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Adsorption of Cadmium Ions on Oxygen Surface Sites in Activated Carbon

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Various types of oxygen functional groups were introduced onto the surface of coconut shell derived activated carbon by oxidation using nitric acid. Fourier-transform infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), and selective neutralization were used to characterize the surface oxygen functional groups. The oxidized carbons were also heat treated to provide a suite of carbons where the oxygen functional groups of various thermal stabilities were varied progressively. The adsorption of cadmium ions was enhanced dramatically by oxidation of the carbon. The ratio of released protons to adsorbed cadmium ions on oxidized carbon was approximately 2, indicating cation exchange was involved in the process of adsorption. Na^+ exchange studies with the oxidized carbon gave a similar ratio. After heat treatment of the oxidized carbons to remove oxygen functional groups, the ratio of H^+ released to Cd^{2+} adsorbed and the adsorption capacity decreased significantly. Both reversible and irreversible processes were involved in cadmium ion adsorption with reversible adsorption having higher enthalpy. The irreversible adsorption resulted from cation exchange with carboxylic acid groups, whereas the reversible adsorption probably involved physisorption of the partially hydrated cadmium ion.

Introduction

The trace heavy metals present in the wastewater are of great concern from an environmental perspective due to their toxicity. The use of activated carbon for the removal of the toxic metal ionic pollutants present in low concentration in aqueous solution is of considerable importance. Activated carbons are widely used as adsorbents and catalyst supports due to their well-developed porous structure comprised of hydrophobic graphene layers and hydrophilic surface functional groups. Most of the applications involve adsorption of organic compounds from either gas phase or solution, which are mainly determined by the porous structural characteristics. In the case of gas or vapor adsorption, microporous carbons are used, whereas organic molecules are removed from aqueous solution using mesoporous carbons. In contrast, the adsorption of ionic species from solution on activated carbon is usually dominated by the surface functional groups.^{1,2} The most important application of activated carbon to the adsorption of heavy metal species from solution is for the recovery of precious metals from gold plant liquors, slurries, and effluents.^{3–5} In the case of the adsorption of $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$, the graphene layers in carbon are probably the main adsorption sites,^{1,6,7} although there is some irreversible adsorption of $\text{Au}(\text{CN})_2^-$ on active carbons.⁸ Second, the adsorption of heavy metals on active carbon is used for the treatment of wastewater

containing trace toxic metals.^{9–15} Finally, the adsorption of metal ion species (either cationic or anionic) on activated carbons from aqueous solutions is of importance in the preparation of metal catalysts supported on carbon. The particle size and dispersion of the metal catalysts in carbon may be controlled by the interaction of metal ions and the carbon surface.^{16,17}

Despite extensive research, the adsorption mechanism of cationic metal species on activated carbon is not fully understood. The objectives of this work were to investigate the effects of oxygen functional groups incorporated into the carbon by oxidation using aqueous nitric acid on the adsorption of cadmium cations on the carbon. Cadmium was chosen for this study because it is a typical transition metal cationic species present in wastewater.

Experimental Section

Materials Used. The activated carbon used in this study was commercially available coconut shell based carbon (Code C) activated in steam at $\sim 900^\circ\text{C}$. The carbon was washed with water by using the Soxhlet extraction method to remove water soluble materials present in the carbon prior to the adsorption study. Carbon C was chemically modified by oxidation using nitric acid in order to introduce various oxygen functional groups on the carbon surface. The procedure was as follows: carbon C was refluxed in 7.5 M HNO_3 solution for 4 and 48 h to assess the influence of reaction time on the incorporation of functional groups. The oxidized carbons were Soxhlet extracted with water, until the pH of aqueous extract was constant, to remove residual HNO_3 and any soluble materials and vacuum-dried at 75°C . The resultant carbons with oxidation times of 4 and 48 h were designated sample code CN1 and CN2, respectively. CN1 and

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Table 1. Characterization Data of Active Carbons Used

sample code	proximate analysis, wt %, ar				ultimate analysis, wt %, daf				pore volume ^a (cm ³ g ⁻¹)			D-R surface area, m ² g ⁻¹ (CO ₂ , 273 K)
	moisture	volatile	ash	fixed carbon	C	H	N	O (by diff)	micropore (CO ₂ , 273 K)	total pore (N ₂ , 77 K)	V _{CO₂} /V _{N₂}	
C	3.1	3.3	3.0	90.7	96.1	0.4	0.3	3.2	0.321	0.323	0.994	683
CN1	2.5	23.9	1.8	71.8	82.8	1.1	0.8	15.3	0.262	0.273	0.960	455
CN1-300	1.2	20.5	0.8	77.5	84.1	1.0	0.9	14.1	0.252	0.291	0.866	537
CN1-400	1.3	17.7	1.3	79.7	86.3	0.7	0.8	12.2	0.262	0.282	0.929	557
CN1-500	1.2	14.5	1.4	82.9	88.4	0.7	0.9	10.0	0.253	0.280	0.904	538
CN1-600	1.1	11.5	1.7	85.7	91.0	0.6	0.9	7.5	0.270	0.298	0.906	574
CN1-800	1.0	4.6	1.4	93.0	95.9	0.5	1.0	2.6	0.291	0.325	0.895	619
CN2	2.9	29.1	1.7	66.3	75.6	1.5	1.0	21.9	0.139	0.207	0.671	295
CN2-300	2.3	27.1	1.1	69.5	77.1	0.9	1.0	21.0	0.163	0.209	0.780	347
CN2-400	1.7	24.2	0.7	74.3	82.1	0.9	1.1	15.9	0.188	0.235	0.800	401
CN2-500	1.5	19.2	1.6	77.7	84.3	1.0	1.1	13.6	0.222	0.237	0.937	473
CN2-600	1.3	14.4	0.7	83.6	86.9	0.8	1.2	11.1	0.213	0.271	0.786	453
CN2-800	1.1	3.9	1.8	93.2	94.3	0.5	1.4	3.8	0.260	0.267	0.974	553

^a Total pore volume was obtained from adsorption at $p/p^\circ = 1$, micropore volume was obtained from extrapolation of Dubinin–Radushkevich equation.

CN2 were heated at 10 °C min⁻¹ under flowing helium to the desired temperature and held for 1 h at the maximum temperature. The resultant carbons were designated as the code of original carbon followed by a number to indicate the heat treatment temperature in degrees Celsius, e.g. CN1–300 represents CN1 heat treated to 300 °C and held at the heat treatment temperature (HTT) for 1 h.

Temperature Programmed Desorption (TPD). Temperature programmed desorption (TPD) studies were carried out on a Thermal Science STA 1500 thermogravimetric analyzer (TGA) connected to a VG Quadrupole 300 amu mass spectrometer by a heated stainless steel capillary lined with deactivated fused silica. Approximately 7 mg of sample was placed in a sample bucket and was heated from ambient temperature to 1200 °C at a heating rate of 15 °C min⁻¹ under flowing argon (50 cm³ min⁻¹). The evolved gas was sampled and analyzed by the mass spectrometer throughout the course of the desorption process. The mass/charge (m/z) values of 28 and 44 were monitored.

Fourier-Transform Infrared Spectroscopy (FTIR). Infrared spectra were recorded on a Nicolet 20-PCIR Fourier-transform infrared spectrometer with CsI optics and a DTGS detector. The KBr disks were prepared by mixing 0.5% of finely ground carbon sample in KBr. The spectral resolution was 4 cm⁻¹.

Titration Studies (Boehm's Method). The selective neutralization method used to evaluate the carbon surface acidity was the scheme suggested by Boehm.¹⁸ The amounts of the various acidic functional groups can be measured by selective neutralization using NaHCO₃, Na₂CO₃, and NaOH solutions, respectively. About 0.2 g of carbon was placed in 25 cm³ of each 0.1 N of solution and the mixtures were allowed to stand for 72 h at room temperature. The mixtures were separated by filtration. The amount of each base neutralized by the carbon was determined by back-titration using 0.1 N HCl solution.

X-ray Absorption Near Edge Structure (XANES). The nitrogen X-ray absorption near edge structure (K edge) spectroscopy measurements were carried out by using beam line Station 1.1 of the synchrotron radiation source (SRS) at Daresbury Laboratory. The details have been reported previously.¹⁹

Adsorption and Desorption Studies of Cadmium. The mixtures of carbon and cadmium nitrate aqueous solution were allowed to stand for 48 h in a water bath of 25 °C. The carbons were separated by filtering and rinsed with water (0 °C) to remove residual solution trapped among carbon particles. Desorption studies were carried out by using Soxhlet extraction for 24 h. The amounts of cadmium adsorbed and desorbed were determined by measuring the solution concentration using a Unicam 701 inductively coupled plasma (ICP) atomic emission spectrometer (University of Newcastle upon Tyne, Chemical Analytical Service Unit).

Flow Microcalorimetry Studies. A Microscal Model 3 Vi immersion flow microcalorimeter was used to measure the enthalpy change of a solid/liquid interaction. Approximately 80 mg of carbon (particle size of 0.212–0.425 mm) was used with a flow rate of 3.3 cm³ h⁻¹. The heats of adsorption were measured by the following procedure. (1) The carbon was equilibrated by passing water until a steady baseline was achieved. (2) Cadmium nitrate solution was passed over the sample and the heat of adsorption was measured by calibration of the thermal profile against a known current/voltage/time calibration peak. (3) After the adsorption and calibration were completed, the water was passed over the sample to obtain the heat of desorption. (4) When a steady baseline was achieved after desorption 1, the cadmium nitrate was passed over the sample bed again to obtain the heat of adsorption for the second adsorption. (5) Finally, the heat of desorption for the second cycle was obtained by passing water over the sample.

Energy-Dispersive X-ray Analysis (EDA). EDA studies were carried out on a JEOL JSM 35 scanning electronic microscope (SEM) with a LINK QX2000 EDA analyzer.

Results

Characterization of Carbons. Analytical and Porous Structure. Table 1 shows the analytical data including proximate and ultimate analysis results and the porous structure characteristic of the carbons used in the study. The proximate analysis data show that the amounts of volatile species increased while ash content decreased as a result of HNO₃ treatment. The volatiles are an indication of the functional groups incorporated by the nitric acid oxidation treatment, which are decomposed during heat treatment. Treatment with HNO₃ results in increases in oxygen, nitrogen, and hydrogen content and decrease in carbon content. It is apparent that large amounts of oxygen were introduced into the carbon after nitric acid oxidation, with the oxidation time of 48 h (CN2) introducing approximately one-third more oxygen functional groups than oxidation for 4 h (CN1). Small amounts of nitrogen were also incorporated into the carbon by the oxidation. The nitrogen K-edge XANES spectrum of oxidized carbon CN2 is shown in Figure 1. According to previous studies,^{1,19} the peak at 401.1 eV is assigned to pyridone groups, whereas the two strong well-resolved peaks at 403.5 and 405 eV are assigned to pyrrolic and possibly pyridine *N*-oxide groups, respectively. The pHs of the carbons were obtained by a modified ASTM method.²⁰ The pHs of CN1 and CN2 were 4.42 and 3.97, respectively, showing that they were weakly acidic.

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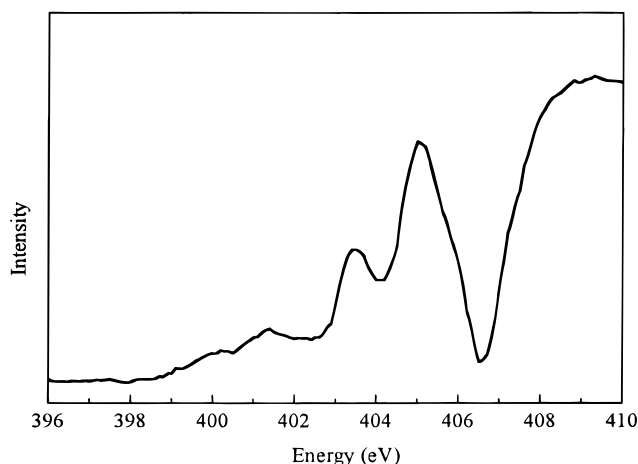


Figure 1. Nitrogen K-edge XANES spectrum of oxidized carbon CN2.

Table 2. Analysis of Leachate from Water Extraction and HNO₃ Treatment of Carbon C

	leachate from water extraction, $\mu\text{mol (g of carbon)}^{-1}$	leachate from HNO ₃ oxidation, $\mu\text{mol (g of carbon)}^{-1}$	leachate from washing oxidized carbon, $\mu\text{mol (g of carbon)}^{-1}$
Al	4.0	1.6	0
Mn	4.3×10^{-3}	9.9×10^{-2}	1.8×10^{-3}
Cu	0	9.6×10^{-2}	
Zn	0	1.8×10^{-2}	
Mg	3.1×10^{-1}	9.9	1.8×10^{-1}
Ca	1.6×10^{-1}	7.8	1.1×10^{-1}
Sr	0	5.1×10^{-2}	
Ba	0	2.2×10^{-2}	
Na	55	27	3.4
K	240	160	30
B	139	3.1	
S	2.1	4.8	3.4×10^{-1}
Si	30	7.8×10^{-1}	8.4×10^{-2}
P	6.6	7.0	6.0×10^{-1}

Heat treatment decreases the oxygen and hydrogen contents gradually, whereas the nitrogen content remained relatively constant, which indicates that nitrogen was incorporated into the carbon structure as relatively stable functional groups. Heat treatment to 300 °C reduced the oxygen contents in the oxidized carbons slightly with release of carbon dioxide. The chemical composition and structure of the oxidized carbons heat treated at 800 °C were similar to those of the original samples.

In addition to the modification to the surface chemical structures of the active carbons, the porous structures were also modified after oxidation with HNO₃. Nitric acid treatments decreased both the CO₂ micropore volume and N₂ total pore volume with the higher oxidation times resulting in greater reduction of pore volumes. Heat treatment increased the surface areas and both the micropore and total pore volumes gradually. However, the structural changes introduced by oxidation were not completely reversible by heat treatment to 800 °C.

The analytical results for the leachates obtained from Soxhlet extraction with water and nitric acid oxidation are given in Table 2. It is apparent that the water extract was composed mainly of potassium, sodium, and boron with smaller amounts of silicon, phosphorus, and sulfur. The nitric acid oxidation extract contained significant quantities of calcium and magnesium in addition to the elements extracted with water.

Titration Studies. The acidic surface groups present in carbons include (1) carboxylic acid groups, (2) derivatives of carboxylic acid groups such as carboxylic anhydride, lactone, and lactol groups, and (3) phenolic groups. These

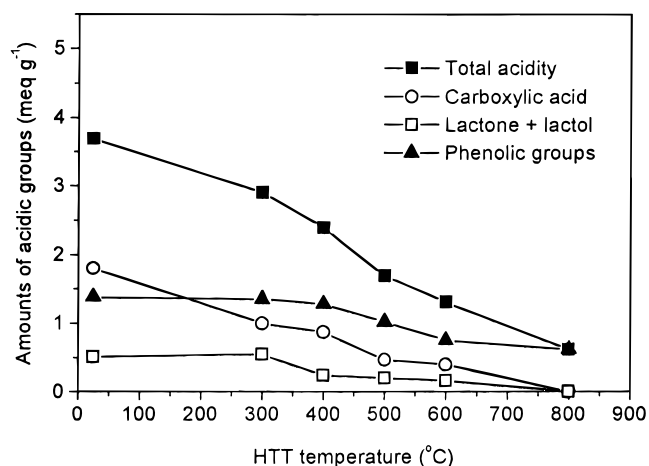


Figure 2. Variation of surface acidic groups with heat treatment for CN1.

groups are weakly acidic and the acidity constants differ by several orders of magnitude.²¹ According to Boehm^{18,22} only the strongly acidic carboxylic groups are neutralized by NaHCO₃, whereas those neutralized by Na₂CO₃ are thought to be lactone, lactol, and carboxyl groups. The weakly acidic phenolic groups only react with strong alkali (NaOH). Therefore, by selective neutralization using bases of different strength, the surface acidic functional groups in carbons can be characterized quantitatively and qualitatively. It is assumed that neutralization with HCl characterizes the amounts of surface basic groups. The basic properties are ascribed to surface basic groups and the π electron system of carbon basal planes.

The titration results for the original activated carbon C, the oxidized carbons CN1 and CN2, and their heat-treated derivatives by both HCl and bases of different strength are shown in Table 3. The results indicate that carbon C is basic H-type carbon since it does not react with sodium carbonate and sodium bicarbonate and therefore does not contain significant quantities of carboxylic acid groups or their derivatives such as anhydride, lactone, and lactol groups. However, the carbon contains a small amount of acidic groups which react with NaOH, but the dissociation is small since the carbon shows only basic properties in aqueous solution. The oxidation by HNO₃ produced considerable amounts of acidic groups in the carbon. Approximately half of the total acidity in the oxidized carbons was due to carboxylic groups. Comparison of titration data for CN1 and CN2 shows that increase in oxidation time leads to the incorporation of greater amounts of all oxygen functional groups into the carbon in approximately the same proportion.

The trends for the concentration of various acidic groups after heat treatment of the oxidized carbons CN1 and CN2 at elevated temperatures to eliminate progressively the surface oxygen complexes are shown in Table 3 and graphically for CN1 in Figure 2. It is evident that heat treatment led to progressive loss of acidic surface groups. In contrast the amounts of HCl required to neutralize basic groups in carbons increased slightly with increasing heat treatment temperature (HTT) with the basicity being similar to that of starting carbon C after heat treatment to 800 °C.

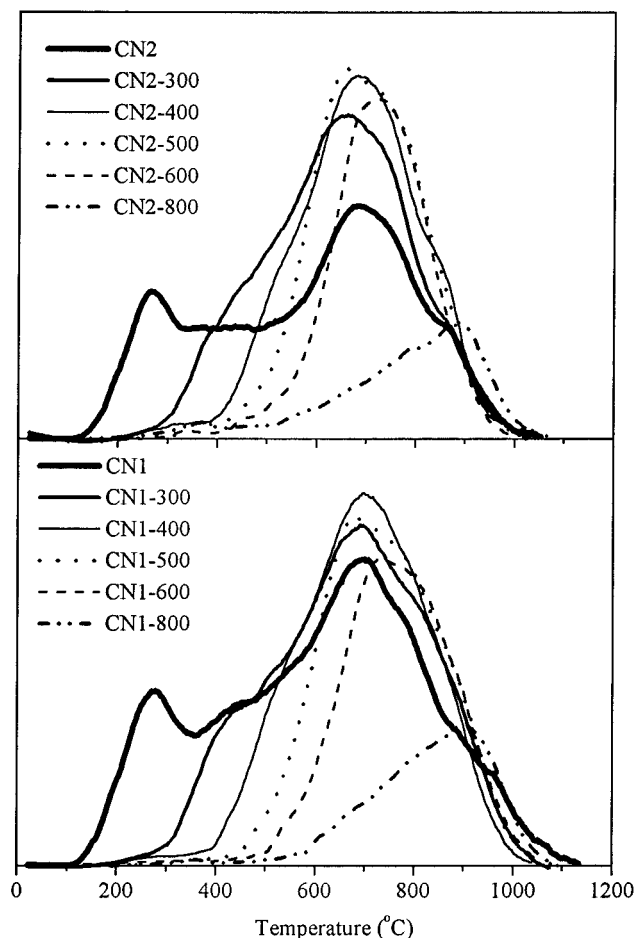
Figure 2 and Table 3 show that the carboxylic acid groups are most sensitive to heat treatment. Approxi-

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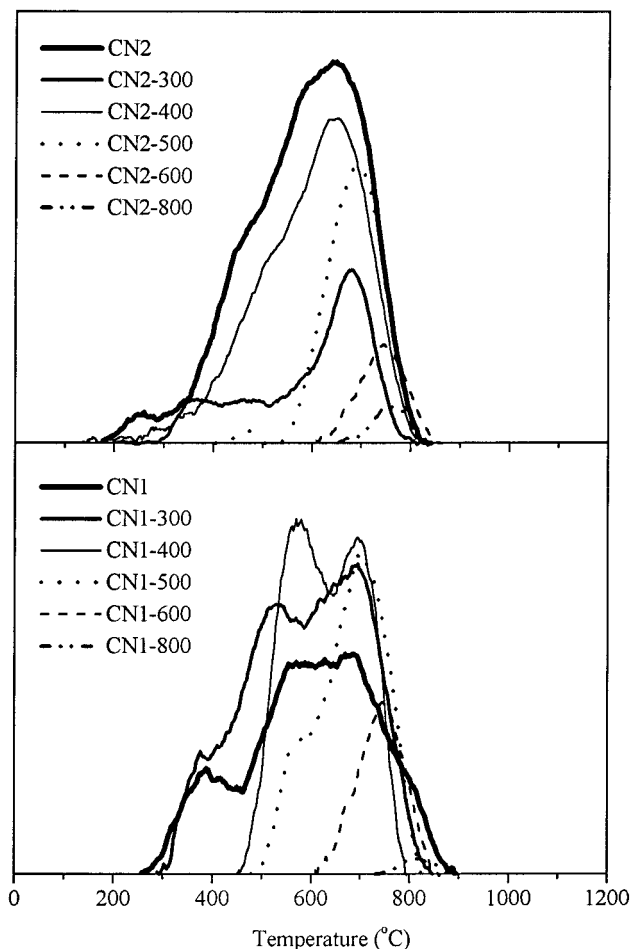
Table 3. Selective Neutralization Results of HNO₃-Oxidized Carbons and Heat Treatment Derivatives

sample code	HCl, (mequiv g ⁻¹)	NaHCO ₃ (mequiv g ⁻¹)	Na ₂ CO ₃ (mequiv g ⁻¹)	NaOH (mequiv g ⁻¹)	acidic groups, %		
					carboxylic	lactone + lactol	phenolic
C	0.40	0	0	0.50	0	0	100
CN1	0.08	1.80	2.31	3.69	48.8	13.8	37.4
CN1-300	0.05	1.00	1.55	2.90	37.5	20.6	41.9
CN1-400	0.14	0.87	1.11	2.39	36.4	10.0	53.6
CN1-500	0.11	0.47	0.67	1.69	24.2	23.2	52.6
CN1-600	0.26	0.40	0.56	1.31	23.0	9.2	67.8
CN1-800	0.35	0	0	0.62	0	0	100
CN2	0	2.52	3.25	4.89	51.5	14.9	33.5
CN2-300	0	1.40	2.06	3.70	37.8	17.8	44.3
CN2-400	0	0.95	1.32	2.96	31.9	12.7	55.4
CN2-500	0.06	0.63	0.78	2.02	23.4	16.3	61.2
CN2-600	0.06	0.24	0.53	1.30	18.5	22.3	59.2
CN2-800	0.50	0	0	0.41	0	0	100

**Figure 3.** Temperature programmed CO₂ desorption profiles for CN1 and CN2.

mately half of the carboxylic acid groups in the oxidized carbons CN1 and CN2 were removed by heat treatment at 300 °C for an hour, whereas the amounts of lactone and phenolic groups remained relatively unchanged at this temperature, indicating that they are more stable toward heat treatment. The amounts of lactone and lactol groups decreased for heat treatment temperatures >300 °C, while the amounts of phenolic groups decreased for heat treatment >400 °C. Small amounts of acidity remained in the carbons after heat treatment at 800 °C, and this is ascribed tentatively to phenolic groups.

Temperature Programmed Desorption (TPD). Temperature programmed desorption (TPD) experiments were carried out to characterize surface oxygen functionality from their thermal stability by monitoring evolved CO₂ and CO (see Figures 3 and 4, respectively). It is apparent

**Figure 4.** Temperature programmed CO desorption profiles for CN1 and CN2.

that the corresponding profiles for CN1 and its heat-treated derivatives are very similar to those for CN2. The interpretation of TPD is complex especially at high temperature where surface mobility is significant.²³ However, it is generally accepted that at low temperatures CO₂ is mainly due to the decomposition of carboxylic acid groups and their derivatives, anhydride, lactone, and lactol groups, whereas CO is derived from the decomposition of phenolic hydroxyl, carbonyl, quinone, ether, pyrone, and anhydride groups.^{24,25} The CO₂ TPD evolution profile of carbon C is not illustrated in the figure due to the negligible

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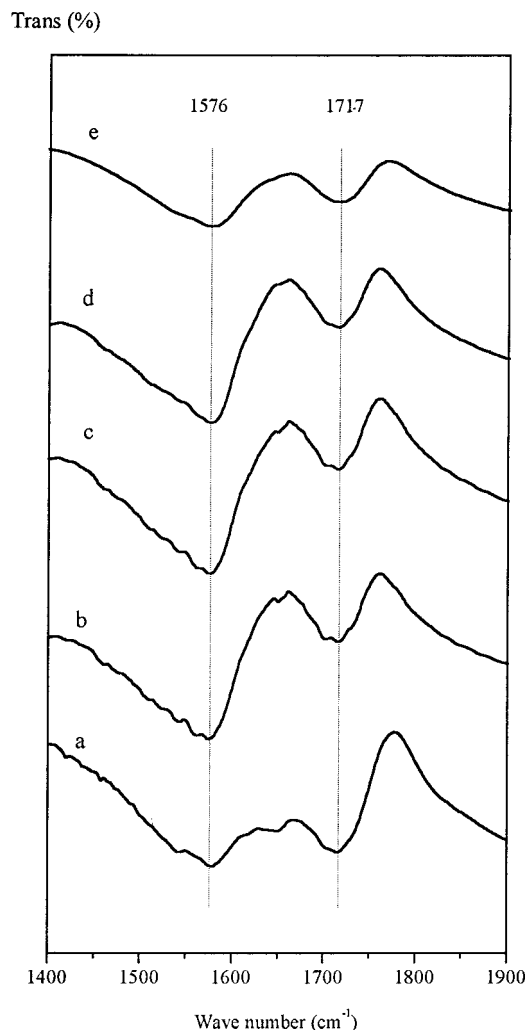


Figure 5. FTIR spectra of (a) CN2, (b) CN2-NaHCO₃, (c) CN2-Na₂CO₃, (d) CN2-NaOH, and (e) CN2 after adsorption of cadmium.

amount of CO₂ evolved during TPD, which is consistent with the above titration results which show that neither Na₂CO₃ nor NaHCO₃ react with carbon C, indicating that carboxylic groups and their derivatives were not present.

Two well-resolved peaks were observed in the carbon dioxide TPD for oxidized carbons, CN1 and CN2, at about 270 and 700 °C, respectively, while the profiles were complex, consisting of a number of unresolved additional peaks. Heat treatment results in decomposition of the surface oxygen functional groups and this results in significant changes in the TPD profiles. The starting points of CO₂ evolution increased gradually with increasing heat treatment temperature, but, in general, CO₂ evolution starts below the HTT of the sample. The initial CO release occurred at higher temperatures than that of the corresponding CO₂, and the CO evolution reached a maximum at 600 °C.

Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectra of original carbon C, oxidized carbon CN2, heat treated CN2, and CN2 reacted with bases of different strength are presented in Figures 5 and 6. For carbon C, the bands observed at 2852 and 2921 cm⁻¹ were assigned to symmetric and asymmetric C-H stretching vibrations in aliphatic CH, CH₂, and CH₃ groups. The band at 1635

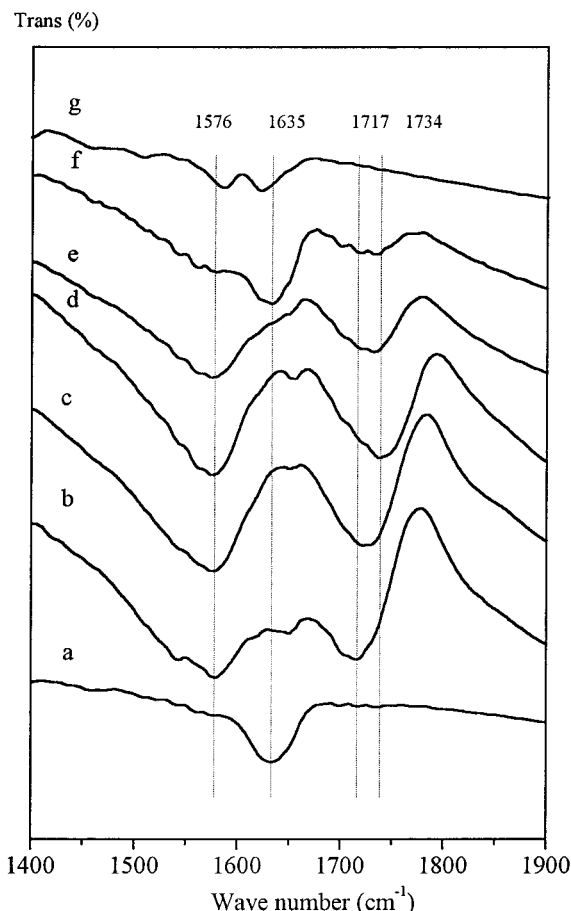


Figure 6. FTIR spectra of (a) original carbon C, (b) CN2, (c) CN2-300, (d) CN2-400, (e) CN2-500, (f) CN2-600, and (g) CN2-800.

cm⁻¹ is a characteristic peak for carbon materials²⁶ and is probably ascribable to carbonyl groups which are highly conjugated in the graphene layer such as quinone and/or ionoradical structure C=O.²⁷ This is consistent with the basic nature of the carbon. The broad weak peak at 1182 cm⁻¹ is assigned to C-O stretching vibrations in phenolic groups.

Two additional bands were observed at 1576 and 1717 cm⁻¹ in the IR spectrum of CN2, while the relative intensity of the broad band at 1182 cm⁻¹ increased considerably and the peak at 1635 cm⁻¹ was obscured by the new bands at 1576 and 1717 cm⁻¹. The 1717-cm⁻¹ band is characteristic of stretching vibrations of carbonyl groups C=O in carboxylic acid groups. The carboxylic acid groups should also have an absorption band at ~3400 cm⁻¹. However, the intense broad peak in the 3400-cm⁻¹ region in the spectrum of CN2 is not an unequivocal identification of O-H stretching vibrations in carboxylic acid groups because of the possibility of adsorbed water present in the sample. The broad band at 1182 cm⁻¹ may have contributions from both C-O stretching and O-H bending modes in phenolic, carboxylic acid groups.^{27,28} The 1576-cm⁻¹ band has contributions from the aromatic ring stretching mode and conjugated carbonyl groups, such as quinone type C=O and/or C=O ionoradical structures. Second, the reaction between COOH groups in the carbon

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and KBr during the preparation of the sample disk cannot be ruled out completely. The resultant carboxylate groups COO^- should display a strong asymmetric COO^- vibrations band in the range $1550\text{--}1610\text{ cm}^{-1}$ and a weak symmetric COO^- stretching band in the range $1360\text{--}1450\text{ cm}^{-1}$.^{29,30} The absence of bands at 1830 and 1760 cm^{-1} confirms the absence of carboxylic anhydride in carbon CN2.

The FTIR spectra of CN2 treated with NaHCO_3 , Na_2CO_3 , and NaOH to selectively neutralize different acidic groups are shown in Figure 5. It is evident that there are changes in the IR spectra of CN2 after reaction with bases of different strength. The relative intensity of 1717 cm^{-1} band assigned to carboxylic acid decreased significantly, accompanied by an increase in the intensity of the 1576 cm^{-1} band assigned to carboxylate groups. The reactions also brought about a decrease in the 1182 cm^{-1} band intensity, which was assigned as C–O stretching and O–H bending modes in carboxylic acid and phenolic groups.^{27,28} Although the band at 1717 cm^{-1} decreased in relative intensity, it did not shift to higher wavenumber after CN2 was reacted with NaHCO_3 . Therefore, it can be inferred that lactone groups were probably absent in oxidized carbon CN2.

The changes in FTIR spectra of CN2 after heat treatment are shown in Figure 6. It is apparent that the bands at 1182 , 1576 , and 1717 cm^{-1} decrease in relative intensity with increasing HTT. Heat treatment to 400°C results in the band at 1717 cm^{-1} shifting to 1734 cm^{-1} , which is assigned as lactone groups. Since the absorption bands due to anhydride were not observed, it is proposed that carboxylic acid groups decompose with partial intermolecular rearrangements to form lactone groups. The concentration of lactone groups decreased gradually at heat treatment temperatures $> 400^\circ\text{C}$ as inferred from the changes in 1734 cm^{-1} band intensity and the titration studies above. The reduction of the band intensities in the 1182 and 1576 cm^{-1} region for heat treatment at 600°C suggests that considerable decomposition of phenolic and quinone groups had occurred. The band at 1635 cm^{-1} split into two bands at 1585 and 1623 cm^{-1} . The 1623 cm^{-1} band was assigned to the quinone-type carbonyl oxygen conjugated with the carbon basal plane. The band at 1585 cm^{-1} in CN2–800 was assigned to ionoradical structure $\text{C}=\text{O}$ caused by heat treatment or further chemisorption of oxygen at room temperature.^{27,31}

The FTIR spectrum of oxidized carbon CN2 after adsorption of cadmium (see Figure 5) shows that the relative intensity of the carboxylic acid band at 1717 cm^{-1} decreased relative to the carboxylate 1576 cm^{-1} band intensity. This is indicative of cation exchange with carboxylic acid groups being involved in the cadmium adsorption on the oxidized carbon. Attempts to detect CdO stretching vibrations for CN2 after adsorption of cadmium using both infrared and Raman spectroscopy were unsuccessful.

Adsorption of Cadmium. The adsorption kinetics were studied in order to assess the time required for equilibrium to be achieved. The results showed that equilibrium was achieved within ~ 3 h. However, the solutions were left for 48 h to ensure complete equilibration. The adsorption isotherms of cadmium on various carbons derived from CN1 are shown in Figure 7. It is

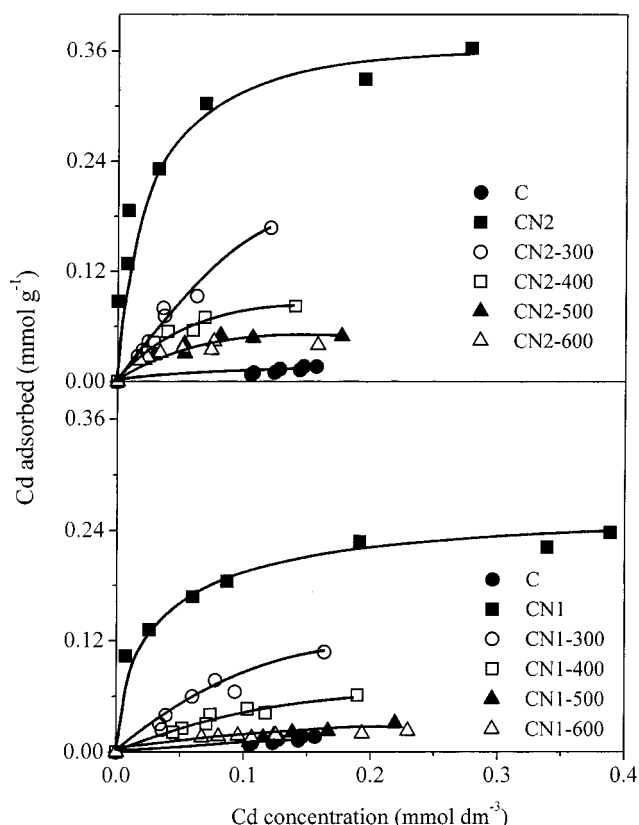


Figure 7. Comparison of adsorption isotherms of cadmium on oxidized carbons CN1 and CN2 and their heat-treated derivatives.

apparent that the adsorption capacities of cadmium were dramatically enhanced after the carbon C was oxidized with HNO_3 . It is apparent that the isotherms for cadmium adsorption on the corresponding carbons derived from CN2 are very similar. After CN1 and CN2 were subjected to progressive decomposition of surface oxygen functional groups by heat treatment at elevated temperatures, the adsorption capacities of Cd^{2+} on the carbons were reduced significantly. Comparison of the adsorption isotherms of cadmium ions on CN1 and CN2 shows that CN2 has a higher adsorption capacity. This indicates that higher extent of oxidation treatment by HNO_3 incorporated more oxygen functionality responsible for cadmium ion adsorption. In contrast, the total and micropore volumes for CN2 were lower than for CN1 (see Table 1).

The changes in pH of residual solution after cadmium adsorption on various carbons were also monitored in this study. Comparison of the cadmium adsorption studies with the corresponding blank reference studies showed that the release of protons from carbon when contacting with cadmium solution was entirely ascribed to the adsorption of cadmium ions which displaced the protons from the carbon surface. The relation between the amounts of adsorbed cadmium and that of released protons after adsorption on oxidized carbon CN2 is shown in Figure 8. It is evident that the ratio of released H^+ to adsorbed Cd^{2+} is approximately 2 in the lower concentration range used in this study. The ratio decreased slightly at higher concentrations. The amounts of corresponding desorbed cadmium from carbon CN2 are also shown in Figure 8. It is apparent that little cadmium was desorbed from carbon CN2 by Soxhlet extraction using water. This was confirmed by EDA studies of the surface of CN2 after adsorption of cadmium followed by Soxhlet extraction with water. The cadmium distribution was relatively uniform

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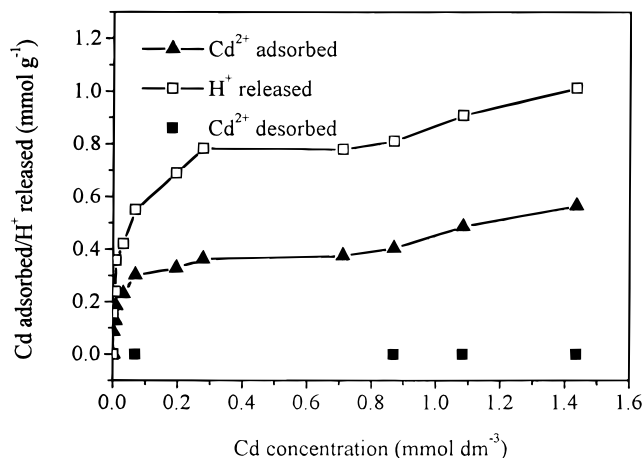


Figure 8. Comparison of the amounts of adsorbed cadmium ions (▲) on oxidized carbon CN2 with that of released H⁺ (□) from the carbon after adsorption and desorbed cadmium ions by Soxhlet extraction (■).

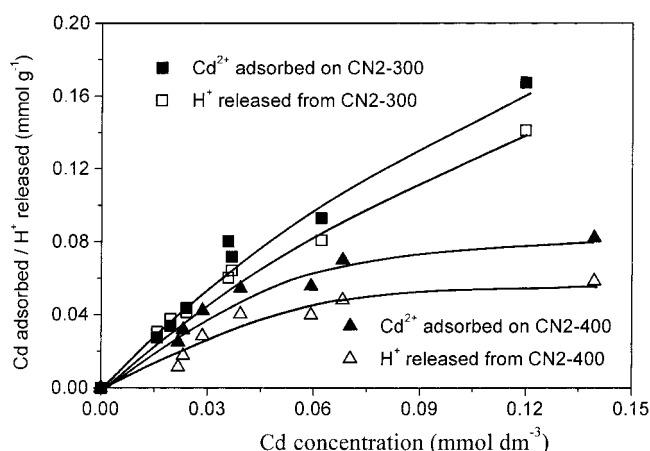


Figure 9. Comparison of the amounts of adsorbed cadmium ions with that of released H⁺ for the carbons CN2-300 and CN2-400.

across the surface of the particle and the cadmium was adsorbed irreversibly on the oxygen surface sites in the carbon. Therefore the carboxylic acid groups on the surface of carbon CN2 are probably the main sites for the adsorption of cadmium cations with the ion exchange of cadmium cations with the protons of carboxylic acid groups.

The relations between adsorbed cadmium and released H⁺ for CN2-300 and CN2-400 are shown in Figure 9. It is apparent that after heat treatment of CN2 to eliminate some surface oxygen functional groups, the ratio of H⁺/Cd²⁺ decreased in addition to the reduction of cadmium adsorption capacity. The H⁺/Cd²⁺ ratio for adsorption on CN2-300 is slightly greater than 1 at lower concentration and less than 1 at higher concentration. The H⁺/Cd²⁺ for adsorption on CN2-400 is much lower than that of CN2-300 and CN2 and this ratio also decreases with increasing equilibrium concentration.

To further investigate the adsorption mechanism of cadmium, the oxidized carbon CN2 was treated with NaOH to neutralize the acidity on the carbon surface and displace H⁺ with Na⁺. Adsorption of cadmium on Na⁺ ion exchanged carbon was studied and the amounts of released Na⁺ and adsorbed Cd²⁺ were monitored (see Figure 10). At lower concentration the amount of desorbed Na⁺ during cadmium adsorption is approximately twice that of adsorbed Cd²⁺, indicating that a cation exchange mech-

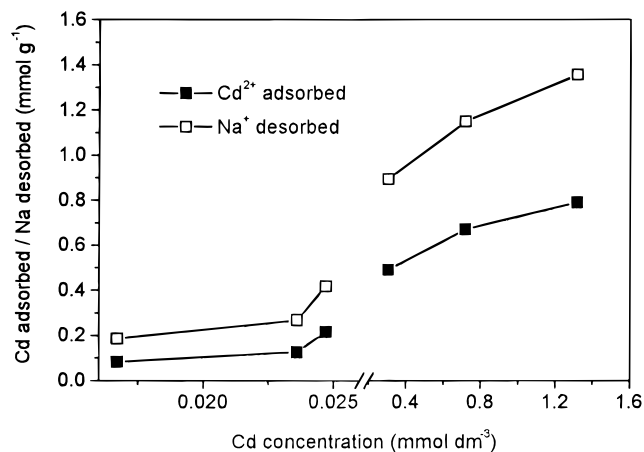


Figure 10. Comparison of the amounts of adsorbed cadmium ions with that of released Na⁺ for carbon CN2 after reaction with NaOH.

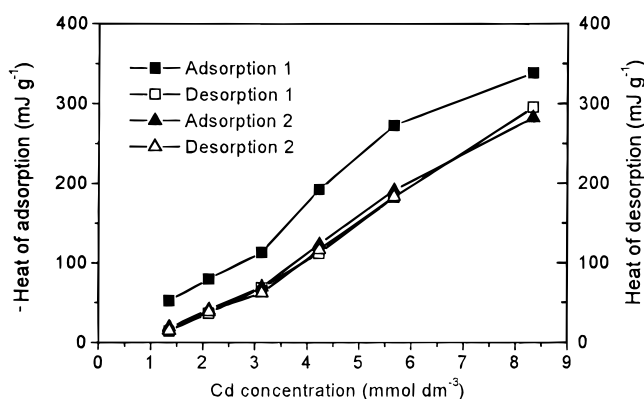


Figure 11. Enthalpies of adsorption and desorption of cadmium on carbon CN2.

anism may be involved in the cadmium adsorption. At higher concentrations the Na⁺/Cd²⁺ ratio is less than 2 and decreases gradually with increasing equilibrium Cd²⁺ concentration.

The enthalpies of adsorption and desorption of Cd²⁺ on oxidized carbon CN2 are shown in Figure 11. There is a large difference between adsorption 1 and other isotherms, while little difference is observed among desorption 1, adsorption 2, and desorption 2. This difference remains relatively constant in the concentration range used in this study. It is apparent that both reversible and irreversible adsorption are involved in the adsorption of cadmium cations on oxidized carbon CN2. The irreversible adsorption is shown from the difference between the heat of adsorption 1 and desorption 1, adsorption 2, and desorption 2. The reversible adsorption is reflected by the similar isotherms of the heat of desorption 1, adsorption 2, and desorption 2.

The heats of adsorption and desorption of cadmium on carbon CN2-300 and CN2-500 are shown in Figures 12 and 13. It is evident that there is little difference between the graphs, indicating mainly reversible adsorption processes for CN2-300 and CN2-500.

The molar heats of adsorption of cadmium ions on CN2, CN2-300, and CN2-500 are shown in Figure 14. It is evident that the molar heats of adsorption increase with increasing concentration for all three carbons, indicating differences in the adsorption sites and mechanism. The enthalpy of adsorption for cadmium on CN2 is very low and similar to that observed for ion exchange reactions

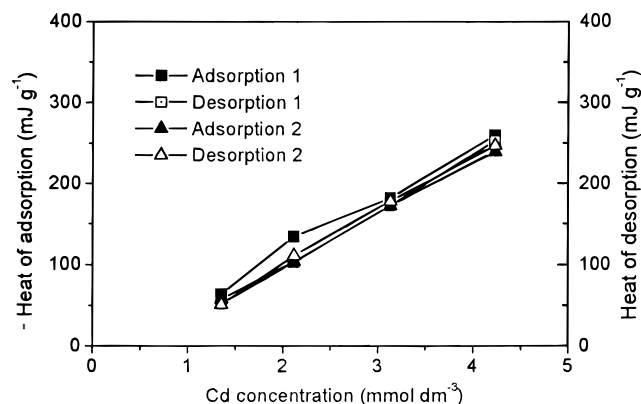


Figure 12. Enthalpies of adsorption and desorption of cadmium on carbon CN2-300.

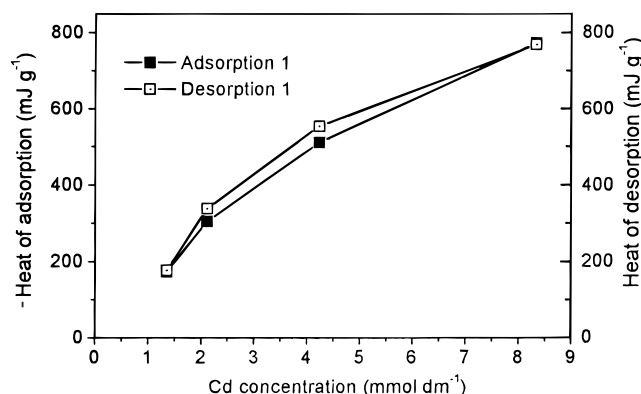


Figure 13. Enthalpies of adsorption and desorption of cadmium on carbon CN2-500.

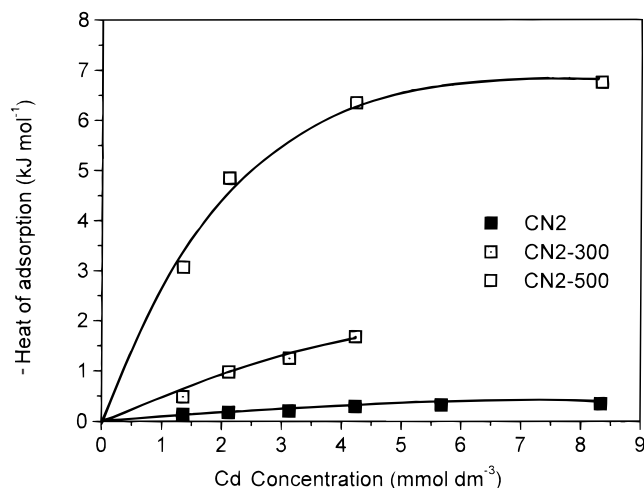


Figure 14. Molar heat of adsorption of cadmium on carbons CN2, CN2-300, and CN2-500.

in resins ($0.0\text{--}0.5\text{ kJ mol}^{-1}$).³² The enthalpy of adsorption of cadmium ions on carbon C (untreated) at a concentration of 1 mmol dm^{-3} was 70 kJ mol^{-1} . Previous studies of Groszek³³ on the adsorption of cadmium ions on Chemviron BPL carbon reported a value of 89 kJ mol^{-1} at the same concentration. It is apparent that oxidation treatment reduced the molar enthalpy of adsorption dramatically to $\sim 0.2\text{ kJ mol}^{-1}$. The enthalpy of adsorption for cadmium adsorption on CN2 is relatively uniform compared with

its heat-treated derivatives. The enthalpy of adsorption increases after the oxidized carbon was heat treated, as shown in Figure 14. This indicates that the changes in adsorption mechanism result from the changes in surface functional groups during heat treatment. Intuitively one would expect the irreversible adsorption to have a higher enthalpy of adsorption. However, in the flow microcalorimeter the net heat of adsorption is measured and a number of processes are involved which may affect the measured heats of adsorption from solution.

Discussion

The oxidation of active carbons by nitric acid involves the incorporation of surface functional groups, which result in significant modification of the surface chemistry of the activated carbon. Heat treatment eliminates oxygen functional groups progressively. The nature of oxygen groups present in carbon was determined by a combination of FTIR, TPD, and selective neutralization analysis. The oxygen functional groups present in HNO_3 oxidized carbon can be divided into carboxylic acid, phenolic, and quinone groups. No strong evidence was observed to support the existence of lactone groups. The titration studies show that heat treatment at $300\text{ }^\circ\text{C}$ eliminated more than half of the carboxylic acid groups, whereas other oxygen functional groups were not removed. The lactone groups were possibly formed during heat treatment at lower than $400\text{ }^\circ\text{C}$ and began to decompose at higher than $400\text{ }^\circ\text{C}$. Small amounts of nitrogen functional groups were also incorporated by the oxidation procedure.

The oxidation with nitric acid brought about the reduction of surface areas, micropore volumes, and total pore volumes of the oxidized carbons. However, the adsorption capacities of cadmium were enhanced dramatically by the nitric acid treatment. Heat treatment of the oxidized carbons increased the surface area and pore volumes, while the adsorption capacities for cadmium decreased dramatically. Carbon CN2 had lower total and micropore volumes than CN1 but adsorbed greater quantities of Cd^{2+} than CN1. These observations indicate that the cadmium adsorption capacities of the carbons are not influenced significantly by changes in the porous structure of the activated carbons during nitric acid oxidation. The amount of nitrogen incorporated into the carbon structure did not change significantly with heat treatment and therefore this is not a factor. The adsorption of cadmium correlated with surface acidic oxygen functional groups present in carbon. The cadmium adsorption capacity was increased dramatically after significant amounts of acidic oxygen groups were introduced by HNO_3 oxidation. However, the various types of oxygen surface groups do not make the same contribution to the adsorption of cadmium. Carboxylic acid surface groups are the least thermally stable. Although heat treatment at $300\text{ }^\circ\text{C}$ only decreased the oxygen contents of CN1 and CN2 slightly, it produced the greatest reduction of cadmium adsorption capacities. This is indicative of the oxygen present as carboxylic acid groups contributing most to the adsorption of cadmium. However, the role of other oxygen functional groups in cadmium adsorption cannot be excluded completely.

The FTIR spectra strongly suggest the formation of carboxylate after the adsorption of cadmium on HNO_3 oxidized carbon. This provides direct evidence that cation exchange with carboxylic acid groups is involved in cadmium adsorption on activated carbon. The adsorption capacity of cadmium was decreased correspondingly with the elimination of carboxylic acid groups by heat treat-

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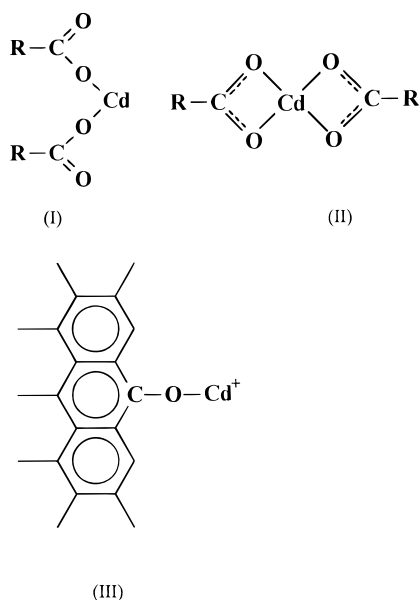


Figure 15. Possible modes of carboxylate and phenolic coordination with cadmium cation.

ment. The ratio of H^+/Cd^{2+} is approximately two for oxidized carbon CN2 in the concentration range used in this study and decreases slightly at higher concentration. It is apparent that surface carboxylate compounds $(RCOO)_2Cd$ were formed during adsorption of Cd^{2+} with two protons being displaced by one cadmium cation. This was confirmed by the ratio of Na^+/Cd^{2+} during cadmium adsorption on the NaOH-neutralized CN2. At higher concentration, the ratio of Na^+/Cd^{2+} decreases slightly, indicating other mechanisms may be involved in the adsorption in addition to the cation exchange mechanism. The possible modes of coordination of the carboxylate to the cadmium cation are illustrated in Figure 15. The coordination modes I and II represent the cation exchange reaction with one cadmium cation displacing two protons or sodium cations.^{34–37} In the case of I some H_2O coordination may also be involved. Studies of the crystal structures of metal carboxylate complexes show that the carboxylate can form a monodentate ligand, a bidentate chelate, or a bridging bidentate structure. In the case of adsorption where H^+/Cd^{2+} or Na^+/Cd^{2+} ratios < 2 were observed, the nitrate anion must also be involved in order to balance the charge. It is also possible for the less acidic phenolic groups to coordinate to the cadmium ions (see Figure 15). However, the major changes in adsorption capacity are associated with carboxylic functional groups which decompose on heat treatment to give mainly carbon dioxide. It is possible that phenolic groups are involved for adsorption on the carbons heat treated to higher temperatures.

Comparison of Figures 8 and 10 shows that after CN2 was treated with NaOH solution, the adsorption capacity for cadmium was enhanced appreciably. This is because neutralization of weakly acidic surface functional groups

with strong alkali solution gives greater dissociation and in this form could be termed as a strong exchanger.³²

For the adsorption of cadmium on CN2–300, the ratio of H^+/Cd^{2+} is approximately 1:1. The contribution from cation exchange to the adsorption of cadmium decreases with increasing heat treatment temperatures of the carbon and with the reduction of the amounts of carboxylic acid groups. In addition to the ion exchange, another mechanism of adsorption of cadmium on carbon may involve the interaction between other oxygen surface groups and cadmium cations by the formation of hydrogen bonding. The hydrogen bonding may be formed by the interaction of oxygen surface groups and hydrated cadmium cations¹³ with charge balance involving nitrate ions.

Both reversible and irreversible adsorption of cadmium ions occurs on oxidized carbons and heat treatment derivatives. In the lower concentration range, the adsorption is dominated by the ion exchange between surface carboxylic acid groups and cadmium cations, which results in irreversible adsorption. When the carboxylic acid groups were removed by heat treatment or reacted with the Cd^{2+} ions, the reversible physisorption takes place. This possibly involves hydrogen bonding between other surface oxygen groups and hydrated cadmium ions,¹³ which may result in the reversible adsorption of cadmium. There is also the possibility of the Cd^{2+} ion interacting with the phenolic groups in the carbon.

Conclusions

Acidic oxygen functional groups were incorporated into activated carbon by HNO_3 oxidation. Carboxylic acid groups were the major surface species incorporated and the oxidation process also introduced phenol and quinone groups, while the lactone groups were probably formed during heat treatment. The functional groups had a range of thermal stabilities with carboxylic acid groups being the least stable. Cadmium adsorption did not correlate with changes in the porous structures of the activated carbons. Cadmium adsorption was dramatically enhanced after the carbon was oxidized and decreased significantly after heat treatment to progressively eliminate the oxygen functional groups of various thermal stability, thereby establishing a link between acidic oxygen functional groups and cadmium adsorption, with the carboxylic acid groups contributing most to the cadmium adsorption. The ratios of H^+/Cd^{2+} for oxidized carbon and Na^+/Cd^{2+} for Na^+ ion exchange form of the carbon after adsorption were approximately 2, coinciding with the stoichiometry of cation exchange. Both reversible and irreversible adsorptions were observed in cadmium adsorption on oxidized carbon. The adsorption was dominated by an irreversible process at relatively low equilibrium adsorbate concentration, whereas reversible adsorption occurred at higher concentration when the cadmium concentration was in excess of the amounts of acidic groups. After heat treatment to eliminate carboxylic functional groups, the irreversible adsorption decreased markedly. The differences in adsorption mechanism were also apparent from the enthalpies of adsorption for various carbons, which varied markedly with adsorbate concentration and surface functional group concentration resulting from heat treatment. The irreversible adsorption is ascribed to cation exchange with carboxylic acid groups while reversible adsorption, probably resulting from the hydrogen bonding between surface functional groups and hydrated cadmium cations, also occurs.

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