Adsorption of Phenol on Surface-modified Carbon Black from Its Aqueous Solution. II. Influence of Surface-chemical Structure of Carbon on Adsorption of Phenol[1)]

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Samples of electronic conductive carbon black (Lion Akzo Co.) were treated with nitric acid, hydrogen peroxide, dried air, or hydrogen gas. These samples had almost the same specific surface areas and pore volumes, except for the one treated with nitric acid. Phenol gas adsorption and aqueous-phase adsorption were carried out in order to study the adsorption mechanism on these treated samples. During aqueous-phase adsorption, the amount of phenol adsorbed increased with a decrease in the number of surface oxygen compounds on the carbon sample. During gas adsorption, the amount of phenol adsorbed decreased with a decrease in the number of oxygen compounds on the carbon surface. The residual amount of phenol also decreased. In the case of gas adsorption, interactions occur not only between the hydrophobic sites on the carbon and the hydrophobic groups of phenol, but also between the surface functional groups on the carbon and the hydrophilic groups of phenol. In the case of aqueous-phase adsorption, competitive adsorption of phenol with water molecules occurs. Water molecules adsorb, selectively, the surface functional groups on the carbon. Thus, the phenol adsorption due to the hydrophobic interaction on the carbon interferes with this selective adsorption.

Municipal wastewaters and industrial wastewaters, which include various organic compounds, are sources of environmental pollution. The use of solid adsorbents as a medium for removing trace quantities of organic compounds from wastewaters is useful at the time of demanding environmental restrictions and a need for the regeneration of water.[2)]

Activated carbon which has a very large surface area has usually been used for solid adsorbents during wastewater treatment.[2–12)] The carbon produced by usual methods, contains considerable amounts of oxygen chemisorbed on the surface.[13)] It seems that the adsorptive properties of such types of carbon are affected by the amount of chemisorbed oxygen. However, the influence of oxygen compounds on the carbon surfaces regarding the adsorption of organic compounds, has not been studied in detail. In this research, a special carbon black having a very large surface area was used as an adsorbent. Using this sample, four types of surface-modified carbon black were prepared. The amount of phenol adsorbed on the modified forms of carbon black was measured in the gas state and in aqueous solution. On the base of the adsorption data, we discuss the influence of the oxygen compounds on the carbon surfaces upon the adsorption of phenol.

Experimental

Materials. The carbon black used as an adsorbent was Electronic Conductive Carbon Black supplied by Lion Akzo Company, Ltd., Tokyo, Japan. The carbon black was treated with nitric acid, hydrogen peroxide, dried air, or hydrogen gas. The modifications were carried out by a method previously reported.[1)] The modification methods and the typical properties of the modified carbon black samples are shown in Fig. 1 and Table 1.

The phenol used for the adsorption experiment was a reagent grade chemical from Wako Pure Chemical Industries Company, Ltd., Tokyo, Japan, it is more than 99% pure.

Procedures. Phenol Gas Adsorption. Prior to adsorption measurements, all samples were evacuated at 120 °C for 5 h under 1.3×10^{-3} Pa. The amount of phenol adsorbed was measured gravimetrically using a Cahn RG-type electromagnetic microbalance at 25 °C and at $P/P_0=0.080$ (where P and P_0 are equilibrium and saturated pressures respectively). After the adsorption experiment, the samples were outgassed for 12 h under 1.3×10^{-3} Pa at 25 °C and the

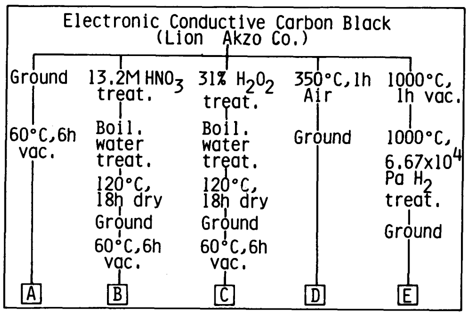

Fig. 1. Surface modifications of carbon black.

Table 1. Properties of surface modified carbon black samples

Carbon black	Surface treatment	Specific surface area[a)] $m^2 g^{-1}$	Pore volume[b)] $ml g^{-1}$	Ash[c)] %
A	Unmodified	886	0.855	0.20
B	13.2 M HNO_3	670	0.562	0.02
C	H_2O_2	826	0.876	0.10
D	Air at 350 °C	959	0.909	0.36
E	H_2	851	0.863	0.25

a) By N_2 BET method. b) Cranston-Inkley method, from 10 to 300 Å pore diameter. c) The ash content was determined with a porcelain crucible, in air.

Table 2. Adsorbed amount and residual amount of phenol on modified carbon black samples

Carbon black	Gas adsorption		Aqueous-phase adsorption
	Adsorbed amount $10^{-5} g m^{-2}$	Residual amount $10^{-5} g m^{-2}$	Freundlich const k[a)] $10^{-5} g m^{-2}$
A	33.6	7.2	4.0
B	42.8	17.8	0.9
C	35.0	7.6	2.1
D	32.4	7.4	2.6
E	25.9	5.3	4.8

a) Data from the previous paper.[1)]

residual amount of phenol at 25 °C was also measured gravimetrically.

The Weight Decrease of the Carbon Black Samples Heated in Vacuum. After the carbon black samples were outgassed for 18 h under 1.3×10^{-3} Pa at 120 °C, the samples were heated to 1000 °C at a heating rate of 4 °C/min in vacuum. The weight decrease of the samples was measured gravimetrically on the basis of the weight at 120 °C, using the Cahn RG-type electromagnetic microbalance.

Results and Discussion

Adsorbed amounts and residual amounts of phenol on the modified carbon blacks are shown in Table 2. The amount of phenol adsorbed on the modified carbon blacks from its aqueous solution, described in the previous paper, is also shown in Table 2. The amount of phenol adsorbed on the carbons treated with various oxidizing agents, especially with 13.2 M[†] HNO_3, increased, and the residual amount of phenol also increased. On the other hand, the amount of phenol adsorbed and the residual amount of phenol decreased on the carbon treated with hydrogen gas. In the previous paper it was reported that the amount of phenol adsorbed from an aqueous solution regarding the carbon treated with various oxidizing agents decreased. That regarding carbon treated with hydrogen gas, increased.

The adsorptive properties of forms of carbon are dependent on the pore structure.[6—11)] However, Table 1 shows that these modified types of carbon black have almost the same specific surface areas and pore volumes, except for the carbon black treated with nitric acid.

Activated carbon and carbon black produced by the usual methods contain considerable amounts of oxygen and hydrogen chemisorbed on their surfaces.[13)] The adsorptive properties of forms of carbon black are presumably affected by the amount of the oxygen and hydrogen on the surface. In order to examine the influence of chemisorbed oxygen and hydrogen on this adsorption, the carbon was evacuated and then heated from 120 to 1000 °C; this treatment decomposed the chemisorbed oxygen and hydrogen. Decomposition products during the heat/evacuation treatment were measured using mass spectrometry. Figs. 2—6 show the variations of mass spectral peaks of the desorbed gas from the modified forms of carbon black with an outgassing temperature up to 1000 °C at a heating rate of 4 °C/min in vacuum. When the samples were heated, the surface compounds decomposed into carbon dioxide, carbon monoxide, water and hydrogen. At higher temperatures, carbon monoxide is more evolved than carbon dioxide. Hydrogen is more difficult to remove than oxygen, but can be removed at very high temperatures.

[†] 1 M=1 mol dm^{-3}.

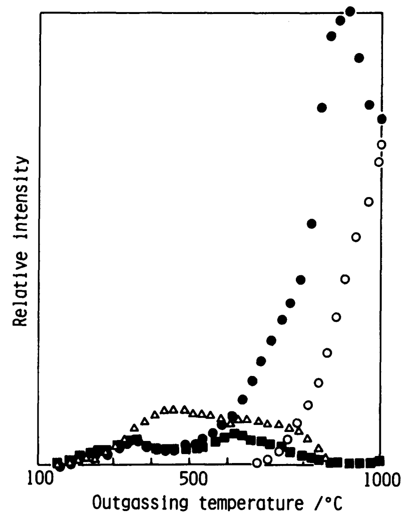

Fig. 2. Variations of mass spectral peaks of the desorbed gas on carbon black A with outgassing temperature up to 1000 °C at a heating rate of 4 °C/min in vacuum. ○: H_2, △: H_2O, ●: CO, ■: CO_2.

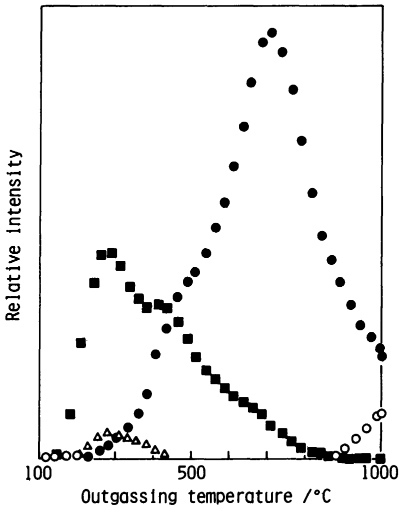

Fig. 3. Variations of mass spectral peaks of the desorbed gas on carbon black B with outgassing temperature up to 1000 °C at a heating rate of 4 °C/min in vacuum. ○: H_2, △: H_2O, ●: CO, ■: CO_2.

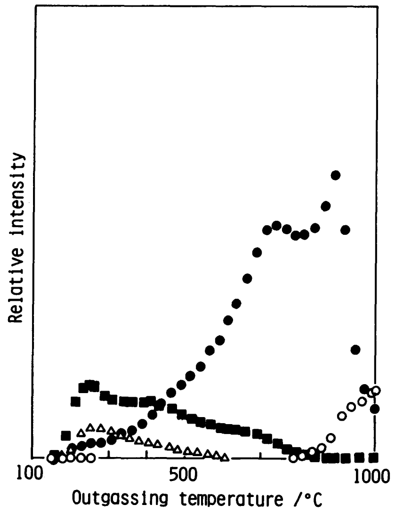

Fig. 4. Variations of mass spectral peaks of the desorbed gas on carbon black C with outgassing temperature up to 1000 °C at a heating rate of 4 °C/min in vacuum. ○: H_2, △: H_2O, ●: CO, ■: CO_2.

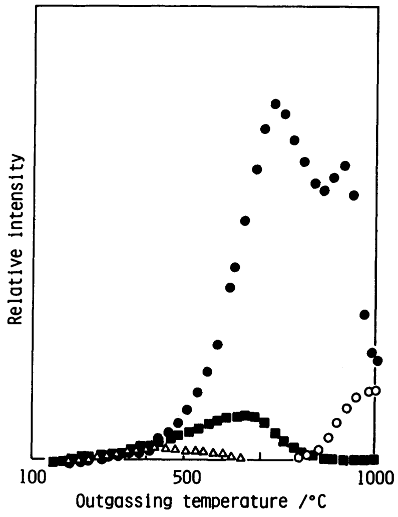

Fig. 5. Variations of mass spectral peaks of the desorbed gas on carbon black D with outgassing temperature up to 1000 °C at a heating rate of 4 °C/min in vacuum. ○: H_2, △: H_2O, ●: CO, ■: CO_2.

The mass spectral peaks of oxygen compounds such as CO and CO_2 from oxidized carbon black, especially from the carbon treated with 13.2 M HNO_3, were very large. However, the mass spectral peaks of H_2 from the oxidized forms of carbon black were low. For the carbon treated with hydrogen gas, the mass spectral peaks of oxygen compounds were very low and the mass spectral peaks of H_2 were rather large. We conclude that the hydrogen gas treatment removes the surface oxygen compounds. Mass spectroscopy showed that they were removed in the forms of H_2O, CO, and CO_2 during the hydrogen gas treatment. The weight decrease of the carbon-black samples heated in vacuum are shown in Table 3. The weight decreases of the oxidized carbon black, especially the carbon treated with 13.2 M HNO_3, were large, while that of the carbon treated with hydrogen gas was small. The weight decrease of various forms carbon, thus, increased along with the increase in the number of surface oxygen compounds.

The relationship between the amount of phenol adsorbed and the weight decrease of the carbon-black

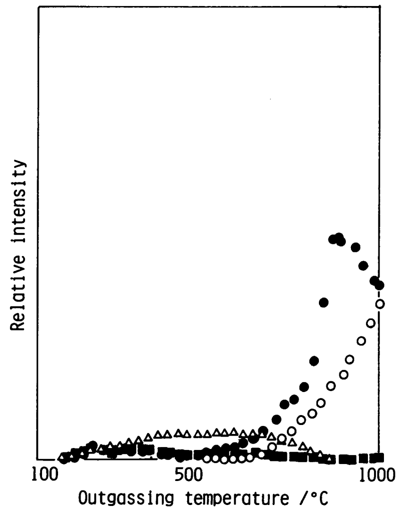

Fig. 6. Variations of mass spectral peaks of the desorbed gas on carbon black E with outgassing temperature up to 1000 °C at a heating rate of 4 °C/min in vacuum. ○: H_2, △: H_2O, ●: CO, ■: CO_2.

Table 3. Weight decrease of modified carbon black samples heated up to 1000 °C at a heating rate of 4 °C/min in vacuum

Carbon black	Weight decrease[a)] wt%
A	2.55
B	15.75
C	5.79
D	7.77
E	2.48

a) Based on the weight at 120 °C in vacuum.

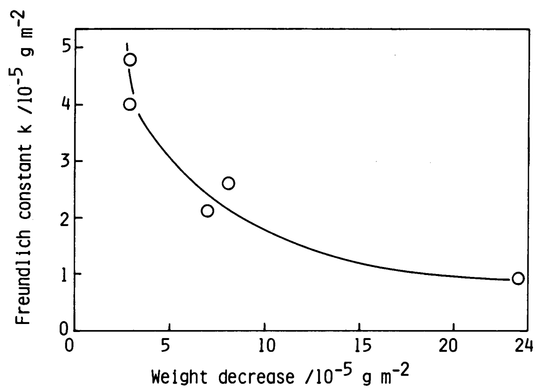

Fig. 7. The relationship between the amount of phenol adsorbed and the weight decrease of the modified carbon black samples in aqueous-phase adsorption.

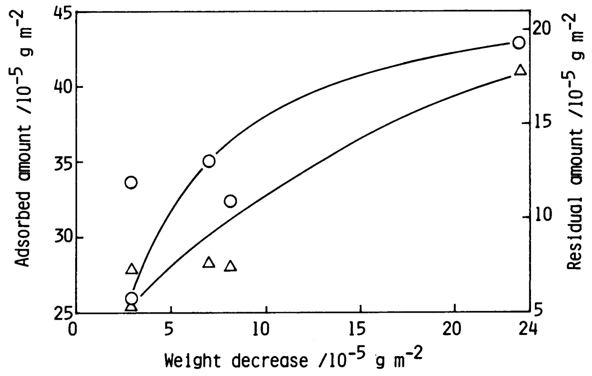

Fig. 8. The relationship between the amount of phenol adsorbed and the weight decrease of the modified carbon black samples in gas adsorption.
○: Adsorbed amount, △: Residual amount.

samples during aqueous-phase adsorption is shown in Fig. 7. In aqueous-phase adsorption, the amount of phenol adsorbed decreased with increasing the amount of the surface oxygen compounds. The relationship between the amount of phenol adsorbed and the weight decrease of the carbon-black samples in gas adsorption is shown in Fig. 8. In gas adsorption, the amount of phenol adsorbed increased with increasing the number of the surface oxygen compounds, and the residual amount of phenol also increased.

From the above results, we propose a model regarding the adsorption mechanism between carbon and phenol (Fig. 9). In the case of gas adsorption, the interactions are not only between the hydrophobic sites on the carbon and the hydrophobic groups of phenol, but also between the surface functional groups on the carbon and the hydrophilic groups of phenol. In the case of aqueous-phase adsorption, there is a competitive adsorption of phenol with water molecules. The adsorption of water may commence by hydrogen bonding to surface oxygen groups.[13)] It is thought that the water molecules adsorb selectively to the surface oxygen groups on the carbon because of their large polarity. The water molecules become secondary adsorption centers and retain other water molecules by means of hydrogen bonds.[12)] The majority of the surface oxygen groups exist near the edges of fused hexagonal carbon rings or aromatic nuclei that make up the basis structure for carbons.[11,14)] As a result, complexes of associated water form at the entrances of the pores of the carbon black. These complexes prevent the phenol adsorption due to the hydrophobic interaction on the carbon and prevent the invasion of phenol into the large surface area within the pores of the carbon. Therefore, the amount of phenol adsorbed on the carbon black in aqueous-phase adsorption decreases upon increasing the number of surface oxygen groups. However, in gas adsorption, the adsorbed amount and the residual amount of phenol on carbon black increased upon

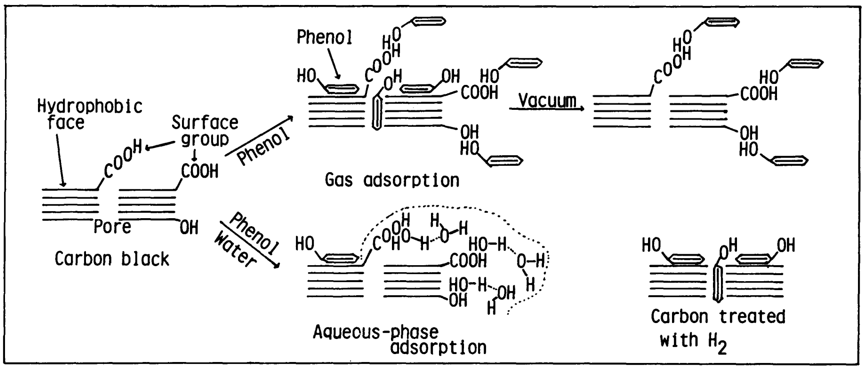

Fig. 9. The model of the adsorption mechanism between carbon and phenol.

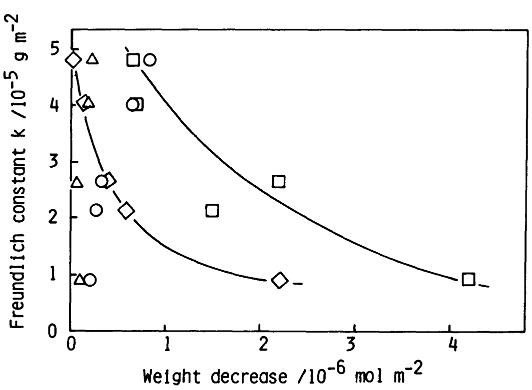

Fig. 10. The effect of surface oxygen compounds on aqueous-phase adsorption of phenol.
○: H_2, △: H_2O, □: CO, ◇: CO_2.

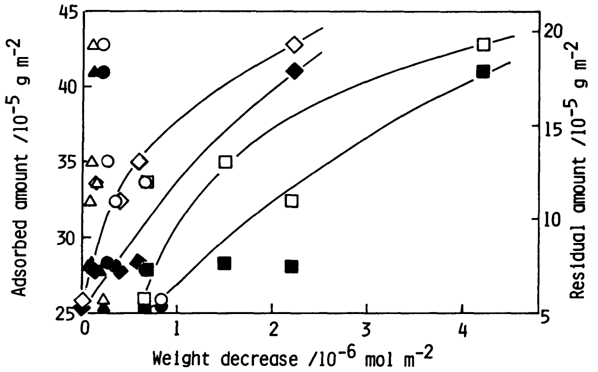

Fig. 11. The effect of surface oxygen compounds on gas adsorption of phenol.
Adsorbed amount: ○; H_2, △; H_2O, □; CO, ◇; CO_2,
Residual amount: ●; H_2, ▲; H_2O, ■; CO, ◆; CO_2.

increasing the number of surface oxygen groups, due to an interaction due to hydrogen bonding to the surface oxygen groups.

In order to investigate the influence of the forms of the surface oxygen groups on the carbon upon the adsorption of phenol, the weight decreases of the carbon for each of the desorbed gases have been evaluated using the mass spectral peaks of the desorbed gases on the modified types of carbon black shown in Figs. 2—6. These results are shown in Table 4. For carbon-black B, the weight decreases according to the desorbed gases, since CO and CO_2 are large and the total weight decrease is also large. For carbon-black C, the weight decreases are rather large for H_2 and H_2O, but the total weight decrease is little. The relationships between the amount of phenol adsorbed on the carbon and the weight decrease of the carbon for each of the desorbed gases are shown in Figs. 10 and 11. In aqueous-phase adsorption, the amount of phenol adsorbed decreased upon increasing the weight decreases based on the gases desorbed as CO and CO_2. In gas adsorption, the amount of phenol adsorbed increased upon increasing the weight decreases based on the gases desorbed as CO and CO_2.

Table 4. The weight decreases of the modified carbon black samples for each of the desorbed gases

Carbon black	Weight decrease				
	mmol g^{-1}				
	H_2	H_2O	CO	CO_2	Total
A	0.58	0.17	0.60	0.11	1.46
B	0.14	0.08	2.82	1.75	4.79
C	0.22	0.08	1.24	0.48	2.02
D	0.33	0.07	2.11	0.38	2.89
E	0.71	0.19	0.56	0.01	1.47

The residual amount of phenol also increased. The variation of the adsorbed amounts on the modified types of carbon black is independent of the weight decreases based on the gases desorbed as H_2 and H_2O in aqueous-phase adsorption and in gas adsorption, because the variation of weight decreases based on the gases desorbed as H_2 and H_2O is little. Suzuki[15] and Walker[16] have reported on the desorbed gases of carbon during the heat/evacuation treatment. The

Table 5. Surface acidities of modified carbon black samples

Carbon black	Surface group meq g^{-1} I	II	III	IV	Total
A	0.01	0	0.06	0	0.07
B	0.40	0.08	0.41	0	0.89
C	0.06	0.07	0.07	0.02	0.22
D	0.08	0.08	0.09	0.01	0.26
E	0	0.01	0	0.04	0.05

I: Carboxyl group. II: Carboxyl group that occurs as a lactone. III: Phenolic hydroxyl group. IV: Carbonyl group that reacts with the carboxyl group II to form the lactone (or lactol).

weight decrease based on the gas desorbed as CO_2 shows that carboxyl groups and carboxylic anhydrides exist on the carbon. The weight decrease based on the gas desorbed as CO shows that hydroxyl groups, carbonyl groups, and quinone exist on the carbon. Since the weight decrease of H_2O is independent of the variation of the amount of phenol adsorbed, it is thought that the surface oxygen groups are present as anhydrides on the carbon. The surface oxygen groups desorbed as CO and CO_2 are carboxylic anhydrides, carboxyl groups that occur as lactones, quinone, and carbonyl groups. The surface acidity of the modified carbon-black samples, which was estimated by the method of Boehm *et al.*[17,18] in the previous paper, is shown in Table 5. The surface acidity of carbon-black B, especially the surface acidity for carboxyl group, is large. The total weight decrease of carbon-black B is also large. The surface acidity of carbon-black E is less than that for the other types of carbon. The total weight decrease of carbon-black E is also less. The surface acidity of the modified types of carbon black for carbonyl group was less than that for other groups. Therefore, the surface oxygen compounds introduced with the oxidation treatments as carboxylic anhydride and as the carboxyl group that occurs as a lactone are probably dependent on the adsorption of phenol.

Consequently, the adsorption character of the various types of carbon black was found to be dependent on the surface oxygen compounds, especially on the carboxylic anhydrides and on the carboxyl groups that occur as lactones. We conclude that carbon black treated with hydrogen gas exhibits excellent adsorbability in the aqueous-phase adsorption. However, carbon black treated with stronger oxidizing agents exhibits better adsorbability regarding phenol gas adsorption.

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