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MODIFICATION OF CATION-EXCHANGE PROPERTIES OF ACTIVATED CARBON BY TREATMENT WITH NITRIC ACID*

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SUMMARY

The uptake of inorganic cations by high-surface-area activated carbon can be increased by an order of magnitude by controlled exposure to high concentrations of nitric acid at elevated temperatures. Distribution coefficients of cations are also increased. Acid strength of the functional groups from the nitric acid treatment is greater than those of the starting material. Surface area measurements and small-angle neutron scattering indicate that the increase in effective ion-exchange capacity is not accompanied by gross changes in the structure of the material. ^{13}C NMR on solid samples suggests that the concentration of carboxyl and phenolic functional groups in the carbon is increased by the treatment.

INTRODUCTION

Adsorption by activated carbon of inorganic ions has received less attention than that of other substances, although there is a considerable literature on the subject. Various aspects have been covered in reviews (see, *e.g.*, refs. 1-3) or in book chapters (*e.g.*, ref. 4). A book⁵, referenced by Smith³, deals with adsorptive properties in terms of ion exchange. Smith also cites a number of Russian papers. Nelson *et al.*⁶ demonstrated the distribution of Fe(III) between activated carbon and concentrated solutions of hydrochloric acid and lithium chloride paralleled in a remarkable way the distribution observed with organic ion exchangers and in solvent extraction.

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Kraus and Nelson⁷ also showed that the distribution of acids from concentrated electrolyte solutions was analogous for activated carbon and ion exchangers. Activated carbon can have either positive or negative surface charge^{2,8}.

The ion-exchange capacity of conventional activated carbons is usually not high except in contact with solutions at high pH. It has been realized for some time that cation-exchange capacity can be sharply increased by exposure to oxidizing environments. Weller and Young⁹ reported the effect on acid and base uptake of activated carbon exposed to oxygen at 400°C. There was a decrease in hydrochloric acid uptake, and an increase in sodium hydroxide, up to *ca.* 2 mequiv./g when the final sodium hydroxide concentration was above 0.1 *M*. Puri *et al.*¹⁰ treated charcoal with nitric acid at elevated temperature and attained neutralizations of barium hydroxide of up to 12 mequiv./g. Ivanova *et al.*¹¹ reported properties of charcoal oxidized by atmospheric oxygen, hydrogen peroxide and nitric acid.

The literature survey here is by no means complete; there are many other citations in the references listed. Here we report effects on ion-exchange properties of nitric acid treatment as a function of time, temperature, and nitric acid concentration. We also report observations on other properties of the materials that we believe shed some light on the changes in the solids accompanying the changes in ion-exchange properties.

EXPERIMENTAL

Activated carbons

Four samples were used in oxidation studies. Three were of high surface area (*ca.* 1000 m²/g) coconut charcoals. One of these was a Nucon material (referred to as N). Two from Barnebey Cheney (referred to as BC-1 and BC-2) differed in some details of preparation not known to us. The other was a low-surface-area coconut charcoal, also from Barnebey Cheney (BC-3). It was stated to have a surface area of about 50 m²/g. Two mesh sizes were investigated, -100, +200 and -6, +14.

A limited evaluation of commercial oxidized carbons from Nuclear Consultants, is also reported.

Oxidation procedures

The charcoal samples were dried at 110°C for at least 2 days. In early experiments, they were outgassed under vacuum at 500°C for 24 h, in conformance with the practice of Puri *et al.*¹⁰. Although the outgassing procedure, as we shall describe, had effects on properties of the as-received material, differences between as-received and outgassed appeared to be insignificant after nitric acid treatment, and the outgassing step was omitted in later stages.

Most oxidations were carried out under reflux on samples of from five to ten grams. Ten ml of nitric acid was added per gram of charcoal. Time, temperature, and nitric acid concentrations were varied. After the desired time, samples were cooled; excess acid was poured off; the samples were neutralized with 0.1 *M* sodium hydroxide, and rinsed with distilled water, with the final wash adjusted to pH 6 by acid or base addition; and samples were dried at 110°C overnight. In presenting results, concentrations in the solid phase are in terms of amounts per kg of dry charcoal. Except for outgassed samples, "dry charcoal" is defined as material dried at 110°C.

Batch equilibrations

With a few exceptions, measurements of uptake and distribution coefficients were carried out by equilibrating a known amount of solid with a solution of known composition tagged with a radioactive tracer. The solution was counted after equilibration, and the amount on the solid determined by difference from the original amount in the solution.

The details of procedures were varied as appropriate, and aspects thought significant will be discussed in connection with presentation of results. Carbon samples were usually pre-equilibrated with the composition desired several times before addition of the tracer. In most cases, tests were carried out in centrifuge tubes, were shaken at least overnight, and were centrifuged at 2000 *g* for 20 min to remove solid. The samples were further equilibrated in cases where there was doubt concerning attainment of equilibrium. In some instances, pH changed during equilibration, owing to adsorption of atmospheric carbon dioxide or other causes; when the shift had significant consequences, the acidity was readjusted to the desired value and the sample re-equilibrated. Tracers used were ^{22}Na , ^{85}Sr , ^{64}Cu , and ^{57}Co .

Activated carbon in the pH range of these measurements behaves as a weak-acid ion exchanger. Consequently, its apparent capacity, if evaluated, *e.g.*, as moles of replaceable sodium ion/kg solid, will vary with pH. We consequently prefer to discuss "uptake", measured under specified conditions, rather than "capacity", which might be defined as the maximum uptake, at pH values high enough for all protons to be replaced from the solid. Uptake was obtained from batch equilibrations by isotope dilution: *w* kg of charcoal is pre-equilibrated with a desired concentration (*c*, moles or equivalents per liter) of electrolyte without tracer, and then with *V* liters of the same concentration plus a known number of counts of tracer of the cation per unit volume per unit time (n_0 , initial; *n* at equilibrium). Uptake in moles or equivalents/kg charcoal is

$$\text{Uptake} = \frac{(n_0 - n)cV}{nw}$$

Distribution coefficients (*D* in l/kg) are measured by the same procedure, the value sought being counts of tracer of the ion whose *D* is being measured per kg of solid after equilibration/counts per liter of equilibrated solution.

$$D = \frac{(n_0 - n)V}{nw}$$

In carrying out measurements as a function of pH, it is frequently desirable to stabilize systems by adding a low concentration of a buffer. Acetate is convenient to maintain pH values around 5; bicarbonate, 8; and carbonate or ammonia in the range 10–11.

*Preloaded column*¹²

Another technique used in some cases for measurements of distribution coefficients, including one set reported here, utilizes a column of carbon which has been precontacted in a batch equilibration with a solution containing the ion of interest, traced with a radioisotope. This approach is particularly convenient for measurement

of high values of D at a fixed solid loading of the ion of interest, over a range of concentrations of a salt of a displacing ion. If distribution coefficients of the ion of interest are high, relatively little of it is removed from the solid in establishing equilibrium with the eluting solution passed through the column. Consequently, the loading changes only at the top of the column, and the bottom stays at the initial loading, which is known from analysis after the initial equilibration. Alternatively, the initial loading may be accomplished by passing a solution of known concentration and known specific activity through a column until the effluent concentration equals the incoming. The loading may be computed from the amount of the ion taken up from the solution put through in the process. In either case, one knows the amount of the ion both in moles and counts per kg of solid and by counting the solution effluent from the column can determine the concentration in equilibrium, and thereby can compute D .

Small-angle neutron scattering

Small-angle neutron scattering from several samples of carbon was measured on the 30-m (source-to-detector) instrument of the National Center for Small-Angle Scattering Research, located at the High Flux Isotope Reactor, Oak Ridge National Laboratory. The maximum range of κ [$\kappa = (4\pi/\lambda) \sin\theta$, where λ is the wavelength of the neutrons, here 4.75 Å, and 2θ is the scattering angle] was about 0.003–0.3 Å⁻¹, attained by using several different sample-to-detector distances from 1.4 to 16 m. Data are collected with a two-dimensional position-sensitive detector, and combined as a radial average corrected for detector background, empty-beam, and detector sensitivity by programs provided by the Center. Intensities were converted to an absolute scale (cm⁻¹) with factors provided by the Center, based on scattering by water, vanadium or other substances of known cross-sections. Runs at different distances may be combined by an available program.

Cross polarization/magic angle spinning-¹³C NMR

Solid state nuclear magnetic resonance measurements were made on a modified Varian-XL-100 spectrometer equipped with an external ¹⁹F field frequency lock, Nicolet NMR-80 data system, and a home-built, double-tuned single coil probe operating at 25.16 and 100.07 MHz for ¹³C and ¹H, respectively. A single contact cross polarization experiment with radio-frequency field strengths $\gamma_C H_{1C} = \gamma_H H_{1H} = 30$ kHz was used. The Hartmann-Hahn match was adjusted with 1 dB precision. Dipolar decoupling during acquisition was accomplished with a *ca.* 40 kHz proton radio frequency field. Spectra were recorded with a 1.0 ms contact time and 2.0 s repetition rate. Spin temperature alternation was employed for the cancellation of artifacts. Powder samples were packed in a hollow screw cap Kel-F rotor (*ca.* 90 μl volume) of the Andrew type and spun at the magic angle ($\pm 0.3^\circ$) at 2.5 ± 0.1 kHz. No attempt has been made to correct the center band areas for the overlap of first order sideband contributions to the spectra. The distortion of the aromatic centerband from the first lower aliphatic resonance sideband, similar for both samples, does not overlies the region of carboxylic acid resonances, and is estimated to introduce less than 2% error in the aromatic resonance areas.

RESULTS

*Uptake. Effect of nitric acid treatment**High-surface-area charcoals*

In comparisons, we frequently used an arbitrary combination of conditions: 90% (fuming) nitric acid at 70°C for 35 minutes. In Table I, we compare the effect of exposure of the three high-surface-area materials on uptake of sodium from 0.01 M sodium carbonate, the measured pH values scattering about 10.5 in most cases.

The uptakes of the as-received carbons varied substantially, over a range of about a factor of five. After oxidation, the values are much more similar, the maximum differences being less than 50%. They are also much greater after oxidation, the uptakes increasing from a few tenths of a mole/kg to about 1.5. Outgassing decreased uptakes in comparison to the values as received, but there is little, if any, difference outside scatter in uptakes of outgassed and as-received after nitric acid treatment. Likewise differences between coarse and fine particle sizes are probably not significant. Apparently the kinetics of the reactions with nitric acid is such that diffusion into the particles is not limiting. The times of contact in batch equilibrations also seem long enough for essential equilibrium in distribution of sodium tracer to be attained for both particle sizes. Reproducibility of uptakes of the same starting material in duplicate oxidations also seems to be good.

Effect of pH. The increase in sodium uptake after nitric acid treatment is found over the range of pH investigated, from slightly below neutral to 10–11 (Figs. 1 and 2). The conditions of the adsorption measurements were not exactly the same in all cases; Na(I) concentration was varied sometimes to obtain maximum precision (50% of initial tracer removed at equilibrium), for example. However, differences in conditions are not enough to obscure the general picture. Fig. 1 shows the lack of effect

TABLE I

SODIUM UPTAKES OF CHARCOALS BEFORE AND AFTER NITRIC ACID TREATMENT

90% HNO₃ at 70°C for 35 min, measured from 0.01 M Na₂CO₃.

Charcoal	Mesh size	As received		Oxidized		Outgassed		Outgassed and oxidized	
		pH	Na(I) equiv./kg	pH	Na(I) equiv./kg	pH	Na(I) equiv./kg	pH	Na(I) equiv./kg
BC-1	-100, +200	10.9	0.047					10.5	1.70
	-6, +14	10.7	0.054	10.4	1.56			10.4	1.72
BC-2	-100, +200	11.1	0.30	10.4	1.81	10.7	0.10	10.5	1.72*
	-6, +14	10.4	0.35			10.8	0.21	10.6	1.68*
Nucon								10.5	1.55
	-100, +200	10.7	0.15			10.4	0.08	10.5	1.47
	-6, +14	10.4	0.15	10.5	1.26	10.4	0.16	10.4	1.40
		11.4	0.30						

* These values are for samples prepared in separate oxidations.

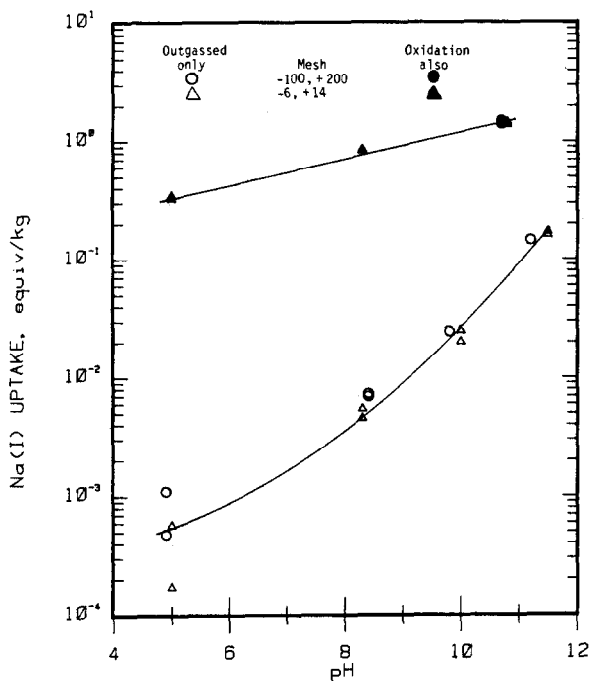


Fig. 1. Effect of particle size on sodium ion uptake of Nucon. Oxidation conditions: 70°C, 90% HNO₃, 35 min.

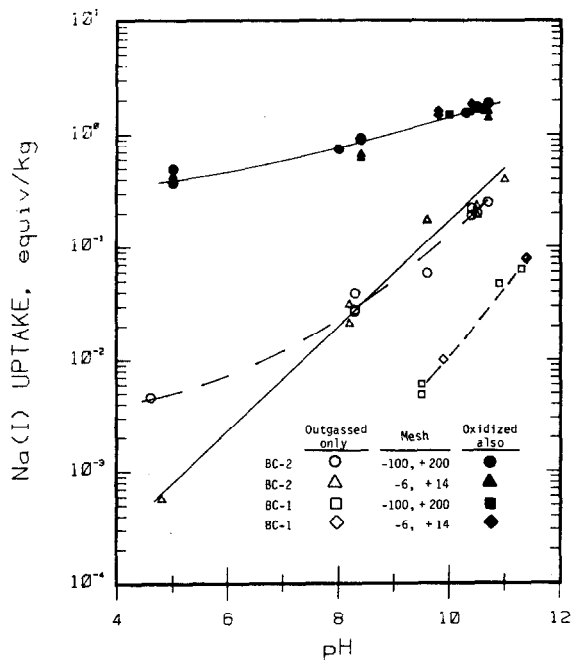


Fig. 2. Comparison of monovalent ion uptake by activated carbons. Oxidation conditions: 70°C, 90% HNO₃, 35 min.

of particle size. Fig. 2 shows that differences between samples disappear after HNO_3 treatment.

A general characteristic of these figures is an increase in sodium ion uptake with pH, the percentage increase being much greater for carbons which had not been subjected to nitric acid treatment. These substances are weak-acid exchangers, and the average $\text{p}K$ of the protonated groups is lower (*i.e.*, the groups are stronger acids) after nitric acid treatment.

Effect of salt concentration. If the increase in uptake with pH arises from neutralization of weak-acid groups, one would expect higher sodium uptakes with higher sodium chloride concentration, owing to $\text{Na}^+ - \text{H}^+$ exchange. Fig. 3 shows that this does occur. Fig. 4 indicates that the effects of salt concentration are relatively somewhat greater for materials not treated with nitric acid than for those that were; the values for oxidized materials fall within a narrow band on a logarithmic ordinate.

Divalent ions. Use of sodium ions to compare capacities avoids ambiguities from possible precipitation or valence state change. However, it is, of course, important to validate that the values obtained are at least relatively applicable to other ions of interest. Cu(II) is convenient to measure at pH 5, buffered with acetate, and at pH above 10, from an ammonia solution. Co(II) poses no problems from acetate buffered solutions at pH 5. Ion exchange of Co(II) from ammonium chloride-ammonia solutions (*ca.* pH 10) were found to be reversible and to follow fairly well predictions of simple theory in short-term experiments. However, on long exposure to activated carbons, distribution coefficients continued to increase and adsorption became irreversible. The reasons are not altogether clear. One possible explanation

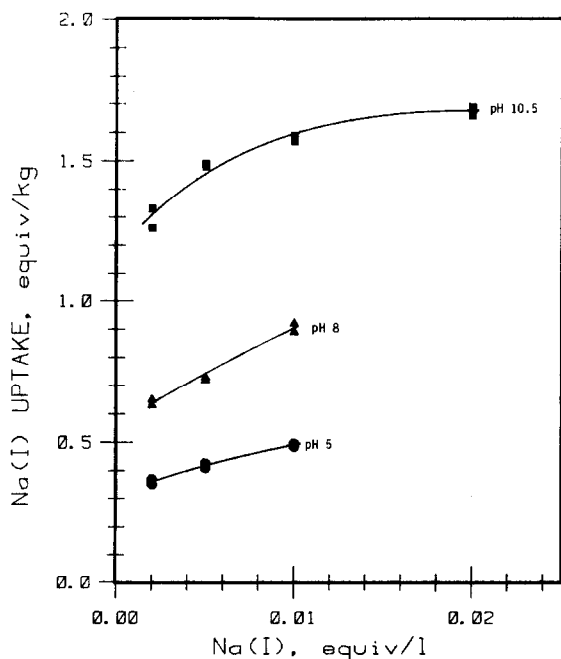


Fig. 3. Effect of salt concentration on uptake of monovalent ion on oxidized BC-2. -100, +200 mesh; oxidation conditions: 70°C , 90% HNO_3 , 35 min.

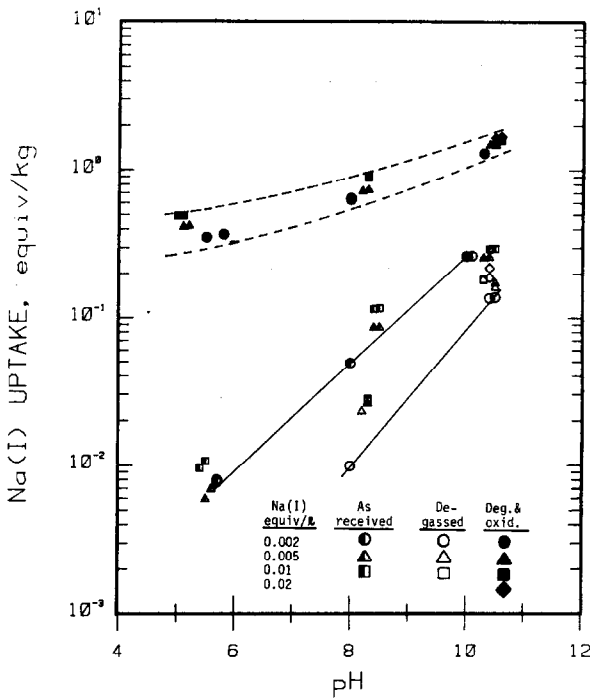


Fig. 4. Salinity and pH effects on monovalent ion uptake on carbons. BC-2; -100, +200 mesh; oxidation conditions: 70°C, 90% HNO₃, 35 min.

is oxidation to Co(III). Arguing against this is the fact that adsorption could not be reversed by reducing agents. In addition, in other studies we have found even oxidized carbon to be itself highly reducing; it will, for example, reduce pertechnetate [Tc(VII)] to lower valence states in solutions of neutral or mildly alkaline pH. The fact that 1 *M* hydrochloric acid rapidly removes irreversibly adsorbed cobalt suggests that precipitation of hydrolyzed species (in spite of the stabilization which might be expected from formation of ammine complexes) is the cause of observed irreversibility.

Fig. 5 compares uptakes of Na(I), Cu(II), and Co(II) as a function of pH for oxidized and outgassed-only Nucon. In these measurements, acetic acid was added to adjust pH to *ca.* 5, and the solutions at pH *ca.* 10 were 0.5 *M* in ammonia. For oxidized carbon, equilibrium concentrations were 0.005 *M* copper chloride or 0.005 *M* cobalt chloride at both pH values. The solutions equilibrated with non-oxidized charcoal were 0.005 *M* at pH 10 and 0.002 *M* Cu(II) or Co(II) at pH 5. Na(I) results reported in other figures are included for comparison. It can be seen that at pH 5, uptake of Cu(II) by unoxidized material is much higher than of Na(I), and Co(II) is intermediate. Relative differences appear to be less at higher pH. For the oxidized material, differences between uptakes of the various ions are not great.

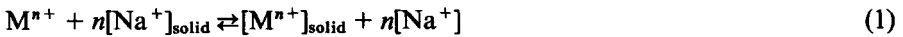
Low-surface-area charcoal

The nominal 50 m²/g BC-3 responded to nitric oxide treatment drastically differently. In contrast to other materials, it appeared to undergo considerable de-

composition, evidenced by blackening of the liquid during oxidation. Subsequently, we were unable to wash from the solid materials which blackened contacting solutions. Solutions of hydrochloric acid, of sodium hydroxide, and of sodium carbonate, as well as acetone, were tried. We carried out no further evaluation of this material, but the results with it show that nitric acid treatment does not replace the standard activation process, even though it does wash out previous differences in ion-exchange properties of various activated carbons.

Selectivity

Cation exchange between solution and solid phases is conventionally represented by an equilibrium of the type



with an equilibrium constant

$$K = \frac{[M^{n+}]_{solid} [Na^+]^n (\gamma_{\pm MCl_n})^{n+1} (\gamma_{\pm NaCl})^{2n}}{[M^{n+}] [Na^+]_{solid}^n (\gamma_{\pm MCl_n})^{n+1} (\gamma_{\pm NaCl})_{solid}^{2n}}$$

$$K = \frac{D_M [Na^+]^n \Gamma}{[Na^+]_{solid}^n} \tag{2}$$

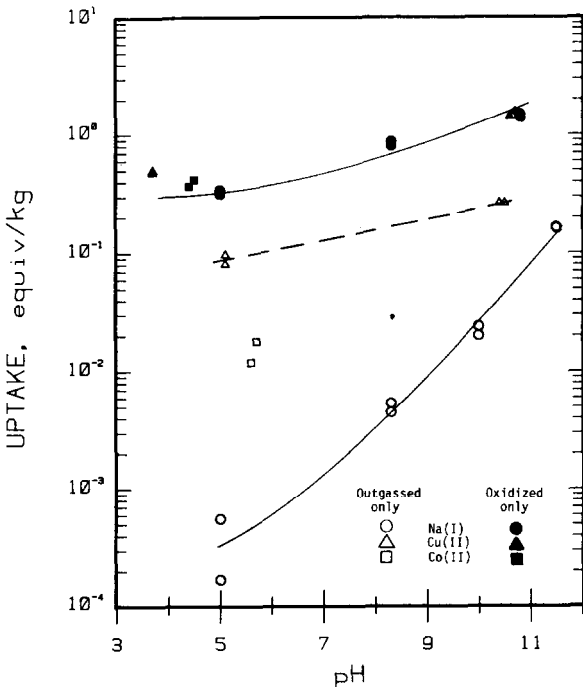


Fig. 5. Uptake of monovalent and divalent ions. Nucon, -6, +14 mesh; oxidation conditions: 70°C, 90% HNO₃, 35 min.

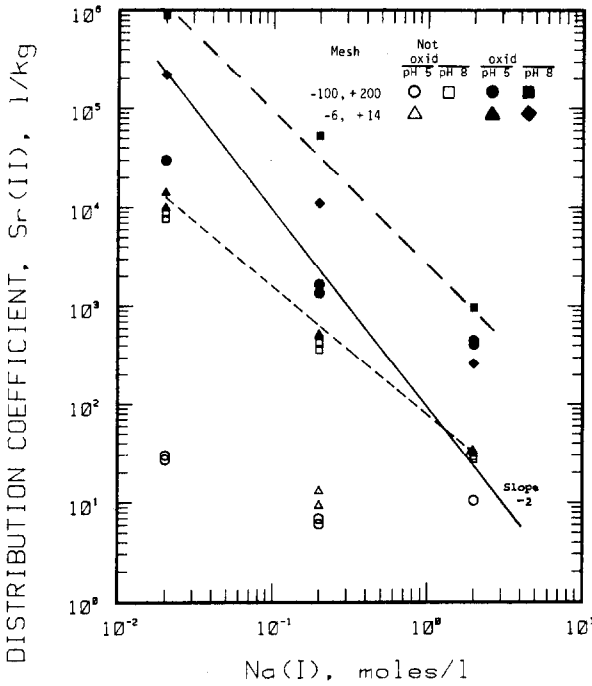


Fig. 6. Distribution of divalent ion between solution and BC-2 as a function of monovalent ion concentration. Sodium chloride + 0.01 *M* acetate, pH 5; +0.01 *M* bicarbonate, pH 8; oxidation conditions: 70°C, 90% HNO₃, 35 min.

Γ summarizing the activity coefficient ratio. If units of concentration are moles/kg solid and moles/l solution (no subscript), the units of the distribution coefficient D will be l/kg. If variations in Γ can be neglected and if coion (chloride in this example) invasion is low enough to be ignored, and if the concentration of M^{n+} is small, so that $[Na^+]_{solid}$ is essentially equal to C , the cation-exchange capacity, and therefore constant, a plot of $\log D_M$ vs. $\log [Na^+]$ should be linear with a slope of $-n$. (This will also be true at appreciable loading of M^{n+} provided loading is constant, *i.e.*, $[M^{n+}]_{solid}/[Na^+]_{solid}$ does not vary.) Similar expressions can be obtained when coion invasion does occur, but we have made no measurements of coion invasion on activated carbons. It is probably small in most cases here, and eqns. 1 and 2 will be adequate for discussion.

Even if Γ is constant, coion invasion small, and the solution concentration of sodium ions constant, eqn. 2 requires that D_M decrease with loading of M on the solid when it becomes appreciable in comparison with the capacity, *i.e.*, $[Na^+]_{solid}$ begins to vary. Another cause of variation of D_M is of significance here, the change in apparent capacity from Na^+H^+ exchange on these weak-acid exchangers.

Low loading of charcoals relative to capacity

Fig. 6 compares distribution coefficients of Sr(II) on BC-2 as a function of sodium ion concentration. The strontium tracer was not carrier-free, and loading of the solid (perhaps up to a tenth of Na^+ uptake) has a small effect at the highest D

value. At pH 8, the slope for the nitric acid-treated charcoal is not far from the ideal ion-exchange value of -2 , at least for the small mesh size. At pH 5, the slope is less for oxidized carbon and D is almost invariant for as-received. Presumably this non-ideality reflects change of effective capacity because of $\text{Na}^+ - \text{H}^+$ exchange. Distribution coefficients are higher for nitric-acid treated solid, other conditions being equal. They are also higher at higher pH. Substantial differences between different particle sizes may imply that equilibrium was not attained in all cases.

High loading

Distribution coefficients of another divalent ion, the Cu(II) -ammonia complex, were measured as a function of monovalent ion solution concentration at appreciable, but constant, Cu(II) loading of the carbons by the preloaded column technique. The carbons were first loaded by passing through columns of them a solution of 0.002 M in Cu(II) and 1 M in ammonium chloride and in ammonia until the effluent reached the influent concentration. The amount of Cu(II) on the carbon was computed from the amount taken up in the process, analyses being by flame atomic absorption. Uptakes of Cu(II) are listed in Fig. 7. The concentration of ammonium chloride and ammonia (always the same) was then varied and the effluents analyzed. The results (Fig. 7) plotted as $\log D_{\text{Cu}}$ vs. $\log[\text{NH}_4^+]$ fall roughly about the ideal ion-exchange slope, -2 .

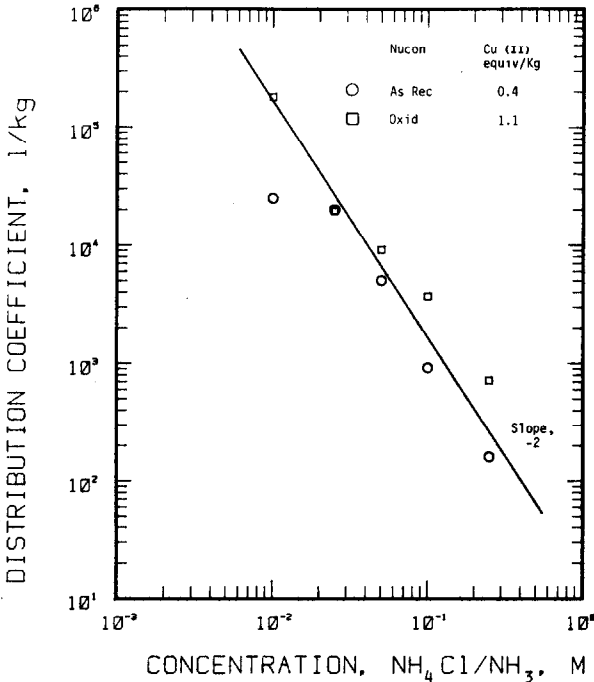


Fig. 7. Distribution of Cu(II) between activated carbon and NH_4Cl solutions at high Cu(II) loading. NH_3 concentration equal to NH_4Cl , pH ≈ 9.4 ; oxidation conditions: 70°C , 90% HNO_3 , 35 min; $-100, +200$ mesh.

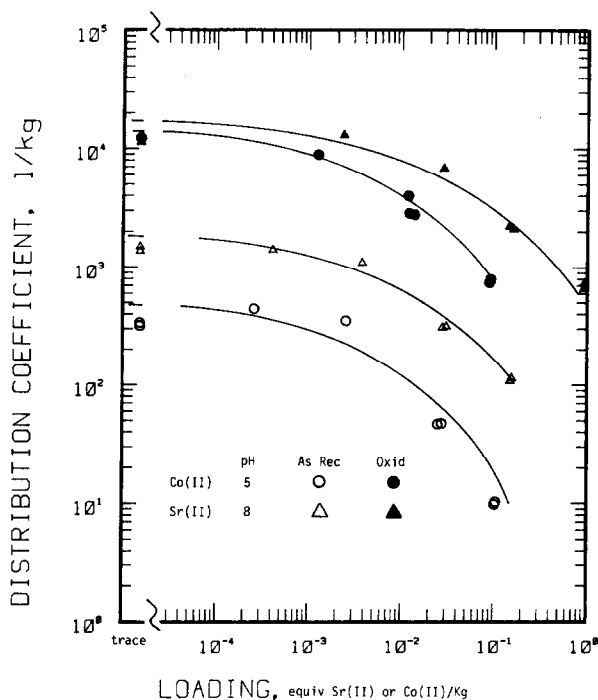


Fig. 8. Effect of loading on distribution of divalent ions. BC-2, -100, +200 mesh; oxidation conditions: 70°C, 90% HNO₃, 35 min; 0.2 M sodium chloride + 0.01 M acetate or bicarbonate.

Loading effects

Distribution coefficients of one ion (here, a divalent ion) in exchange with a constant solution concentration of another (here, monovalent) are expected to decrease as the concentration of the first on the solid increases (eqn. 2, as $[\text{Na}^+]_{\text{solid}}$ decreases). Fig. 8 shows that this is indeed the case for Co(II) and Sr(II) adsorbed from 0.2 M sodium chloride on both oxidized and as-received charcoal. The pH values were selected to avoid possible difficulties with hydrolysis. We do not have measurements of sodium ion uptake on these materials from 0.2 M sodium chloride, but we estimate from other results that they would be about 0.01 equiv./kg at pH 5 and 0.1 at pH 8 for as-received and about 0.5 equiv./kg at pH 5 and 1 at pH 8 for oxidized. If these numbers are correct, significant declines in D are seen sooner (*i.e.*, at lower ratios of loading of divalent ion to sodium uptake) than ideal ion-exchange behavior (eqn. 2, constant Γ , constant equivalent Na^+ plus divalent on solid) would predict, at least for the oxidized material. The estimates of Na(I) uptake are too uncertain for a detailed analysis to be worthwhile.

Effect of conditions of nitric acid treatment

Our initial attempt at nitric acid treatment was adapted from Puri *et al.*¹⁰: charcoal was degassed for 28 h at 500°C in a vacuum, 5 g were treated with 150 ml of fuming nitric acid added in increments, with increasing temperature to a final value of about 110°C. This procedure converted the charcoal we used almost com-

pletely to a colloidal material, unusable as a solid adsorbent. However, milder treatment such as that used to obtain the results described so far (exposure to 90% nitric acid at 70°C) gave solids on which batch equilibrations could be carried out and from which columns could be prepared. The next three figures show the effect of variation of these treatment parameters.

Fig. 9 gives the dependence on nitric acid concentration of sodium ion uptake on Nucon exposed for 100 min at 70°C. Uptake rises with nitric acid concentration as expected.

Fig. 10 gives the variation of uptake with temperature of oxidation treatment. As one would expect, uptake increased, although the dependence (a large increase over untreated, but about the same at 60 and 70°C, and a sharp rise thereafter) seems odd.

Fig. 11 shows increase of uptake with increasing oxidation time for several combinations of temperature and nitric acid concentration.

Characterization of charcoals

We have attempted in several ways to obtain information contributing to an understanding of the effects of nitric acid treatment on charcoals.

Surface area

The increase in ion-exchange uptakes could plausibly result either from an

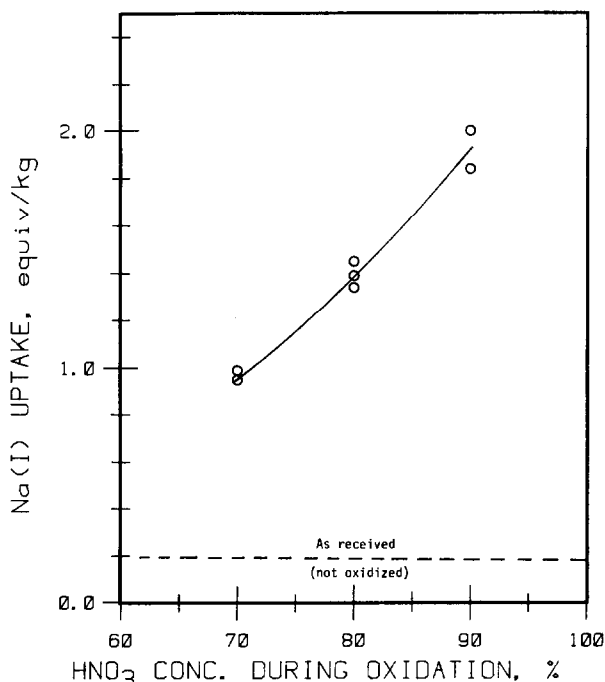


Fig. 9. Dependence of uptake on acid concentration during oxidation. Nucon, -6, +14 mesh; oxidation conditions: 70°C, 100 min; uptake from 0.01 M Na₂CO₃, pH 10.7.

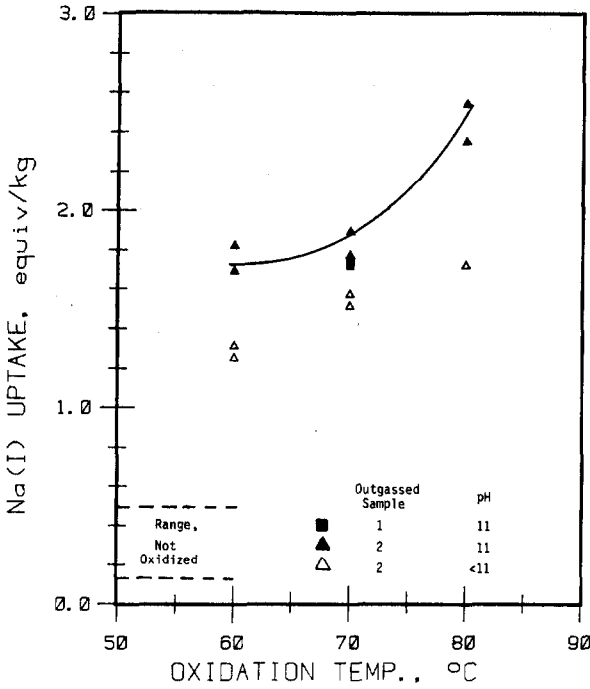


Fig. 10. Effect of oxidation temperature. BC-2; oxidation conditions: 90% HNO₃, 35 min.

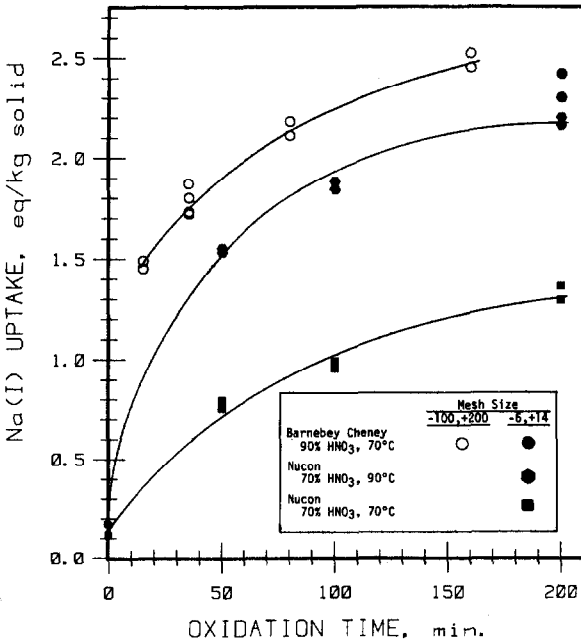


Fig. 11. Effect of oxidation conditions on monovalent ion uptake by charcoals. Measured from 0.01 M Na₂CO₃, pH 10.5.

TABLE II

SURFACE AREAS AND HELIUM DENSITIES OF NUCON CHARCOAL SAMPLES*

	Sample wt. (g)	Helium density (g/cm ³)	Surface area (m ² /g)
As received	0.0507	2.013	1020
After HNO ₃ treatment	0.0509	2.062	970

* Carried out by J. D. Kintigh of the ORNL Metals and Ceramics Division.

increase in surface area or from an increase in density of ionizable groups per unit area. BET nominal surface area measurements were carried out on as-received, -100, +200 mesh, Nucon and on the same material after treatment with 90% nitric acid at 70°C for 35 min. The results are given in Table II. The sorbing gas was nitrogen. There is no significant increase in gas adsorption or exposed nominal surface area, from oxidation. Differences between samples in both area and in helium apparent density are considered insignificant.

NMR characterization

We carried out ¹³C NMR scans on solid samples of hydrogen-form, -100, +200 mesh, BC-2 as-received and after nitric acid treatment (90% acid at 70°C for 35 min). Conversion to the hydrogen form in this case was by two contacts with 10 ml of 1 M hydrochloric acid solution. The results are shown in Fig. 12. The spectra resemble those of bituminous coals with exaggerated low field "aromatic" resonances which represent phenolic (145–165 ppm) and carboxylic acid (170–185 ppm) moieties. The integrated intensity of the spectra in Fig. 12 is only about 10% of that obtained for coals measured under similar conditions. The bulk of this hydrogen-poor material apparently does not yield a cross polarization signal. However, relative peak areas of the detected signal in these two samples show significant differences. The carboxylic acid group resonance is substantially higher in the oxidized sample. There also appears to be a less well-defined area increase in the phenolic region of the spectrum.

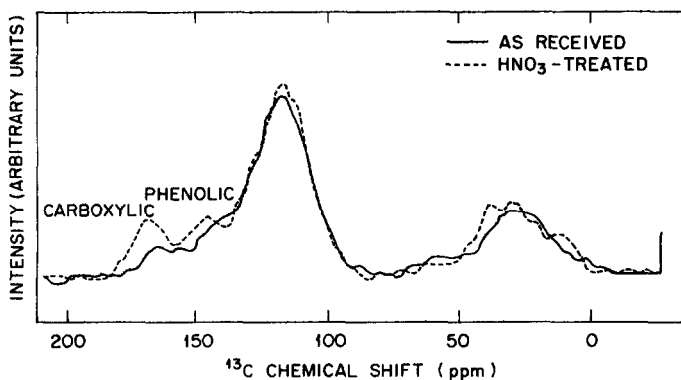


Fig. 12. NMR scans of -100, +200 mesh BC-2 activated carbon, before and after nitric acid treatment. 90% HNO₃ at 70°C for 35 min.

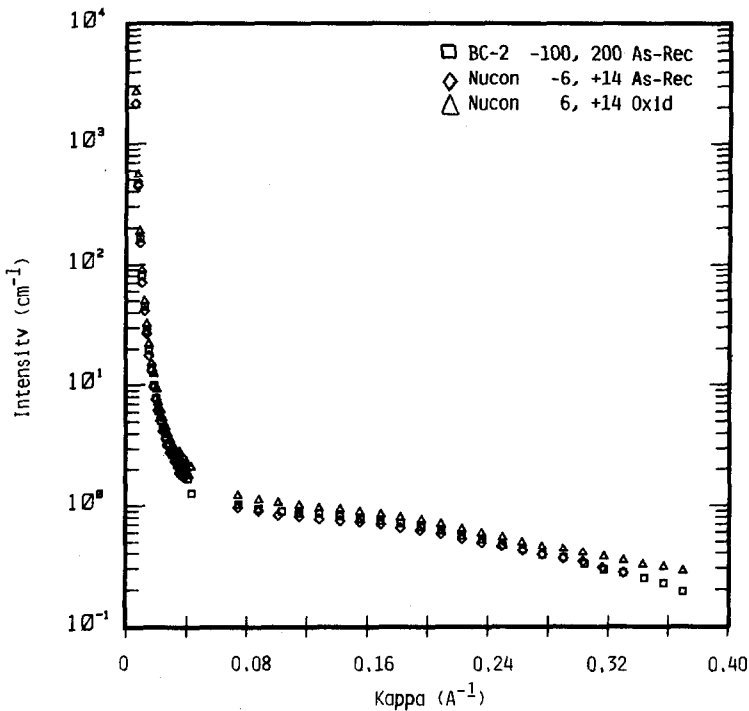


Fig. 13. Small-angle neutron scattering from as-received and HNO₃-treated carbons. Oxidation conditions: 70°C, 90% HNO₃, 35 min.

Taken together with ion-exchange behavior, these observations suggest strongly that increased sodium uptake with nitric acid treatment arises from an increase in the density of carboxylic and phenolic groups on the charcoal.

Small-angle neutron scattering

Neutrons are scattered at small angles from these charcoals because of inhomogeneities arising from the existence of pores. Patterns can therefore be used to detect changes in pores arising from treatment with nitric acid. Recently Hall and Williams¹³ reported scattering from activated carbon. We obtained a pattern for as-received Nucon extending from $\kappa \approx 0.003$ to 0.3. We do not reproduce it here because our inferences are essentially the same as theirs: that there is a distribution of void sizes, difficult to analyze in detail; and that from the results at the high end of the κ range, where the effect of interpore interferences is diminished, a Guinier dimension¹⁴ of about 6 Å can be obtained.

More pertinent to present concerns is a comparison of patterns taken at two distances from an as-received charcoal and from the same material exposed to 90% nitric acid for 35 min at 70°C (Fig. 13). Differences are slight, in agreement with the comparison of surface areas. A pattern from BC-2 included in the figure is similar to those from Nucon.

DISCUSSION

The results presented here, in agreement with the literature, show that oxidative treatment can increase the effective cation exchange capacity of active carbon at a given pH by an order of magnitude. The functional groups contributing to uptake are more strongly acidic than those on the untreated charcoal. Distribution coefficients are also enhanced by oxidative treatment. There is some sacrifice in particle strength, but probably not to a prohibitive extent for many column applications.

In contrast to the observations of Coughlin and Ezra¹⁵, the increases in uptake with oxidation were not accompanied by change in surface area. They found increases in uptake (as measured by base consumption from aqueous solutions of bases of different strength) similar to ours, but the nominal surface area of the active carbon they investigated (Union Carbide Columbia carbon LC325) was less than half the original 1200 m²/g) after oxidation. They also found that the increase in uptake of ions was accompanied by a decrease in adsorption of phenol and nitrobenzene both per unit weight and per unit surface area. Because small-angle neutron scattering also indicated that no great changes in the structure of our material resulted from nitric acid treatment, we conclude that there are basic differences between their activated carbon and ours.

In much of the literature, increase in ion exchange capacity with oxidation has been attributed to "chemisorption" of carbon dioxide, which then forms salts when contacted with alkaline solutions. In at least some authors' minds, formation of carboxylate groups attached to hydrocarbon-type structures would appear to be included under this term. Puri *et al.*¹⁰ for one has a more specific model, however, based on such evidence as equivalence between adsorption of Ba²⁺ and carbon dioxide removed by outgassing. Such a picture would imply here that there is carbon dioxide held entrapped by the carbon surface, not rapidly exchangeable under the conditions of our equilibrations with carbonate in solution phases. The ready exchange of other inorganic ions raises questions concerning this mechanism in our case.

Puri's conditions in nitric acid treatment and in other experiments were considerably more severe than ours. To us, the simplest inference is that the increase in uptake results from increase in carboxylate and phenolate groups on the carbon. The NMR results support this explanation of capacity increase. In this connection, if ortho diphenols were formed, their acid strength would be greater than monophenols. We had analyses carried out on as-received and nitric acid-treated samples by a commercial laboratory. There were increases in oxygen content with oxidation, but we are not sure how much adsorbed gases may have contributed to the results. One inference can be safely drawn from the analyses. Nitrogen was low with samples before and after oxidation and increased only slightly from the treatment. Nitration of the carbon thus appears to have made only a small contribution.

We measured as a function of pH uptakes of two commercial samples of oxidized activated carbon, Spherical Oxycarbon G-30-16 × 35 and Oxycarbon G-80-16 (Nuclear Consulting Services, Columbus, OH, U.S.A.). Uptakes were comparable to nitric acid samples we prepared, with somewhat greater dependence on sodium ion concentration.

Particle attrition is frequently a serious problem in use of adsorbents in col-

umns, and the effect of oxidation procedures on particle strength is of concern. Evaluation by crushing tests has been carried out, and is the subject of another planned communication¹⁶. Here we comment only that there is an appreciable loss of strength accompanying the increased ion-exchange capacity, but that it does not appear prohibitive for many applications. Our hope that this proves correct is increased by the fact that the increased capacity may not only be helpful in separations using the materials discussed here, but it also increases the amounts of other adsorbents with which the pores of the carbons can be loaded¹⁷. Adsorbents of desirable selectivity but difficult to make in forms of size, homogeneity, and stability suitable for chromatography can frequently be used when held in carbon.

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