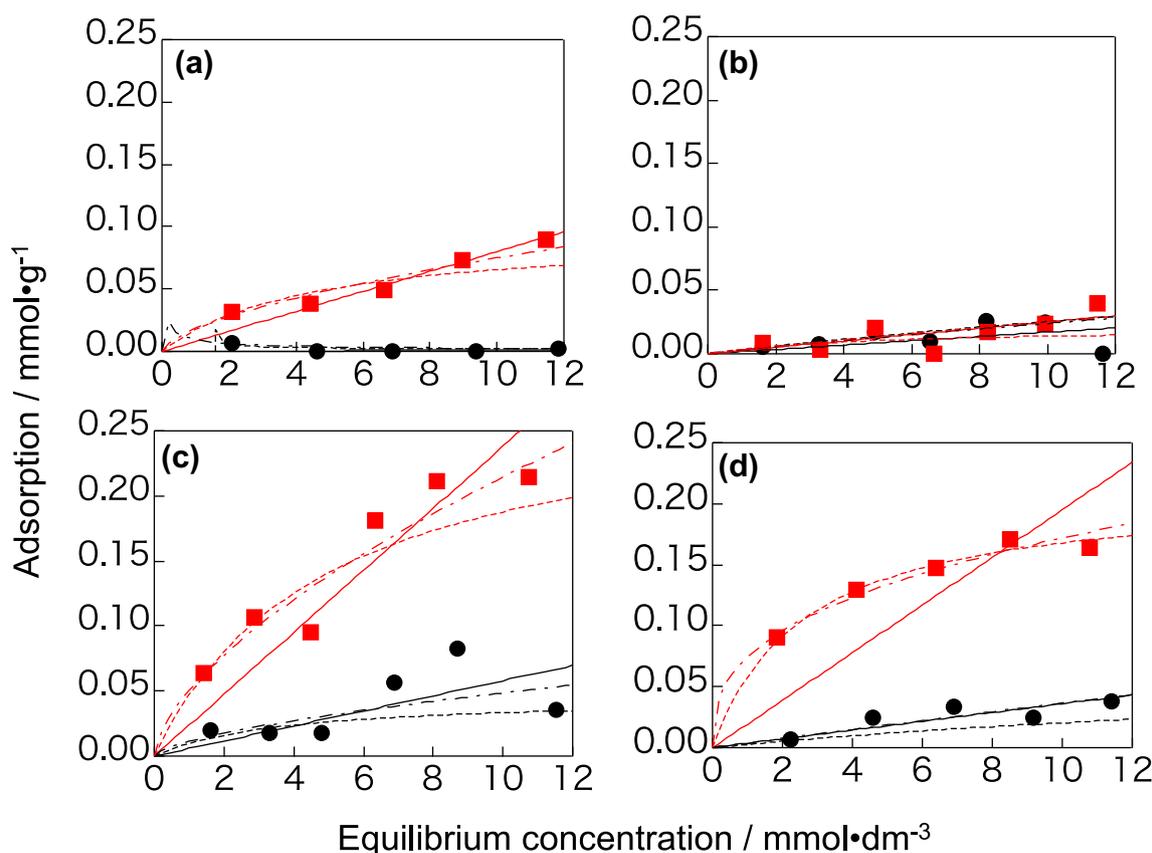
Figure 4. Isotherms for the adsorption of aniline by fullerene and fullerene nanowhiskers at pH (**a**) *x*, (**b**) 2, (**c**) 5 and (**d**) 8.5. The solid black circles and solid red squares refer to fullerene and fullerene nanowhiskers, respectively. The solid, dotted and dash-dotted lines show the Henry, Langmuir and Freundlich models, respectively. The black and red lines correspond to fullerene and fullerene nanowhiskers, respectively.

Fullerene nanowhiskers more effectively adsorb aniline than fullerene, except at pH 2. It is difficult to explain the different adsorption behaviour of these materials. The number of adsorption sites in fullerene may be different from that in fullerene nanowhiskers. As shown in figure 1, the purchased fullerene shows granular-shaped particles. The particle size is not uniform. Contrarily, the shape of fullerene nanowhiskers is typically like sticks. A number of adsorption sites in fullerene are located on its surface; however, all sites inside the granules will not contribute to the adsorption behaviour. In this work, fullerene nanowhiskers were prepared by recrystallization from a toluene solution of fullerene, and their adsorption sites were more accessible than those in granular fullerene.

3.3 *Adsorption of benzoic acid*

The isotherms for the adsorption of benzoic acid by fullerene and fullerene nanowhiskers at pH 2, 4 and 11 in figure 5 are almost linear with the equilibrium concentration. No plateaus are observed in the adsorption isotherms under the experimental conditions. For fullerene nanowhiskers, the adsorption at pH 2 is similar to that at pH 4. At pH 11, the adsorption is

very low, that is, benzoic acid is not adsorbed by fullerene nanowhiskers. The adsorption on fullerene at pH 2 is lower than that on fullerene nanowhiskers. In the case of fullerene, the isotherm at pH 2 is very similar to that at pH 4. At pH 11, the adsorption extent is lower than at pH 2 and 4. As shown in figure 5, the adsorption at pH 11 by fullerene is slightly lower than that on fullerene nanowhiskers. The reason for this difference in the adsorption with fullerene and fullerene nanowhiskers is the same as that described for the adsorption of aniline.

As benzoic acid contains a carboxyl group ($pK = 4.21$), it attains a negative charge at high pH values. At pH values below 4.21, benzoic acid is neutral, while at values above pH 4.21, benzoic acid is negatively charged. At pH 11, most benzoic acid molecules have a negative charge, hampering its adsorption on fullerene and fullerene nanowhiskers. The adsorption of benzoic acid by fullerene and fullerene nanowhiskers at pH 11 is lower than at pH 2 and pH 4. Since pH 4 is close to the dissociation constant, some benzoic acid molecules are ionized, while others remain neutral. The adsorption on fullerene and fullerene nanowhiskers at pH 4 is higher than at pH 11 and slightly lower than at pH 2, as most benzoic acid molecules bear no charge at this pH.
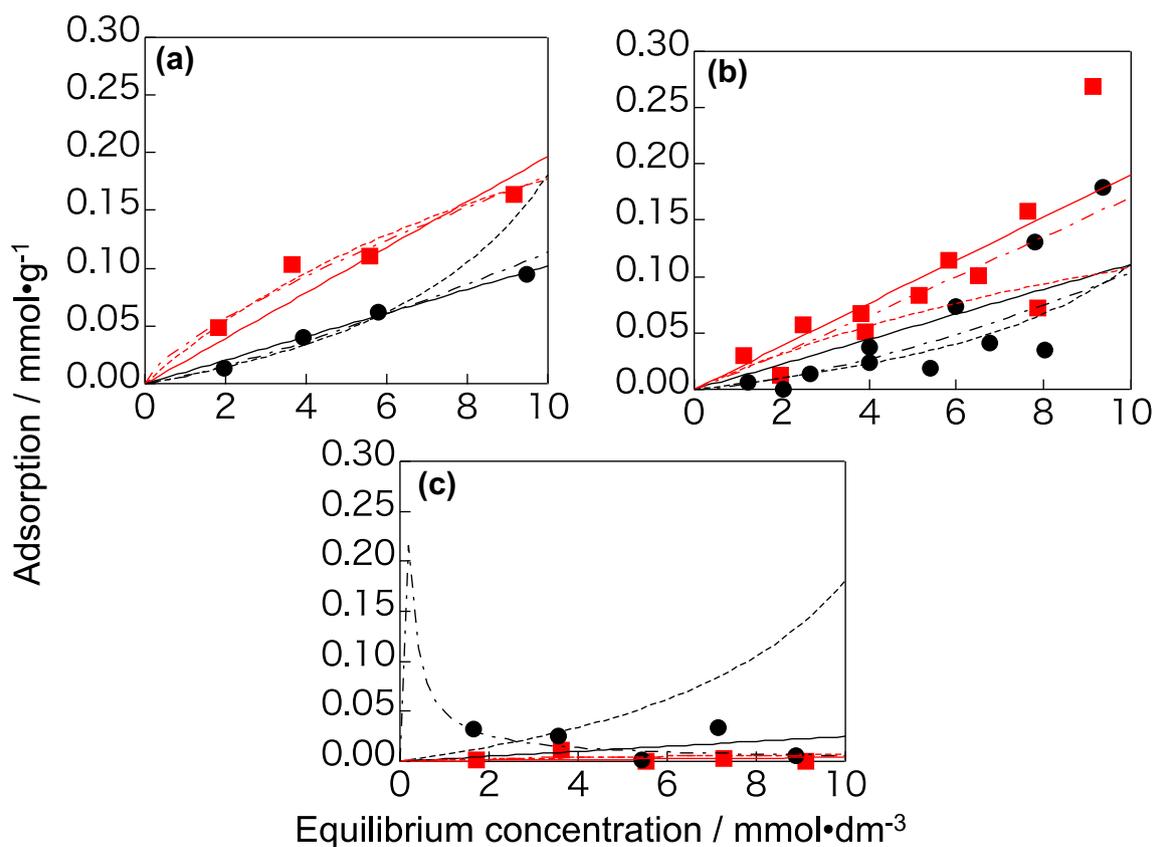
Figure 5. Isotherms for the adsorption of benzoic acid by fullerene and fullerene nanowhiskers at pH (**a**) 2, (**b**) 4 and (**c**) 11. The solid black circles and solid red squares refer to fullerene and fullerene nanowhiskers, respectively. The solid, dotted and dash-dotted lines show the Henry, Langmuir and Freundlich models, respectively. The black and red lines correspond to fullerene and fullerene nanowhiskers, respectively.

4. Discussion

4.1 *Comparison of the adsorption isotherms of benzene, aniline and benzoic acid*

The adsorption isotherms of fullerene and fullerene nanowhiskers were fitted to the Henry, Langmuir and Freundlich models following the equations:

Henry's equation: $A = K_h C$ (1)

Langmuir's equation: $A = aW_s C/(1 + aC)$ (2)

Freundlich's equation: $A = K_f C^{1/n}$ (3)

where A (mol g^{-1}) is the extent of adsorption, C (mol dm^{-3}) is the equilibrium concentration, K_h (g dm^{-3}) is the coefficient of Henry's equation, a is the coefficient for the adsorption equilibrium, W_s (mol dm^{-3}) is the extent of saturated adsorption in the Langmuir's equation, and K_f (g dm^{-3}) and n are the coefficients in Freundlich's equation. The fitting coefficients for the three equations are shown in tables 1 and 2. The R^2 values refer to the linear regression correlations. The fitting curves using the parameters from the adsorption

isotherms are shown in figures 3–5. For the adsorption of benzene (figure 3), the three equations show a similar trend in the case of fullerene; in contrast, the curved line for the Langmuir's equation in the case of fullerene nanowhiskers is lower than the other two lines. The adsorption isotherms for fullerene according to the Henry and Freundlich models are similar to those for the fullerene nanowhiskers. In figure 4, the experimental data have been fitted to the three equations. However, the experimental data for the adsorption by fullerene at pH x cannot be fitted by Langmuir's and Freundlich's equations at low concentrations in figure 4a as the extents of adsorption at pH x are very low and the data points are significantly dispersed. In figure 5, most fitting curves are consistent with the plotted data, with the exception of the adsorption isotherm of fullerene at pH 11. This is because the extent of adsorption is very low and the data points are widely scattered, as in the above-mentioned case for aniline adsorption by fullerene at pH x.

As shown in figures 3–5, both fullerene nanowhiskers and fullerene adsorb benzene more efficiently than aniline and benzoic acid. As the surfaces of fullerene and fullerene nanowhiskers are highly hydrophobic, benzene, which does not have any hydrophilic functional groups, is easily adsorbed

Table 1. Coefficients of the Henry's, Langmuir's and Freundlich's equations for fullerene.

	Henry		Langmuir			Freundlich		
	K_h	R^2	a	W_s	R^2	K_f	n	R^2
Benzene	0.058	0.55	0.014	4.75	0.75	0.083	1.22	0.76
Aniline								
pH x	0.0001	0.31	−0.70	0.0020	1	0.0093	−1.73	1
pH 2	0.0017	0.16	0.022	0.022	0.86	0.0031	1.13	0.81
pH 5	0.0058	0.29	0.046	0.27	0.36	0.011	1.58	0.47
pH 8.5	0.0036	0.61	0.38	0.21	0.91	0.0038	1.02	0.80
Benzoic acid								
pH 2	0.010	0.99	−0.066	−0.095	0.98	0.0066	0.81	0.98
pH 4	0.011	0.54	−0.062	−0.069	0.95	0.0035	0.68	0.75
pH 11	0.0025	0.90	−0.67	0.0036	0.48	0.049	−1.09	0.22

Table 2. Coefficients of the Henry's, Langmuir's and Freundlich's equations for fullerene nanowhiskers.

	Henry		Langmuir			Freundlich		
	K_h	R^2	a	W_s	R^2	K_f	n	R^2
Benzene	0.058	0.60	0.11	0.77	0.48	0.085	1.20	0.66
Aniline								
pH x	0.0080	0.89	0.22	0.096	0.81	0.018	1.63	0.89
pH 2	0.0025	0.53	0.21	0.020	0.16	0.0031	1.11	0.54
pH 5	0.024	0.74	0.20	0.28	0.88	0.052	1.59	0.89
pH 8.5	0.020	0.87	0.038	0.075	0.92	0.074	2.75	0.96
Benzoic acid								
pH 2	0.019	0.80	0.077	0.41	0.98	0.034	1.39	0.95
pH 4	0.019	0.65	0.063	0.28	0.36	0.016	0.96	0.69
pH 11	0.0004	0.32	0.077	0.016	0.53	0.0020	2.08	0.13

on them. The adsorption of benzene by fullerene and fullerene nanowhiskers is likely facilitated by the hydrophobic interactions. Moreover, fullerene and fullerene nanowhiskers have π-electrons, similar to benzene. The interactions between these π-electrons also affect the adsorption behaviour [28]. The mechanism of adsorption can be related to the solvation between fullerene or fullerene nanowhiskers and benzene. In contrast, aromatic hydrocarbons with hydrophilic functional groups such as aniline and benzoic acid are barely adsorbed on fullerene and fullerene nanowhiskers. After pH adjustment, aniline and benzoic acid become neutral molecules, and are more easily adsorbed by fullerene and fullerene nanowhiskers than in the ionized form. The different adsorption behaviour of benzene and aniline/benzoic acid by fullerene and fullerene nanowhiskers can be explained by the polarization effects on the molecules, that is, fullerene and fullerene nanowhiskers more effectively adsorb benzene than aniline and benzoic acid even when they are not charged. The amino group of aniline and the carboxyl group of benzoic acid still possess

small $+\delta$ and $-\delta$ charges on the nitrogen or oxygen atoms, respectively. Therefore, the adsorption of aniline and benzoic acid on fullerene and fullerene nanowhiskers is generally difficult. In addition, the hydration of aniline and benzoic acid can possibly prevent the adsorption of aniline and benzoic acid on fullerene and fullerene nanowhiskers.

4.2 *Comparison of the adsorption of benzene, aniline and benzoic acid by fullerene and fullerene nanowhiskers with that using carbon materials and clay minerals*

The adsorption of aromatic hydrocarbons has been investigated using other carbon materials, such as CNTs and active carbon. Su *et al* [29] reported the adsorption of benzene, toluene, ethylbenzene and *p*-xylene by CNTs, NaOCl-oxidized CNTs and granular activated carbon (GAC). GAC adsorbed four of these aromatic hydrocarbons effectively, whereas the performance of CNTs was poor. The extent of adsorption of benzene by GAC was ten times higher than that

Table 3. Parameters of the Henry, Langmuir and Freundlich models for the adsorption of benzene, aniline and benzoic acid by talc [5], pyrophyllite [6] and FSM-16 [4].

| | Talc | | | | | Pyrophyllite | | | | | FSM-1 |
| | Henry | Langmuir | | Freundlich | | Henry | Langmuir | | Freundlich | | Henry |
	K_h	a	W_s	K_f	n	K_h	a	W_s	K_f	n	K_h
Benzene	0.208	0.00498	41.5	0.211	1.004	0.173	0.202	1.169	0.1948	1.194	0.0156
Aniline	—	—	—	—	—	0.0025	−0.028	−0.054	0.0012	0.776	—
Benzoic acid	—	—	—	—	—	0.0025	−0.102	−0.0046	0.0006	0.611	0.00491

by CNTs. The adsorption of benzene on CNTs is similar to that on the fullerene or fullerene nanowhisker materials employed in this work. Goto *et al* [30] reported the adsorption of benzene and nitrobenzene by bead-shaped activated carbon (BAC), which efficiently adsorbed benzene and nitrobenzene. Upon modification of the surface of BAC *via* treatment with HNO_3 or $KMnO_4$, the adsorption performance decreased compared to that of the original BAC. This was ascribed to the increase in the number of carboxyl groups on the BAC surface. The adsorption isotherms for fullerene and fullerene nanowhiskers were similar to those for BAC treated with HNO_3. In general, the adsorption by BAC was superior to that obtained in this work.

Some clay minerals can also adsorb aromatic hydrocarbons. Such clay minerals, such as talc, pyrophyllite and serpentine, do not have any surface charges. As their surface ideally bears no charges, benzene and toluene should be easily adsorbed on these materials. Indeed, it has been reported that talc and pyrophyllite are able to efficiently adsorb benzene [5,6]. Contrarily, the adsorption of hydrophobic organic compounds such as benzene is not favoured on materials with surface charges such as FSM-16 [4]. The parameters of the Henry, Langmuir and Freundlich models for the adsorption isotherms of benzene, aniline and benzoic acid by FSM-16, talc and pyrophyllite are summarized in table 3. Upon comparison of the adsorption isotherms of benzene on fullerene nanowhiskers, fullerene, talc and pyrophyllite, the Henry parameters for talc and pyrophyllite are larger than those of fullerene nanowhiskers. Additionally, fullerene and benzene are barely adsorbed on FSM-16, while benzoic acid is barely adsorbed on pyrophyllite, fullerene and fullerene nanowhiskers. In contrast, FSM-16 is able to adsorb benzoic acid effectively. This is because the surface of FSM-16 possesses exposed hydroxide groups, thus favouring the adsorption of benzoic acid.

5. Conclusion

The adsorption isotherms of aromatic hydrocarbons on fullerene and fullerene nanowhiskers are reported. Benzene is more efficiently adsorbed on fullerene nanowhiskers and fullerene than aniline and benzoic acid. Aromatic

hydrocarbons with hydrophobic functional groups are more favourably adsorbed by fullerene and fullerene nanowhiskers. Contrarily, aromatic hydrocarbons with hydrophilic functional groups, such as aniline and benzoic acid, are barely adsorbed on fullerene and fullerene nanowhiskers. However, upon adjusting the pH, the functional groups of the aromatic hydrocarbons are neutralized and fullerene and fullerene nanowhiskers are able to adsorb such compounds. Fullerene and fullerene nanowhiskers thus exhibit good characteristics for the removal of aromatic hydrocarbons, and are promising adsorbents for the removal of aromatic hydrocarbons and other harmful hydrophobic organic molecules, with a similar efficiency to that of clay minerals such as talc and pyrophyllite.

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