

Adsorption isotherms for benzene on diatomites from China

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In this paper, benzene adsorption isotherm and their hysteresis on two important local diatomites were determined at 25°C, and their silicon hydroxyl group (SiOH) number was determined, their properties were reported, and the relationship between surface structure, surface SiOH number per nm² and adsorption isotherm with hysteresis was discussed. The specific surface was also calculated from the isotherms, and pore-size distribution was determined.

Keywords Benzene, adsorption isotherm, diatomites, surface structure

Introduction

Diatomite is a kind of nonmetal mineral formed of the remains of diatoms, which grew and deposited in the sea or lake, and were changed through ages by natural environmental action. Although there were some ten thousand varieties of diatoms, they are all secrete silica, so that their remains, diatomite, consist principally of hydrated silica. In a study of the infrared spectra of water and hydroxyl-containing diatomite, we found¹ the existence of hydrogen bonding with a polymeric hydroxyl band at 3650 cm⁻¹, and also detected another band at 1630—1640 cm⁻¹ corresponding to that of free water which was physi-sorbed on to the surface. Brunauer *et al.*² have shown that the hydroxyl groups on the diatomite were situated above each silicon atom, and we³ attributed the activity of the silica of diatomite, including its acidic character, to the presence of these hydroxyl groups.

Diatomite products are used in a variety of ways,

including (1) reinforcing, stiffening, and hardening organic solids, (2) reducing adhesion between solid surface, (3) increasing adhesion, (4) increasing viscosity, thixotropy, (5) surfactant effects, (6) hydrophobing effects, (7) absorbent, (8) catalysts, (9) cloud seeding, in which the specific surface, silicon hydroxyl groups on the surface of diatomite and adsorption properties of diatomite are important parameters.

The BET method, for the determination of specific surface of powdered substances from benzene adsorption isotherms, is a standard procedure. Our previous determination of the specific surface of untreated and acid-treated diatomite showed that acid-washing decreased the specific surface of the diatomite by approximately 40%.⁴ Subsequently both untreated and acid-treated diatomite were heated to different temperatures, and the specific surface of the heated samples determined by benzene adsorption. These results are shown in Table 1.

A typical adsorption isotherm exhibits several stages: first, an increasing fraction of the surface is covered by adsorbed molecules from zero pressure to certain point around P (see Fig. 1), and at point P, the surface becomes covered with a single layer of benzene molecules. When P is near P₀, benzene liquids fill all pores and give a measure of pore volume.

Adsorption isotherms often exhibit hysteresis phenomenon which has been widely discussed on the basis of the capillary condensation theory, stemmed from Kelvin equation⁵ which relates the vapour pressure above the liquid adsorbate in a capillary, to the radius of curvature of the meniscus of the liquid and hence to the radius of

the capillary in which the condensation took place. The equation is of the form

$$\ln(P/P_0) = (-2\gamma V \cos\theta)/r_k RT \quad (1)$$

where P is the pressure of adsorbate at temperature T (K), P_0 the saturation vapour pressure at the same temperature, γ surface tension of liquid adsorbate, θ the angle of contact between liquid adsorbate and capillary wall, V the molar volume of adsorbate, and r_k the radius of curvature of the meniscus.

Previous work using benzene as adsorbate studied the adsorption isotherms of American Kenya diatomite (diatom belonged to Pennales), and it was found that the isotherms belonged to three types, that is, type II, IV and V,^{2,6,7} but all without adsorption hysteresis. In this paper, types of adsorption isotherms and adsorption hysteresis of diatomite produced in Sheng county, Zhejiang province, and Changbaishan county, Jilin province, China were determined and results discussed. This would provide theoretical basis and useful reference for the development and application of diatomite resource.

Experimental

Materials

The diatomite ore studied was supplied by Sheng county, Zhejiang province, and Changbaishan county, Jilin province, China.

The ore was digested with 80–90 dilute hydrochloric acid, in the ratio of 3 g of diatomite to 50 mL of acid, followed by washing with distilled water, then it was free from chloride ions.

The benzene was of analytical grade.

Heat treatment

Heating of the diatomite was done in air, in a muffle furnace at temperatures of 200, 400, 600, 800, 950 and 1150, for durations of 4 hours.

Adsorption measurement

The weights of benzene adsorbed by one gram of diatomite sample at different pressures of adsorbates were

measured in a standard gravimeter sorption apparatus of BET using a quartz helix. The helix was calibrated with standard weights and its extensions were measured with a 100 cm cathetometer. By this arrangement changes in the weights of adsorbent-adsorbate system could be measured with an accuracy of $\pm 1 \times 10^{-4}$ g. Pressure of adsorbate was obtained by means of a wide bore mercury manometer, read by means of the same cathetometer as above. The adsorption cell was placed in a water bath, thermostated at $25 \pm 0.05^\circ\text{C}$ with the rest of adsorption system being enclosed in an air thermostat kept at $25 \pm 0.1^\circ\text{C}$. Pore-size distribution was determined by mercury penetration method using 9310 type mercury porosimetry.

Determination of numbers of SiOH

Drying of the diatomite was done in vacuum drying oven at temperature of 105°C for durations of 4 hours, to desorb physi-sorbed water. Then the drying diatomite was determined by differential thermal analysis (DTA-TG) method, and according to amount of dehydration of SiOH groups and specific surface by BET method, the number of SiOH groups was calculated.⁸

Results and discussion

The diatomite samples were analysed for silica and acid-soluble contents, and the results showed that Zhejiang and Jilin diatomite contained 64.80 and 92.75% silica respectively, the acid-treated Zhejiang diatomite contained 86.96%. The first lost 2.91% of its weight, the second lost 0.50% and the third lost 3.10% of its weight on heating to 300°C .

The results of BET method, DTA-TG and mercury penetration method on the different samples of two important local diatomites are shown in Table 1.

Diatomite surface structure and adsorption isotherm type

Diatom species of Zhejiang and Jilin diatomite belonged to *Melosira agardh* and *Coscinodiscus ehrenbergi*⁹ respectively. At normal temperature (298 K), adsorption isotherms all belonged to type II, giving a reverse shape (Figs. 1 and Fig. 2). Because adsorption isotherm type depends on relative numerical values of adsorption heat ($-\epsilon_1$) and heat of liquification ($-\epsilon_L$)

of benzene on diatomite surface,¹⁰ when $(-\epsilon_1) > (-\epsilon_L)$, adsorption isotherm will be of type II.

Table 1 Results of BET method, DTA-TG and mercury penetration method

Item	Temperature (°C)						
	Room temp.	200	400	600	800	950	1150
Specific surface (m ² /g)	64.70	51.70	43.86	39.03	13.74	12.77	9.28
Pore volume (mL × 10 ⁻³ /g)	100.57	90.29	104.00	100.10	77.71	4.71	3.42
SiOH (nm ⁻²) ^a	4.20	—	6.00	2.20	1.20	0.50	0.06
Pore-size	1.34—			2.81—		5.87—	
	2.81 μm			9.59 μm		300 μm	
Distribution	6.00—			3.95—			0.50—
	7.67 nm			35.00 μm			1.00 nm
Medium pore	115—						
	147 nm						
Average diameter (μm)	2.0398	—	2.3712	9.0066	—	21.6409	0.0060
Specific surface (m ² /g)	40.01	35.56	35.97	30.03	18.2	7.19	3.50
Pore volume (mL 10 ⁻³ /g)	100.23	108.22	114.29	108.57	74.29	2.65	1.29
SiOH (nm ⁻²) ^b	2.60	—	2.40	1.90	1.10	0.30	0.02
Pore-size	2.81 μm	—	—	9.59—		42.0—	
				25.70 μm		300 μm	
Distribution							0.50—
							1.00 nm
Specific surface (m ² /g)	19.11	19.95	22.58	17.42	14.63	12.60	12.60
Pore volume (mL 10 ⁻³ /g)	43.43	48.00	45.71	45.71	41.94	6.95	4.45
SiOH (nm ⁻²) ^c	3.70	—	4.70	1.90	1.10	0.90	0.00
Pore-size	50.0—	—	—	50.0—		1.00—	
	70.0 nm			114 nm		2.00 nm	
Distribution				3.59—			0.50—
				12.3 nm			0.80 nm

^a Zhejiang diatomite, ^b acid-washed Zhejiang diatomite, ^c Jilin diatomite.

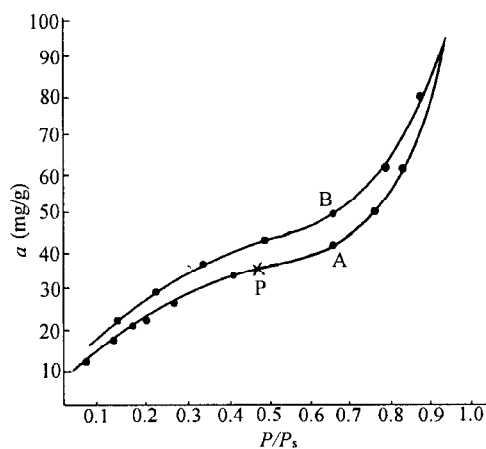


Fig. 1 Adsorption isotherm of Zhejiang diatomite (A is adsorption isotherm, B is desorption hysteresis).

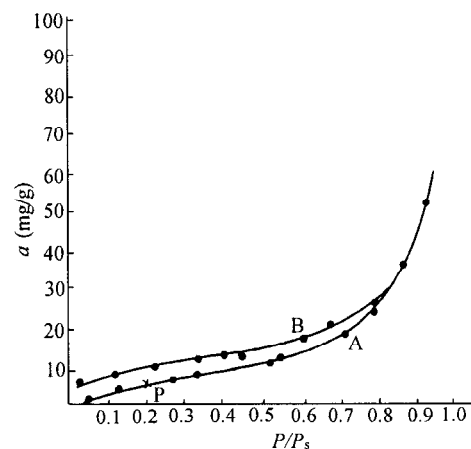


Fig. 2 Adsorption isotherm of Jilin diatomite (A is adsorption isotherm, B is desorption hysteresis).

At point P ($P/P_s = 0.5$) in Fig. 1, curve of Zhejiang diatomite adsorption isotherm and at point P' ($P/P_s = 0.2$) in Fig. 2, curve of Jilin diatomite adsorption isotherm, benzene completed its monolayer adsorption. The explanation of the difference of the two P/P_s values seems most probably to be linked to difference of pore structure of the diatomites. Through scan electron microscope it was observed that diatom body in Zhejiang diatomite was single cylindrical or double joint cylindrical, with capillaries of different sizes arranging on the cylinder wall and that diatom body in Jilin diatomite was disc shaped with capillaries of different sizes arranging inside the disc.⁴ By mercury porosimetry, sizes of micropores were determined. Those of Zhejiang diatomites centered round 6.00—7.67 nm and 115—147 nm, whereas those of Jilin diatomite around 50.0—70.0 nm and 5.0—20.0 nm. All micropores of both samples were of cylindrical shape. The former sample had comparatively smaller micropore size and larger curvature of inner pore with the more stable OH groups⁵ and more number of SiOH per nm^2 (see Table 1), thus, with hydroxyl groups of the inner surface packed more closely and hydrogen bond formed between the hydroxyl groups more strongly. The interactions of adsorbing benzene molecules at $P/P_s = 0.50$, with the previously formed hydrogenbond type adsorbed species in molecular size capillaries could be expected to lead to a temporary rise in adsorption heat ($-\epsilon_1$) liberated. This possibility would be enhanced by the existence of some of the adsorbing hydroxyl groups in dense islands,¹¹ and more hydroxyl groups, thereby increasing the likelihood of the occurrence of lateral interactions among the adsorbed molecules.

Effect of acid washing and roasting on the type of adsorption isotherm

When diatomite was acid-washed, rearrangement of surface hydroxyl groups and increase of average diameter of medium pore took place and the number of adjacent silicon hydroxyl groups decreased from 4.2 OH/ nm^2 at room temperature to 2.6 OH/ nm^2 at acid-washed (see Table 1), thus strength of hydrogen bond of these groups with benzene ring decreased. As a result, adsorption heat ($-\epsilon_1$) also decreased this time, $(-\epsilon_1) < (-\epsilon_L)$ and adsorption isotherm changed from type II to type III (Fig. 3).

When diatomite was roasted, some of the adjacent

silicon hydroxyl groups of diatomite were dehydrated and the number of silicon hydroxyl groups decreased gradually with increase of average diameter of medium pore (see Table 1). There is infrared evidence that after heat treatment at 800°C, only isolated hydroxyl groups remain on diatomite surfaces, and it is stressed that the hydrogen bonding arrangement is proposed for extremely low surface hydroxyl group concentrations outside the scope of detection by present infrared techniques.

According to Iler,⁵ adsorption heats of samples roasted at variable temperature are in accord with their higher hydroxyl group concentrations and hence with the increased possibility that hydroxyl groups would be more favorably spaced to accommodate more than one $\text{OH}\cdots\text{C}_6\text{H}_6$ type of linkage with adsorbed benzene molecules. Confirmation of this possibility is evident from Fig. 1, Fig. 4 and Fig. 5 which show that the amount of benzene adsorbed depends significantly on the hydroxyl group concentration. Thus as temperature rising at 400°C, the adsorption heat ($-\epsilon_1$) decreased, $(-\epsilon_1) < (-\epsilon_L)$, adsorption isotherm changed from type II to type III (Fig. 4).

But in the case of acid washed diatomite, when acid-washed diatomite was roasted, adsorption isotherm did not change in type, because of decrease of adjacent silicon hydroxyl group number from 2.6 OH/ nm^2 at room temperature to 0.02 OH/ nm^2 at 1150°C (see Table 1), and hence with adsorption heats ($-\epsilon_1$) of adsorbed benzene molecules on diatomite surface decreasing. So $(-\epsilon_1)$ kept less than $(-\epsilon_L)$ from beginning to end.

When Zhejiang diatomite was roasted at 950°C, average diameter of medium pore of *Melosira agardh* increased at maximum value, but with decrease of silicon hydroxyl group number by a wide margin (see Table 1), and when roasted at 1150°C, macropore of *Melosira agardh* diatom body collapsed, and the silicon hydroxyl group number decreased to 0.06 OH/nm. As a result, adsorption isotherm changed from type III to type I (Fig. 5).

When Jilin diatomite was roasted at 950—1150°C, micropore of *Coscinodiscus ehrenberg* diatom body disappeared, with some melted into the shell body, and the number of silicon hydroxyl groups decreased by a wide margin, from 3.7 OH/ nm^2 at room temperature to 0.0—0.9 OH/ nm^2 at 950—1150°C, and this time, the strength of hydrogen bond between benzene and inner

pore surface of diatomite decreased greatly, so adsorption isotherm changed from III to type I (Fig. 6).

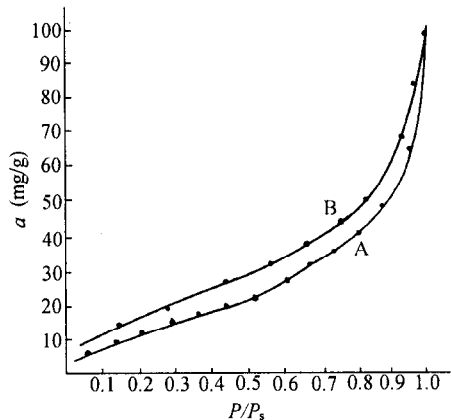


Fig. 3 Adsorption isotherm of acid washed Zhejiang diatomite.

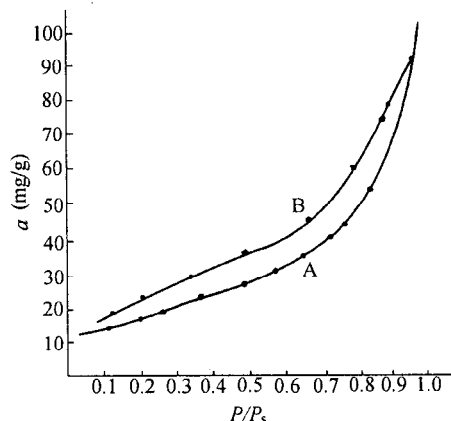


Fig. 4 Adsorption isotherm of Zhejiang diatomite roasted at 400°C.

The effect of adsorption isotherm type, pore structure and roasting temperature on adsorption hysteresis

At ordinary temperature, adsorption hysteresis of untreated diatomite belonged to a combination of type B adsorption hysteresis and type II isotherm, while acid-washed diatomite to type B adsorption hysteresis and type III isotherm (Fig. 1 to Fig. 3). This showed that pore structure of diatomites studied was of cylindrical capillaries. After roasting, adsorption hysteresis type of diatomite changed into a complex of type B adsorption hysteresis and type III isotherm (Fig. 4). Macropore of *Melosira agardh* diatom bodies was reduced to micropore when roasted to 1150°C and the desorption portion of the curve formed a hysteresis cycle with the adsorption portion (Fig. 5), which conformed to the H4 type of IUPAC classification of adsorption hysteresis showing the

presence of micropore. After roasting at 1150°C, micropores at the surface of *Coscinodiscus ehrenberg* diatom bodies melted and disappeared. Then adsorption of benzene only took place at the outside surface and, as a result, adsorption hysteresis coincided with adsorption isotherm (Fig. 6).

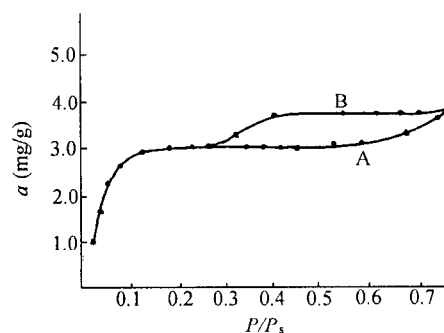


Fig. 5 Adsorption isotherm of Zhejiang diatomite roasted at 1150.

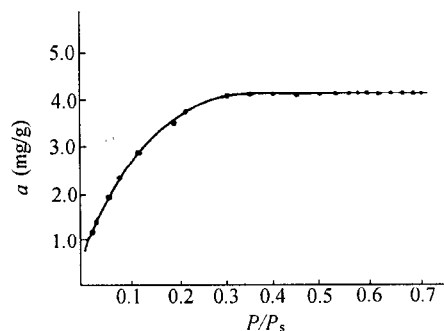


Fig. 6 Adsorption isotherm of Jilin diatomite roasted at 1150°C.

Equation of adsorption isotherms and constant D with relation to types of adsorption isotherm

For adsorption isotherms of diatomite roasted at different temperatures and from the curves of $\log a$ versus $(\log P_s/P)^2$, a plot of $\log a$ against $(\log P_s/P)^2$ should therefore give a straight line of intercept $\log a_m$. The adsorption data on samples of *Melosira agardh* diatom and *Coscinodiscus ehrenberg* diatom roasted at different temperatures are plotted in Fig. 7 and Fig. 8, and the monolayer capacities so obtained are given in Table 2. The monolayer capacities of the two species diatomite were of the same order.

From Fig. 7 and Fig. 8, an equation was obtained as the following: $\log a = \log a_m - D(\log P/P_s)^2$, where a is the adsorption amount of monomolecular layer, a_m ,

the saturation adsorption amount; D , a constant depending on the type of adsorption isotherm and P/P_s , specific pressure = 0.05—0.35.

The pore volume of an adsorbent may be obtained by means of the Gurvitsch rule,¹⁰ provided there was

some identifiable sign of pore filling on the adsorption isotherm. Pore volumes of the diatomite samples were therefore calculated by the Gurvitsch rule from the amount of benzene adsorbed at the high pressure ends of the hysteresis loops. The results are given in Table 2.

Table 2 The relationship between pore volume V_m , constant D and roasting temperature

Item	Room temp	200°C	400°C	600°C	800°C
V_m (mL 10 ⁻³ /g)	100.57	90.29	104.0	100.1	77.7
a_m (mg/g)	28.18	22.39	21.13	18.30	6.68
D	0.2	0.2	0.3	0.3	0.6
V_m (mL 10 ⁻³ /g)	111.2	108.2	114.3	108.6	74.3
a_m (mg/g)	19.5	17.28	17.28	17.28	10.90
D	0.4	0.5	0.5	0.5	0.5
V_m (mL 10 ⁻³ /g)	43.4	48.0	45.7	45.7	41.9
a_m (mg/g)	10.29	10.57	10.59	9.58	9.30
D	0.3	0.3	0.3	0.3	0.5

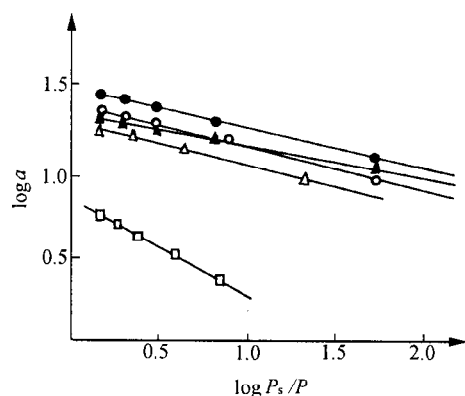


Fig. 7 Plot of $\log a$ vs. $(\log P_s/P)^2$ for the adsorption of benzene vapour on *Melosira agardh* diatom roasted at different temperatures: ● Original, ▲ 200, ○ 400, △ 600, □ 800°C. The average relation coefficient $r = 0.976$.

Every micropore structure was characterized by a and D , two parameters, and the constant D was of pore structure characteristic. When effective radius increased, constant D also increased, and the adsorption isotherm did not curve upward at initial terminal.⁵

Adsorption isotherms of both *Melosira agardh* and *Coscinodiscus ehrenberg* diatomite all curved upward and thus belonged to type II. The former had D equal to

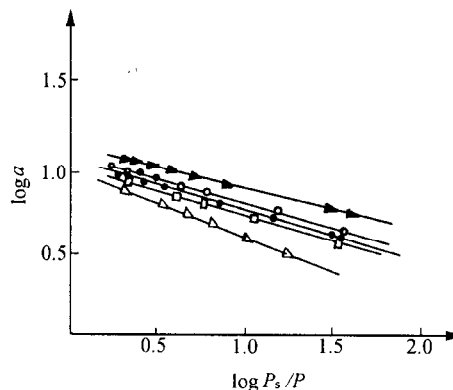


Fig. 8 Plot of $\log a$ vs. $(\log P_s/P)^2$ for the adsorption of benzene vapour on *Coscinodiscus ehrenberg* diatom roasted at different temperatures: ● Original, ▲ 200, ○ 400, △ 600, □ 800°C. The average relation coefficient $r = 0.983$.

0.2 and the latter equal to 0.3. After acid-washing, both D values increased to 0.4, pore-size of both increased also (see Table 1), and the adsorption isotherms did not curve upward, and hence belonged to type III, the saturation adsorption amount a_m decreased.

After roasting, D value of the former increased to 0.3, pore-size increased, but a_m and V_m decreased

gradually (see Table 2), while that of the latter kept unchanged, and a_m and V_m of latter changed quite a little with roast temperature. The adsorption isotherms did not curve upward, indicating that they had changed from type II to type III.

Conclusion

At ordinary temperature, adsorption isotherms of both Sheng county, Zhejiang province diatomite and Changbaisan county, Jilin province diatomite all belonged to type II, after roasting or acid washing, adsorption isotherms changed from type II to type III. Adsorption hysteresis of both diatomites belonged to combined complex form of type B hysteresis and type II isotherm. There was an intimate relationship between surface structure and type of adsorption isotherm. The number of surface hydroxy groups varied with the change of the type of adsorption isotherm. Pore structure and adsorption hysteresis type varied with roasting temperature. Equation of adsorption isotherm of diatomite was obtained as: $\log a = \log a_m - D(\log P_s/P)^2$, constant D of which is closely related with the type of adsorption isotherm. The higher the value of D is, the less the up-

ward curvature of the adsorption isotherm is. As a final result, isotherms changed from type II to type III.

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