

The Dynamic Adsorption of Benzene Vapor on the ACF Activated by Phosphoric Acid

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ABSTRACT: The dynamic adsorption behaviors of benzene vapor on phosphoric acid-activated carbon fiber (ACF-P) were investigated by gas chromatography. The experimental results showed that ACF-P that was activated at $>350\text{ }^{\circ}\text{C}$, like steam-activated carbon fiber (ACF-W), has good dynamic adsorption properties for benzene vapor. However, the saturation adsorption capacities of ACF-P and ACF-W are different. The dynamic adsorption conditions apparently do not affect the effluent concentration before the breakthrough point, but do change the operation loading and usage efficiency. The adsorbed ACF-P can be regenerated, and good dynamic adsorbability can be recovered by heating treatment. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1841–1847, 2002

Key words: activated carbon fiber; phosphoric acid activation; dynamic adsorption; benzene vapor

INTRODUCTION

Activated carbon fiber (ACF) is a new kind of functional fiber with high adsorption efficiency. It can be widely used in environmental protection, chemical engineering, source recovery, and other fields because of its novel adsorption properties.^{1–3} However, ACF is more expensive than commonly used adsorbents (e.g., granular activated carbon), so its applications are limited. Recently, a new kind of chemically activated carbon fiber, which was made from a natural fiber precursor and activated with phosphoric acid (ACF-P), has been prepared by us to decrease the cost of product. The ACF-P prepared possesses high yield (30–40 wt %) and large surface area (900–950 m^2/g). Similar to the ACF activated with stea-

m(ACF-W), ACF-P also has abundant micropores with diameters are concentrated in the range 0.5–2.0 nm.⁴ Therefore, the ACF-P possesses high static adsorption capacities for organic vapors and small molecular substances in the water,^{5, 6} like general microporous ACF, because of micropore filling. However, ACF-P presents much lower adsorption capacity than ACF-W for methylene blue in aqueous solution because of its smaller micropore diameter.^{5, 6}

Although ACF-P has better static adsorption characteristics for vapors, as we know, most industrial adsorption applications are dynamic systems. So the assessment of dynamic adsorption properties for ACF-P is of great significance in theoretical and real use. Therefore, in this paper, the dynamic adsorption behaviors of ACF-P for benzene vapors were further studied by gas chromatography. At the same time, the effects of activation conditions, adsorption conditions, pretreatment, and regeneration processes on the dynamic adsorption properties of

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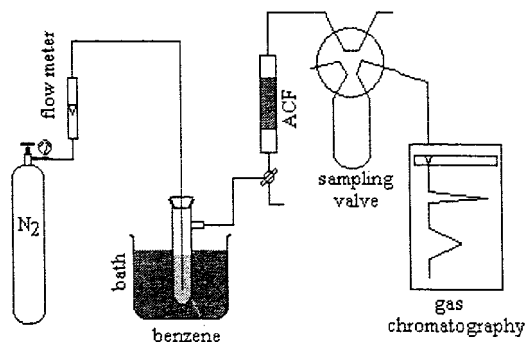


Figure 1 The experimental apparatus.

different ACF-P were systematically investigated.

EXPERIMENTAL

Preparation of ACF-P (Chemical Activation)

About 40 g of natural sisal fiber was immersed in 35% H_3PO_4 for 24 h and then taken out from solution and dried. The treated fiber was hung in a carbonization-activation furnace, heated to a predetermined temperature, and then kept in this temperature for 90 min in the protection of nitrogen gas. After cooling to ambient temperature, the product was fetched out and noted as ACF-P-xxx-0. Here, xxx represents the activation temperature. When ACF-P-xxx-0 was fully washed with water and then dried, the obtained fiber was noted as ACF-P-xxx-1.

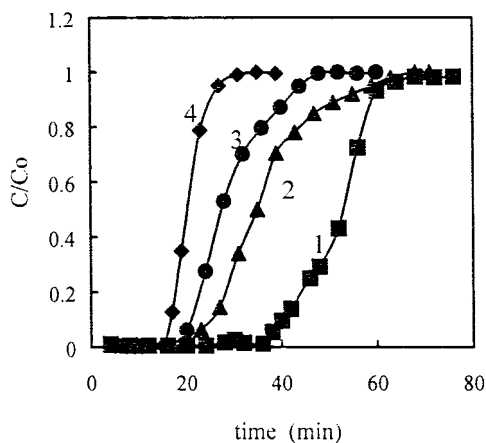


Figure 2 The dynamic adsorption of various ACFs towards benzene vapor. Key: (1) ACF-W; (2) ACF-Zn; (3) ACF-P; (4) ACF-K.

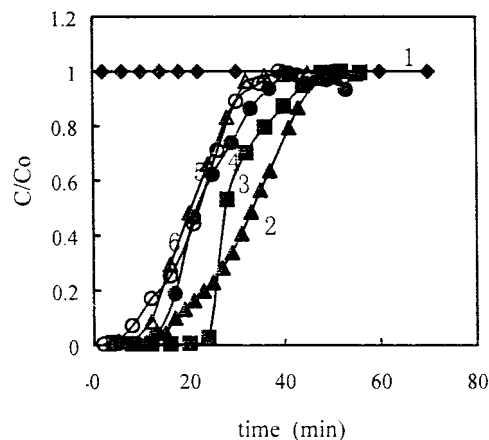


Figure 3 The dynamic adsorption of ACF-P activated at different temperatures towards benzene vapor. Key: (1) 300 °C; (2) 350 °C; (3) 830 °C; (4) 750 °C; (5) 500 °C; (6) 400 °C.

Preparation of ACF-Zn (Chemical Activation)

About 40 g of natural sisal fiber was immersed in 35% $ZnCl_2$ and then carbonized-activated following the same procedures as for the preparation of ACF-P. The product was noted as ACF-Zn.

Preparation of ACF-K (Chemical Activation)

About 40 g of natural sisal fiber was immersed in 5% $(NH_4)_2HPO_4$ for 24 h and then taken out from solution and dried naturally in the air. Next, the dried sample was precarbonized at 450 °C for 30 min. Then the carbonized fiber was immersed in saturated KOH solution for 24 h and finally activated following the same procedure as for the preparation of ACF-P. The product was noted as ACF-K.

Preparation of ACF-W (Thermal Activation)

About 40 g of natural sisal fiber was immersed in 5% $(NH_4)_2HPO_4$ for 24 hours and then taken out

Table I Breakthrough Times, Specific Surface Areas, and Yields of ACFs

Parameter	ACF-W-830	ACF-P-830-1	ACF-Zn-830-1	ACF-K-830-1
Breakthrough time (min)	36	17	18	14
Specific surface area (m^2/g)	1367	1020	954	660
Yield (%)	12.5	30.5	27.6	20.5

Table II Dynamic Adsorption of Benzene on ACF-P

Parameter	ACF-P-xxx-1					
	P-300-1	P-350-1	P-400-1	P-500-1	P-750-1	P-830-1
Surface area (m ² /g)	740	938	615	530	822	960
Yield (%)	/	48.4	41.9	37	32.5	30.5
Breakthrough time (min)	0	12	8	5	10	17
Saturation adsorption capacity (mg/g)	0	238	150	164	152	218

from solution and dried naturally in the air. The treated fiber was hung in a carbonization–activation furnace, heated to predetermined carbonization temperature, and then activated with steam for 90 min in the protection of nitrogen gas. After being cooled to ambient temperature, the product, noted as ACF-W, was fetched out.

Measurement of Specific Surface Areas of ACFs

The Brunauer–Emmett–Teller (BET) surface areas of ACFs were calculated with the adsorption isotherms of nitrogen ($P/P_0 = \sim 0.01\text{--}0.2$, helium as carrier gas) that were measured with a model ST-03 Surface and Pore Distribution Detector made in Beijing, China.

DETERMINATION OF BREAKTHROUGH CURVES OF ACF-P FOR BENZENE VAPOR

About 400 mg of testing ACF was packed in an adsorption column (1-cm diameter). The benzene

vapor was carried over with nitrogen and flowed continuously through fixed bed. The effluent gas was sampled on schedule through sampling valve and then analyzed by a Perkin-Elmer Autosystem 2000 gas chromatograph. The experimental apparatus is shown in Figure 1.

RESULTS AND DISCUSSION

Comparison of the Dynamic Adsorption of Different ACFs

As a fundamental assessment, the breakthrough curve of ACF-P for benzene vapor was detected and compared with those of different ACFs, such as ACF-Zn, ACF-K and ACF-W (Fig. 2). The experimental results indicate that ACF-P, as well as other chemically activated ACFs (e.g., ACF-Zn and ACF-K) have good dynamic adsorption behavior for benzene vapor that is as good as that of ACF-W. The effluent concentrations before the breakthrough point for all tested ACFs are de-

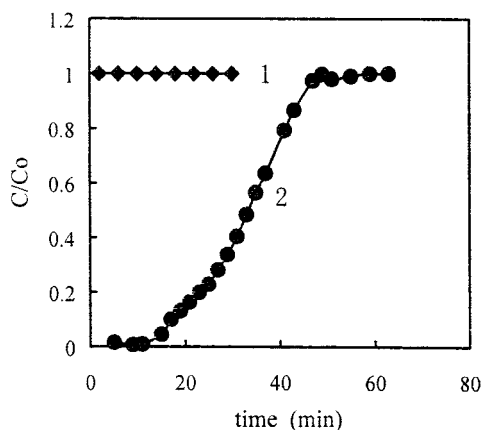


Figure 4 The influence of after-washing on dynamic adsorption of ACF-P-350 towards benzene vapor. Key: (1) ACF-P-350-0; (2) ACF-P-350-1.

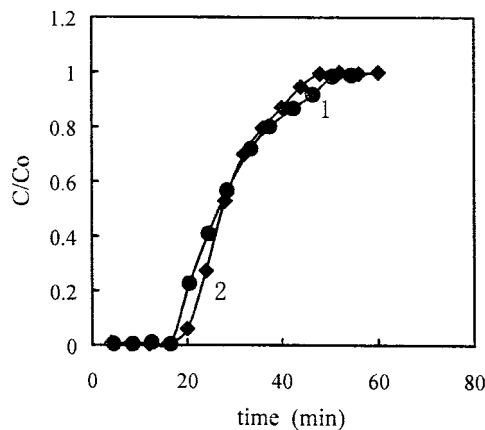


Figure 5 The influence of after-washing on dynamic adsorption of ACF-P-830 towards benzene vapor. Key: (1) ACF-P-830-0; (2) ACF-P-830-1.

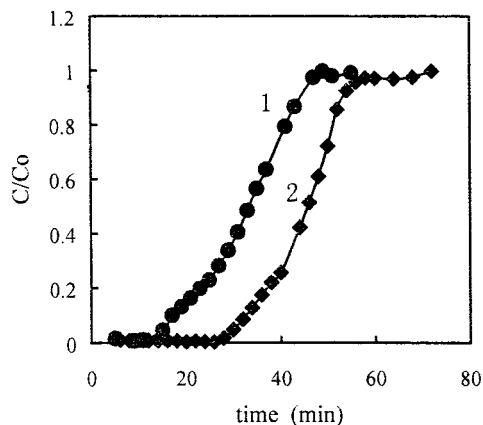


Figure 6 The influence of the amount of ACF-P-350-1 used on dynamic adsorption of benzene vapor. Key: (1) 383 mg; (2) 505 mg.

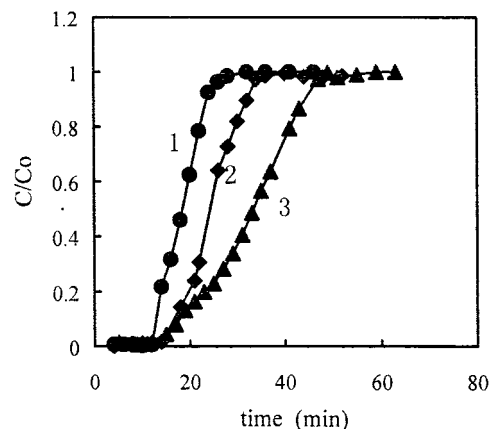


Figure 7 The effect of the initial concentration of benzene vapor on the dynamic adsorption of ACF-P-350-1. Key: (1) 14,000 ppm; (2) 11,000 ppm; (3) 7000 ppm.

creased from an initial 7000–14,000 ppm to <15 ppm. The removal efficiencies of all tested ACFs are >99%. However, various ACFs possess different adsorption capacities (breakthrough time) that are related to their specific surface areas. Here, the breakthrough time of the ACF-W column is larger than that of the ACF-P and ACF-Zn columns, which are larger than that of ACF-K. This order mostly matches the order of their specific surface area. The breakthrough times, specific surface areas, and yields of relevant ACFs are shown in Table I. It can be concluded from a comprehensive survey of the breakthrough time, specific surface area, and yield that ACF-P is able to be used in the industrial treatment of waste gases.

Effect of Preparation Conditions on Dynamic Adsorption

The breakthrough curves of various ACF-P-xxx-1 activated at different temperatures are shown in Figure 3. It can be seen that all ACF-P-xxx-1 activated at >350 °C have certain dynamic ad-

sorption abilities for benzene vapor, although their breakthrough times and saturation adsorption capacities are somewhat different (Table II). Here, the dynamic adsorption abilities are related to the specific surface areas as well as the surface structures. The experimental results clearly showed that the ACF-P-300-1 could not adsorb benzene under dynamic conditions even though it has large specific surface area. The reasons for this result may be that the graphite-like microcrystal in fiber is not yet formed at such low temperature and the adsorption force of fiber is quite weak so that it can not catch the adsorbates under dynamic conditions. This conclusion can also be supported by the comparison of the breakthrough curves of ACF-P-350-1 and ACF-P-830-1. Although both fibers have similar surface areas, the latter has an obviously larger breakthrough time than the former. Moreover, ACF-P-350-1 presents a longer mass transfer zone than ACF-P-830-1, although it possesses a larger saturation adsorption capacity than the latter. This phenomenon can also be explained because ACF-P-830-1

Table III Influence of Amount of ACF-P-350-1 on Dynamic Adsorption

Weight of ACF-P (mg)	L/D Ratio	Breakthrough time (min)	Saturation Adsorption Capacity (mg/g)	Breakthrough Loading (mg/g)	Usage Efficiency (%) ^a
505.2	2:1	26	254	168	66
382.9	1.5:1	13	240	111	46

^a Usage efficiency = breakthrough loading/saturation adsorption capacity.

Table IV Dynamic Adsorption of ACF-P-350-1 under Different Concentrations of Benzene

Concentration of Benzene (ppm)	Breakthrough Time (min)	Saturation Adsorption Capacity (mg/g)	Mass Transfer Zone (min)	Usage Efficiency (%)
7000	13	240	36	42
11000	13	250	23	55
14000	12	254	16	64

has more perfect and larger graphite-like microcrystals,⁷ which will afford it strong adsorption ability and high adsorption speed.

Because the ACF-P was prepared at low temperature (i.e., 350 °C) and simultaneously not further washed with water, it would not have dynamic adsorption ability for benzene vapor (Fig. 4). Under the condition of low temperature activation, most phosphoric compounds would remain in the matrix of ACF-P, which would block up the micropores of fiber. In this case, the ACF-P-350-0 almost had no BET surface area and, therefore, no dynamic adsorption ability towards benzene vapor.

However, when ACF-P samples were activated at high temperature, they presented good dynamic adsorption properties for benzene vapor even if they were not further washed with water (Fig. 5). It was known from former studies that most of phosphoric compounds have been volatilized from fiber and clear micropores are obtained at high temperature.⁴ So, the washing process can be omitted in practical applications for the high-temperature activated ACF-P.

Effect of Adsorption Conditions on Dynamic Adsorption

The effect of the amount of ACF-P used on breakthrough curves is shown in Figure 6. When the amount of ACF-P packed increases but the packing density of column is kept constant, the breakthrough time increases but the shape of curves is

kept in almost the same. Further calculations with the results in Figure 6 indicate that the increase of length (L)/diameter (D) ratio is to a certain extent, advantageous to increase the dynamic usage efficiency of ACF-P (Table III).

The effect of benzene concentration on dynamic adsorption of ACF-P is shown in Figure 7 and Table IV. It can be seen that with the increase of initial concentration, the saturation adsorption capacity of ACF-P increases to some extent, whereas the usage efficiency obviously increases. At the same time, the mass transfer zone is shortened (i.e., the mass transfer front in fixed bed is more precipitous). According to the mass transfer theory of fixed bed in the literature,⁸ when the adsorption in a fixed bed presents a favorable isotherm (in this case, $K_d = (q^*/C)(C_o - C)/(q_o^* - q^*) > 1$, $d^2q^*/dC^2 < 0$), then the high concentration mass transfer front in the fixed bed moves more quickly than in lower one. Therefore, the mass transfer front in the fixed bed becomes more precipitous and the mass transfer zone length will be reduced with the increase of influent concentration. It has been found from the determination of specific surface area and pore distribution that the adsorption isotherm of N_2 on ACF-P is a favorable (I type isotherm).⁴

It is also known that a decrease of influent low rate is advantageous to the contact between adsorbate and adsorbent that can also shorten the mass transfer zone length.⁸ The experimental results (Table V) indicate that high flow rate of influent will decrease both the saturation adsorp-

Table V Dynamic Adsorption of ACF-P-350-1 under Different Flow Rates of Influent

Flow Rate of Influent (mL/min)	Breakthrough Time (min)	Saturation Adsorption Capacity (mg/g)	Breakthrough Loading (mg/g)	Usage Efficiency (%)
51	28	255	182	71
108	13	257	165	64
150	7	234	134	57

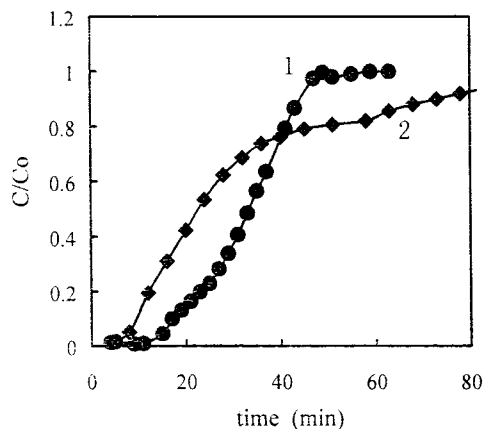


Figure 8 The dynamic adsorption of ACF-P-350-1 towards benzene after being placed in the air for 2 days. Key: (1) original ACF-P-350-1; (2) after being placed in the air for 2 days.

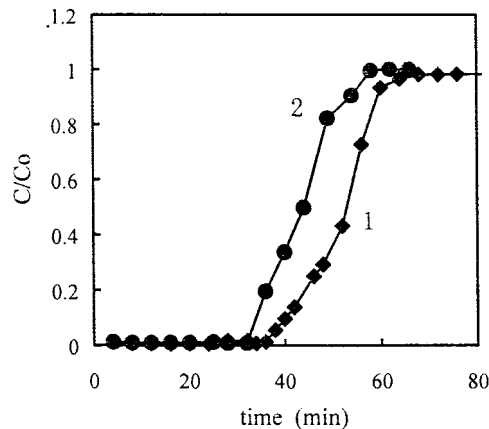


Figure 10 The dynamic adsorption of ACF-W-830 towards benzene after being placed in the air for 2 days. Key: (1) original ACF-W-830; (2) after being placed in the air for 2 days.

tion capacity and usage efficiency of ACF-P for benzene vapor.

Pretreatment and Regeneration of ACF-P

If the ACF-P is exposed to the air for a certain time and then used without any pretreatment, its dynamic adsorption ability will greatly decrease (Figs. 8 and 9). This result is very different with ACF-W, whose dynamic adsorption ability will not be affected much in the same case (Fig.10). Structural analysis has proven that ACF-P possesses lower carbon content but much more hydroxyl and other oxygen-containing surface

groups than ACF-W.⁴ Additionally, there are also many phosphoric-oxygen compounds on ACF-P. Therefore, ACF-P has a strong tendency to adsorb polar substances.⁹ When ACF-P has been exposed to the air and therefore adsorbed large amounts of water and other polar molecules, its adsorption ability for benzene, of course, will greatly decrease.

However, ACF-P exposed to the air or adsorbed to saturation can be regenerated by heating treatment over 150 °C. The regenerated ACF-P can be reused and still possesses dynamic adsorption ability for benzene that is as good as original samples (Figs. 11 and 12).

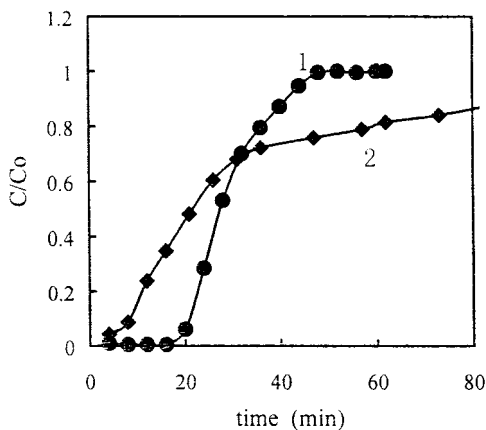


Figure 9 The dynamic adsorption of ACF-P-830-1 towards benzene after being placed in the air for 2 days. Key: (1) original ACF-P-830-1; (2) after being placed in the air for 2 days.

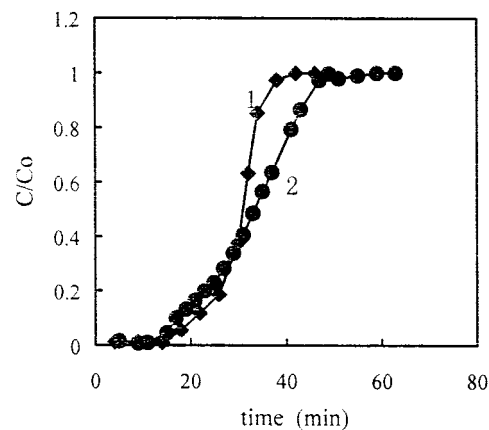


Figure 11 The regenerated dynamic adsorption of ACF-P-350-1 towards benzene. Key: (1) original ACF-P-350-1; (2) regenerated ACF-P-350-1.

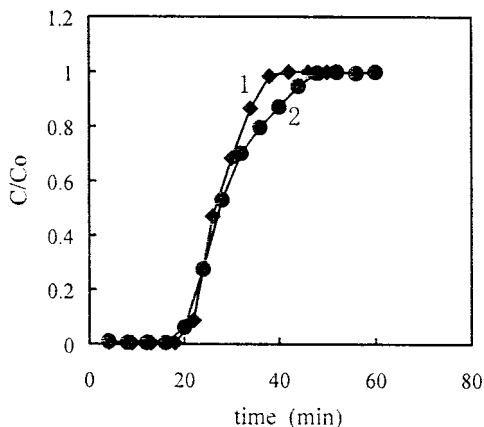


Figure 12 The regenerated dynamic adsorption of ACF-P-830-1 towards benzene. Key: (1) original ACF-P-830-1; (2) regenerated ACF-P-830-1.

CONCLUSION

Various ACF-P samples, activated at $>350\text{ }^{\circ}\text{C}$, have dynamic adsorption properties for benzene vapor that are as good as those of ACF-W, although their saturation adsorption capacities are different. In contrast, those ACF-P samples activated at $<350\text{ }^{\circ}\text{C}$ have no dynamic adsorbability. Evidently, the dynamic adsorption conditions do not affect the effluent concentration before the breakthrough point, but will change the operation loading and usage efficiency. When the initial concentration of benzene increases and the influent flow rate decreases, the mass transfer zone

length of ACF-P bed is reduced and usage efficiency increases. If the ACF-P has been placed in the air for long time, it must be pretreated by heating to renew the adsorbability before use. The adsorbed ACF-P can be regenerated and recover good dynamic adsorbability by heating treatment.

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