

USE OF CARBON FOR REMOVAL OF AMMONIA FROM WATER*

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Introduction

Ammonia is produced in waste water and sewage treatment plants. The presence of ammonia in water is undesirable because ultimately it gets converted into nitrites and nitrates which act as nutrients for algae growth. The present study describes the use of surface-modified carbons for the removal of ammonia.

Experimental

Activated carbons supplied by five different companies, namely A (12x40 mesh), B (4x10 mesh), C (8x30 mesh), D (6x8 mesh) and E (4x10 mesh) were used. These carbons had N_2 areas (77°K) in the range 750-830 m^2/g and CO_2 areas (298°K) in the range 540-825 m^2/g . Aqueous suspensions of the carbons had alkaline pH values in the range 7.1-9.1.

The as-received carbons were given oxidative treatments with dry and moist air at 285°C, HNO_3 , 0.2N $(NH_4)_2S_2O_8$ (ammonium persulfate), and 2N H_2O_2 . 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. For treatment with HNO_3 , carbon was heated with concentrated HNO_3 (10 $cm^3 HNO_3/g$ carbon) to dryness at 80°C. For treatment with $(NH_4)_2S_2O_8$ and H_2O_2 , 2g portions were mixed with 50 cm^3 of the oxidizing solution. The suspensions were shaken mechanically for 48 hr at room temperature. After oxidative treatment with different oxidizing solutions, the carbons were washed free of excess oxidants with water and dried at 110°C.

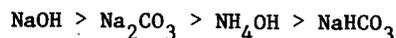
Neutralization of 0.1N solutions of NaOH, $NaHCO_3$, Na_2CO_3 and NH_4OH by carbons was determined by mixing 1g portions with 100 cm^3 of solution. After attainment of equilibrium, the fall in concentration of NaOH, $NaHCO_3$ and Na_2CO_3 solutions was determined by titration with HCl, whereas decrease in concentration of ammonia was determined using an Orion ammonia electrode.

The efficacy of carbons for removal of ammonia 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 equalled the inlet concentration. The 'spent' carbon was regenerated with 0.1N HCl followed by washing with water until free from chloride ions.

Results and Discussion

The as-received carbons did not adsorb noticeable amounts of ammonia. However, following oxidation all the carbons adsorb significant amounts of

ammonia (Table 1). The pH values of aqueous suspensions of various oxidized samples and the amounts of various bases neutralized by the carbons are listed in Table 1. The efficiency of various oxidative treatments to enhance ammonia uptake of a given carbon follows the order: $HNO_3 > (NH_4)_2S_2O_8 > H_2O_2 > \text{moist air} > \text{dry air}$. Amounts of $NaHCO_3$, Na_2CO_3 and NaOH neutralized by various samples follow the same trend as the adsorption of ammonia, whereas pH values of the aqueous suspensions decrease in the reverse order. For a given carbon, the amounts of different bases neutralized vary in the order



Various oxidative treatments had little or no effect on surface areas of carbons. Although for each oxidative treatment surface areas of samples derived from carbon C are lower than those of the other carbons, samples from carbon C have the highest ammonia removal capacities. The high surface area of activated carbon often determines its use in most industrial applications. However, in the present study the chemical nature of the surface, rather than the magnitude of the surface, determines ammonia removal capacity.

Boehm (1) has suggested a selective neutralization technique using $NaHCO_3$, Na_2CO_3 and NaOH for estimating the concentration of carboxylic, lactonic and phenolic acid 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. Boehm also found that for completely oxidized carbons twice as many acid 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 were plotted against amounts of NaOH neutralized, the data points in each case fell more or less on straight lines passing through the origin. From the plots, 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 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 the total surface acidity is more or less constant.

Since the amount of Na_2CO_3 neutralized by a carbon has been suggested to be a measure of the concentration of carboxyl and lactone groups (1), the amount of CO_2 evolved on outgassing a carbon at elevated temperatures should be theoretically equivalent to the Na_2CO_3 neutralization capacity.

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However, in this study amounts of CO₂ evolved were invariably greater than the Na₂CO₃ values.

Carbons A and C oxidized with HNO₃ were used in dynamic studies. Breakthrough times and bed capacities for different flow rates are listed in Table 2. Breakthrough times increase with decreasing flow rates, as expected. Capacities are independent of flow rate after the first cycle, indicating the presence of minimal external mass transport resistance to adsorption. Regeneration of the carbon beds between successive runs was conducted by treatment with HCl. Following the first ammonia adsorption run, about 95% of the ammonia adsorbed could be 'desorbed' with HCl. In subse-

quent runs, essentially all adsorbed ammonia could be desorbed. The irreversibly adsorbed ammonia has been suggested to be due to the presence of some, as yet unidentified, surface functional group (2).

In conclusion, the results of the present study suggest that oxidized carbons, preferably those oxidized with HNO₃, should be strong contenders for ammonia removal from waste waters.

References

1. Boehm, H. P. in "Advances in Catalysis", Vol. 16, Academic Press, New York, 1966, pp. 179-268.
2. Puri, B. R. and Mahajan, O. P., J. Indian Chem. Soc., 41, 586 (1964).

Table 1 - BASE NEUTRALIZATION CAPACITIES AND pH VALUES OF CARBONS

Oxidizing Agent	Carbon	pH	Base neutralization capacity, m-equiv/g			
			NaHCO ₃	NH ₄ OH	Na ₂ CO 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) ₂ S ₂ O 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 ₂ O 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

Table 2 - BREAKTHROUGH TIMES AND BED CAPACITIES

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