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O. P. Mahajan[a]; A. Youssef[ab]; P. L. Walker Jr.[a]
[a] DEPARTMENT OF MATERIAL SCIENCES, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA [b] National Research Center, Cairo, Egypt

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Surface-Treated Activated Carbon for Removal of Ammonia from Water

O. P. MAHAJAN, A. YOUSSEF,* and P. L. WALKER, JR.

DEPARTMENT OF MATERIAL SCIENCES
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA 16802

Abstract

As-received commercial activated carbons do not adsorb noticeable amounts of ammonia from aqueous solution. Following oxidation, pH values of aqueous carbon suspensions decrease appreciably with a concomitant increase in their ammonia adsorption capacities. Oxidative treatment with nitric acid is most effective for enhancing ammonia adsorption capacity of a carbon. Irrespective of the oxidative treatment, the relative concentration of carboxylic, lactonic, and phenolic groups on different oxidized carbons is more or less constant. Breakthrough curves have been measured at different flow rates for two oxidized carbons. Bed capacities are essentially constant after the first cycle and could be regenerated with 0.1 *N* HCl.

INTRODUCTION

Ammonia is produced in wastewater and sewage treatment plants by the enzymatic breakdown of urea, proteins, and other nitrogen-containing materials. The presence of ammonia in water is undesirable because ultimately it gets converted into nitrites and nitrates which act as nutrients for algae growth. Several methods have been suggested for the removal of ammonia, namely, selective ion exchange (*1*), air stripping (*2*), breakpoint chlorination (*3*), biological nitrification-denitrification (*4*), and physical-chemical treatment (*5*). Activated carbons are used in several

*Present address: National Research Center, Dokki, Cairo, Egypt.

industrial applications, including wastewater treatment. However, their potential use for the removal of ammonia has not been thoroughly investigated. The present paper describes the results of such an attempt.

EXPERIMENTAL

Adsorbents

Five commercial activated carbons supplied by different companies were used in the present study. Their important characteristics are shown in Table 1. Nitrogen and CO_2 surface areas were determined from their adsorption isotherms measured at -196 and 25°C, respectively (*6*). For measuring pH values of aqueous suspensions of carbons, 1 g portions of carbons were mixed with 20 ml CO_2-free distilled water in 50 ml capacity stoppered Pyrex bottles. The suspensions were shaken mechanically for 8 hr following which their pH values were determined using a glass electrode. The pH values of various carbons are seen to vary in the range 7.58 to 9.88 (Table 1). For each carbon, the N_2 area is appreciably higher than the corresponding CO_2 area. This is presumably due to the presence of small pores in which reversible capillary condensation of N_2 occurs at very low relative vapor pressures before the apparent monolayer capacity is reached (*7*).

Oxidation

The as-received carbons were given oxidative treatment with dry and moist air, concentrated HNO_3, 0.2 *N* ammonium persulfate $[(NH_4)_2S_2O_8]$, and 2 *N* hydrogen peroxide (H_2O_2). For treatment with HNO_3, carbon

TABLE 1

Characteristics of As-Received Activated Carbons

Carbon	Mesh size	Ash (%, dry)	pH of aqueous suspension	Surface area (m^2/g)	
				N_2	CO_2
A	12 × 40	7.18	9.88	975	836
B	4 × 10	1.60	9.06	945	540
C	8 × 30	0.70	7.58	835	566
D	6 × 8	1.11	8.83	890	566
E	4 × 10	4.70	8.67	902	799

was heated with the concentrated acid (10 ml HNO_3/g carbon) to almost dryness at 80°C. For treatment with $(NH_4)_2S_2O_8$ and H_2O_2, 1 g portions of carbons were mixed with 50 ml of the respective oxidizing solution. The suspensions were shaken mechanically for 48 hr at room temperature. After treatment with different oxidizing solutions, the carbons were washed free of excess oxidants with distilled water and dried in an air-oven at 110°C.

Oxidative treatment with dry and moist air was carried out at 285°C. Moist air refers to an air–water vapor mixture at a total pressure of 1 atm containing water vapor at a partial pressure of 17 Torr. This pressure was generated by bubbling air through deaerated distilled water maintained at 20°C. For the oxidative treatment, about 5 g carbon were spread uniformly in a quartz boat. The boat was placed in a horizontal tube furnace maintained at 285°C. Dry or moist air was passed over the carbon bed at 400 cm^3/min for 20 hr. The effect of reaction temperature on oxygen chemisorption (as measured by weight increase of carbon) was studied in a few exploratory runs. It was found that for each carbon a maximum amount of oxygen chemisorption occurred at 285°C.

Base Neutralization

Neutralization of 0.1 *N* solutions of NaOH, $NaHCO_3$, and Na_2CO_3 by carbons was studied by mixing 1 g portions with 100 ml of the respective solution in 250 ml capacity stoppered Pyrex glass bottles. The suspensions were flushed with N_2 to remove O_2 present. This step was essential to circumvent the possibility of base-catalyzed autoxidation of carbons in the presence of O_2 (*8*). The suspensions were shaken mechanically for 48 hr. It was ascertained that in each case equilibrium was attained well within this period. The fall in concentration of each solution was determined by titrating an aliquot of the supernatant liquid against HCl.

For studying adsorption of ammonia, 1 g of carbon was mixed with 100 ml NH_4OH solution of a desired concentration. The suspensions were shaken mechanically for different intervals of time. Fall in concentration of NH_4OH was then determined using an Orion ammonia electrode.

Column Experiments

Removal of ammonia by carbons under dynamic (flow) conditions was studied in a Pyrex glass column of 2 in. diameter. The carbon bed (height,

4 in.) was held between two glass wool plugs (height, 2 in.). During the runs, the level of ammonia in the column was always kept constant (about 2 in. above the upper glass wool plug). Ammonia was passed through the bed at a constant flow rate. The concentration of ammonia in the effluent was followed as a function of time until the outlet concentration equaled the inlet concentration. The "spent" carbon was regenerated with 0.1 *N* HCl. The concentration of NH_4Cl in the effluent was also determined as a function of time using the ammonia electrode. The carbon bed was then washed with water until free from chloride ions.

RESULTS AND DISCUSSION

The as-received carbons were found not to adsorb any noticeable amounts of ammonia when 1 g portions were contacted with 100 ml of 0.1 *N* NH_4OH for 24 hr. This is perhaps not surprising. The pH values of aqueous suspensions of these carbons fall in the alkaline range (Table 1). Since an aqueous NH_4OH solution is basic in nature, it cannot be removed by carbons having alkaline surfaces. In other words, carbons associated with acidic surfaces would be expected to be the preferred adsorbents for ammonia. The acidic surface functional groups on carbons are carboxylic, lactonic, and phenolic (*9*). The activation step in the production of activated carbons involves heat treatment in an oxidizing atmosphere, generally steam, at temperatures higher than 700°C. Heat treatment at these temperatures is known to result in more or less complete elimination of acidic functional groups (*10*). Therefore, as-received activated carbons are expected to be poor adsorbents for ammonia removal, as is observed in the present study.

Prior to studying ammonia adsorption on various oxidized samples, it was considered desirable to evaluate the optimum experimental conditions under which different carbons showed maximum adsorption capacities. The effect of concentration of ammonia and reaction time on adsorption was studied on HNO_3-oxidized Carbons A and C. The choice of the two carbons was warranted by the following considerations. From the mercury intrusion data obtained up to 30,000 psi* and from pore volume distribution curves calculated from N_2 adsorption isotherms (−196°C) using the Cranston and Inkley method (*11*), it was found that of all the as-received carbons studied, Carbons A and C possessed the extremes of porosity—Carbon C was most microporous and Carbon A was least microporous. When 1 g portions of the two carbons were shaken

*At 30,000 psi, pores larger than 70 Å in diameter would be filled with mercury.

mechanically with 100 ml of 0.1 *N* NH_4OH solution for different intervals of time, equilibrium was attained within 2 hr in each case. The effect of concentration of ammonia on adsorption was studied by shaking 1 g portions of Carbons A and C with 100 ml of NH_4OH solution of different concentrations for 24 hr. It was found that in each case the extent of adsorption became essentially independent of concentration above 0.1 *N*. Therefore, in all subsequent runs carbons were contacted with 0.1 *N* NH_4OH for 24 hr.

The pH values of aqueous suspensions of various oxidized carbons and the amounts of different bases neutralized by them are listed in Table 2. When the pH values of the oxidized samples are compared with those of the as-received samples (Table 1), it is seen that following oxidation,

TABLE 2

Base Neutralization Capacities and pH Values of Carbons

Oxidizing agent	Carbon	pH	Base neutralization capacity (mequiv/g)			
			$NaHCO_3$	NH_4OH	Na_2CO_3	NaOH
HNO_3	A	4.40	1.40	1.80	2.30	3.60
	B	4.40	1.25	1.60	2.10	3.20
	C	4.02	2.15	2.80	3.55	5.55
	D	4.35	1.30	1.70	2.20	3.60
	E	4.35	1.35	1.80	2.25	3.65
$(NH_4)_2S_2O_8$	A	4.95	0.95	1.40	1.70	2.65
	B	4.95	0.90	1.40	1.70	2.65
	C	4.14	1.70	2.60	3.25	4.95
	D	4.92	1.65	1.60	1.95	3.00
	E	4.82	0.95	1.40	1.75	2.65
H_2O_2	A	5.25	0.60	0.90	1.05	1.60
	B	5.30	0.65	0.90	1.05	1.65
	C	4.28	0.80	1.20	1.40	2.20
	D	5.22	0.45	0.70	0.80	1.25
	E	5.11	0.60	0.90	1.05	1.65
Moist air	A	5.60	0.40	0.65	0.65	1.05
	B	5.27	0.40	0.65	0.70	1.15
	C	5.14	0.55	0.85	0.85	1.40
	D	5.28	0.40	0.65	0.60	1.00
	E	5.65	0.45	0.85	0.75	1.20
Dry air	A	5.81	0.20	0.40	0.45	0.70
	B	5.31	0.20	0.40	0.45	0.65
	C	5.15	0.35	0.70	0.85	1.25
	D	5.30	0.20	0.40	0.45	0.65
	E	5.65	0.32	0.60	0.75	1.10

the pH values fall appreciably. Concurrent with a decrease in pH value, the amount of ammonia neutralized by a carbon increases significantly upon oxidation. In fact, the lower the pH value of the aqueous suspension of an oxidized carbon, the greater is its capacity to adsorb ammonia. The efficacy of various oxidative treatments to enhance ammonia uptake of a given carbon follows the order: HNO_3 > $(NH_4)_2S_2O_8$ > H_2O_2 > moist air > dry air. It is noteworthy that even though as-received Carbon C did not adsorb any noticeable amount of ammonia, following oxidation with HNO_3 it can neutralize ammonia to the extent of 2.8 mequiv/g carbon. For a given carbon, the amounts of different bases neutralized vary in the order: NaOH > Na_2CO_3 > NH_4OH > $NaHCO_3$.

Various oxidative treatments had little or no effect on surface areas of carbons. Even though for each oxidative treatment surface areas of oxidized samples prepared from Carbon C were found to be lower than those of the other carbons studied, they show the highest ammonia removal capacities (Table 2). The high surface area of activated carbon often determines its use in most industrial applications. However, the results of the present investigation show that the chemical nature of the carbon surface (as determined by pH value and acidic surface complexes), rather than the magnitude of the surface, determines ammonia removal capacity.

Boehm (*9*) has suggested a selective neutralization technique using $NaHCO_3$, Na_2CO_3, and NaOH for estimating the concentration of carboxylic, lactonic, and phenolic groups. He has concluded that $NaHCO_3$ neutralizes carboxylic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups, and NaOH neutralizes carboxylic, lactonic, and phenolic groups. That is, NaOH gives a measure of total surface acidity of carbons. However, Rivin (*12*) has cautioned that the selective neutralization technique sets arbitrary limits on acidity ranges for each group which may not be realistic for all carbons. He has argued that the acidity of surface groups may depend upon the carbon crystallite to which they are attached and to their point of attachment. Thus it is probable that the same acidic functional group, depending upon its location, may have different strengths.

Using the selective neutralization technique, Boehm (*9*) found that for completely oxidized carbons twice as many acidic groups were neutralized with Na_2CO_3 as with $NaHCO_3$, whereas with NaOH three times the $NaHCO_3$ neutralization was achieved. In the present study, when the amounts of $NaHCO_3$, Na_2CO_3, and NH_4OH neutralized by different samples are plotted against the corresponding amounts of NaOH neutralized (Fig. 1), the data points in each case are seen to fall more or less

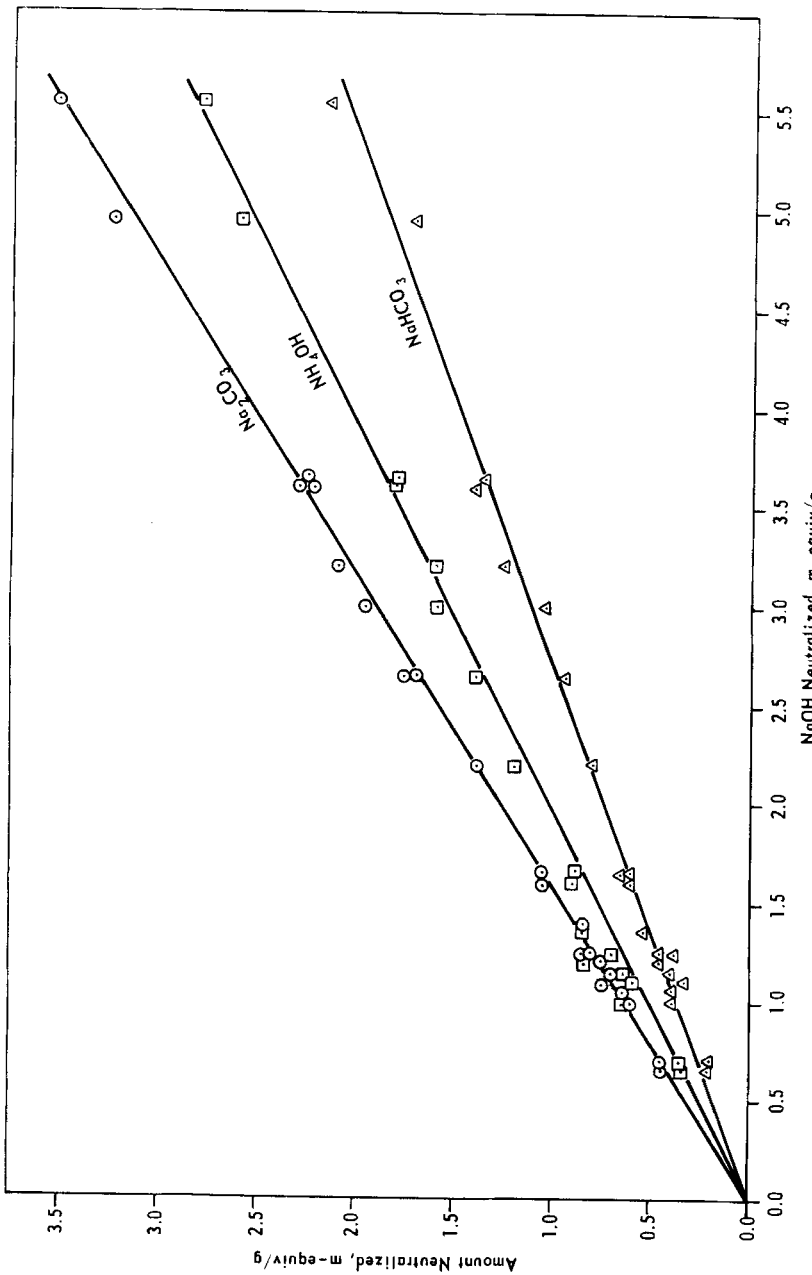

FIG. 1. Amounts of $NaHCO_3$, NH_4OH, and Na_2CO_3 neutralized by different carbons in relation to the amounts of NaOH neutralized.

on straight lines passing through the origin. From the slopes, ratios of $NaHCO_3$, NH_4OH, and Na_2CO_3 neutralized relative to NaOH were found to be 0.36, 0.51, and 0.63, respectively. These results thus show that for a given carbon, irrespective of the organic precursor, amount and nature of inorganic impurities present, the activation process, the degree of activation, and subsequent oxidative treatment, the concentration of acid groups of different strengths relative to total surface acidity is more or less constant.

It has been referred to earlier in this paper that for all oxidative treatments, oxidized samples prepared from carbon C have the highest ammonia adsorption capacities. This may be due to the following reasons. It is known that oxygen is chemisorbed on active sites (ASA); that is, carbon atoms located at the edges of carbon crystallites (*13*). A part of the total chemisorbed oxygen on polycrystalline carbons constitutes acidic functional groups (*10*). Obviously, in order to have a higher concentration of acidic groups, it is desirable to chemisorb oxygen on a highly disordered carbon associated with as small an average crystallite size as possible. ASA in the activated carbon can be dependent upon a number of variables selected for its preparation such as nature of starting carbonaceous material, heating rate, maximum temperature, soak time at maximum temperature, and atmosphere used during its activation. The activation step involves (a) enlarging of pores that were open in the carbon precursor, and (b) opening up of closed pores, that is, pores which were initially inaccessible to helium at room temperature. During activation, ASA increases (*13*). For the same degree of activation (carbon burn-off) in a given atmosphere, the increase in ASA may be different for different carbons due to inherent differences in the nature of the precursor carbons. However, the recent work of Cariaso and Walker (*14*) shows that for a given carbon the gaseous atmosphere used during activation can also affect ASA development. They found that a relatively pure carbon (prepared by the carbonization of Saran, which is a copolymer of PVC and PVDC) activated to the same level of carbon burn-off in O_2 and CO_2 subsequently showed marked differences in its capacity to chemisorb oxygen. The O_2-activated sample chemisorbed 3 times as much oxygen per unit total surface area as did the sample activated in CO_2. Cariaso and Walker (*14*) suggested that chemisorption of oxygen was strongly sensitive to the geometry of the carbon sites on the surface, and that activation in O_2 created a template more susceptive to subsequent oxygen chemisorption than the template created by CO_2 activation.

It is instructive to compare the neutralization capacities of samples

TABLE 3

Concentration of Acidic Groups on Carbons Oxidized with Dry and Moist Air

	Acidic groups (mequiv/g)					
	Carboxylic		Lactonic		Phenolic	
Sample	Dry air	Moist air	Dry air	Moist air	Dry air	Moist air
A	0.20	0.40	0.25	0.25	0.25	0.40
B	0.20	0.40	0.25	0.30	0.20	0.45
C	0.35	0.55	0.50	0.30	0.40	0.55
D	0.20	0.40	0.25	0.20	0.20	0.40
E	0.32	0.45	0.43	0.30	0.35	0.45

oxidized with dry and moist air. The concentration of carboxylic, lactonic, and phenolic groups, calculated by the Boehm approach from the data in Table 2, are given in Table 3. It is seen that the presence of water vapor in air is very conductive for the formation of carboxylic and phenolic groups; in some cases the concentration of these groups increases by 100%. The effect of water vapor on lactone groups is peculiar. For Sample A, the concentration of lactone groups remains unchanged, whereas a 20% increase is observed for Sample B. For the remainder of the samples, the concentration of lactone groups decreases in the presence of water vapor; the decrease is most pronounced for Sample C.

The formation of carboxylic and phenolic groups on treatment with dry air is intriguing. In the complete absence of moisture, it would be expected that oxidative treatment with air would result in the formation of only one acidic group, namely lactonic. The "extra dry" grade air used for oxidation in the present study was rated to have a maximum of 10 ppm moisture as an impurity. It can be shown by simple calculations that under the experimental conditions used in the present study (that is, sample weight $\simeq 5$ g, flow rate = 400 cm^3/min, reaction time = 20 hr), the amount of water vapor present in the dry air stream would be insufficient to account quantitatively for the amounts of carboxylic and phenolic groups formed on different carbons. Presumably treatment with air at 285°C involves both chemisorption of oxygen as well as gasification of carbon. A net gain in weight during the oxidative treatment is indicative of a higher rate of chemisorption compared to the gasification rate. Polycrystalline carbons, including activated carbons, are always associated with carbon–hydrogen surface complexes. It is known that during gasification, hydrogen is preferentially oxidized to carbon (*15*). In the

presence of O_2 (air), the evolved water could react with carbon by a hitherto unknown mechanism to form carboxylic and phenolic groups. Support for this "mechanism" comes from the fact that in the presence of added water vapor the concentration of carboxylic and phenolic groups is significantly enhanced (Table 3).

Carbons A and C oxidized with HNO_3 were used in dynamic (flow) studies. Adsorption was studied from 0.1 *N* NH_4OH solution using flow rates between 90 and 280 cm^3/min. Breakthrough times and bed capacities for different flow rates are given in Table 4. Breakthrough curves for Carbon A for different flow rates, plotted in Fig. 2, are seen to be very sharp. Corresponding curves for Carbon C are of the same general shape as those for Carbon C and are not plotted for reasons of space. Breakthrough times increase with decreasing flow rate, as expected. Following the first ammonia adsorption run, about 95% of ammonia adsorbed on both the carbons studied could be "desorbed" with HCl. In subsequent runs, essentially all adsorbed ammonia could be desorbed. This is shown in Table 4 for Runs I and II at a flow rate of 95 cm^3/min. Bed capacities after the first cycle are more or less constant and are independent of flow rate (Table 4). These results suggest that carbon beds can probably be used *ad infinitum* without any noticeable loss in bed capacity.

The different breakthrough curves in Fig. 2 can be normalized into one curve (Fig. 3). Normalization was done in the following manner. Ratios of breakthrough times for different flow rates were calculated with

TABLE 4

Breakthrough Times and Bed Capacities

Sample	Flow rate (cm^3/min)	Breakthrough time (min)	Bed capacity (mequiv/g)
C	95 (I)	30	2.63
	95 (II)	30	2.48
	125	22	2.46
	165	16	2.46
	200	13	2.44
	280	10	2.42
A	90 (I)	20	1.68
	90 (II)	20	1.58
	130	14	1.59
	165	11	1.56
	200	9	1.56
	260	7	1.52

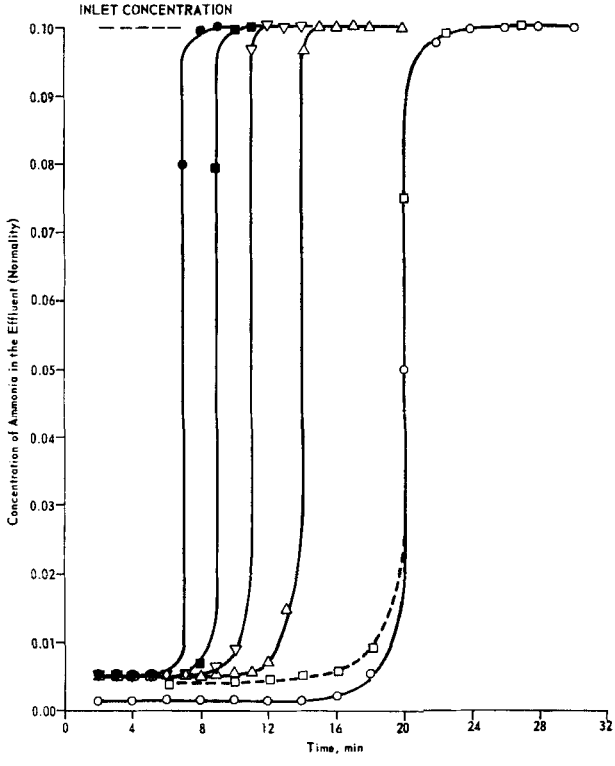

FIG. 2. Ammonia breakthrough curves for Carbon A oxidized with HNO_3. Flow rate (cm^3/min): ○, 90 (I); □, 90 (II); △, 130: ▽, 165; ■, 200; ●, 260.

respect to that for a flow rate of 165 cm^3/min (any other flow rate could also be used). For a given flow rate, the product of the ratio and "reaction" time was plotted against the corresponding effluent concentration. The normalization of the data and constancy of bed capacities, referred to above, are strongly indicative of the presence of minimal external mass transport resistance to adsorption.

It has been referred to above that following the first ammonia adsorption run, a part of the adsorbed ammonia could not be desorbed with HCl. Adsorption of ammonia on carbons in a nonhydrolyzable form has been reported in the literature (*16–18*). Puri and Mahajan (*18*) concluded that irreversibly adsorbed ammonia was due to the presence of an unidentified surface functional group.

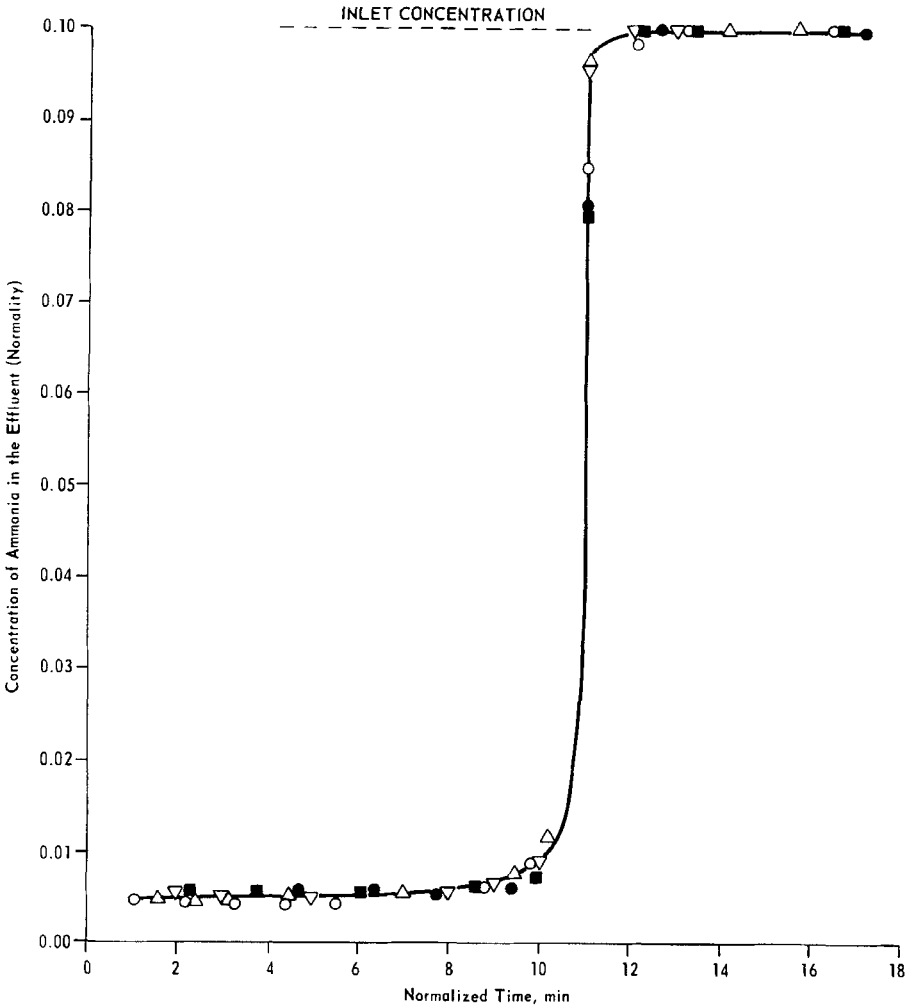

FIG. 3. Normalized ammonia breakthrough curve for Carbon A oxidized with HNO_3. Flow rate (cm^3/min): ○, 90 (I); △, 130; ▽, 165; ■, 200; ●, 260.

In conclusion, the results of the present study suggest that oxidized carbons, preferably those oxidized with HNO_3, should be strong contenders for ammonia removal from wastewaters.

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