Ordered Mesoporous Carbon as an Efficient and Reversible Adsorbent for the Adsorption of Fullerenes

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ABSTRACT. An ordered mesoporous carbon, CMK-3, was synthesized using mesoporous siliceous material, SBA-15, as the template. The CMK-3 was characterized and used for the adsorption of fullerenes, C_{60} and C_{70}. It was found that the adsorption capacity of CMK-3 is four times higher than that of activated carbon (AC), while the other two adsorbents being investigated, alumina and silica gel, have little adsorption capacity for fullerenes. A detailed study was undertaken to determine the adsorption equilibrium isotherms of C_{60} and C_{70} on CMK-3 for both single and binary systems. The reversibility of fullerene adsorption on CMK-3 was also studied. It was found that nearly 24 % adsorbed C_{60} and 8 % adsorbed C_{70} can be desorbed from CMK-3 within 10 minutes at 25 ℃ when a volume of 200 ml pure toluene is used to desorb 25 mg of pre-saturated adsorbent in a batch desorption process. The effects of time, volume of toluene, and temperature on the desorption of fullerenes from CMK-3 were examined. It was shown that the volume of toluene and the temperature are two important factors for fullerenes, especially for C_{70}, to be desorbed from CMK-3. Increasing the volume and the temperature will help C_{70} to be desorbed from CMK-3. The above results indicate that CMK-3 is an efficient and reversible adsorbent for the separation of fullerenes by adsorption.

KEYWORDS: mesoporous carbon; fullerenes C_{60} and C_{70}; adsorption; desorption.

• Introduction

The discovery of fullerene series, C_{60} and C_{70}, was first reported by Kroto, Curl and Samlley in 1985.[1] Fullerenes are described as the third form of ordered carbon having a structure very different from diamond and graphite. Over the last decade many scientists have been intrigued by the exploitation of the physical and chemical properties of these novel molecules.[2] It is found that fullerenes has installed in scientists a variety of application hopes, such as superconductors, large-scale industrial catalysts, and perhaps even antiviral agents.[3] Because the preparation of pure fullerene compounds on a large scale is very difficult, the number of their successful applications is still limited.[4] This academic interest and enthusiasm in fullerene science has prompted us to develop a safe, fast, effective, and inexpensive method for the separation and purification of fullerenes, which can produce large quantities of pure C_{60} and C_{70}, the most popular members of the fullerene family.[5]

The main methods for the separation and purification of C_{60} and C_{70} are selective complexation,[6-10] fractional crystallization,[11-14] and liquid chromatography.[15-19] Fractional crystallization is a very useful method to separate C_{60} and C_{70}, but it requires stirring for a long time at elevated temperature, and repeating the precipitation-filtration sequence a few times.[20] Liquid chromatography seems to be so far the most convenient method for the laboratory-scale separation of C_{60} and C_{70}, but it also has fundamental limitations in its application.[4] The most serious problem limits the application of liquid chromatography is the unavailability of an effective and reversible adsorbent for fullerene adsorption. Many researchers have carried out studies on the adsorption of fullerenes on different adsorbents. Taylor[16] firstly used neutral alumina as the stationary phase to separate C_{60} and C_{70} and found that large amounts of expensive alumina and intensive labor are needed. Then, activated carbon, for its huge specific surface area and high adsorption capacity, becomes the most popular adsorbent for fullerene separation during the following years.

The high capacity of activated carbon to adsorb C_{60} and C_{70} allows the quantity of the stationary phase to be reduced.[19] However, the drawback of this method is the microporous structure of activated carbon (AC), leading to irreversible adsorption of some C_{60} and nearly all of the C_{70}. The discovery of ordered mesoporous materials[21-25] has opened new possibilities in the field of adsorption and catalysis. The template synthesis of ordered mesoporous materials has received widespread attention recently since this technique allows the preparation of materials with a controllable architecture.[26] In 2000, in order to solve the irreversibility problem in fullerene adsorption, Piwonski et al.[27] first reported the adsorption of pure C_{60} from toluene solution on ordered mesoporous silica material, MCM-41. Although the amount of C_{60} adsorbed on MCM-41 was much smaller than that obtained with AC,[4] the whole process appeared to be completely reversible. This quality gave MCM-41 certain advantages over other stationary phase materials. Thus, if a new adsorbent can be found, which not only have a good adsorption ability for fullerene, but also is reversible for this process, the overall cost of fullerene production can be significantly reduced.[4] Ordered mesoporous carbon, which has a well-defined mesoporous pore structure, a large surface area, and a high adsorption capacity, is an ideal adsorbent to solve the problems in fullerene adsorption.

In this study, a new type of adsorbent, ordered mesoporous carbon (CMK-3) is synthesized in our group and firstly used for the adsorption of fullerenes for both single and binary systems.

• Materials and Methods

Synthesis of CMK-3. Siliceous material SBA-15 was synthesized by the sol-gel method. The tri-block copolymer (Pluronic 123, pure, Aldrich) and the organic silica material, tetraethylorthosilicate (TEOS, 98 %, Aldrich), were employed as sources of template and silica, respectively. In a typical synthesis, 4 g of Pluronic 123 was first dissolved in 150 g of 1.6 M HCl to form a template solution. It was then stirred vigorously until a milky solution was observed, followed by adding 8.5 g of TEOS into the milky solution at 35 ℃. The resulting solution was aged at 35 ℃ for 24 h and subsequently at 110 ℃ for another 24 h. Afterwards, the SBA-15 was obtained by calcination at 550 ℃ for 9 h in air.

The template-free SBA-15 material was then used as a mold for the synthesis of mesoporous carbon. Sucrose and sulfuric acid were used as the carbon source and the dehydrating agent, respectively. Sucrose solution is obtained by dissolving 1.25 g of solid sucrose into 5 ml of water. Then, 0.14 g of sulfuric acid was added into the sucrose solution under stirring. Finally, 1 g of the template-free SBA-15 was impregnated in the acid-containing sucrose solution and the mixture was put into an oven at 100 ℃ for 6 h and subsequently at 160 ℃ for another 6 h. The impregnation step was repeated once again but with different amounts of the substances (0.8 g sucrose, 0.09 g H_2SO_4, and 5 ml H_2O). After the impregnation step, the dark brown solid products, which were the composites of carbon and SBA-15, was carbonized at 1050 ℃ under vacuum for 6 h. The generated black powders (composites) were leached with a mixture of ethanol and 1 M sodium hydroxide solution to remove the silica, and further recovered by filtration, washed with distilled water and dried at 60 ℃ overnight to produce the ordered mesoporous carbon (CMK-3).

Fullerenes. C_{60} (99.5 %) and mixture of fullerenes (approx. 79 % C_{60}, 13 % C_{70}) were supplied by Frontier Carbon Corp., Japan. C_{70} (98 % +) was obtained from Nano-C, USA.

Characterization. Low angle X-ray diffraction patterns of samples were recorded with a powder x-ray diffraction system (Model X'pert, Panalytical). The step width was 0.02°at an acquisition time of 8 s per step in the range of $2\theta = 0.85° – 5.0°$. TEM image was obtained using a JEOL JEM-2010F transmission electron microscope. The TEM image was taken from the thin edges of carbon particles mounted on a porous carbon grid.

Nitrogen adsorption isotherms were measured with an ASAP2010 adsorption analyzer (Micromeritics) at liquid nitrogen temperature. Prior to the measurements, all the samples were degassed at a temperature of 200 ℃ for 6 h. The adsorption data in the relative pressure range from 0.04 to 0.2 were used to determine the BET surface area. The pore size distribution (PSD) was calculated by the BJH method from the desorption branch.

Measurement of Concentrations of C_{60} and C_{70}. High Performance Liquid Chromatography (HPLC) was used to determine the concentrations of C_{60} and C_{70} in the solution. Different known concentrations of pure C_{60} and pure C_{70} solutions in toluene were prepared to calibrate the relationship between the peak area and the fullerene concentration, which was found to be linear. The HPLC analysis was performed on a Hewlett Packard I090 liquid chromatography equipped with a YMC-Pack ODS-A column (4.6×150 mm). The detection was performed with UV-visible light at 330 nm. Toluene/2-propanol (1:1 v/v) was used as the mobile phase and the flow rate was set to 1 ml/ min.

Determination of Fullerene Adsorption Equilibrium Isotherm on Different Adsorbents. The time required for the adsorption of fullerene to reach equilibrium on different adsorbents was studied in a batch system. Because the adsorption equilibrium time is much longer for a binary system than a single component system, a mixture of C_{60} and C_{70} was used to determine the required equilibrium time. Once this equilibrium time is obtained, it is used to measure the adsorption equilibrium isotherms of pure C_{60} and pure C_{70} as well as their mixture. The adsorption process of mixed C_{60} and C_{70} from its solution in toluene (initial concentration of fullerene was 100 mg/L, weight ratio of C_{60}:C_{70} = 79:13) by different adsorbents at 25 ℃ was studied in a batch system. The four adsorbents were alumina, activated carbon mixed with silica gel (weight ratio is 1:1), activated carbon, and ordered mesoporous carbon (CMK-3). The alumina was Aluminium Oxide 90 Active Neutral for column chromatography, 0.063-0.2 mm (70-230 mesh ASTM) supplied by Merck. Activated carbon was Norit Row 0.8 Supra supplied as cylindrical extrudate but cruched into around 0.1 mm particles before usage, and silica gel was Silica gel 60, (0.04~0.063 mm) for column chromatography, (230-400 mesh ASTM), also supplied by Merck. The weight of each adsorbent used was 25 mg. The adsorption solution volume was 20 ml. During the adsorption process, samples were drawn out (0.3 ml per sample) at different time intervals and the fullerene concentrations in the samples are analyzed by the HPLC.

Adsorption isotherms of Binary C_{60} and C_{70} on Different Adsorbents. Once the time required to reach equilibrium was determined (24 hours), it was used to measure the adsorption equilibrium isotherms of fullerenes on CMK-3 and AC at 25 ℃. A volume of 20 ml of different initial concentrations of fullerene in the toluene solutions was mixed with 25 mg adsorbent and stirred for 24 hours for the equilibrium to be established.

Adsorption of pure C_{60} and pure C_{70} on CMK-3. The adsorption equilibrium isotherms of pure C_{60} and pure C_{70} on CMK-3 at 25 ℃ were measured by changing the initial concentrations of pure C_{60} or pure C_{70} solutions. The weight of CMK-3 was 25 mg. The adsorption volume was 20 ml. After 24 h, the adsorption equilibrium was reached in the system.

Desorption of pure C_{60} and pure C_{70} from CMK-3 and AC.

25 mg of CMK-3 or AC was placed in 200 ml solution of 100 mg/L pure C_{60} or C_{70} at 25 ℃ for 24 h for the equilibrium to be established. Then the solution was filtered and the solid was dried under vacuum at 60 ℃ for 10 h to remove toluene. The recovered solid was then placed in 200 ml fresh toluene to start the desorption of pure C_{60} or pure C_{70}.

Effect of solvent volume on the desorption of pure C_{60} and pure C_{70} from CMK-3

25 mg of dried CMK-3 pre-saturated with pure C_{60} or C_{70} was placed in different toluene volumes of 50 ml, 150 ml, 250 ml, 450 ml, 650ml, 1000ml for the desorption to proceed. The desorption time for each desorption volume was 12 h.

Effect of temperature on the desorption of pure C_{60} and pure C_{70} from CMK-3

25 mg of dried CMK-3 pre-saturated with pure C_{60} or C_{70} was placed in 250 ml fresh toluene. Again the desorption time was 12 h. The desorption was done for different temperatures. The recovered CMK-3 was placed into another 250 ml fresh toluene solution to start the second desorption cycle. This was repeated for 4 desorption cycles.

• Results and Discussion

The structures of SBA-15 template and the corresponding CMK-3 were studied using low angle XRD. Their XRD patterns are shown in Figure. 1. The well resolved XRD peaks of SBA-15 which can be assigned to (100), (110), and (200) diffractions, indicate that such a material has an ordered structure with 2-D hexagonal symmetry. Therefore, CMK-3 should have a hexagonal structure, which corresponds to the negative replication of silica template. The XRD pattern of CMK-3, characteristic of the hexagonal structure, was similar to that of SBA-15 as shown in Figure. 1. The d-spacing values of the peak (100) of SBA-15 and CMK-3 are 9.7 nm and 8.3 nm, respectively.

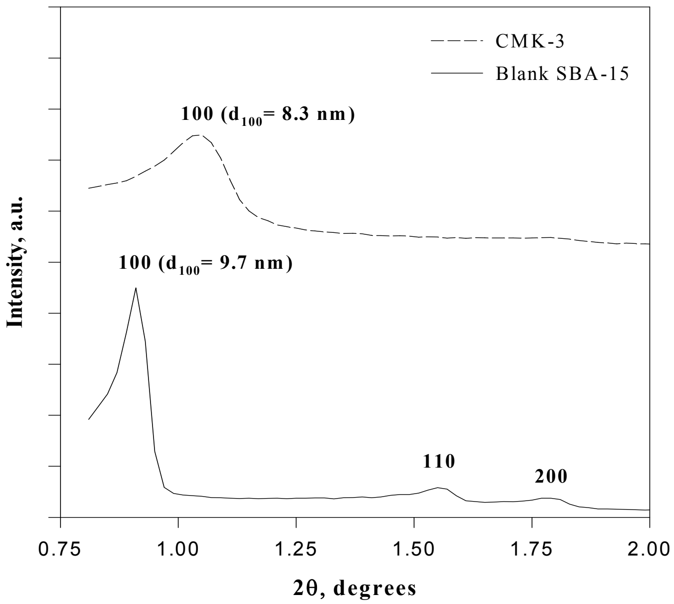

Figure 1. XRD spectrums of SBA-15 and CMK-3

The transmission electron microscopy (TEM) image of the CMK-3 mesoporous carbon was shown in Figure 2, which illustrates the hexagonal arrays of carbon rods, 6.5 nm diameter, similar to the structure of CMK-3 reported in the literature.

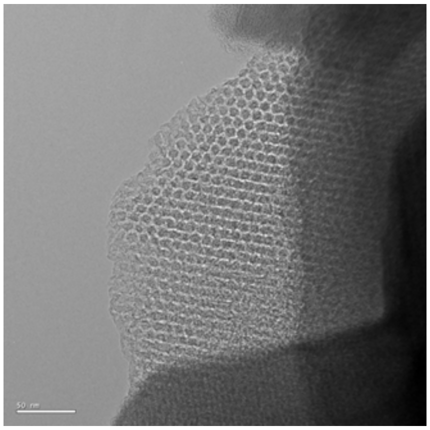

Figure 2. TEM image of CMK-3

The porosity of the SBA-15 and CMK-3 were investigated by nitrogen sorption measurements. The isotherms are presented in Figure. 3. The corresponding pore structure parameters, including BET surface area, mean pore diameter and particle size, are listed in Table 1 together with those of Norit activated carbon for comparison. The nitrogen sorption isotherm (Fig. 3) is of essentially type IV with a small hysteresis loop, indicating that the pore structure of CMK-3 is reasonably regular. Compared with SBA-15, CMK-3 has a smaller pore size and a higher surface area.

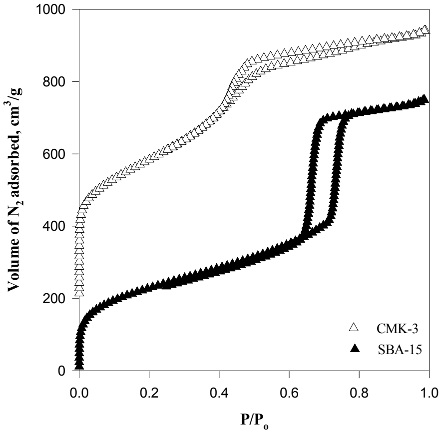

Figure 3. Nitrogen sorption isotherms of SBA-15 and CMK-3

Table 1. Texture parameters of SBA-15, the corresponding CMK-3 and AC

Sample	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	V_{im} (cm^3 g^{-1})	Pore Size (nm)
SBA-15	815	1.02	0.06	6.5
Ordered Mesoporous Carbon (CMK-3)	1366	1.14	0.12	3.5
Norit Row 0.8 Supra (AC)	911	1.18	0.58	1.16

V_t, total pore volume calculated at $p/p_0= 0.99$. V_{im}, microporous volumes (diameter < 2.0 nm) calculated by (Haba and Kleinert) HK method.

The pore size distributions of SBA-15 and CMK-3 are shown in Figure. 4, which possess mode values of. 6.5 nm and 3.5 nm, respectively. For comparison, the pore size distribution of Norit activated carbon is also plotted in Figure 4, which has a peak at around 1.1 nm, much smaller than those of SBA-15 and CMK-3. The specific pore size of the CMK-3 depends on both the wall thickness of SBA-15 and also the structural shrinkage effect during the carbonization process. It is noted that such a pore size (3.5 nm) is large enough for the adsorption of large organic molecules such as benzene, toluene, dyes, and especially in this study, fullerenes.

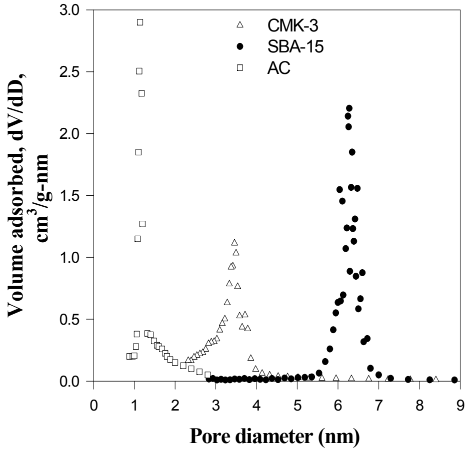

Figure 4. Pore size distributions of SBA-15, CMK-3 and AC

Fullerene Adsorption Equilibrium Time on Different Adsorbents. Figure 5. shows the binary adsorption process of C_{60} and C_{70} at 25 □ on four different adsorbents versus time. The four adsorbents were silica gel, neutral alumina, Norit activated carbon Row 0.8 Supra (AC) and CMK-3. It is seen that the adsorbed phase concentration becomes stable after 10 h for all CMK-3, AC and silica gel. Alumina has nearly no adsorption capacity for fullerenes and the process is very slow. Because the adsorption process is quicker for a single component system than a binary system, 24 h was considered long enough to reach adsorption equilibrium and was chosen as the equilibrium time in the following experiments for both single and binary systems.

It is also seen that alumina and silica gel have almost no adsorption capacity for both C_{60} and C_{70}. The two carbon based adsorbents, AC and CMK-3, showed significant adsorption capacity for the fullerenes. The difference in the adsorption capacity of different adsorbents may be explained by the interaction between fullerenes and the adsorbents. CMK-3 and AC are carbon based materials. Fullerenes are also made up of carbon atoms. Therefore, the adsorption of fullerenes on AC and CMK-3 is caused by the π-π interaction between the fused aromatic rings in the pores of carbons and the surface of fullerenes. This interaction is much stronger than the Van der Waals forces between the pores of alumina/silica gel and the surface of fullerenes.

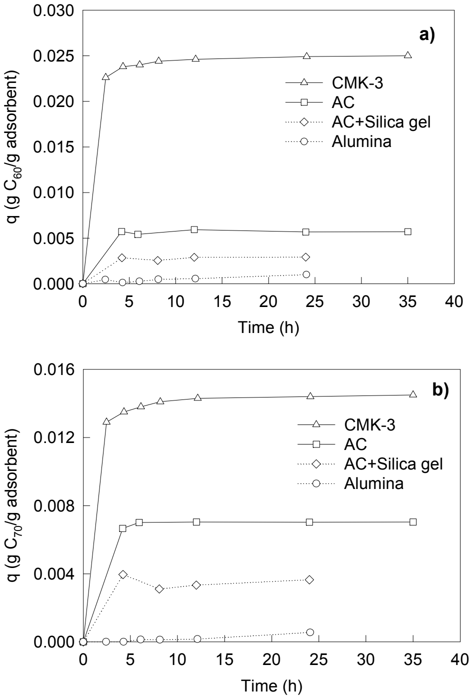

Figure 5. Binary adsorption of C_{60} and C_{70} versus time on different adsorbents:
(a) C_{60}; (b) C_{70}.

Binary Adsorption Isotherms of C_{60} and C_{70} on Different Adsorbents. The binary adsorption equilibrium isotherms of fullerenes on CMK-3 and AC are shown in Figures 6. It is seen that the adsorption capacity of fullerenes on CMK-3 is nearly four times higher than that on activated carbon. This indicates that ordered mesoporous carbon is a more effective adsorbent than activated carbon for the adsorption of fullerenes. This can be explained by the pore size distribution and pore structure of these two adsorbents. Because the size of C_{60} and C_{70} molecules is around 1.0 nm to 2.0 nm, CMK-3, having a well-defined mesoporous structure and a pore size distribution centered at 3.5 nm, can accommodate the molecules of fullerenes efficiently. However, activated carbon is a microporous material and its pore size distribution is peaked at 1.1 nm, as shown in Figure 4. This pore size is too small to adsorb fullerenes.

Since CMK-3 is the best adsorbent for binary C_{60} and C_{70} adsorption, further study on the adsorption of fullerenes on CMK-3 will be carried out as below.

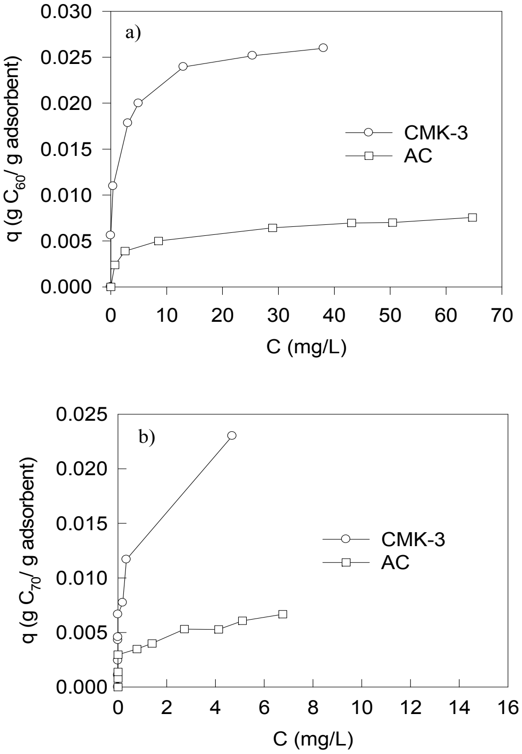

Figure 6. Binary adsorption isotherms of fullerenes on CMK-3 and AC at 25℃. (a) C_{60}; (b) C_{70}.

Adsorption Equilibrium Isotherms of Pure C_{60} and Pure C_{70} on CMK-3. The adsorption equilibrium isotherms of pure C_{60} and pure C_{70} on CMK-3 from its toluene solutions at 25 ℃ are shown in Figure 7. It can be seen that C_{70} is adsorbed more strongly than C_{60} on CMK-3 at the same liquid phase concentration. The interaction between C_{70} and the pores of CMK-3 is stronger than that between C_{60} and the pores of CMK-3. This is due to the shape of the fullerene molecules. C_{60} molecules are spherical whereas C_{70} molecules are elliptical. Hence, the interaction area between C_{70} and CMK-3 is relatively larger due to the C_{70} molecular shape being flatter. It is easy for C_{70} to be adsorbed on CMK-3 and difficult to be desorbed. The difficulty of desorption of C_{70} from the adsorbent has been a problem for a long time which remains unsolved.

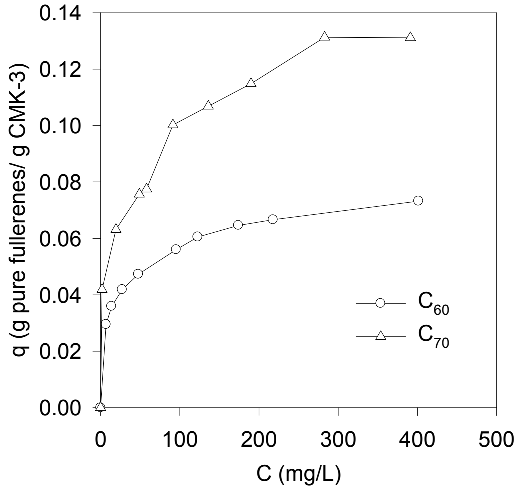

Figure 7. Adsorption equilibrium isotherms of pure fullerenes on CMK-3 at 25℃

Adsorption Equilibrium Isotherms of Binary C_{60} and C_{70} on CMK-3. The equilibrium isotherms of binary C_{60} and C_{70} adsorption on CMK-3 at 25 ℃ are shown in Figure 8. The adsorption equilibria of C_{60} and C_{70} mixture were also measured and the results showed that the temperature effect is not significant for the adsorption of fullerenes on CMK-3.

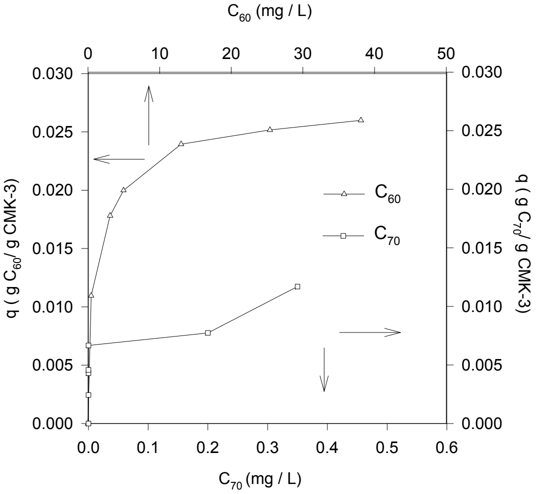

Figure 8. Adsorption equilibrium isotherms of binary C_{60} and C_{70} on CMK-3 at 25℃.

Desorption of Pure C_{60} and Pure C_{70} from CMK-3 and AC.

The desorption process of pure C_{60} and pure C_{70} from CMK-3 and AC at 25 ℃ is shown in Figure 9. For both cases, 25 mg adsorbents of pre-adsorbed pure C_{60} or pure C_{70} at 25 ℃ were added to 200 ml pure toluene. It is seen that for both adsorbents the desorption process can quickly reach the new equilibrium in five minutes. Nearly 24% of adsorbed pure C_{60} and 8% of adsorbed pure C_{70} can be desorbed from CMK-3. For comparison, only 9.5% of adsorbed pure C_{60} and 6% of adsorbed pure C_{70} can be desorbed from activated carbon. Thus, the ordered mesoporous carbon, CMK-3, not only has a higher adsorption capacity, but also is a more reversible adsorbent than activated carbon.

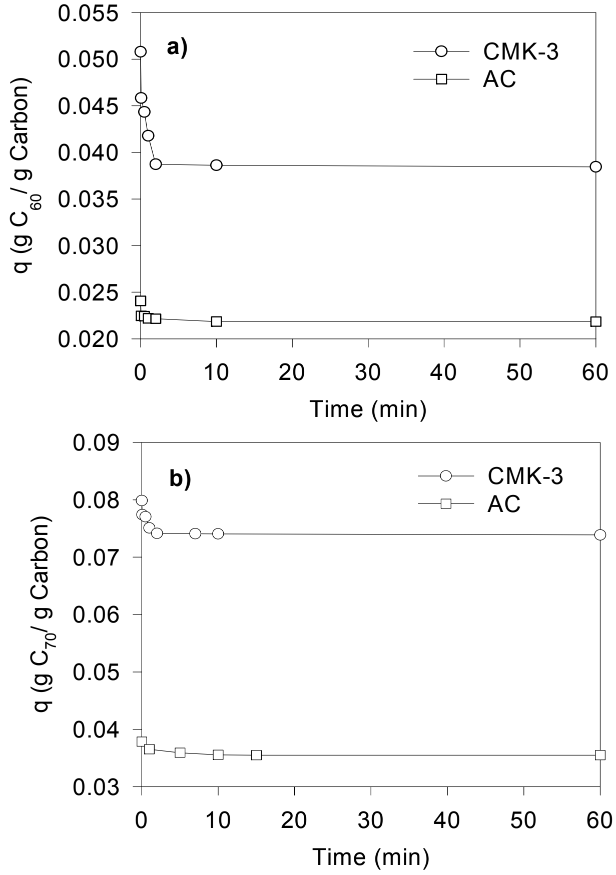

Figure 9. Desorption evolution of pure fullerene from CMK-3 and AC at 25℃: (a) pure C_{60}; (b) pure C_{70}

Effect of solvent volume on the desorption of pure C_{60} and pure C_{70} from CMK-3

The effect of solvent volume on the desorption from 25 mg CMK-3 of pre-adsorbed pure C_{60} or pure C_{70} at 25 ℃ is shown in Figure 10. As expected, the amount of fullerenes desorbed increases with more solvent volume used. About 25 % pure C_{60} and 13 % pure C_{70} can be desorbed when a solvent volume of 1000 ml is used to desorb 25 mg of pre-saturated CMK-3 at 25 ℃. When only 200 ml toluene is used, only 8 % pure C_{70} can be desorbed. The desorption of C_{70} can be significantly improved by using more solvent. The desorption of C_{60} can also be improved by using more solvent but not as significantly as C_{70}.

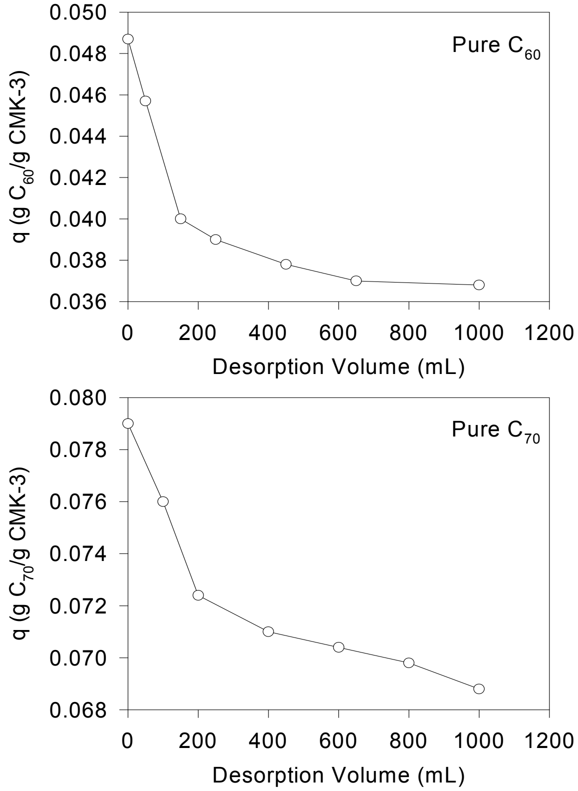

Figure 10. Effect of solvent volume on the desorption of pure fullerene from CMK-3 at 25℃.

Effect of temperature on the desorption of pure C_{60} and pure C_{70} from CMK-3

Because adsorption is an exothermic process, increasing the temperature will be helpful for the desorption. The effect of temperature on the desorption from 25 mg CMK-3 pre-adsorbed pure C_{60} or pure C_{70} at 25 □ is shown in Figure 11. The solvent volume used is 250 ml. It is seen that the amount of pure C_{60} desorbed from CMK-3 changes very little by increasing the temperature from 25 □ to 55 □. However, the amount of pure C_{70} desorbed from CMK-3 increases with the temperature increasing. At the highest temperature of 55 □, the amount of pure C_{70} desorbed from CMK-3 is the highest. Therefore, temperature is another important factor for C_{70} desorption. High temperature will help to improve the reversibility of CMK-3 for C_{70}. Figure 11 also shows the effect of desorption cycles on the desorbed quantity of pure fullerenes. In the subsequent desorption cycles, the desorption is repeated by drying the desorbed adsorbent from the previous cycle and then placing it into another 250 ml fresh toluene. Nearly 47 % pure C_{60} can be desorbed from CMK-3 after four cycles of desorption process. About 16 % pure C_{70} can be desorbed from CMK-3 after three cycles of desorption process.

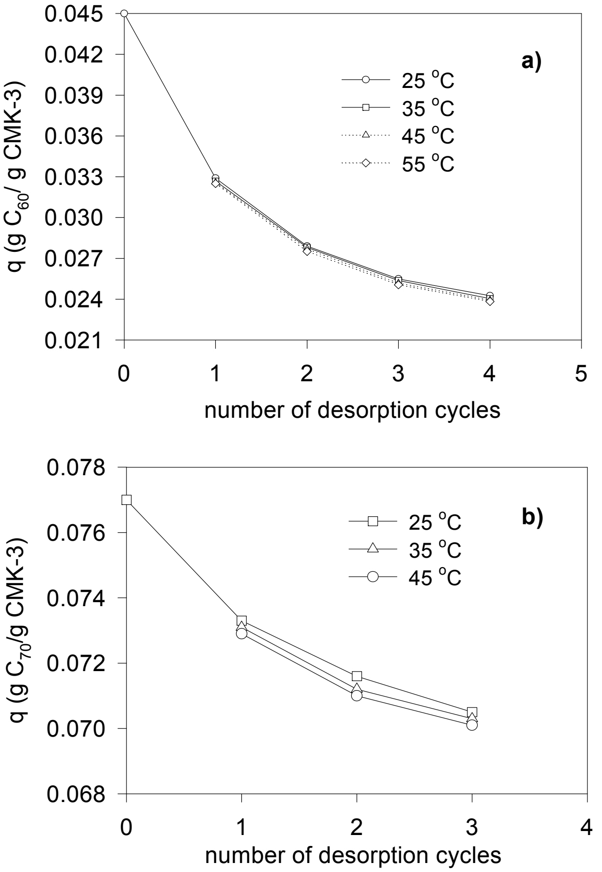

Figure 11. Effect of temperature on the desorption of pure fullerene from CMK-3:
(a) pure C_{60}; (b) pure C_{70}

• Conclusions

The adsorption of fullerenes, C_{60} and C_{70}, on four adsorbents including alumina, silica gel, activated carbon (AC), and ordered mesoporous carbon (CMK-3) was investigated using a batch system. Alumina and silica gel have little adsorption capacity for fullerenes. Both CMK-3 and activated carbon can adsorb fullerenes but the adsorption capacity of CMK-3 is four times higher than that of AC. The detailed study shows that C_{70} is more strongly adsorbed on CMK-3 than C_{60}. The effect of temperature on the adsorption equilibrium of fullerenes on CMK-3 is marginal.

The reversibility of fullerene adsorption on CMK-3 was also studied. Nearly 24 % adsorbed pure C_{60} and 8 % adsorbed pure C_{70} can be desorbed from 25 mg pre-saturated CMK-3 within 10 minutes at 25 □ using 200 ml pure toluene. More fullerenes can be desorbed by using more solvent. For a toluene volume of 1000 ml, about 25 % pure C_{60} and 13 % pure C_{70} can be desorbed at 25 □. The desorption can also be improved by using more cycles of desorption process. Nearly 47 % pure C_{60} can be desorbed after four cycles of desorption and around 16 % pure C_{70} can be desorbed after three cycles of desorption. The amount of pure C_{70} desorbed increases with increasing temperature.

• Acknowledgment

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