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# Effect of Activated Carbon Surface Oxygen- and/or Nitrogen-Containing Groups on Adsorption of Copper(II) Ions from Aqueous Solution<sup>†</sup>

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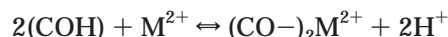
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The adsorption properties of a modified activated carbon with various oxygen- and/or nitrogen-containing surface groups toward copper ions was studied. Previously de-ashed and chemically modified commercial activated carbon D-43/1 (Carbo-Tech, Essen, Germany) was used. The chemical properties of the modified carbon surface were estimated by standard neutralization titration with HCl, NaOH, and NaOC<sub>2</sub>H<sub>5</sub>. The adsorption of Cu<sup>2+</sup> ions on three modified activated carbons from aqueous CuSO<sub>4</sub> solution of various pH was measured. The carbon samples with adsorbed Cu<sup>2+</sup> ions were analyzed by spectroscopic methods (X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy). In addition, an electrochemical measurement (cyclic voltammetry) was performed using powdered activated carbon electrodes. While the modification procedures employed alter the surface only slightly, they strongly influence the surface chemical structure. Basic groups are predominant in the heat-treated samples; acidic functional groups are predominant in the oxidized sample. Both the copper cation adsorption studies and the spectral and electrochemical measurements show that adsorbed ions interact with the carbon surface in different ways. The number of adsorbed ions depends on the nature and quantity of surface acid–base functionalities and on the pH equilibrium in the aqueous solution. The possible mechanisms of interactions between metal ions and carbon surface functionalities are summarized and discussed.

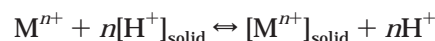
## Introduction

Because of their large surface area and their high degree of surface reactivity, activated carbons are regarded as very good adsorbents for the removal of heavy metal ions from aqueous phases<sup>1,2</sup> and can be used in a number of possible technological and analytical applications. An understanding of the interaction of metal ions with the carbon surface is essential for the control of the sorption/desorption processes applicable to activated carbon sorbents as well as for the recognition of catalytic properties of carbon materials promoted by adsorbed metal species. The mechanism of cationic species adsorption has been widely discussed but is not yet adequately explained.<sup>1–11</sup> Heavy metal adsorption equilibrium has been modeled by using the empirical adsorption isotherms (linear,

Langmuir, Freundlich)<sup>1</sup> or by applying mechanistic models as surface complex formation<sup>6</sup> and surface ionization models.<sup>9</sup> Removal of heavy metal cations from water is influenced by various factors, such as solution concentration and pH, contact time, carbon dosage, and sorbent surface modification procedure. Some investigators have reported an increase in adsorption with increase in pH of the medium,<sup>5,6</sup> while others have reported effective adsorption from acid or slightly acidic solutions.<sup>7,8</sup> Generally, the process depends on the cationic species to be adsorbed, the adsorbent, and the adsorption conditions. A variety of interactions between metal ions and the carbon surface could be occurring, e.g., the formation of surface complexes<sup>1</sup>



ion-exchange processes with the participation of a strong acidic surface group<sup>10</sup>



and redox reactions with a change of metal valence.<sup>11</sup>

In the present study, we have investigated the influence of surface oxygen and/or nitrogen groups on the adsorption of Cu<sup>2+</sup> ions from aqueous solution on modified activated carbon. Furthermore, we have attempted to ascertain the real nature of the adsorbed ionic species-modified carbon surface interactions using spectral (X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy) and electrochemical (cyclic voltammetry) measurements.

## Experimental Section

Three samples of de-ashed (with concentrated HF and HCl) and chemically modified commercial active carbon (AC) D-43/1 (Carbo-Tech, Essen, Germany) were studied. Annealing in a

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**Table 1. Summary of Physicochemical Properties of Modified Samples of Active Carbon**

modified sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	pH <sup>a</sup>	functional groups (mequiv/g)					total O/N (wt %)
			–COOH	–COO–	>C–OH	>C=O	basic	
D-H	1133	10.1	0.00	0.01	0.12	0.09	0.42	0.6/0.2
D-O	1171	3.08	0.72	0.38	0.56	0.39	0.13	10.8/0.6
D-N	1078	10.4	0.00	0.04	0.10	0.21	0.62	0.4/1.9

<sup>a</sup> In 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 6.42).

vacuum at 1000 K (D-H sample), oxidation with concentrated HNO<sub>3</sub> (D-O sample), as well as heat treatment in an ammonia atmosphere at 1170 K (D-N sample) were used as modification procedures.<sup>12</sup> For all the carbons, the BET surface area, total oxygen/nitrogen content (accurate to 0.2%), and the pH of carbon slurries (1 g of AC in 100 cm<sup>3</sup> of 0.1 M Na<sub>2</sub>SO<sub>4</sub>) were determined. The chemical properties of the modified carbon surface were estimated by standard neutralization titration with HCl, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, and NaOC<sub>2</sub>H<sub>5</sub> (0.1 M). These results presented in Table 1 were interpreted according to Boehm's method.<sup>13</sup> The excess adsorption isotherms of the Cu<sup>2+</sup> cations on the modified carbon samples were determined at 298 K for aqueous solutions of copper(II) sulfates at different pHs (adjusted with sulfuric acid or sodium hydroxide). The amount adsorbed was obtained by determining spectrophotometrically the concentrations of the metal ions in the solutions before and after adsorption.

The transmission IR spectra of the carbon samples with preadsorbed copper ions were obtained using the KBr technique and a Perkin-Elmer FTIR Spectrum 2000 spectrometer. The 1:300 carbon–KBr mixtures were ground in an agate mortar, desorbed under vacuum (10<sup>−2</sup> Pa), and finally pressed in a hydraulic press. The number of interferograms of nominal resolution 4 cm<sup>−1</sup> was fixed at 25. Before the spectrum of a sample was drawn, the background line was obtained arbitrarily and subtracted.

The X-ray photoelectron spectra (XPS) were obtained with an Escalab 210 (V.G. Scientific Ltd.) photoelectron spectrometer using nonmonochromatized Al K $\alpha$  radiation (1486.6 eV), the source being operated at 15 kV and 34 mA. Prior to XPS measurement, all carbons were dried for 2 h at 373 K. The vacuum in the analysis chamber was always better than 5  $\times$  10<sup>−10</sup> Pa.

The carbons without and with adsorbed copper species were used as electrode materials. Cyclic voltammetry (CV) was performed using the typical three-electrode system and the electrochemical cell described elsewhere.<sup>14,15</sup> The design details of the operating powdered activated carbon electrode are also described there. Previously vacuum desorbed (10<sup>−2</sup> Pa), the powdered carbon (grain size 0.075–0.067 mm, weight 100 mg) was placed in an electrode container and drenched with a deaerated solution to obtain a ~5 mm sedimentation layer. CV curves were recorded when stationary potential was established (3–4 h) in potential range from −0.6 to +0.8 V and for a sweep potential range from 2 to 10 mV s<sup>−1</sup>. All potentials were measured and reported against a potassium chloride saturated calomel electrode (SCE).

## Results and Discussion

Modification of activated carbons alters their surface area (BET) only slightly, but strongly influences their surface chemical structure. These structure were highly diverse and depended on the modification procedure applied. The data given in Table 1 show that D-H and D-N type modification of carbon samples display a basic character whereas after D-O modification carbon sample is acidic. Oxidation with nitric acid caused the fixation of large amounts of oxygen on the carbon surface (Table 1), and part of surface oxygen formed functional groups. According to Boehm<sup>13</sup> only the strongly acidic carboxylic groups can be neutralized by NaHCO<sub>3</sub>, whereas those

neutralized by Na<sub>2</sub>CO<sub>3</sub> are believed to be lactones, more likely lactols. The NaOH additionally neutralized weakly acidic hydroxylic (phenolic) groups.<sup>12,13</sup> These stable, protogenic groups are responsible for ion-exchange capacity of the oxidized carbon. Using a still stronger base, sodium ethoxide, NaOC<sub>2</sub>H<sub>5</sub>, in ethanol, carbonyl groups (neutral in aqueous solutions) are additionally detected. Pairs of carbonyl groups arranged at the periphery of the graphene layers in such a way that a system of conjugated double bonds can be formally drawn in, behaving similar to quinone functions.<sup>13</sup> According to some authors,<sup>16,17</sup> the existence of pyrone-like structures incorporated in the carbon matrix is partly responsible for the carbon's basicity. As pyrones are very slightly basic ( $pK_b \approx 13$ ), the recorded pH values of carbon suspension (near 10) indicate the presence of relatively strong basic sites with a  $pK_b$  of about 4. These sites may be the result of the adsorption of molecular oxygen and the form of superoxide ions O<sub>2</sub><sup>−</sup>, which can act as a strong Brønsted base.<sup>18,19</sup> The more pronounced basic properties of the ammonia-treated carbon (D-N) are due to the presence of additional basic sites—probably nitrogen structures incorporated into the carbon matrix.<sup>20,21</sup> Because surface modification procedures applied to the tested carbon alter its surface area only slightly (see Table 1), the nearly 10% differences in apparent surface area ( $S_{\text{BET}}$ ) could not explain the marked differences in adsorption capacity toward copper cations (Figure 1). The amount adsorbed is closely dependent on the pH of the solution and the modification procedure (Figure 2). Cu<sup>2+</sup> adsorption on studied AC samples was examined from external solutions of different pHs covering a range close to 1–6. For greater pH values the possibility of precipitation of copper as Cu(OH)<sub>2</sub> is also increased. The cation uptake increases linearly (0.07 mmol/pH) in the studied pH range for the heat-treated sample (D-H), increases sharply between 1 and 3 in the case of an oxidized sample (D-O), and, in the case of the ammonia-treated sample (D-N), increases smoothly with an increasing pH (0.03 mmol/pH). In acidic solutions (adjusted by the addition of sulfuric acid), adsorption increases on modification of the carbon with ammonia and on oxidation with nitric acid. In a strong acidic solution (pH = 1) Cu<sup>2+</sup> adsorption is much larger for the D-N modified sample; however, in a slightly acidic solution (pH = 3) it is the D-O modified sample that displays the greater adsorption. On the other hand, from nearly neutral solutions (adjusted by sodium hydroxide), adsorption is greatest on D-H modified active carbon. The jump in the adsorption found in the pH range 1 to 3 for the D-O sample might indicate that the zero point of charge of the oxidized AC lies between these two values. It seems to indicate that for D-O sample at low pHs electrostatic repulsion between Cu<sup>2+</sup> ions and the positively charged surface of carbons takes place. As the pH increases, the cations replaced hydrogen ions from

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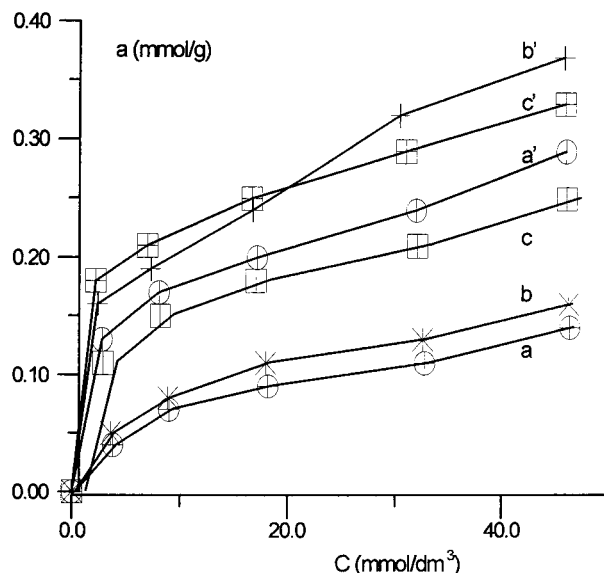
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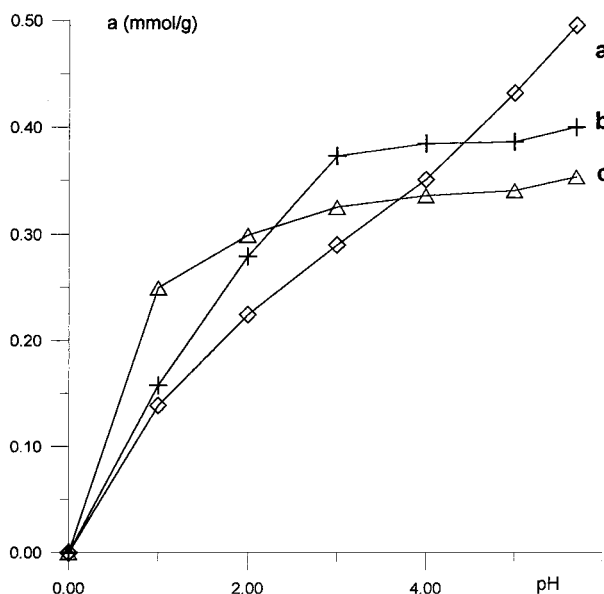
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**Figure 1.** Adsorption isotherm of  $\text{Cu}^{2+}$  from copper sulfate solutions at different pH (a–c, 1.0; a'–c', 3.0) on modified carbon samples: a, a', D-H; b, b', D-O; c, c', D-N.



**Figure 2.** Adsorption of  $\text{Cu}^{2+}$  by modified carbon samples as a function of pH of external solution: (a) D-H, (b) D-O, (c) D-N.

the carbon surface and, therefore, the adsorption extent will increase rapidly.<sup>9</sup> Thus the adsorption of  $\text{Cu(II)}$  ions by carbons is influenced principally by the presence of surface functional groups. Adsorption from copper sulfate solution (0.05 M, pH = 4.68) with no additives leads to changes in final (equilibrium) pH of the solution (Table 2). The fall of pH of the external solution for D-O sample is caused by the release of the active hydrogen ions from the surface during ion exchange. The increase of pH values for copper sulfate solutions with D-H and D-N samples is insignificant in relation to changes observed for  $\text{Na}_2\text{SO}_4$  solution (Table 1). Therefore, the surface group influences the amount of adsorbed copper cations both by direct interaction and by the modification of external solution's pH. The addition of any pH-adjusting electrolyte (acid or base) leads to competitive adsorption of ions present in solution and influences the dissociative ionization of functional groups. In further studies the carbon samples were selected with copper adsorbed from 0.05 M  $\text{CuSO}_4$ . The quantities of adsorbed ions are given in Table 2.

The recorded differences in adsorption capability indicate a different mechanism of interaction between the carbon surface and the ionic metal species present in the aqueous solution (aqua and hydroxy complexes, hydroxide ions, and electronegative complexes).

To discover the state of the adsorbed species, some independent measurements of the surface layer of adsorbent were carried out. All carbon samples were studied by the XPS method in powdered form before and after copper uptake. Several peaks attributable to carbon, oxygen, nitrogen, and copper (in samples after adsorption) were present. The XP survey spectra of the initial modified carbons (before adsorption) were discussed in an earlier paper.<sup>12</sup> A more detailed discussion of the XP spectral changes in the C 1s, O 1s, and N 1s signals following adsorption will be undertaken soon for a number of activated carbons with different surface nature and some adsorbed cations. The surface elemental composition estimated from XPS data for each sample is shown in Table 2. The amounts of surface copper correlated with  $\text{Cu}^{2+}$  ion adsorption. Figure 3 shows the high-resolution copper 2  $p_{3/2}$  spectra from the carbon samples investigated. There were marked differences between experimental (dots) and synthesized (continuous lines) values in all the spectra. The positions of the fitted peaks (dashed lines) were determined according to both the literature data<sup>22,23</sup> and empirically derived values. Table 3 shows the results obtained from the curve fitting of the Cu 2  $p_{3/2}$  (928–942 eV) spectra of copper uptake on the carbons. The binding energy (BE), the relative peak area (rpa), and the full width at half-maximum (fwhm) for separate peaks were estimated and collected. According to the literature data,<sup>22–31</sup> the XPS Cu 2  $p_{3/2}$  lines calibrated with standard samples were found at binding energies (BE) of 932.4, 933.4, and 934.8 eV for copper in oxidation states 0, +1, and +2, respectively. Beyond the difference in energy shift, another important feature of the copper(II) XP spectrum is the presence, or absence, of a satellite peak at 942.5 eV. However, with the copper in the +1 and zero oxidation states, no such satellite peaks are observed. In the other research,<sup>25,26</sup> the binding energies of the Cu 2  $p_{3/2}$  transitions on copper-impregnated (5%) Cu activated carbon samples were reported as 933.4 and 934 eV and respectively interpreted as  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ . The samples produced in their work were prepared in ammoniacal<sup>25</sup> or carbonate<sup>26</sup> solutions, dried, and heat-treated in air. This would result in the greater proportion of copper oxides. The BEs near 935 eV were ascribed the presence of  $\text{CuCO}_3$  and  $\text{Cu(OH)}_2$  species.<sup>27</sup>

In our study, the binding energies of the Cu 2  $p_{3/2}$  lines for copper adsorbed on activated carbon samples (below 2.5 wt %) presented in Table 3 approach to a certain extent the literature data. The main binding energy peaks recorded for D-O and D-N samples (near 80% relative peak area) in the 934.1–934.3 eV region can be ascribed to  $\text{Cu(II)}$  species adsorbed with participation of carbon

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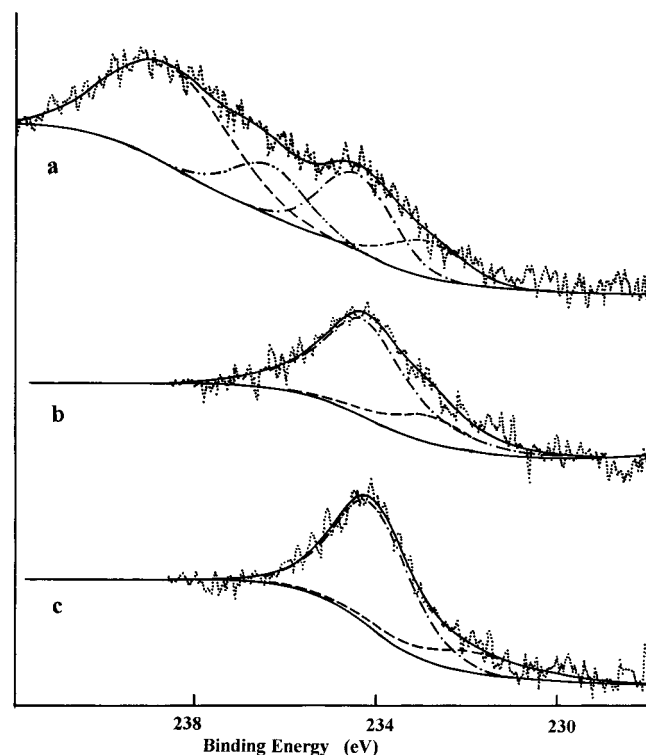
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**Table 2. Adsorption Cu<sup>2+</sup> Data and Surface Composition from XP Spectra**

modified sample	cation up-take (mmol/g)	pH <sup>a</sup>	C (%)	O <sup>b</sup> (%)	N (%)	Cu (%)
D-H			96.88	2.72	0.40	
D-H/Cu <sup>2+</sup>	0.43	4.97	95.54	3.60	0.61	0.23
D-O			88.70	10.10	1.20	
D-O/Cu <sup>2+</sup>	0.25	2.45	87.20	10.30	0.90	0.11
D-N			90.89	6.20	2.81	
D-N/Cu <sup>2+</sup>	0.32	5.05	91.17	5.10	3.60	0.13

<sup>a</sup> Initial pH of 0.05 M CuSO<sub>4</sub>, 4.68. <sup>b</sup> Oxygen from water excluded.

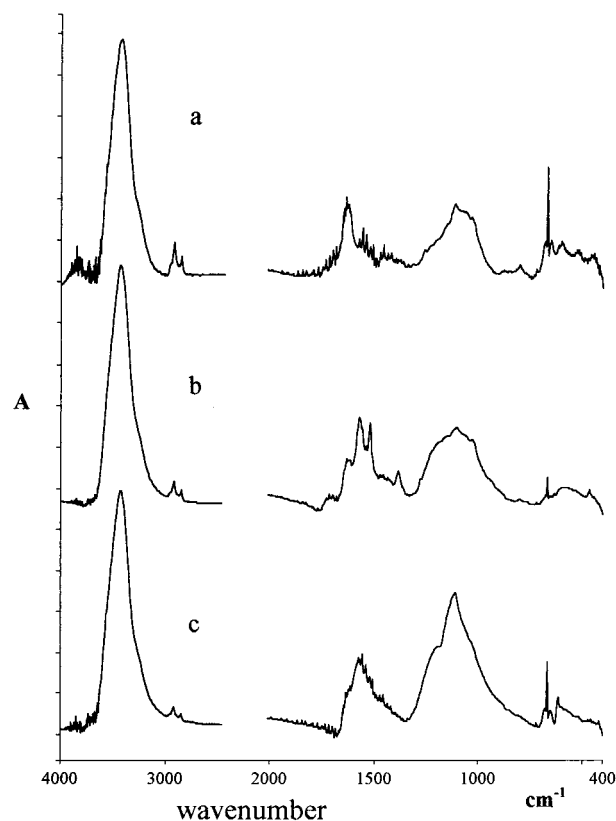


**Figure 3.** Comparison of Cu 2p<sub>3/2</sub> XP spectra of copper ions adsorbed on modified carbon samples: (a) D-H, (b) D-O, (c) D-N.

**Table 3. Cu 2p<sub>3/2</sub> Peak Parameters Deduced from XPS**

modified sample	BE (eV)	rpa (%)	fwhm (eV)
D-H	938.7	48.8	3.22
	936.4	15.7	1.94
	934.5	23.7	1.93
	932.9	11.8	2.00
D-O	934.3	79.4	2.29
	932.8	20.6	2.00
	934.1	80.8	2.12
D-N	931.9	19.2	2.80

surface functionalities. The second peak, with the lower binding energy, suggests the presence of nearly 20% of species with copper in a reduced form: Cu(I) and Cu(0) for D-O and D-N modified samples of active carbon, respectively. Unexpectedly, two other forms with higher binding energies are present (Figure 3) for D-H carbon besides the Cu(I) (11.8%) and Cu(II) (23.7%) species. They can be assigned to Cu(OH)<sub>2</sub> specimens (936.4 eV, 15.8%) and Cu(III) (938.7 eV, 48.8%), which may be viewed as Cu(II) and a hole in the carbon matrix.<sup>24</sup> Additionally, the positive shift in binding energy values could be explained as the consequence of the decreased relaxation in highly dispersed copper specimens.<sup>23</sup> The influence of the chemical interaction of copper with surface functionalities (active adsorption centers) on binding energies cannot be ruled out either.



**Figure 4.** FTIR spectra of modified carbon samples recorded after Cu<sup>2+</sup> ion adsorption: (a) D-H, (b) D-O, (c) D-N.

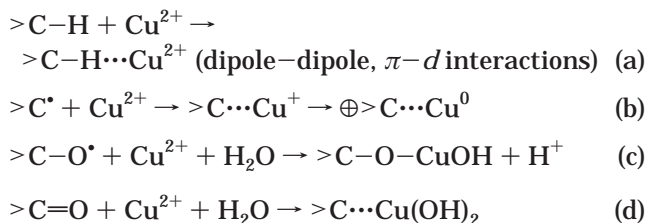
Because the FTIR spectra of modified D-H, D-O, and D-N samples of active carbon were discussed in detail previously,<sup>12</sup> Figure 4 shows only the transmittance IR spectra of carbons with preadsorbed copper ions. The IR measurement procedure applied here (KBr-pellet technique) precludes quantitative comparison of the FTIR spectra obtained for different carbon samples, but it does clearly indicate which individual surface structures could be present or absent in the carbon. In the FTIR spectra of the carbon materials, the band of stretching OH vibrations (3600–3100 cm<sup>-1</sup>) was due to the existence of surface hydroxylic groups, chemisorbed water as well as adsorbed copper hydroxy and aqua complexes.<sup>32</sup> Below 2000 cm<sup>-1</sup> the shape of FTIR spectrum depends on the kind of carbon (modification procedure).

For a heat-treated carbon sample (D-H) the presence of complex absorption bands in the 1650–1550 cm<sup>-1</sup> region suggests that aromatic ring stretching and double bond (C=C) vibration bands overlap the C=O stretching vibration and OH binding vibration bands. The presence ion–radical structures with chemisorbed oxygen molecules is also possible.<sup>18,19,33</sup> Another broad band in the 1330–1000 cm<sup>-1</sup> range consists of a series of overlapping

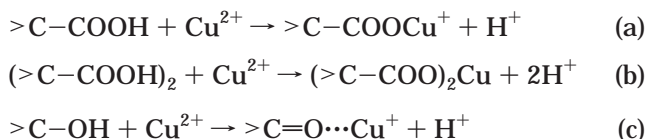
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absorption bands ascribable to the etheric (symmetrical stretching vibration) epi-oxide and OH bending modes. These results suggest that copper hydroxide species ( $\text{CuOH}^+$ ,  $\text{Cu}(\text{OH})_2$ ) and copper(II) aqua complexes may be adsorbed on the carbon surface. The presence of bands below  $800\text{ cm}^{-1}$  is characteristic of out-of-plane deformation vibrations of C-H moieties in aromatic structures. Additionally, the presence of narrow absorption peaks near  $1110$ ,  $1000$ , and (the highest)  $670\text{ cm}^{-1}$  points to the presence of sulfate ions (internal vibration of the  $\text{SO}_4^{2-}$ ) adsorbed on the carbon surface. Furthermore, after active carbon oxidation (D-O) and copper adsorption, there appear a band characteristic of carbonyl moieties in a carboxylic acid ( $1720\text{ cm}^{-1}$ ) and bands  $1600$  and  $1580\text{ cm}^{-1}$  ascribable to metal chelates with carboxylate functionalities.<sup>32</sup> The presence of a peak at  $1390\text{ cm}^{-1}$  characteristic of carboxylic ions is indicative of the partial ion-exchanging nature of  $\text{Cu}^{2+}$  adsorption on this carbon. For the D-N carbon sample the presence of overlapping peaks in the  $1600\text{--}1500\text{ cm}^{-1}$  region and broad overlapping bands in the  $1350\text{--}900\text{ cm}^{-1}$  region is observed following copper adsorption. An increase in the intensity of the bands in those regions is characteristic of pyridine-, pyridine *N*-oxide-, or/and pyridone-like surface structures and related complexes with copper ions.<sup>32</sup> The peaks near  $1100$  and  $670\text{ cm}^{-1}$  indicate the presence of adsorbed  $\text{SO}_4^{2-}$  ions. In accordance with the results of the spectroscopic study presented above, the possible surface structures containing adsorbed copper can be shown schematically as follows:

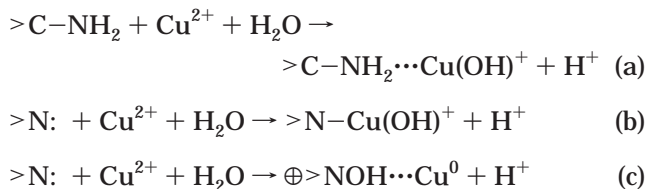
for D-H carbon (Scheme 1)



for D-O (Scheme 2)

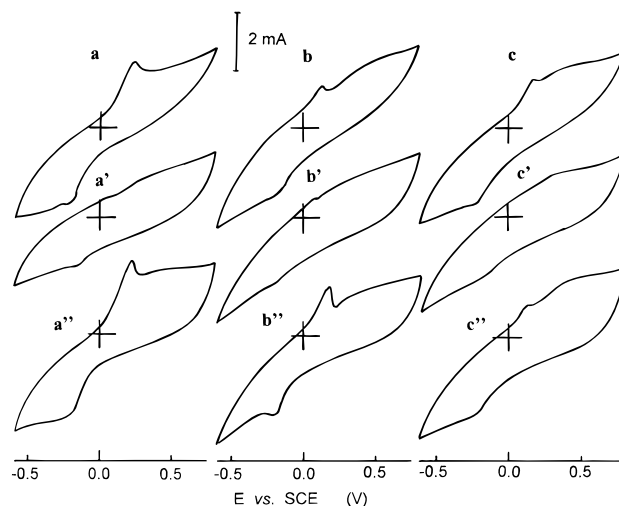


for D-N carbon (Scheme 3)



where symbols  $\bullet$  and  $\oplus$  marked the ion radical and positive holes in carbon structure, respectively. In the interest of clarity, the coadsorbed counterions (mainly  $\text{SO}_4^{2-}$ ) are not marked.

The possible interactions and surface structures (Schemes 1–3) presented above describing copper species sorbed on various modified active carbon samples are deduced from obtained results. The presence of proposed surface structures is partially confirmed by spectral (FTIR, XPS) studies. It seems that dominant mechanisms of



**Figure 5.** Cyclic voltammograms of carbon electrodes without (a–c) and with preadsorbed (a'–c', a''–c'')  $\text{Cu}^{2+}$  ions recorded in different electrolyte systems: (a–c)  $0.1\text{ M CuSO}_4 + 0.5\text{ M Na}_2\text{SO}_4$  (pH = 4.46); (a'–c')  $0.5\text{ M Na}_2\text{SO}_4$  (pH = 6.02); (a''–c'')  $0.1\text{ M CuSO}_4 + 0.5\text{ M Na}_2\text{SO}_4$  (pH = 4.46) for D-H (a–a''), D-O (b–b'), and D-N (c–c''); ( $v = 3 \times 10^{-3}\text{ V s}^{-1}$ ).

copper adsorption on heat-treated active carbon (D-H sample) could be dipole–dipole ( $\pi-d$ ) interactions between graphene layers and metal ionic species as well as spontaneous electrochemical reduction of copper ions. For the oxidized active carbon sample (D-O), the surface ionization and ion-exchange mechanism can describe the cations sorption from aqueous solutions. Heat-treatment with ammonia (D-N sample) involves incorporation of nitrogen atoms into the graphene layers (presumably at their periphery), and these adatoms can play a dominant role during copper ions adsorption act as ligands, which additionally may explain the low dependence of adsorption on pH.

The proposed various forms of adsorbed copper can change the electrochemical behavior of modified carbon samples used as electrode materials (powdered working electrodes in cyclic voltammetry). Figure 5 shows cyclic voltammograms (CVs) for powdered carbon electrodes without (curves a–c) and with preadsorbed copper (curves a'–c' and a''–c'') recorded in solution containing (curves a–c and a'–c') or not containing  $\text{Cu}^{2+}$  ions (curves a'–c'). An aqueous solution of  $0.5\text{ M Na}_2\text{SO}_4$  as background electrolyte was employed. The CV curves recorded in the solution containing copper ions exhibit a pair of cathodic and anodic peaks, the potentials of which are dependent on the carbon modification procedure and the electrolyte's pH. The estimated peak potentials as well as the midpoint potential ( $E_{p,a} - E_{p,c}$ )/2 values are given in Table 4.

The electrochemistry of  $\text{Cu}(\text{II})$  ions in aqueous solution is well documented<sup>34–36</sup> and can be summarized as follows:



In the absence of any complexing anions,  $\text{Cu}(\text{I})$  is unstable

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**Table 4. Characteristic Potentials for the Cu<sup>+</sup>/Cu<sup>2+</sup> Redox Couple in Various Systems Studied ( $\nu = 3 \times 10^{-3}$  V/s)**

system studied	pH	$E_{p,a}$ (V)			$E_{p,c}$ (V)			$(E_{p,a} + E_{p,c})/2$ (V)		
		D-H	D-O	D-N	D-H	D-O	D-N	D-H	D-O	D-N
in 0.1 M CuSO <sub>4</sub> + 0.5 M Na <sub>2</sub> SO <sub>4</sub>	4.46	+0.22	+0.12	+0.16	-0.22	-0.18	-0.21	0.00	-0.02	-0.02
in 0.1 M CuSO <sub>4</sub> + 0.5 M Na <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub>	2.97	+0.25	+0.12	+0.20	-0.30	-0.19	-0.26	-0.03	-0.03	-0.03
ads. Cu from 0.1 M CuSO <sub>4</sub> ; in 0.5 M Na <sub>2</sub> SO <sub>4</sub>	6.02	+0.06	+0.06	+0.31	-0.16	-0.20	-0.15	-0.05	-0.06	-0.08
ads. Cu from 0.1 M CuSO <sub>4</sub> ; in 0.1 M CuSO <sub>4</sub> + 0.5 M Na <sub>2</sub> SO <sub>4</sub>	4.46	+0.21	+0.17	+0.12	-0.20	-0.21	-0.21	+0.01	-0.02	-0.04
ads. Cu from 0.1 M CuSO <sub>4</sub> ; in 0.1 M CuSO <sub>4</sub> + 0.5 M Na <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub>	2.97	+0.23	+0.18	+0.13	-0.23	-0.25	-0.23	-0.01	-0.02	-0.05

and undergoes disproportionation. In the presence of complexing ligands Cu(I) becomes stabilized and the Cu(II)/Cu(I) redox couple appears in cyclic voltammetry as a quasi-reversible wave.<sup>34</sup>

The presence on recorded CV curves of peaks of anodic response to one-electron reduction of Cu<sup>2+</sup> ions and the values of midpotentials ( $E_{p,a} - E_{p,c})/2$  close to  $E^\circ$  for the couple (1) (Table 4) suggests the existence both the Cu(I) and Cu(II) surface-bound species in studied systems. For modified carbon samples the CV curves in the presence of Cu<sup>2+</sup> in bulk solution (Figure 5, curves a–c), the redox peaks are the tallest for D-H samples, which corresponds well with adsorption capacity toward copper ions (see Table 2). The higher anodic peaks observed for D-H and D-N samples of modified active carbons indicate that partial spontaneous reduction of adsorbing copper ions (see Schemes 1b, 2c, and 3c) and/or the disproportionation of reduced Cu(I) ions is occurring:



The CV curves obtained for carbons with preadsorbed copper (Figure 5, curves a'–c') exhibit only slightly marked peaks of the Cu(II)/Cu(I) couple and broad waves due to the redox reaction of surface carbon functionalities.<sup>15</sup> However, the preadsorbed copper enhanced the peaks of the redox process in bulk solution (especially the anodic peaks for D-H and D-O samples), as can be seen in Figure 5 (curves a''–c''). The low electrochemical activity of samples with preadsorbed copper species observed in neutral solution (curves a'–c') is the result of partial desorption (ion exchange with Na<sup>+</sup>) of copper as well as the formation of an imperfect metallic layer (microcrystallinities). Deactivation of the carbon electrode as a result of spontaneous reduction of metal ions (silver) was observed earlier.<sup>37</sup> The increase in anodic peaks for D-H and D-O modified samples with preadsorbed copper suggests that despite electrochemical inactivity, the surface copper species facilitate the electron-transfer reactions between the carbon electrode and the ionic form at the electrode–solution interface. The smallest electrochemical activity of the D-N sample points to the

formation of strong complexes between adsorbed cations and surface nitrogen-containing functionalities (similar to porphyrin).<sup>38</sup> The copper(II) in porphyrin complex (modifier of carbon electrode) is not reduced between -0.35 and +0.80 V, so the reoxidation peak of copper(0) cannot be observed.<sup>38</sup>

## Conclusion

The modification procedures employed alter the apparent surface area only slightly but strongly influence the surface chemical structure. Basic groups (Lewis base centers, nitrogen adatoms) are predominant in the heat-treated samples; acidic (mainly carboxylic) functional groups are predominant in the oxidized sample. The copper cation adsorption studies together with spectral and electrochemical measurements show that these ions interact with the carbon surface in different ways. The number of adsorbed ions depends on the nature and quantity of the surface acid–base and ion–radical functionalities as well as on the pH equilibrium in the external solution. A possible dominant interaction between metal ions and various modified surface of active carbon could be considered: physical adsorption of ion (dipole–dipole interaction) and hydroxo complexes as well as redox reactions with a change in metal valence (D-H sample); an ion-exchange process with the participation of a strong acid surface group (D-O sample); formation of surface complexes with nitrogen- or/and oxygen-containing surface groups (D-N sample). The electrochemical behavior of the powdered carbon electrode depends on the surface chemistry, and cyclic voltammetry can be used as simple method of characterizing activated carbon materials.

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