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Sorption of Hydrogen Cyanide onto Activated Carbon Cloth Impregnated with Metallo-organic Compounds

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ABSTRACT

Activated carbon cloth (ACC) was impregnated with metallo-organic compounds consisting of the following cations: copper, silver, iron, magnesium, and aluminum, and the following anions: acetate, oxalate, tartrate, stearate, and citrate. Impregnation was performed in order to increase the chemisorptive capacity of the cloth for bonding hydrogen cyanide. Characterization of all carbon samples by determining the cation and anion contents of impregnants on the cloth was performed by atomic absorption spectrometry and ion and gas chromatography. The image of the surface composition and morphology of the materials were made by scanning electronic microscopy (SEM) with simultaneous local energy-dispersive analysis (EDS). The surface analysis was also performed by ESCA and XPS techniques. Another purpose of the investigation was to find an optimal mechanism for metallo-organic salts impregnation of ACC. Sorption properties of ACC were examined for hydrogen cyanide and benzene in the gas phase by a standard gravimetric procedure with the use of a Cahn RG electrobalance. It was concluded that samples impregnated with copper(II) tartrate, silver(I) citrate, and iron(III) citrate have an optimal sorption capacity from the point of view of both physical adsorption and chemisorption. The salts of magnesium and aluminum which were used have no affinity for HCN bonding.

Key Words. Activated carbon cloth; Impregnation; Metallo-organic salts; Chemisorption; Hydrogen cyanide

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INTRODUCTION

The sorptive properties of activated carbon in the form of granules have been widely studied (1, 2). In recent years particular attention has been given to fibers in the form of textiles (3, 4). These activated carbon fibers can be prepared from the precursor of viscose rayon by using pyrolysis and activation (5, 6).

Activated carbon cloth (ACC) is useful as a sorbent in processes for the complex purification of air and the separation of toxic pollutants from air (7, 8). In this work, hydrogen cyanide was used as a pollutant; it represents extremely toxic pollutants which may be found in the air following chemical accidents. There are several papers dealing with the sorption of hydrogen cyanide on activated carbon (9, 10). The purpose of this work was to find a convenient separation technique and a convenient carbon material for removing cyanide from the air by a chemisorption process. For that purpose, ACC was additionally activated by chemical impregnation. In this way it could be possible to separate cyanides efficiently by bonding them to an active chemical agent inside the cloth (11–17). Chemical impregnation was done by using metallo-organic compounds. The role of metallic ions was to introduce a catalytic function, while the role of organic components was to increase the sorptive capacity of the cloth. The motivation for this work was the idea of investigating sorption on carbon "atoms," which was experimentally achieved by using organic acids which have one, two, or more carboxyl groups. Benzene was used as the standard adsorbate for physical adsorption control.

In this work, the complete results of ACC impregnation, its characterization, and the sorption capacity of the cloth are given.

EXPERIMENTAL

The basic material used in this research was microporous ACC with a specific surface of 1491.12 m^2/g, made by carbonization and activation of viscous rayon, a standard production type, produced by Toyobo, Osaka, Japan. Acetates, oxalates, tartrates, stearates, and citrates of copper, silver, iron, magnesium, and aluminum were used as impregnation reagents. The concentrations of solutions of these salts were 0.1 mol/dm^3, and they were made from Merck and Zorka chemicals.

Portions of the cloth were impregnated with salts as follows. Five pieces, about 10×10 cm^2 each, were placed in a beaker and 250 cm^3 of a standard 0.1 mol/dm^3 aqueous solution of the salts was added. The solutions were prepared by synthesis. Impregnation was done by immersing the pieces of ACC in the aqueous solutions of the salts for 45 minutes.

For salts which are not soluble in water, synthesis was performed on the cloth: cloth was immersed for 20 minutes in a solution which contained the metallic cations and for 20 minutes in a solution which contained the organic anions. The cloth pieces were washed with distilled water and dried on filter paper at room temperature. For comparison, samples with and without washing after impregnation were tested.

Hydrogen cyanide was synthesized immediately before use from potassium cyanide and sulfuric acid (1:1). Before HCN was used it was dried by passage through a column packed with calcium chloride.

In order to evaluate the characteristics of ACC and obtain standard adsorption isotherms, benzene was used as a second adsorbate.

Metallic ions were determined by atomic absorption flame spectrometry with a Perkin-Elmer 5000 model spectrometer. Samples were prepared as follows: samples with an average weight of about 60 mg were placed in Tecator holders, and 5 cm^3 of 65% HNO_3 with a trace of Carborundum was added. The holders were heated to 120°C, at which temperature a yellow gas was liberated and the cloth disintegrated. Then 1 cm^3 concentrated $HClO_4$ was added to holders and heated to 160°C. The moment the color of the solution disappeared, 2 cm^3 of 65% HNO_3 was added, which was followed by liberation of the white gas of perchloric acid. The temperature was increased to 250°C and the solution was heated until a solid residue was left in the holder. Finally, 25 cm^3 distilled water was added and, after mixing the solution vigorously by shaking, it was kept in the holder and used for measurements.

The contents of acetates, oxalates, tartrates, and citrates were determined by ion chromatography (single-column ion chromatography). The following apparatuses were used: a LKB Bromma 2150 HPLC pump, a Rheodyne injector with 100 a μL loop, a Waters IC PAK A column, and a Waters Model 430 Conductivity detector. The flow was 1 cm^3/min. The mobile phase was KH-phthalate, pH 4.1. The standard addition method was used for all anions.

Sample preparation was performed in the following manner: 1 cm^2 of the cloth was measured, immersed in 2 cm^3 distilled water, and left for 30 seconds in an ultrasonic bath. The solution was then separated, passed through a Millex-GX 0.22 μm filter, and injected in the column.

The stearate content was determined by gas chromatography on a Sigma 3B Perkin-Elmer with a Sigma 15 Perkin-Elmer integrator. The conditions were as follows: column temperature (10% FFAP on chromosorb WHP, glass length 2 m) 220°C, injector temperature 230°C, and FID temperature 240°C. The carrier gas was nitrogen at a pressure of 80 kPa.

In order to determine stearates, a sample was prepared in the following manner: a previously measured sample was placed in a test tube and 1

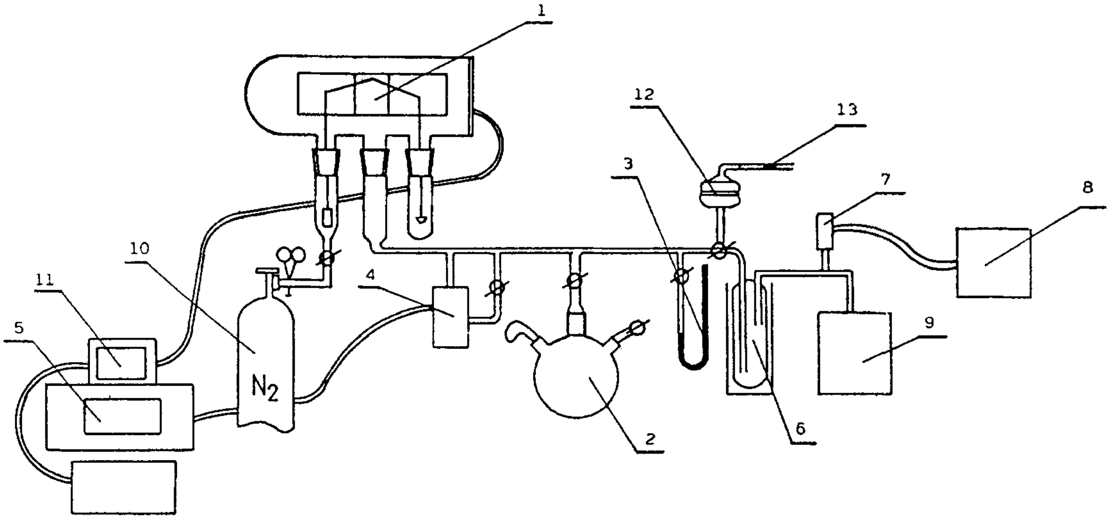


FIG. 1 Scheme of the apparatus for gravimetric adsorption: (1) Cahn RG electrobalance, (2) container for synthesis of HCN, (3) pressure gauge, (4) measuring unit of pressure gauge, (5) pressure gauge, (6) cold trap, (7) measuring unit of pressure gauge, (8) vacuum meter, (9) vacuum pump, (10) N_2 cylinder, (11) measure unit of Cahn electrobalance, (12) respitator container, (13) indicator tube for HCN.

cm^3 BF_3 (50% solution in methanol) was added. The test tube contents were mixed for 30 seconds and then heated at 80°C in a water bath for 2 minutes. Demineralized water (1 cm^3) and 0.2 cm^3 *n*-hexane were added, and the contents were mixed for 1 minute. After layering occurred, 5 μL was taken from the upper layer and dissolved in 0.5 cm^3 *n*-hexane. The sample was injected into a gas chromatograph.

In order to analyze the impregnation process, elementary analysis of ACC both with and without impregnation was performed by an energy-dispersive method on an Edax 9900 apparatus. For this purpose, samples were mounted on stubs 1 cm in diameter and pumped to a vacuum level of 1.33×10^{-6} Pa. Simultaneously, morphological analysis was done by scanning electron microscopy, and the images were obtained by secondary electrons on a Philips SEM 515.

Characterization of ACC was also performed by Auger electronic spectroscopy on a Riber apparatus. The spectroscopic system consisted of an ultrahigh vacuum system (1.33×10^{-7} Pa), an electronic gun of 100 μm diameter for exciting the sample, and an energetic analyzer for detection of Auger electronic peaks in the total secondary distribution. This part of the analysis was successfully performed only with samples impregnated with copper salts. The rest of the samples were not successfully analyzed due to poor conductivity or insufficient impregnation.

The sorptive properties of the samples were examined on a gravimetric adsorption apparatus (Fig. 1) by a standard procedure under static conditions.

A Cahn RG electrobalance was used. Measurements were taken at intervals of relative pressures ranging from 0.0 to 0.3. The increase of mass of adsorbates during the introduction of portions of gas into the system was measured with the Cahn electrobalance. The gas portion was determined by the pressure change. Adsorption was performed at an initial pressure of 13.2 Pa. The sample had been previously vacuumed for 120 minutes to clean the surface of impurities. The results were processed using Langmuir adsorption isotherms.

RESULTS AND DISCUSSION

Quantitative analysis of impregnants indicated that cations and anions show various affinities toward ACC. Affinity of anions decreases in the following order: acetates, tartrates, citrates, oxalates, and stearates, which corresponds to increasing ion size. Good adherence of tartrates and citrates to the surface can be explained by electrostatic attraction and also by the geometry and dimensions of the molecules. Tartrates and citrates attach to electropositive locations on the surface of ACC by their electronegative hydroxyl OH^- and carboxyl COO^- groups by van der Waals forces. Cations remain on the "other" side. Because of its size, the stearate molecule, can attach to the fiber surface only with its "tail." Therefore it does not react with cyanide ions and probably blocks some of the micropores because of its size. The aim of impregnating the ACC with such salts was to find out whether the carbon atoms from the impregnants will be free and active for adsorbing the cyanide. However, it seems that the number of carbon atoms is not decisive; rather, the copper and silver cations are optimally bonded if the salts are properly chosen.

The cation content, as determined by the AAS method, is given in Table 1. It is noticeable that there is a difference in the percentage of impregnant held within the samples that were washed after impregnation and those that were not. Generally, the silver salts [silver(I) acetate with 12.26 mass% silver] and copper salts [copper(II) acetate with 6.72 mass% copper] attach strongly to the surface of the fibers. This is not puzzling when we bear in mind that all silver salts are very slightly soluble in water. For

TABLE 1
Cations in ACC Determined by AAS and EDS Techniques

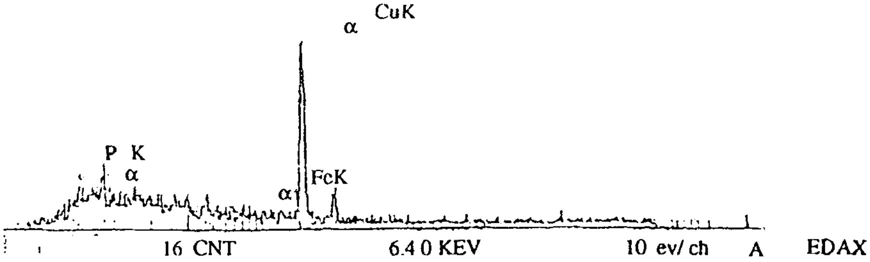
	AAS techniques				EDS techniques, cation content (%)	
	Washed samples		Unwashed samples			
Adsorbent	Cation content (%)	Standard deviation	Cation content (%)	Standard deviation	Washed samples	Unwashed samples
ACC + Cu(II) acetate	6.72	0.680	10.84	1.73	16.32	20.40
ACC + Cu(II) oxalate	0.53	0.045	3.33	0.32	10.53	17.30
ACC + Cu(II) tartrate	2.19	0.018	7.30	0.62	9.20	15.25
ACC + Cu(II) stearate	0.39	0.011	8.77	0.79	8.24	13.80
ACC + Ag(I) acetate	12.26	0.814	14.55	0.73	9.49	13.95
ACC + Ag(I) oxalate	6.78	0.370	8.92	0.77	9.40	13.15
ACC + Ag(I) tartrate	5.62	0.525	7.02	0.59	7.90	12.36
ACC + Ag(I) citrate	3.50	0.202	3.53	0.40	3.20	7.50
ACC + Fe(II) acetate	0.68	0.042	0.76	0.05	4.70	9.20
ACC + Fe(II) oxalate	0.41	0.018	1.28	0.51	3.80	7.65
ACC + Fe(II) tartrate	0.49	0.099	0.96	0.18	4.10	7.80
ACC + Fe(III) citrate	1.08	0.311	1.34	0.31	5.30	10.40
ACC + Mg(II) acetate	0.24	0.021	0.25	0.04	7.20	10.20
ACC + Mg(II) oxalate	0.23	0.032	0.55	0.19	7.40	11.20
ACC + Mg(II) stearate	0.09	0.09	0.33	0.11	3.85	6.45
ACC + Al(III) acetate	0.17	0.021	0.35	0.06	6.50	9.15
ACC + Al(III) oxalate	0.03	0.023	0.27	0.07	1.70	2.75

the same reason, the smallest percentage of impregnants was removed by washing when silver salts were already present on the ACC surface. Generally, about 20% of an impregnant was removed by washing.

The cation content, as determined by the EDS method, is given in Table 1. It is important to emphasize that phosphorus was found in all samples, but not as a result of the impregnation process. It could appear as a result of the preparation of viscous rayon in the activation process. Also, it was established that silicon (12.99 at.%) and potassium (24.70 at.%) were present in the original sample. These two elements are present in the precursors which are usually used in producing ACC. Sulfur was also found in most samples. Spectrograms of some samples are shown in Figs. 2 and 3.

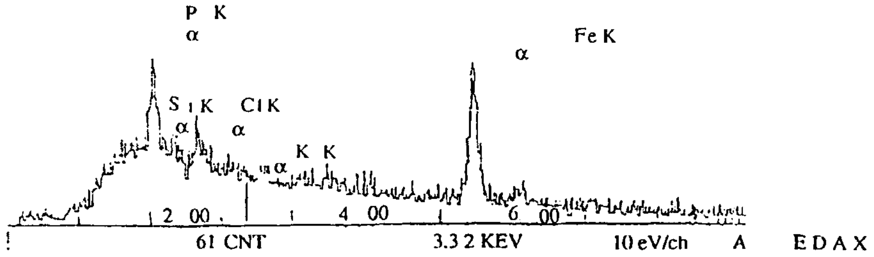
From Table 1 it is seen that there are differences between the values of the impregnant content obtained by EDS and AAS analysis. This is due to the substantial difference between these two techniques. The EDS technique determines the elemental content in a very small surface area while the AAS method determines the content in bulk. EDS can be successfully used for morphological qualitative analysis of cloth as well as for preliminary characterization. The advantages of this method are that it is nondestructive and does not require any additional sample preparation.

The anion content for samples with and without washing after impregnation is given in Table 2. All tartrates and citrates were adsorbed on the cloth excellently. A very high percentage of adherence was achieved only



ELEM	CPS	WT % ELEM
P K	3.5800	21.99
CU K	30.6800	76.01
TOTAL		100.00

FIG. 2 EDS spectrogram of sample impregnated with copper(II) acetate and washed after impregnation.



ELEM	CPS	WT % ELEM
SI K	2.1500	1.99
P K	38.5500	36.87
CL K	9.0000	8.36
K K	2.0000	1.27
FE K	75.8000	51.51
TOTAL		100.00

FIG. 3 EDS spectrogram of sample impregnated with iron(III) citrate and washed after impregnation.

TABLE 2

Anions in ACC Determined by Ion Chromatography

	Washed samples		Unwashed samples	
Adsorbent	Anion content, %	Standard deviation	Anion content, %	Standard deviation
ACC + Cu(II) acetate	19.34	0.83	19.99	0.72
ACC + Cu(II) oxalate	0.03	0.01	0.15	0.04
ACC + Cu(II) tartrate	5.60	0.86	6.68	0.71
ACC + Cu(II) stearate	2.77	0.54	4.11	0.45
ACC + Ag(I) acetate	1.79	0.10	2.70	0.43
ACC + Ag(I) oxalate	0.25	0.06	0.28	0.09
ACC + Ag(I) tartrate	8.42	0.67	14.11	1.26
ACC + Ag(I) citrate	2.58	0.56	3.55	1.27
ACC + Fe(II) acetate	2.07	0.28	2.27	0.43
ACC + Fe(II) oxalate	0.04	0.01	0.05	0.02
ACC + Fe(II) tartrate	10.32	2.00	10.87	1.21
ACC + Fe(III) citrate	2.82	0.25	3.38	0.31
ACC + Mg(II) acetate	0.22	0.12	0.24	0.11
ACC + Mg(II) oxalate	0.04	0.01	0.04	0.01
ACC + Mg(II) stearate	2.18	0.19	5.46	0.93
ACC + Al(III) acetate	1.50	0.18	3.18	0.40
ACC + Al(III) oxalate	0.07	0.02	0.07	0.04

by copper(II) acetate, as high as 19.34 mass% with samples washed after impregnation. All oxalates were adsorbed very poorly: from 0.027 mass% for a cloth impregnated with copper(II) oxalate to 0.25 mass% for a cloth impregnated with silver(I) oxalate.

From Table 2 it is seen that in the sample impregnated with copper(II) stearate there was 2.77 mass% of stearate, while in the sample impregnated with magnesium(II) stearate there was 2.18 mass%. However, stearate was deposited on cloth mainly in the form of a powder which falls off when the cloth is shaken, so it does not achieve the desired function. Also, it visibly covered the surface of the cloth and the micropores. This was confirmed by the adsorption of hydrogen cyanide.

Micrographs obtained by SEM helped to determine the morphological structure of ACC. Figure 4 shows samples impregnated by copper salts. These micrographs show that particles of copper(II) acetate salts are visibly and strongly adsorbed on carbon fibers. The distribution of impregnants was obviously not homogeneous.

The micrographs in Fig. 5 show that silver salts were adsorbed on the cloth better than were the other salts. Because they are the least soluble, they coated the surface of each fiber with particles about 1 μm in diameter. Carbon fiber is about 15 μm thick (18).

With samples impregnated by iron salts, there were no conspicuous traces of salts. Only with some difficulty are traces of these salts seen on the surface of fibers; the particles are smaller than 1 μm. The fibers were smooth and shiny.

Fibers impregnated with aluminum salts looked similar. Salt particles were not visible in interfibrous space, but traces of salt adsorbed on the fiber itself were visible.

For samples impregnated with magnesium salts, particles of salts, both those adsorbed on the fiber and those in interfibrous space, are highly visible. These values are close to the fiber diameter.

The results of AES analysis show that the composition of the surface is not homogeneous, but the ratio of elements generally remains the same. The presence of N, S, P, and Ca can be attributed to impurities in the carbon (Fig. 6).

C 1s, O 1s, Cu 2p, and Cu Auger spectra were recorded by the XPS method. The Cu Auger spectrum was found at 574 and 670 eV. The shape of C 1s spectrum shows that there are no chemical bonds between carbon and metal, while its asymmetry toward higher bonding energies suggests possible connections with O, N, or S. The presence of a doublet (20.1 eV) Cu 2p spectra and its shape show that copper is present as CuO, which is confirmed by the position of the O 1s spectrum. However, the amounts of O and Cu obtained by AES analysis suggest that their ratio

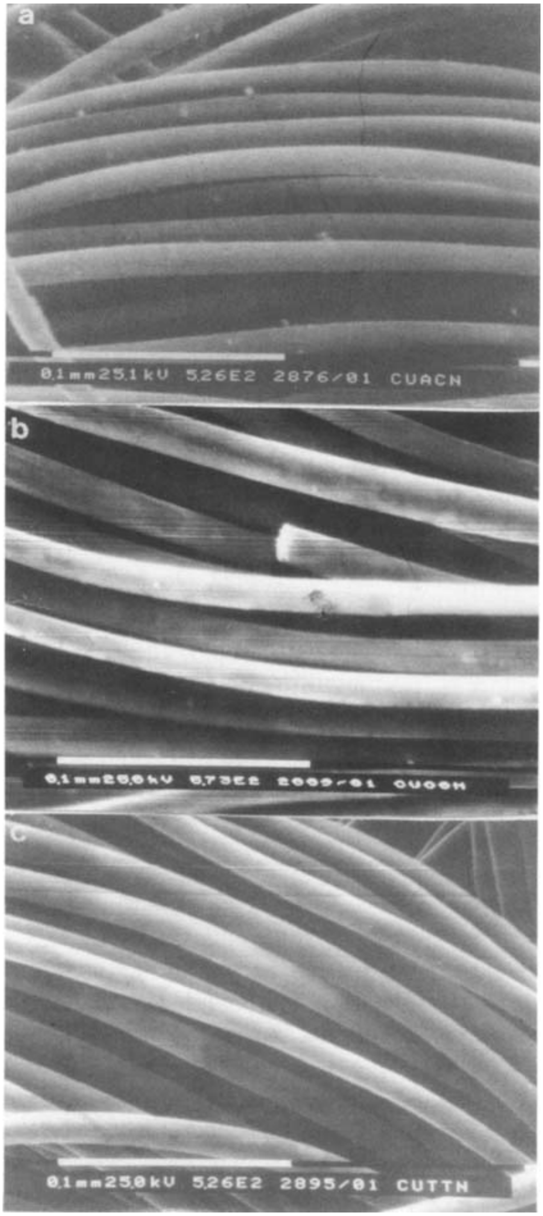


FIG. 4 Micrographs of samples impregnated with copper salts, magnification 526×: (a) ACC + Cu(II) acetate, (b) ACC + Cu(II) oxalate, (c) ACC + Cu(II) tartrate.

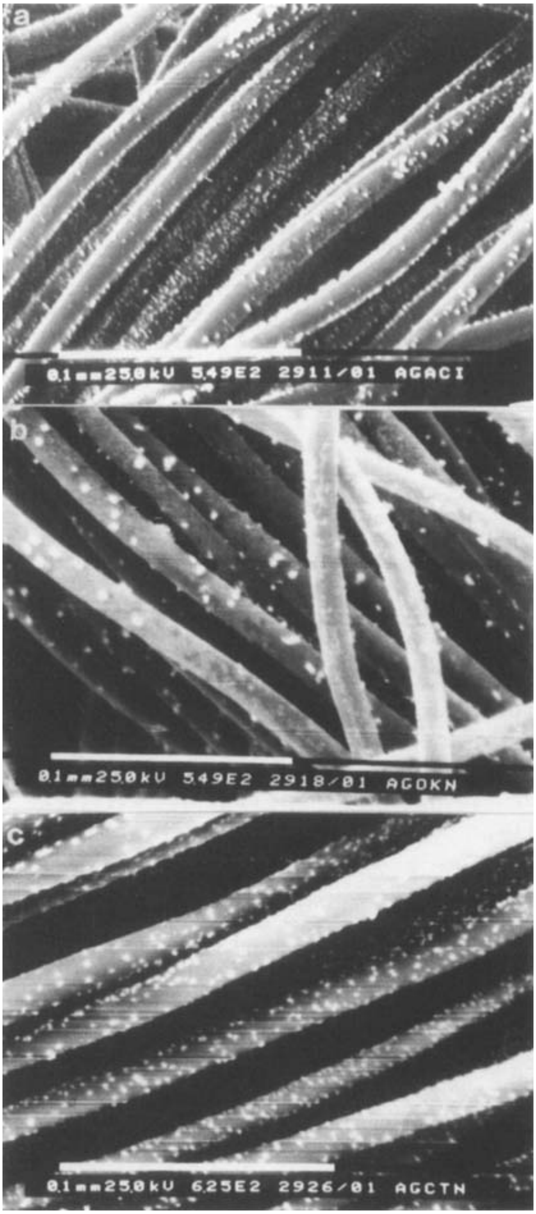


FIG. 5 Micrographs of samples impregnated with silver salts, magnification 549×: (a) ACC + Ag(I) acetate, (b) ACC + Ag(I) oxalate, (c) ACC + Ag(I) citrate.

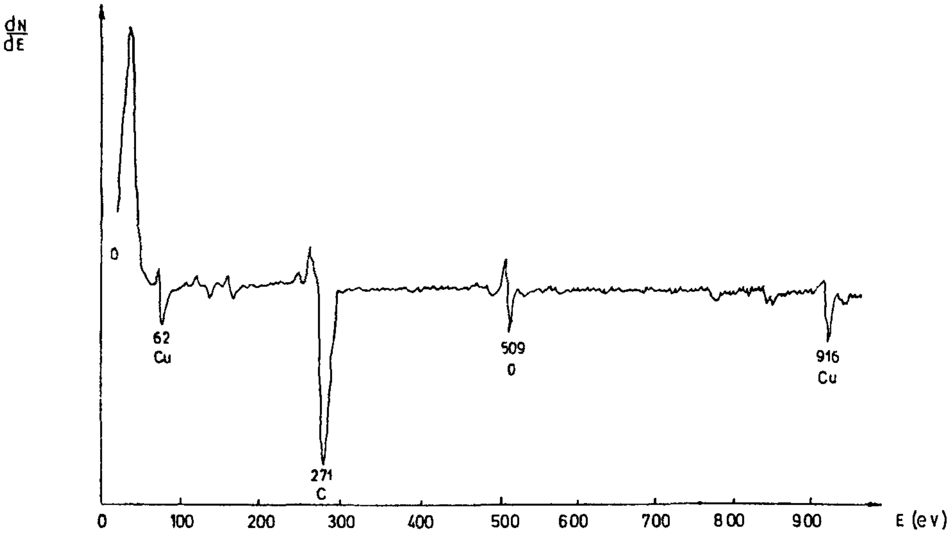


FIG. 6 Auger spectrogram of sample impregnated with copper.

does not fit CuO. In addition, the Cu 2p spectra show wide peaks, that is, several maximums; for this reason, it is believed that on the surface of the sample a part of the copper is present as CuO and another part as Cu_2O. The ratio of copper and oxygen deeper in the sample shows that elementary copper probably dominates (Fig. 7).

The results of determining of specific surface by benzene isotherms are given in Table 3.

Specific surfaces differ from sample to sample because of the differing percentages of impregnants added to ACC. As Kloubek shows in his work (15), impregnants may partly close the pores. Chiou and Reucroft (16) reached the same conclusion. If more impregnant is used, more space is blocked, and therefore the specific surface is further reduced. It is logical to assume that the highest percentage of salts was imposed on ACC when copper(II) acetate was used: 6.72 mass% copper (Table 1) and 19.34 mass% acetate (Table 2). This led to a reduction of the specific surface from 1491.12 to 853.75 m^2/g, which is about 40%. All salts caused a greater or smaller reduction of specific surface, which was expected. Drastic reduction was observed after impregnation with copper(II) stearate and magnesium(II) stearate for which the specific surface was reduced to 270.76 and 473.13 m^2/g, respectively, which is unsatisfactory. For samples which were not washed after impregnation, these values are even lower, namely,

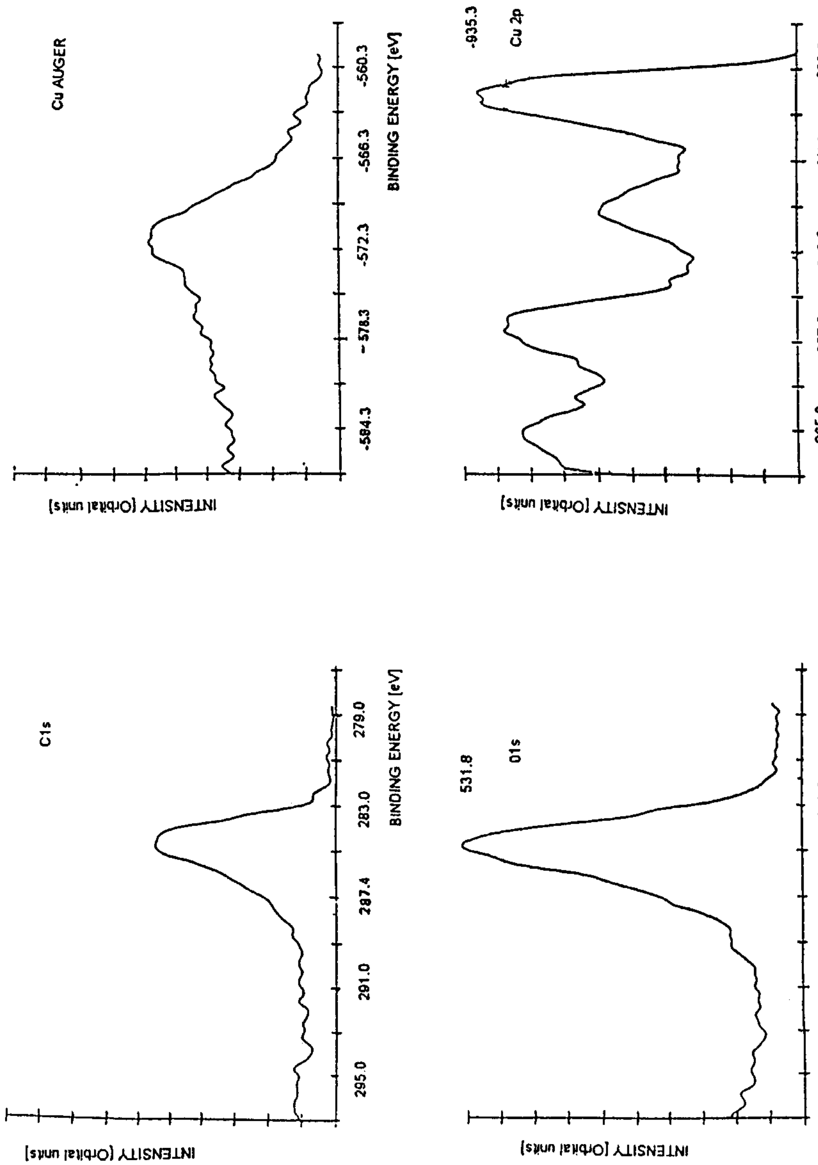


FIG. 7 XPS characterization of sample impregnated with copper.

TABLE 3
Specific Surface Area and Specific Volume of Micropores

Adsorbent	Washed samples		Unwashed samples	
	Specific surface of micropores, m^2/g	Specific volume of micropores, cm^3/g	Specific surface of micropores, m^2/g	Specific volume of micropores, cm^3/g
ACC + Cu(II) acetate	853.75	0.3130	802.91	0.2911
ACC + Cu(II) oxalate	1299.80	0.4739	1183.69	0.4385
ACC + Cu(II) tartrate	896.62	0.3225	848.10	0.3100
ACC + Cu(II) stearate	270.76	0.0924	205.06	0.0692
ACC + Ag(I) acetate	1147.29	0.4218	1025.21	0.3721
ACC + Ag(I) oxalate	1223.61	0.4480	1133.03	0.4162
ACC + Ag(I) tartrate	1307.37	0.4818	1225.32	0.4567
ACC + Ag(I) citrate	1341.60	0.4929	1242.52	0.4631
ACC + Fe(II) acetate	1370.70	0.5050	1244.43	0.4648
ACC + Fe(II) oxalate	1471.30	0.5396	1372.88	0.5126
ACC + Fe(II) tartrate	834.98	0.3088	797.78	0.2954
ACC + Fe(III) citrate	1143.85	0.4211	1068.89	0.3974
ACC + Mg(II) acetate	1250.85	0.4584	1177.48	0.4367
ACC + Mg(II) oxalate	1480.95	0.5436	1298.74	0.4854
ACC + Mg(II) stearate	473.13	0.1680	405.08	0.1407
ACC + Al(III) acetate	1413.85	0.5212	1320.69	0.4907
ACC + Al(III) oxalate	1340.05	0.4933	1252.13	0.4640
ACC	1491.12	0.5482	1491.12	0.5482

205.06 m^2/g for copper(II) stearate and 405.08 m^2/g for magnesium(II) stearate. This means that between 70 and 80% of the micropores were covered.

Table 2 also shows that oxalates attach very poorly to ACC. The consequence of this was that the specific surfaces remained large in samples impregnated by oxalates as compared to samples impregnated by other salts. The reduction of the specific surface was from 1 to 20%.

By comparing the samples which were washed after impregnation and those which were not, it was found that the sorptive capacity of benzene for all types of salts used was lower by about 15% in unwashed samples where the concentration of impregnants was greater and, therefore, more pores were blocked.

Chiou and Reucroft (16) showed that chemisorption is important at lower pressures while physical adsorption dominates at higher pressures. By comparing adsorption isotherms it is seen that adsorptive capacity is lower in regions of higher pressure. This suggests that an impregnant blocked or occupied a part of the adsorption area of the pores, which resulted in a smaller volume of micropores. Such effects reduce adsorptive abilities in regions of higher relative pressure. In the region of lower relative pressure, adsorptive capacity is greater than in nonimpregnated carbon cloth. Based on the types of cupric salts, the greatest adsorptive capacity of benzene was found in material impregnated by copper(II) oxalate (0.44 $g_{C_6H_6}/g_{ACC}$ at a relative pressure of 0.3), copper(II) tartrate (0.28 $g_{C_6H_6}/g_{ACC}$), copper(II) acetate (0.27 $g_{C_6H_6}/g_{ACC}$), and copper(II) stearate (0.17 $g_{C_6H_6}/g_{ACC}$), all at the same relative pressure (Fig. 8a).

When the sorption isotherms of hydrogen cyanide were analyzed, it was seen that adsorption capacity did not follow the above given order. The greatest sorptive capacity for hydrogen cyanide was found in the sample impregnated with copper(II) tartrate (0.32 g_{HCN}/g_{ACC} at a relative pressure of 0.3 with a tendency of further increase, which is seen from the shape of the isotherm). Sorptive capacity decreases in the following order: copper(II) oxalate (0.27 g_{HCN}/g_{ACC}), copper(II) acetate (0.17 g_{HCN}/g_{ACC}), and copper(II) stearate (0.09 g_{HCN}/g_{ACC}), all at the same relative pressure (Fig. 8b).

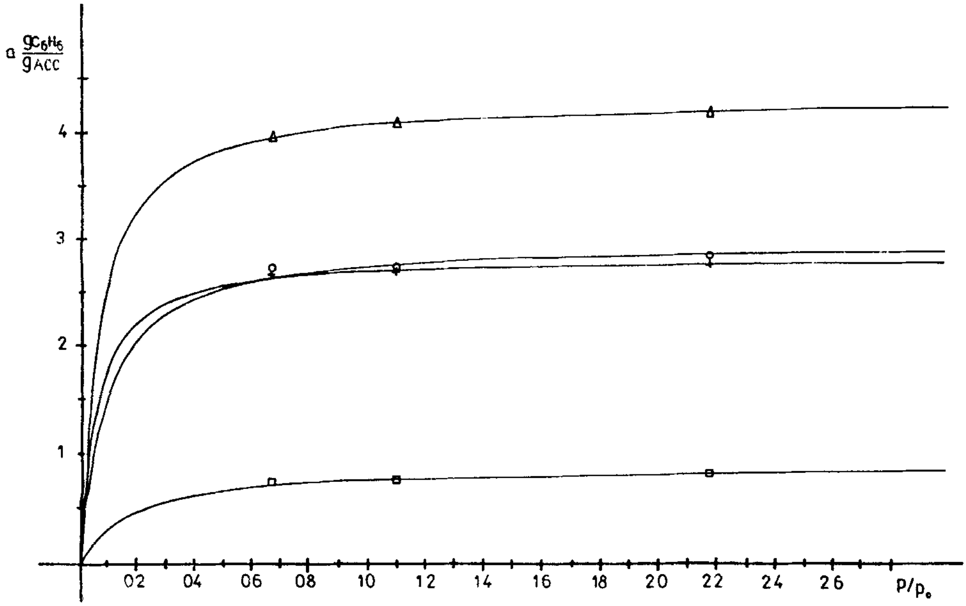


FIG. 8a Adsorption isotherms of benzene for samples impregnated with copper salts: (+) ACC + Cu(II) acetate, (Δ) ACC + Cu(II) oxalate, (O) ACC + Cu(II) tartrate, (□) ACC + Cu(II) stearate.

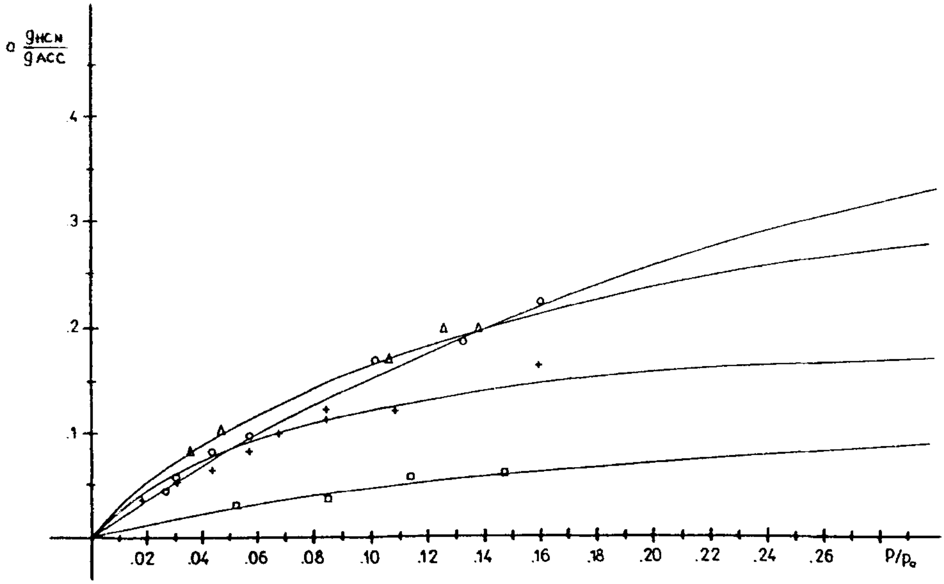


FIG. 8b Adsorption isotherms of hydrogen cyanide for samples impregnated with copper salts: (+) ACC + Cu(II) acetate, (Δ) ACC + Cu(II) oxalate, (O) ACC + Cu(II) tartrate, (□) ACC + Cu(II) stearate.

If these results are compared with the sorptive capacity of samples which were not washed after impregnation, it will be obvious that there are certain discrepancies. The sorptive capacity for HCN with the sample impregnated with copper(II) acetate increased by about 50%, while with other types of salts this capacity was reduced by about 40%, which means that a large number of pores were blocked for adsorption. A characteristic example is impregnation with copper(II) stearate, which has been discussed above.

Sorptive capacities are very high with all types of silver salts used for impregnation, and they are located in a very narrow range (0.36–0.43 $g_{C_6H_6}/g_{ACC}$ at a relative pressure of 0.3). The sorptive capacity decreases in the following order: silver(I) citrate, silver(I) tartrate, silver(I) oxalate, and silver(I) acetate (Fig. 9a).

It is interesting that the same order holds for sorption of HCN. The sorptive capacity of the sample impregnated with silver(I) acetate and washed after impregnation was 0.13 g_{HCN}/g_{ACC} (Fig. 9b) compared with

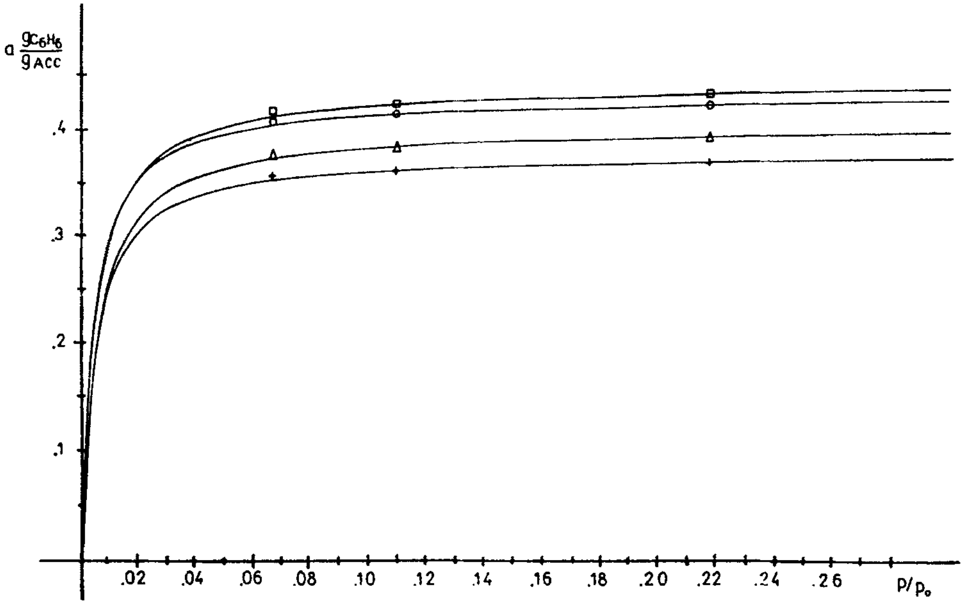


FIG. 9a Adsorption isotherms of benzene for samples impregnated with silver salts: (+) ACC + Ag(I) acetate, (△) ACC + Ag(I) oxalate, (○) ACC + Ag(I) tartrate, (□) ACC + Ag(I) citrate.

$0.26\ g_{HCN}/g_{ACC}$ for the unwashed sample, both at the same relative pressure of 0.3. This suggests that, in this case, it is possible to achieve better chemisorptive ability by increasing the quantity of impregnant. Samples impregnated with silver(I) citrate did not show significant changes in sorptive capacities for HCN whether they were washed or unwashed. Sorptive capacity at a relative pressure of 0.3 was $0.30\ g_{HCN}/g_{ACC}$ and $0.31\ g_{HCN}/g_{ACC}$, respectively. It means that adding more impregnant beyond a certain percentage does not produce any effect.

It can be concluded that all the silver salts tested are efficient as impregnants, although the material impregnated with silver(I) citrate has somewhat better characteristics.

The adsorptive isotherms of benzene in the samples impregnated witn iron salts showed that the highest capacity was obtained with samples impregnated with iron(II) oxalate and subsequently washed ($0.47\ g_{C_6H_6}/g_{ACC}$ at a relative pressure of 0.3). The capacity of iron(II) acetate was

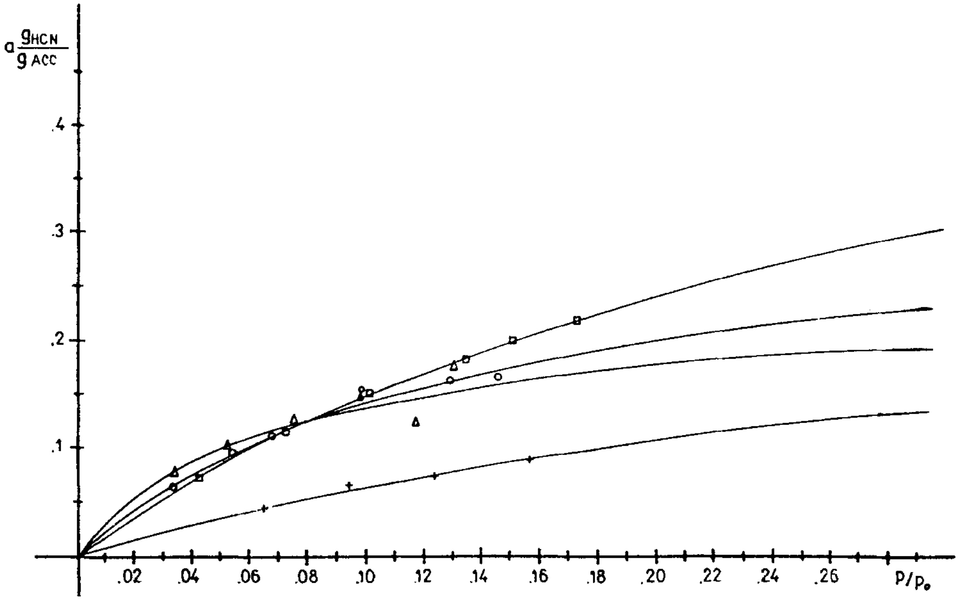


FIG. 9b Adsorption isotherms of hydrogen cyanide for samples impregnated with silver salts: (+) ACC + Ag(I) acetate, (Δ) ACC + Ag(I) oxalate, (○) ACC + Ag(I) tartrate, (□) ACC + Ag(I) citrate.

0.45 $g_{C_6H_6}/g_{ACC}$, of iron(III) citrate 0.36 $g_{C_6H_6}/g_{ACC}$, and of iron(II) tartrate 0.28 $g_{C_6H_6}/g_{ACC}$, all at the same relative pressure (Fig. 10a).

The sorptive capacity for HCN increases from samples impregnated with iron(II) acetate (0.20 g_{HCN}/g_{ACC}), iron(II) oxalate (0.23 g_{HCN}/g_{ACC}), iron(II) tartrate (0.29 g_{HCN}/g_{ACC}), to iron(III) citrate (0.38 g_{HCN}/g_{ACC}), the last showing excellent sorptive capacity (Fig. 10b).

Taking into consideration both the sorption of benzene and that of hydrogen cyanide, material impregnated with iron(III) citrate possesses the best sorption characteristics. As expected, the sorptive capacity of benzene of samples impregnated with magnesium(II) acetate and magnesium(II) oxalate can be very high, but this is not the result of the impregnant used. Material impregnated with magnesium(II) stearate confirms the theory discussed above, namely, magnesium(II) stearate blocks pores completely, so the sorptive capacity of benzene is very low (0.15 $g_{C_6H_6}/g_{ACC}$). The sorptive capacity for HCN is very low for all samples impregnated with magnesium salts; it was not higher than 0.20 g_{HCN}/g_{ACC} with

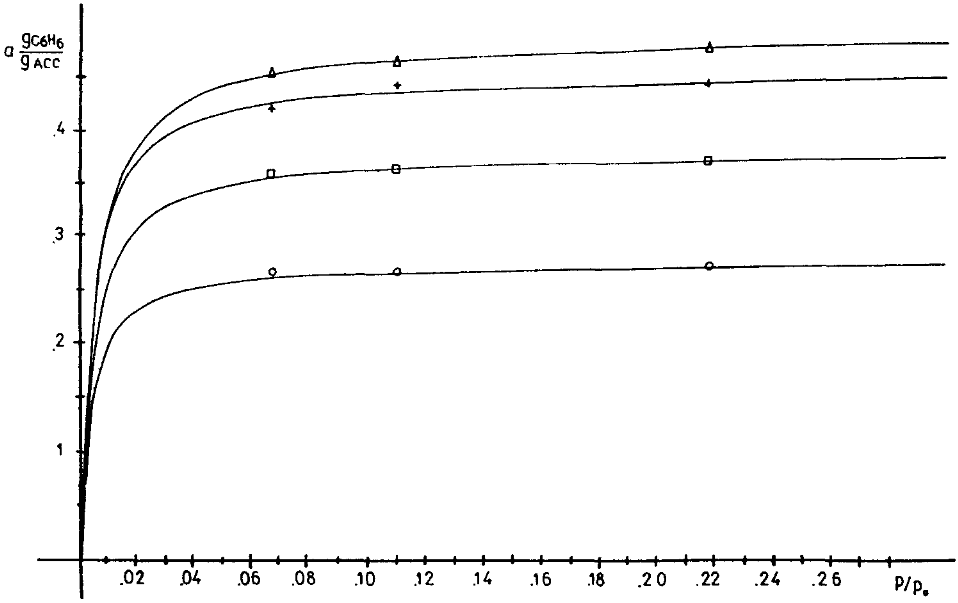


FIG. 10a Adsorption isotherms of benzene for samples impregnated with iron salts: (+) ACC + Fe(II) acetate, (△) ACC + Fe(II) oxalate, (○) ACC + Fe(II) tartrate, (□) ACC + Fe(III) citrate.

any of the samples. If, as in the case of the chemisorption of hydrogen cyanide, the abilities of an impregnant as a chemisorbent were to be examined, it is obvious that magnesium salts are not adequate because they do not show an affinity for HCN; therefore, they will not be considered any further.

Materials impregnated with aluminum salts showed a very high sorptive capacity for benzene, above 0.40 $g_{C_6H_6}/g_{ACC}$. Isotherms for HCN show that this case is similar to the previous one. The sorptive capacity of these materials for HCN is very low, barely above 0.20 g_{HCN}/g_{ACC}. Therefore, *they will not be considered any further.*

Adsorption isotherms for benzene and hydrogen cyanide for nonimpregnated ACC are given in Fig. 11.

When cyanide ions chemically bond on ACC, precipitates and complex compounds are formed. These processes are carried out in two stages, with the formation of characteristic compounds in both cases. By favoring the conditions for producing complex compounds, it is possible to achieve

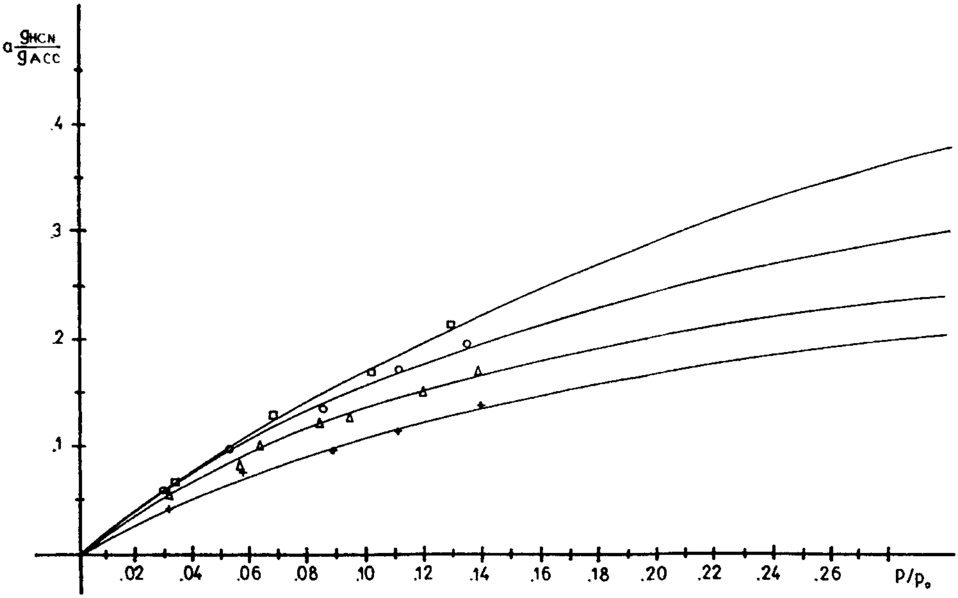


FIG. 10b Adsorption isotherms of hydrogen cyanide for samples impregnated with iron salts: (+) ACC + Fe(II) acetate, (Δ) ACC + Fe(II) oxalate, (○) ACC + Fe(II) tartrate, (□) ACC + Fe(III) citrate.

a higher stoichiometric utilization of the chemical impregnant (17–19) which, in turn, gives an ACC with a higher sorptive capacity. ACC is a convenient medium for the bonding of complex compounds due to the adsorptive and chemical driving forces inside the structure of the cloth (20–22).

Based on the experimental results and on analysis of the chemistry of cyanide ion bonding, possible mechanisms of bonding of this pollutant can be proposed and confirmed. The structural activity of ACC is twofold: the ACC itself (without any chemical impregnant) maintains its adsorptive functions, but an impregnant added to ACC acts chemically toward the formation of precipitates and complex compounds. Beside the adsorptive and chemical forces which affect the active bonding of the pollutant, other important factors are the geometry of the system, the flow of air through the pores of the system, the diffusion rate, and the kinetics of surface reactions. The system is obviously complex. For nonspecific pollutants, the mechanism of bonding to a chemical agent is very important. The movement of a chemical agent and cyanides inside ACC, and the mecha-

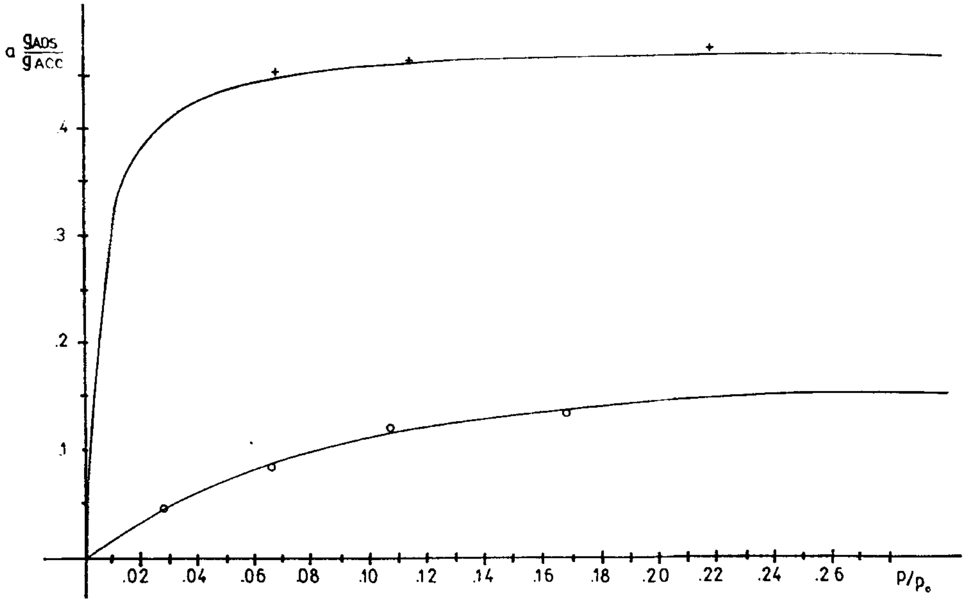


FIG. 11 Adsorption isotherms for nonimpregnated ACC: (+) adsorption isotherm of benzene, (O) adsorption isotherm of hydrogen cyanide.

nism of bonding, may be presented as follows: in the first stage, cyanide ions and copper form the precipitate of copper(I) cyanide, Cu(CN). In the second stage, new quantities of cyanide ions decompose the precipitate, and the tetracyanocuprate(I) complex ion, $[Cu(CN)_4]^{3-}$, is formed. Further quantities of cyanide ions can only be adsorbed, and this process continues until the sorptive capacity of the cloth is completely exhausted.

CONCLUSION

The purpose of this work was to study, investigate, and develop impregnated activated carbon cloth and to determine its structure as well as its adsorptive and chemisorptive properties. This would contribute to the study and application of such materials for air purification from toxic gases, especially cyanides.

On the basis of the results obtained in this experimental work, the following conclusions were reached.

1. ACC impregnation with metallo-organic compounds was performed with acetates, oxalates, tartrates, citrates, and stearates of copper, silver, iron, magnesium, and aluminum. The impregnant was bonded to the fiber's surface or deposited in interfibrous space. Samples with and without washing after impregnation were tested.
2. Characterization of impregnated ACC was performed by modern techniques. The content of metallic cations was determined by atomic absorption spectrometry, while the content of organic acid anions was determined by ion and gas chromatography. The surface composition images and the material's morphology were made by scanning electron microscopy, by energy-dispersive analysis, by Auger electron spectroscopy, and by x-ray photoelectron spectroscopy. It was found that there was a affinity difference to ACC of the salts used, so that the impregnant contents varied from 0.027 mass% for oxalates to 19.44 mass% for acetates. The greatest percentage of metallic cations bonding was found for silver (12.26 mass%), copper (6.72 mass%), and iron (1.08 mass%).
3. Adsorption isotherms for benzene and hydrogen cyanide in impregnated ACC were obtained with a gravimetric adsorption apparatus. It was found that chemisorptive activity was realized by adding of active chemical agent (impregnant) to the material's structure. The effects of metallic ions and their organic salts on hydrogen cyanide and benzene were studied. The bonding efficacy of the pollutants was analyzed, and it was found that the greatest contribution was made by the following materials: ACC impregnated with copper(II) tartrate, then silver(I) citrate, and iron(III) citrate. The chemisorptive process is based on the activity of Cu^{2+} and Ag^{+} ions bonded to activated fiber. A metallic ion in the structure of ACC has a catalytic effect on the chemisorptive process of bonding of the pollutant. The adsorptive capacity of material impregnated with copper(II) tartrate was 0.32 g_{HCN}/g_{ACC} for hydrogen cyanide and 0.28 $g_{C_6H_6}/g_{ACC}$ for benzene. For material impregnated with silver(I) citrate the respective values were 0.30 g_{HCN}/g_{ACC} and 0.43 $g_{C_6H_6}/g_{ACC}$, and for material impregnated with iron(III) citrate the respective values were 0.38 g_{HCN}/g_{ACC} and 0.36 $g_{C_6H_6}/g_{ACC}$.
4. By analysis of the possible chemistry in the structure of ACC, it was found that precipitates and complex compounds were formed in the pollutant and chemical agent (impregnant) reaction. The precipitates and complex compounds ratio depends directly on the pollutant concentration. At higher concentrations the formation of complex compounds predominates, and at lower concentrations the formation of precipitates predominates.

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