

Adsorption of Phenol on Mesoporous Carbon CMK-3: Effect of Textural Properties

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Mesoporous carbon CMK-3s with different textural properties have been used for the adsorption of phenol to understand the necessary physicochemical properties of carbon for the efficient removal of phenol from contaminated water. The kinetic constants (both pseudo-second order and pseudo-first-order kinetics) increase with increasing pore size of carbons. The maximum adsorption capacities correlate well with micropore volume compared with surface area or total pore volume even though large pore (meso or macropore) may contribute partly to the adsorption. The pore occupancies also explain the importance of micropore for the phenol adsorption. For efficient removal of phenol, carbon adsorbents should have large micropore volume and wide pore size for high uptake and rapid adsorption, respectively.

Key Words: Phenol, Mesoporous carbon, CMK-3, Adsorption, Textural property

Introduction

Removal of phenolic compounds from water is very important because phenols are classified as hazardous pollutants.^{1,2} Based on the regulation of US environmental protection agency (EPA), the phenol content in the waste water is asked to be less than 1 ppm.³ For the removal of the phenols from contaminated water, several methods, including adsorption, oxidation, extraction, etc. have been investigated.^{1,2} Among the proposed methods, removal of phenols by adsorption technologies is regarded as one of the competitive methods because adsorption does not need a high operation temperature and the operation procedure is relatively simple.^{1,2}

Several adsorbents have been tried for the removal of phenols, and activated carbons have been one of the typical adsorbents.^{1,2} Recently alternative adsorbents such as zeolites, coals, clay, mesoporous materials, etc. have been searched to decrease the cost or increase the performances.^{1,2,4-6} Adsorbents, including activated carbon, made from wastes attract attention to decrease the cost of adsorption.⁷⁻¹⁰ New adsorbents for achieving a high adsorption capacity, a low residual phenol concentration or increased rate of adsorption have also been developed.¹¹⁻¹⁶ Recently phenols have also been removed with new adsorbents and/or reactions.¹⁷⁻¹⁹

Mesoporous carbon, CMK-3 is a fascinating material and exhibits a high surface area, a large pore volume, narrow pore size distribution, and well-ordered mesoporous structure.^{20,21} CMK-3 has been widely used as adsorbents for several chemicals including biomaterials such as L-histidine and vitamin E.²²⁻²⁸ CMK-3, with or without modification, has also been used in the removal of phenol.^{15,16} However, to the best of our knowledge, there has been no study on the role of the textural parameters of the CMK-3 carbons to affect the adsorption of phenol. In this work, we report on the results of the adsorption of phenol over CMK-3s having different textural properties to

understand the necessary physicochemical properties of adsorbents for phenol adsorption.

Experimental

The CMK-3 samples were prepared using SBA-15 (SBA: Santa Barbara Amorphous) as a hard template to follow the method described by Jun *et al.*²⁰ and Hartman and Vinu.²¹ The samples are denoted as CMK-3-T where T denotes the temperature used for the synthesis of its respective template. Active carbon was purchased from Duksan chemical company (granule, size: 2 - 3 mm). The textural properties of the adsorbents were analyzed on a Quantachrome Autosorb 1MP analyzer after evacuation. The surface area, pore volume and average pore size were calculated using the nitrogen adsorption isotherms.

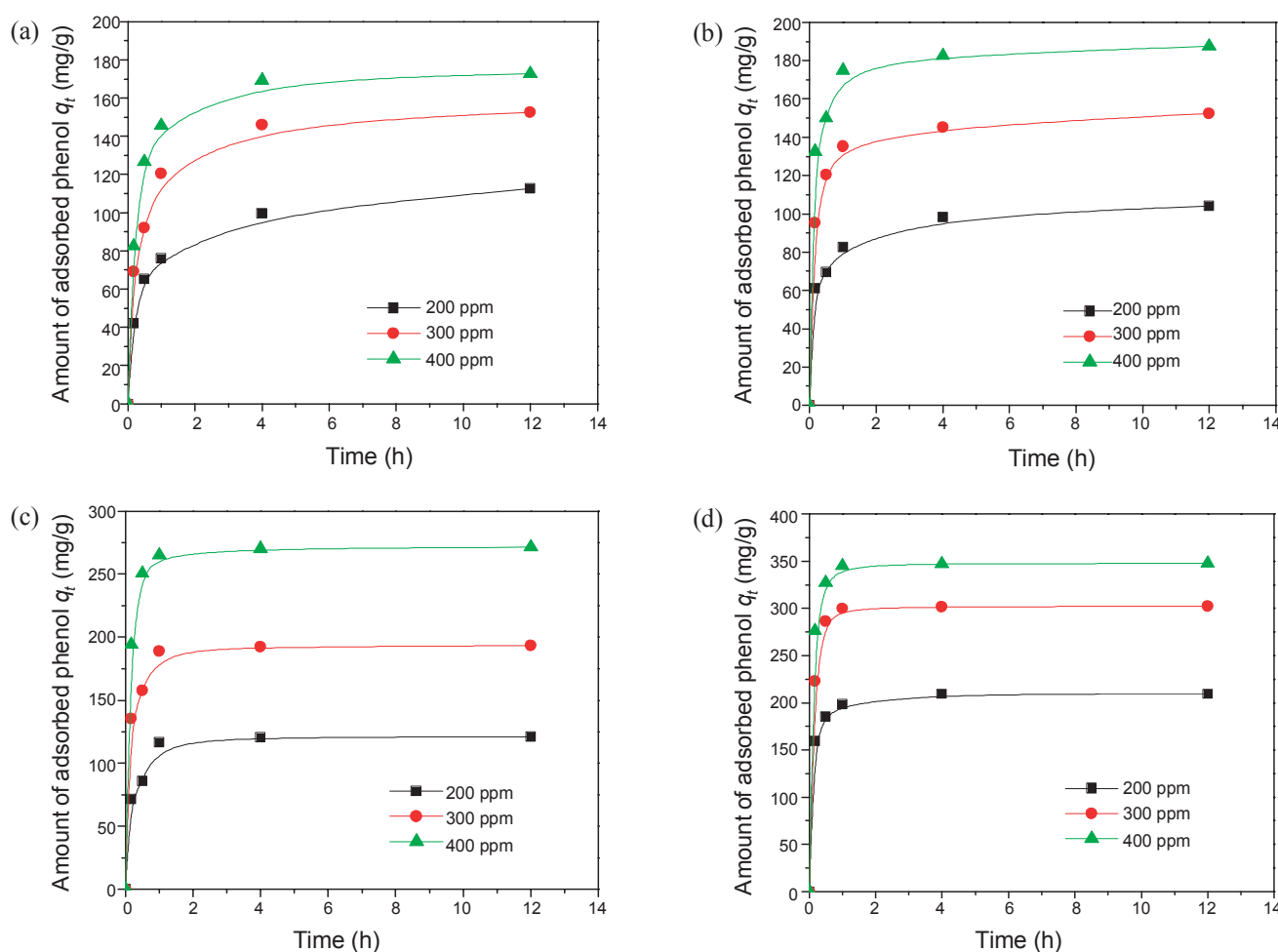
An aqueous stock solution of phenol (10,000 ppm) was prepared by dissolving phenol (98%, DC Chemicals co. Ltd, Korea) in deionized water. Aqueous phenol solution with different concentration of phenol (5 - 1000 ppm) was prepared by successive dilution of the stock solution with water. The phenol concentration was determined using the absorbance (at 269 nm) of the solution after getting the UV spectra of the solution with a spectrophotometer (Shimadzu UV spectrophotometer, UV-1800). The calibration curve was obtained from the spectra of the standard solutions (5 - 400 ppm).

Before the adsorption, the adsorbents were dried overnight under vacuum at 100 °C, and were kept in a desiccator. Exact amount of the adsorbents (~ 10 mg) was put in aqueous phenol solution (25 mL) having fixed phenol concentration (200 ppm to 1000 ppm). The phenol solutions (pH: 5.3 - 5.8) containing adsorbents were mixed well under magnetic stirring and maintained for a fixed time (10 min to 12 h) at 20 °C. After the adsorption for a pre-determined time, the solution was separated from the adsorbents with a syringe filter (PTFE, hydrophobic, 0.5 µm), and the phenol concentration was calculated, after dilution (if

Table 1. The pseudo-second-order kinetics constants (k_2), maximum adsorption capacity (Q_0) and pore occupancies of the four adsorbents.

Adsorbent	Pore diameter, BJH ^a (nm)	BET Surface area (m ² /g)	Micropore volume ^b (cm ³ /g)	Total pore volume ^c (cm ³ /g)	k_2 [g/(mg·h)]			Q_0 (mg/g) ^e	Micropore occupancy (%) ^f	Total pore occupancy (%) ^f
					200 ppm ^d	300 ppm ^d	400 ppm ^d			
active carbon	-	1068	0.32	0.50	0.0195	0.0227	0.0373	257	75.1	48.2
CMK-3-100	3.0	1260	0.41	1.1	0.0392	0.0521	0.0589	347	79.1	29.5
CMK-3-130	4.3	1250	0.46	1.3	0.0703	0.0734	0.0826	428	87.0	30.8
CMK-3-150	6.5	1350	0.49	1.6	0.0962	0.105	0.111	473	90.2	27.6

^aCalculated from the adsorption branch of the isotherm. ^bDetermined with t-plot. ^cTotal pore volume calculated at $p/p_0 = 0.88$. ^dInitial phenol concentration. ^eCalculated from Langmuir plot. ^fCalculated as [volume of adsorbed phenol]/[pore volume] × 100.

**Figure 1.** The variation of adsorbed phenol with adsorption time over various adsorbents: (a) active carbon; (b) CMK-3-100; (c) CMK-3-130; (d) CMK-3-150. The initial phenol concentrations are displayed in the Figures. Note that the scales of y-axes are different one another.

necessary), with absorbance obtained using UV spectra. The adsorption rate constant was calculated using pseudo-second or pseudo-first order reaction kinetics^{3,29,30} and the maximum adsorption capacity was calculated using Langmuir adsorption isotherm^{1,3} after adsorption for 12 h.

Result and Discussion

Textural properties, determined from nitrogen adsorption, are summarized in Table 1 and the pore size distributions of the tested adsorbents are shown in Supporting Fig. 1. As previ-

ously reported,^{21,27} the pore size of the mesoporous carbon increases with increasing the pore size of the templates which were prepared at different synthesis temperature (CMK-3-100 < CMK-3-130 < CMK-3-150). Similarly, the porosity of the mesoporous carbon increases slightly in the same order. The pore size and porosity of active carbon are smaller than those of CMK-3 samples.

Fig. 1 shows the change of the adsorbed amount of phenol for the four adsorbents with adsorption time from solutions having various initial phenol concentrations. The uptake of phenol increases with increasing the initial phenol concentration for

all of the adsorbents. A similar trend has also been reported previously.^{2,3,31} The amount of adsorbed phenol increases sharply up to 4h for active carbon; however, the adsorption is nearly completed in 1 h in the case of CMK-3s. Generally the saturation time increases in the order of CMK-3-150 \leq CMK-3-130 < CMK-3-100 < active carbon, showing the fastest adsorption on the CMK-3-150 which has the largest pore diameter and the largest pore volume among the tested samples. To compare the adsorption kinetics precisely, the changes of adsorption amount with time were treated with the versatile pseudo-second-order kinetic model because the whole data during adsorption time can be treated successfully:^{3, 29, 30}

$$dq_t/dt = k_2 (q_e - q_t)^2$$

$$\text{or, } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where, q_e : amount adsorbed at equilibrium (mg/g);
 q_t : amount adsorbed at time t (mg/g);
 t : adsorption time (h).

Therefore, the second order kinetic constant (k_2) can be calculated by $k_2 = \text{slope}^2 / \text{intercept}$ when the t/q_t is plotted against t .

Fig. 2 shows the plots of the pseudo-second-order kinetics of the phenol adsorptions over the four carbons at various initial phenol concentrations. The calculated kinetic constants (k_2) are shown in Table 1. The rate constants for adsorption over active carbon are similar to the reported ones over active carbons from various sources (0.0292 - 0.0396 g/(mg min);² 0.018 - 0.149 g/(mg h);³). The kinetic constants increase with increasing the initial phenol concentration, showing the rapid adsorption in the presence of phenol in high concentration. The kinetic constants are in the following order: CMK-3-150 > CMK-3-130 > CMK-3-100 > active carbon, illustrating the fastest adsorption over CMK-3-150. The kinetic constant over CMK-3-150 is around 2 - 5 times larger than that of the active carbon. Moreover, the kinetic constant is in the same order of pore size (Table 1), confirming the beneficial role of large pore of mesoporous carbon on the phenol adsorption even though the kinetic diameter of phenol (~ 0.66 nm) is relatively small³² compared with the pore size of the adsorbents. The adsorption data were also analyzed using pseudo-first-order kinetic model:³

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Therefore, the first order kinetic constant (k_1) can be calcu-

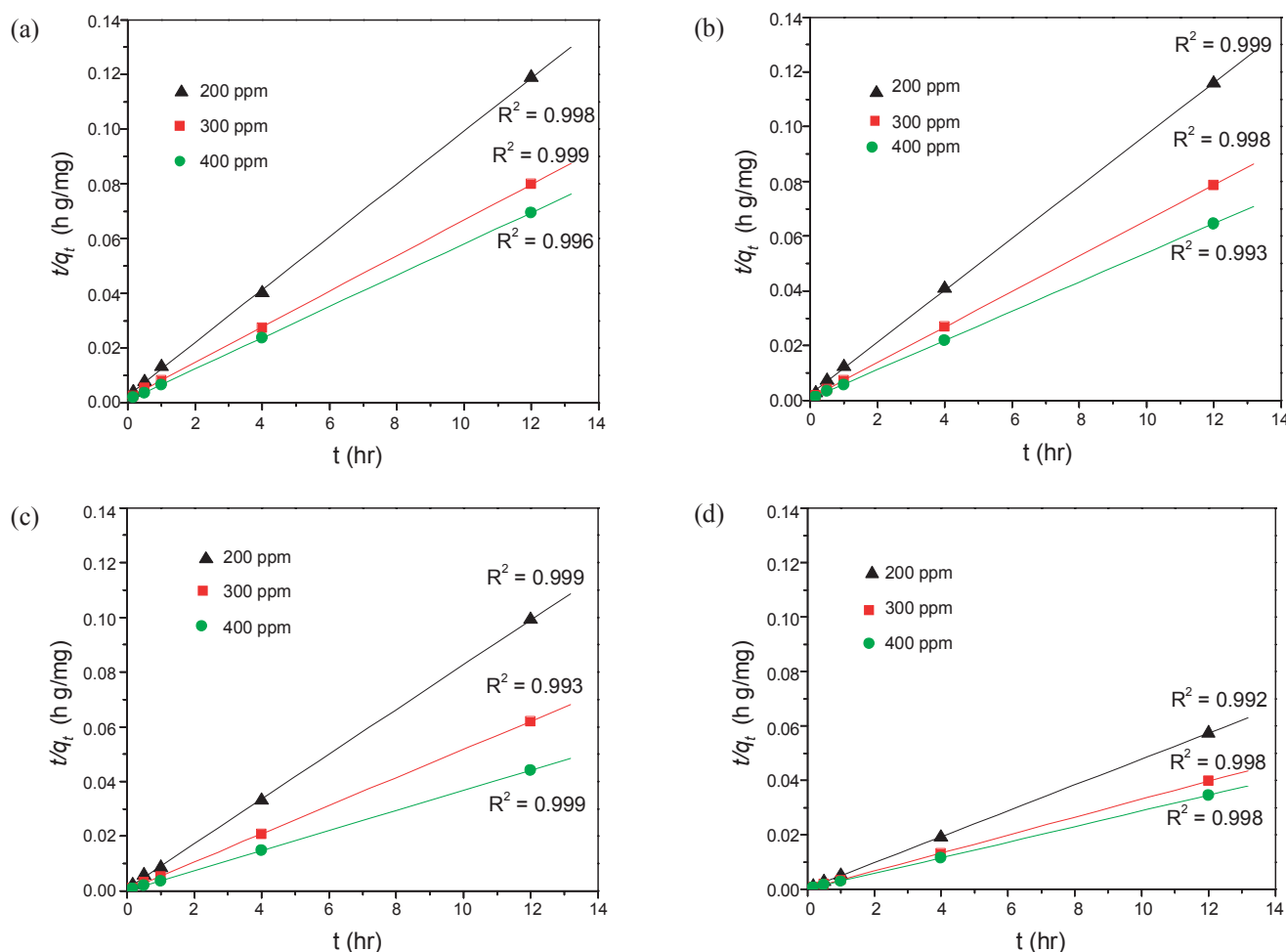


Figure 2. The plots of pseudo-second-order kinetics for phenol adsorption over various adsorbents: (a) active carbon; (b) CMK-3-100; (c) CMK-3-130; (d) CMK-3-150. The initial phenol concentrations are shown in the Figures.

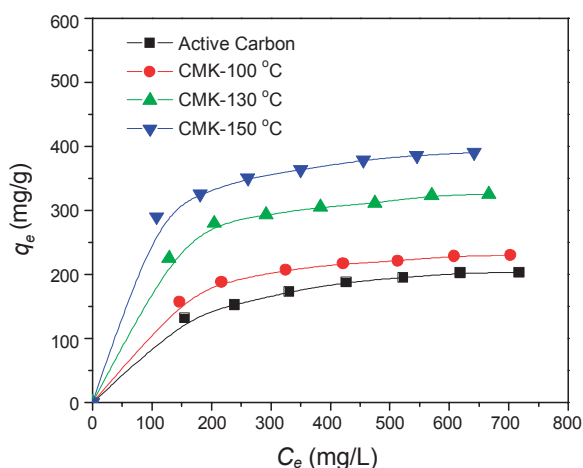


Figure 3. The adsorption isotherms of phenol on four adsorbents.

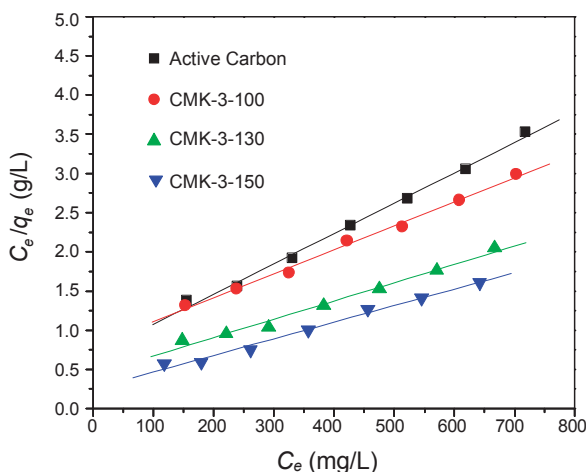


Figure 4. Langmuir adsorption isotherms of phenol on four adsorbents.

lated by $k_1 = -slope$ when the $\ln(q_e - q_t)$ is plotted against t .

The plots of the pseudo-first-order kinetics of the phenol adsorptions over the four carbons at various initial phenol concentrations are shown in Supporting Fig. 2 (adsorption time is only 0 - 1 h for good linearity³ and the kinetic constants are displayed in Supporting Table 1. Similar to the second-order kinetic constants, the rate generally increases in the order of active carbon < CMK-3-100 < CMK-3-130 < CMK-3-150, confirming once again the beneficial effect of large pore size on the rapid adsorption. However, the tendency of increasing the kinetic constant with increasing the pore size is not clear for 200 ppm solution and the linearity is relatively poor, suggesting the efficiency of using pseudo-second-order kinetics.²⁹

The adsorption isotherms were obtained after adsorption for sufficient time of 12 h, and the results are compared in Fig. 3. The amount of adsorbed phenol is in the order of CMK-3-150 > CMK-3-130 > CMK-3-100 > active carbon for the investigated concentrations, suggesting the efficiency of the CMK-3s especially having large porosity. As shown in Fig. 4, the adsorption isotherms were plotted to follow the Langmuir adsorption isotherm:^{1,3}

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b}$$

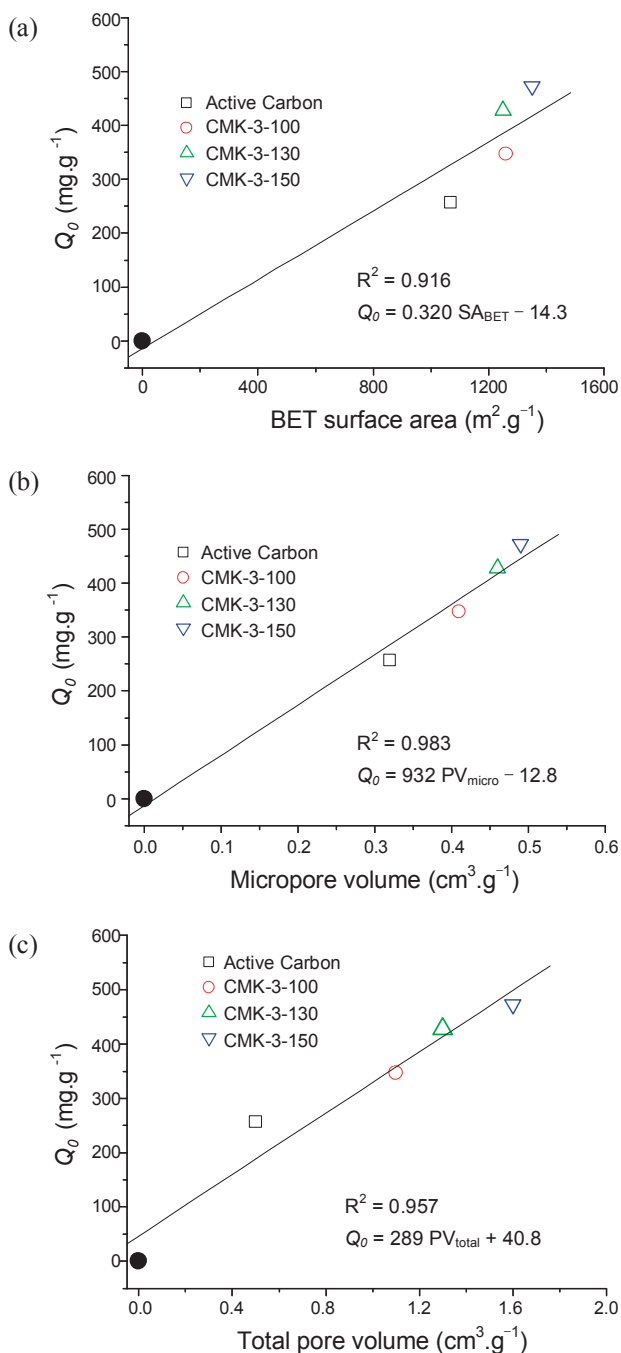


Figure 5. The dependence of maximum adsorption capacity (Q_0) with textural properties: (a) BET surface area; (b) micropore volume; and (c) total pore volume. The filled circles mean (0, 0) points and are included in the linear plots.

Where,

C_e : equilibrium concentration of adsorbate (mg/L)

q_e : the amount of adsorbate adsorbed (mg/g)

Q_0 : Langmuir constant (maximum adsorption capacity)

b : Langmuir constant (related to rate of adsorption)

So, the Q_0 can be obtained from the reciprocal of the slope of a plot of C_e/q_e against C_e .

The Q_0 for all of the samples is determined from Fig. 4 and the values are summarized in Table 1. Generally the Q_0 increases in the order of active carbon < CMK-3-100 < CMK-3-130 < CMK-3-150, and the adsorption capacity of CMK-3-150 is 473 mg/g. So far many adsorbents have been evaluated as a candidate to remove phenol from water, and the adsorption capacity varies widely from 0.33 to about 500 mg/g depending on adsorbents.^{1,2,7} To shed a light on the noticeable performance of CMK-3 mesoporous carbons, the adsorption capacity was compared with textural properties (Table 1) of the used adsorbents. As shown in Fig. 5, the maximum adsorption capacity correlates fairly well with pore volumes or BET surface area; importantly, the adsorption capacity Q_0 correlates most nicely with micropore volume. The plot of Q_0 against textural properties (including (0, 0) point) shows that the correlation factor is the highest and the intercept is the lowest when the plot is based on micropore volume (Fig. 5). The nice correlation with micropore volume represents the importance of micropore volume in the adsorption of phenol. Very recently, Fierro *et al.*³³ have pointed out the importance of micropore volume in the uptake of phenol on active carbon. The pore occupancies (the portion of pore that is occupied by phenol after adsorption) were calculated and are displayed in Table 1. The micropore occupancy increases in the order of active carbon < CMK-3-100 < CMK-3-130 < CMK-3-150; however, the total pore occupancy is in the reversed order. These pore occupancies may be explained with the fact that phenol is adsorbed preferentially on micropore (mesopore or macropore partly contribute to the adsorption). For example, the CMK-3-150 has relatively low contribution of micropore so the micropore occupancy is high due to the contribution of the adsorption on meso or macropore. On the other hand, the total pore occupancy of the CMK-3-150 is low because of low contribution of micropore in the CMK-3-150. Therefore, it may be suggested that suitable carbon adsorbents should have a high micropore volume and mesoporous structure (with large pore size) for high adsorption capacity and rapid uptake, respectively. CMK-3 having large pore size and high micropore volume is found to be one of the suitable adsorbents for the adsorptive removal of phenol.

Conclusion

The mesoporous carbon CMK-3 may be used efficiently to remove phenol *via* liquid-phase adsorption of phenol from contaminated water. Based on the rate constants (pseudo-second or pseudo-first-order kinetics for adsorption) it can be suggested that wide pore size is necessary for rapid uptake of phenol. From the maximum adsorption capacities, calculated from adsorption isotherms using Langmuir equation, and pore occupancies, it can be presumed that large micropore volume is important to increase the adsorbed amount even though larger pore (such as meso and macropore) may partly contribute to the adsorption. Mesoporous carbons like CMK-3 having large micropore volume and wide pore size could be an efficient adsorbent to remove phenol from contaminated water.

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Supporting Information. Pore size distributions and results of pseudo-first-order kinetics are available on request from the correspondence author (email: sung@knu.ac.kr, fax: 82-53-950-6330).

References

1. Lin, S.-H.; Juang, R.-S. *J. Environ. Manag.* **2009**, *90*, 1336.
2. Srivastava, V. C.; Swamy, M. M.; Mall, I. D.; Prasad, B.; Mishra, I. M. *Colloid Surf. A* **2006**, *272*, 89.
3. Hameed, B. H.; Rahman, A. A. *J. Hazard. Mater.* **2008**, *160*, 576.
4. Yousef, R. I.; El-Eswed, B. *Colloid Surf. A* **2009**, *334*, 92.
5. Kuleyin, A. *J. Hazard. Mater.* **2007**, *144*, 307.
6. Khalid, M.; Joly, G.; Renaud, A.; Magnoux, P. *Ind. Eng. Chem. Res.* **2004**, *43*, 5275.
7. Girods, P.; Dufour, A.; Fierro, V.; Rogaume, Y.; Zoulalian, A.; Celzard, A. *J. Hazard. Mater.* **2009**, *166*, 491.
8. Srihari, V.; Das, A. *Ecotoxicology Environ. Safety* **2008**, *71*, 274.
9. Ahmaruzzaman, Md. *Adv. Colloid Interf. Sci.* **2008**, *143*, 48.
10. Mukherjee, S.; Kumar, S.; Misra, A. K.; Fan, M. *Chem. Eng. J.* **2007**, *129*, 133.
11. Caetano, M.; Valderrama, C.; Farran, A.; Cortina, J. L. *J. Colloid Interf. Sci.* **2009**, *338*, 402.
12. Huang, J.-H.; Huang, K.-L.; Wang, A.-T.; Yang, Q. *J. Colloid Interf. Sci.* **2008**, *327*, 302.
13. Xu, M.-C.; Zhou, Y.; Huang, J.-H. *J. Colloid Interf. Sci.* **2008**, *327*, 9.
14. Nabais, J. M. V.; Gomes, J. A.; Suhas, Carrott, P. J. M.; Laginhas, C.; Roman, S. *J. Hazard. Mater.* **2009**, *167*, 904.
15. He, J.; Ma, K.; Jin, J.; Dong, Z.; Wang, J.; Li, R. *Micropor. Mesopor. Mater.* **2009**, *121*, 173.
16. Guo, Z.; Yuan, Y. *Gaodeng Xuexiao Huaxue Xuebao* **2007**, *28*, 289.
17. Xu, H.-Y.; Prasad, M.; Wang, P. *Bull. Kor. Chem. Soc.* **2010**, *31*, 803.
18. Kim, J.; Kwak, B. S.; Kang, M. *Bull. Kor. Chem. Soc.* **2010**, *31*, 344.
19. Jung, M.-W.; Kim, K.-P.; Cho, B.-Y.; Paeng, I. R.; Lee, D. W.; Park, Y. K.; Paeng, K.-J. *Bull. Kor. Chem. Soc.* **2006**, *27*, 77.
20. Jun, S.; Joo, S.H.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Oh-suna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 10712.
21. Hartmann, M.; Vinu, A. *Langmuir* **2002**, *18*, 8010.
22. Vinu, A.; Hossain, K. Z.; Srinivasu, P.; Miyahara, M. *J. Mater. Chem.* **2007**, *17*, 1819.
23. Vinu, A.; Hossain, K. Z.; Kumar, G. S.; Ariga, K. *Carbon* **2006**, *44*, 530.
24. Liu, G.; Zheng, S.; Yin, D.; Xu, Z.; Fan, J.; Jiang, F. *J. Colloid Interf. Sci.* **2006**, *302*, 47.
25. Wang, H.; Lam, F. L. Y.; Hu, X.; Ng, K. M. *Langmuir* **2006**, *22*, 4583.
26. Hartmann, M.; Vinu, A.; Chandrasekar, G. *Chem. Mater.* **2005**, *17*, 829.
27. Vinu, A.; Miyahara, M.; Ariga, K. *J. Phys. Chem. B* **2005**, *109*, 6436.
28. Vinu, A.; Streb, C.; Murugesan, V.; Hartmann, M. *J. Phys. Chem. B* **2003**, *107*, 8297.
29. Ho, Y. S.; McKay, G. *Process Biochem.* **1999**, *34*, 451.
30. Wang, S.; Li, H.; Xu, L. *J. Colloid Interf. Sci.* **2006**, *295*, 71.
31. Din, A. T. M.; Hameed, B. H.; Ahmad, A. L. *J. Hazard. Mater.* **2009**, *161*, 1522.
32. Webster, C. E.; Drago, R. S.; Zerner, M. C. *J. Am. Chem. Soc.* **1998**, *120*, 5509; The kinetic diameter of benzene is 0.66 nm, and the kinetic diameter of phenol may be very similar to that of benzene.
33. Fierro, V.; Torné-Fernández, V.; Montané, D.; Celzard, A. *Micropor. Mesopor. Mater.* **2008**, *111*, 276.