

Comparative Study of Cu(II) Adsorption by As-Prepared and Oxidized Multi-Walled N-Doped Carbon Nanotubes

Viktoria Simon^a, Maryna Manilo^b, Laszlo Vanyorek^c, Zoltan Csoma^a, and Sandor Barany^{a, c, d, *}

^aThe Transcarpathian II. Ferenc Rakoczi Hungarian Institute, Beregovo, Ukraine

^bF.D. Ovcharenko Institute of Biocolloidal Chemistry, Kyiv, Ukraine

^cInstitute of Chemistry, University of Miskolc, Miskolc-Egyetemváros, 3515 Hungary

^dMTA-ME Materials Science Research Group, Miskolc-Egyetemváros, 3515 Hungary

*e-mail: akmsab@uni-miskolc.hu

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Abstract—The laws and mechanisms of adsorption of Cu(II) ions by well characterized and oxidized N-doped multi-walled carbon nanotubes (N-CNTs) are discussed. The samples were synthesized by catalytic chemical vapour deposition method using *n*-butylamine as a carbon source and their surface was functionalized by oxidation with mixture of concentrated H₂SO₄ and HNO₃. The morphology, chemistry and charge of surface groups were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy and micro-electrophoresis methods. It has been shown that: adsorption of Cu(II) reached equilibrium value within 60 min; the degree of extraction of these ions from the solution increased with its dilution; adsorption resulted in a moderate decrease in the suspension pH for as-prepared N-CNTs (1.5 pH unit) and its considerable lowering for the oxidized sample (up to 2.5 pH unit); the adsorption isotherms can be described by the Langmuir model and the plateau amounts of adsorption (28–35 mg/g) were almost the same for both as-prepared and oxidized samples; at pH 6.5 and higher a sharp increase in adsorption was observed which was attributed to hydroxides precipitation. The spectroscopic, adsorption, electrophoretic and pH measurements data showed that below pH of hydroxide precipitation, the major mechanism of adsorption by as-prepared N-CNTs is the donor-acceptor interaction between the free electron pair of N atoms incorporated into nanotubes lattice and vacant *d* orbital of the adsorbing Cu(II) ions. For the oxidized N-CNTs ion-exchange processes with a release of H⁺ ions play also a role.

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INTRODUCTION

Among variety of practical applications of carbon nanotubes (CNTs) an increasing important segment is related to their use as sorbents for toxic substances, heavy metal ions, and organic compounds [1]. For example, CNTs are intensely studied as sorbents for water purification from individual nickel and lead [2], copper and cobalt [3], chromium [4] ions, and other individual or mixed ions of different metals [5].

Copper is an essential nutrient for which the World Health Organization (WHO, 1998) recommends a daily intake of 30 µg/kg body weight. Drinking water standards have been established to prevent adverse health effects resulting from ingestion of too much copper. WHO (1998) recommends a limit of 2 mg/dm³ Cu to prevent adverse health effects from copper exposure. There are few studies devoted to extraction of these ions by carbon nanotubes, both pristine and oxidized by different oxidizing agents. The kinetics of adsorption, shape of adsorption isotherms, impact of pH and degree of CNTs surface functionalization has

been elucidated. A short review of the recent results obtained is summarized below.

Carbon nanotubes was shown to possess good adsorption properties and high capacity (3.5 mg/g at initial concentration of Cu²⁺ ions of 20 mg/dm³) with respect to Cu(II) ions. The affinity of this ion to the CNTs surface and the adsorbed amounts were found to be higher compared to other heavy metal ions such as Co, Zn, Pb, and Mn. The adsorption data were well described by the Freundlich isotherm [6]. The adsorption capacity of oxidized (by H₂O₂, HNO₃ or HClO₄) N-doped bamboo like multi-walled carbon nanotubes (MWCNTs) with respect to Cu(II) ions reached 15–18 mg/g [7]. Bulushev et al. have shown that the interaction of Cu(II) ions deposited on the N-doped carbon nanotubes (N-CNTs) surface by thermal decomposition of copper acetate proceeds via their strong coordination by pyridine nitrogen atoms at the edge of the graphene sheets of the adsorbent [8]. Rao and co-authors [9] reviewed the laws and mechanisms of sorption of divalent metal ions (Cd²⁺, Cu²⁺, Ni²⁺, Pb²⁺, and Zn²⁺) from aqueous solution by various kinds of

raw and surface oxidized carbon nanotubes. The sorption mechanisms appear mainly relevant to chemical interactions between the metal ions and the surface functional groups of the CNTs. The sorption capacity of CNTs remarkably increased after oxidation by NaOCl, HNO₃ and KMnO₄ solutions. Similar results were obtained by the authors [10] who have shown that CNTs with an average diameter between 40 and 60 nm can be successfully used for the removal of heavy metals from aqueous solution. A competition among the metal ions for binding sites was revealed on the MWCNTs surface with affinity in the following order: Cu(II) > Zn(II) > Pb(II) > Cd(II). Gadhave and Waghmare [11] have analysed in detail the impact of CNTs properties (adsorption sites, pore volume, BET surface area, surface total acidity) and solution properties (ionic strength, pH value) on the adsorption of heavy metal ions by carbon nanotubes. The contribution of physical adsorption, electrostatic attraction, precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs was discussed. Gao et al. [12] measured the adsorption isotherms of Cu(II), Ni(II), Zn(II) and Cd(II) onto carbon nanotubes oxidized by concentrated HNO₃ in single, binary, ternary and quaternary systems and have shown that isotherms reveal the effect of competition for adsorption sites as a decrease in the amount adsorbed. The uptakes at the equilibrium concentration 0–0.04 mmol/dm³ in a single-component system and at 0–0.15 mmol/dm³ in a binary system are changed in the order Cu²⁺ > Ni²⁺ > Cd²⁺ > Zn²⁺, whereas in the ternary and quaternary systems the order was different (Cu²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺).

Summarizing the literature review, we can say that the major factors affecting the adsorption of Cu(II) by carbon nanotubes and the mechanisms of the process have at large been clarified. Surprisingly, there is not so much information about the laws and mechanisms of adsorption of these ions by N-doped carbon nanotubes, i.e. adsorbents containing surface nitrogen atoms in different state, potentially capable to form complexes with Cu(II) ions. In this work, we made an attempt to fill in, at least in part, this gap.

EXPERIMENTAL

Materials

The N-doped carbon nanotubes (N-CNTs) were synthesized by catalytic Chemical Vapour Deposition (CCVD) method using *n*-butylamine (VWR) as carbon source and Ni(NO₃)₂ (Sigma Aldrich) plus magnesium oxide, MgO (Merck) as catalyst materials, as described in the paper [13]. The product was purified from the catalyst by treatment with concentrated hydrochloric acid (VWR). The surface functionalization of N-CNTs was performed using oxidation with mixture of concentrated sulphuric acid and nitric acid in a volume ratio 3 : 1 at 80°C overnight using contin-

uous stirring. After the acidic treatment, the N-CNTs were filtered and washed with distilled water until pH 5–6 was reached, and then dried at 120°C. The mixture of H₂SO₄ and HNO₃ turned out to be very efficient for oxidation of carbon nanotubes as it was shown in our previous work [14].

Methods

A VERTEX 70 FTIR spectrometer (Bruker, Germany) was used to record the spectra of the samples in a range 4000–400 cm⁻¹ and a resolution about 0.8 cm⁻¹. Before the measurements, the samples were exposed for 24 h at 25°C and mixed with spectroscopically dry potassium bromide.

The electrophoretic mobility of CNTs in aqueous media was determined using the Zetasizer Nano ZS instrument (Malvern, United Kingdom). Before the measurements, 0.01 wt % (hereafter %) CNTs dispersion was treated in an ultrasonic bath (Tesla, Czech Republic) at a frequency of 35 kHz for 30 min. A sample was taken with a pipette from the upper part of the dispersion for the measurements which were performed at room temperature ($T = 298$ K) in the range of external electric field gradients of 6–15 V/cm. The electrophoretic mobility was transformed into ζ -potential using the classical Smoluchowski equation approach with the software of the instrument. The presented values of the ζ -potential were obtained by averaging three to six measurement results; the measurements error was about 3%.

The morphology of the N-CNTs was studied by High Resolution Transmission Electron Microscopy, HRTEM (Fei Technai G2, 200 kV). The samples for measurements were prepared by dropping aqueous dispersion onto carbon coated copper grids (Carbon/Copper grids, 300 Mesh, Ted Pella Inc.). The X-ray Photoelectron Spectroscopy (XPS) was used to identify the chemical bounds of the incorporated nitrogen atoms and surface functional groups by applying SPECS instrument with PHOIBUS 150 MCD 19 detector.

Copper ions were adsorbed by the carbon nanotubes (typical adsorbent concentration of 0.1%) at room temperature in a pH range of 2.0–12.0 under mechanical shaking the reaction mixtures for designated period of time. The kinetic dependencies were measured during 36 h. The concentration of Cu(II) ions before and after adsorption was determined in acetylene flame with an Agilent 240A atomic absorption spectrophotometer (Agilent Technologies, USA) operating at a wavelength of 429.0 nm and an optical gap width of 0.5 nm. The chosen conditions enable to determine the concentration of ions in the range of 1–100 $\mu\text{g}/\text{dm}^3$. The adsorbed amount was calculated from the material balance of ions in solution prior and after adsorption.

RESULTS AND DISCUSSION

Characterization of N-Doped Carbon Nanotubes

The HRTEM picture demonstrates that non-oxidized N-CNTs represent uneven fibers with length of 2–3 μm and diameter between 7 and 22 nm, with a mean value of 12.4 nm (Fig. 1a). As a result of oxidative treatment, the N-CNTs fibers were broken into shorter fibers, with about 200–800 nm sections in length (Fig. 1b). This can be attributed to the fact that the N-doped bamboo-like carbon nanotubes are easily ruptured, because their mechanical strength is lower compared to their non-doped counterparts. The extraordinary structure of these nanotubes is demonstrated on their schematic illustration (Fig. 1c). A number of graphene edges are seen on the wall of N-CNTs, containing sp^3 hybridized carbon atoms and nitrogen atoms, which easily react with oxidants (Fig. 1d). Therefore, the N-CNTs can be oxidized to higher extent than the non-doped, conventional MWCNTs or single-walled (SWCNTs) nanotubes. The fiber edges can serve as high energy adsorption sites on the wall of bamboo-like nanotubes which are easily accessible for different ions or molecules and can form relatively strong bounds with the adsorbent surface (due to ion exchange adsorption, surface complexes or π - π interactions).

XPS and FTIR measurements were applied to identify the binding types and the nature of surface functional groups. Figure 2 shows the XPS spectra of non-oxidized and oxidized N-CNTs characterizing the binding energy of C–N and C–O bounds. The XPS spectrum of non-oxidized N-CNTs demonstrates the presence of specific chemical binding, which is typical for the N-CNTs (Fig. 2a) [14]. The peak at 398.6 eV binding energy can be attributed to the pyridine type nitrogen atoms (Fig. 2a), the next peak at 401.1 eV originates from the nitrogen incorporation into graphite. A peak of the oxidized nitrogen (pyridine $\text{N}^+ - \text{O}^-$ species) can be also observed on the spectrum, at 404.7 eV binding energy. The N-doped carbon nanotubes are easily oxidized at crystal distortions in the graphitic structure. During the acidic treatment oxygen containing functional groups are developed, which are located at the C1 s band (Fig. 2b). The appearance of $-\text{C}=\text{C}-$ and $-\text{C}-\text{C}-$ bounds is reflected by a highly intensive peak at 284.6 eV, and the $\text{C}=\text{O}$ peak was also identified at 287.5 eV (Fig. 2b). The peak of the carboxyl groups is shown at 291.2 eV binding energy. These oxygen-containing functional groups are visible on the FTIR spectra (Figs. 2c, 2f): stretching vibration of the C–O bond at 1205 cm^{-1} , carbonyl bond at 1628.7 cm^{-1} , carboxyl groups at 1713.7 cm^{-1} and hydroxyl groups at 3440.7 cm^{-1} (Fig. 2c). The latter bond originates from the alcohol or phenolic hydroxyl groups and from the $-\text{COOH}$ groups. Adsorbed water can contribute to the appearance of this absorption bond as well. The vibration mode of N-CNT structure ($\nu\text{C}=\text{C}$) was also

found in the FTIR spectrum at 1565.4 cm^{-1} wavenumber.

Visual presentation of the positions and states of the N-atom in the N-doped carbon nanotubes lattice with corresponding binding energies is given by Fig. 3. Theoretically, all of these atoms can participate in binding the Ni(II) ions to the CNTs surface alongside with cation exchange with surface functional groups.

The FTIR spectrum of the oxidized N-CNTs is characterized by an appearance of a band of hydroxyl groups stretching vibration at 3419 cm^{-1} wavenumber (Fig. 4a). This band is shifted by 22 cm^{-1} as a result of copper ion adsorption. This shift can be explained by the interactions (electrostatic, complexation or ion-exchange adsorption) between the Cu(II) ions and $-\text{OH}$ functional groups of the nanotubes surface (Fig. 4b). Furthermore, the mentioned interactions are confirmed by the shift of $\nu\text{C}-\text{O}$ vibration band from 1164 cm^{-1} to 1208 cm^{-1} . Similar shift from 1561 cm^{-1} to 1584 cm^{-1} was revealed for $\nu\text{C}=\text{C}$ vibration band due to the donor-acceptor interaction between the metal ion and N-CNTs. A new band at 596 cm^{-1} appeared after copper adsorption indicating the metal–oxygen stretching of CuO (Fig. 4b). The vibration band of carboxyl groups is also visualized at 1709 cm^{-1} in the spectrum of the oxidized carbon nanotubes (Fig. 4a).

Electrokinetic Potential

Figure 5 shows the pH dependence of the N-CNTs electrokinetic potential in aqueous suspension. For the pristine N-CNT samples, the isoelectric point (IEP) is observed near pH 7.2, which is higher than the IEP values reported for non-doped MWCNTs: pH 4.0 [15] or pH 6.0 [16]. This observation implies, that the surface is charged positively at lower pH. The positive charge of the surface in acidic media (pH 3–7) is due to the presence of small amounts of oxidized species in the original N-CNTs (see spectra on Fig. 2) as well as to the presence of the pyridine-type N atoms in the lattice capable to acquire positive charge due to proton transfer. The shift of the IEP to higher values probably reflects the contribution of protonated N-atoms into the CNTs surface charge.

After the acidic treatment, the IEP is not reached, and the surface charge remains negative in the whole pH interval studied (pH 2–12). This effect is due to the dissociation of oxidized negative species of various natures on the N-CNTs surface. An increase in the number of oxidized fragments and a decrease in the number of low oxidized groups formed on the surface overcompensate the contribution of the positive surface charge.

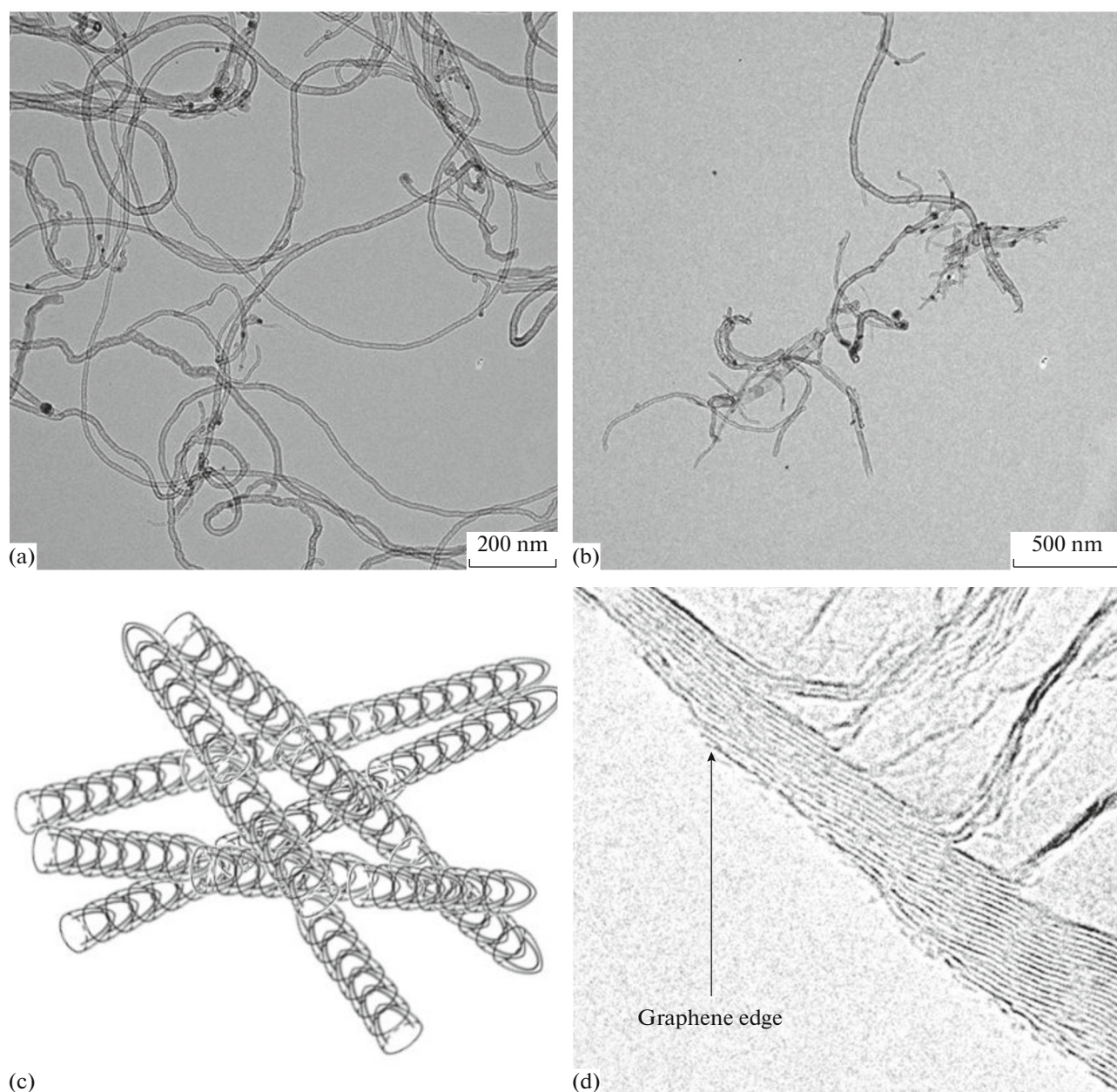


Fig. 1. HRTEM images of the (a) non-oxidized and (b) oxidized N-CNTs. (c) Schematic illustration of the bamboo like structure. (d) The image of the graphene edges on the nanotube wall.

Kinetics of Cu(II) Adsorption

Figure 6 demonstrates the time dependencies of adsorption of Cu (II) ions by as-prepared and oxidized N-CNTs at pH 5.5. The kinetics of adsorption of heavy-metal ions by carbon-containing sorbents is a rather complex process. The majority of published works consider a two-step adsorption kinetics, i.e. an initial rapid uptake and a much slower second stage of adsorption, which may last for several days and even weeks [17–20]. Some authors reported an optimal contact duration of several minutes [20], while others

believe that the optimal time required to establish equilibrium is equal to several hundred hours [17, 19]. Generally, most authors suppose the optimal contact time to be 1–5 hours [17, 18].

Two regions can be distinguished on the kinetic dependences of adsorption in our experiments. During the first 60 min contact of the N-CNT samples with salt solution, the adsorption of Cu(II) ions rapidly increases with time. In a contact time range of 60–100 min, the adsorption equilibrium is established; at $t > 60$ min the saturation value of adsorption

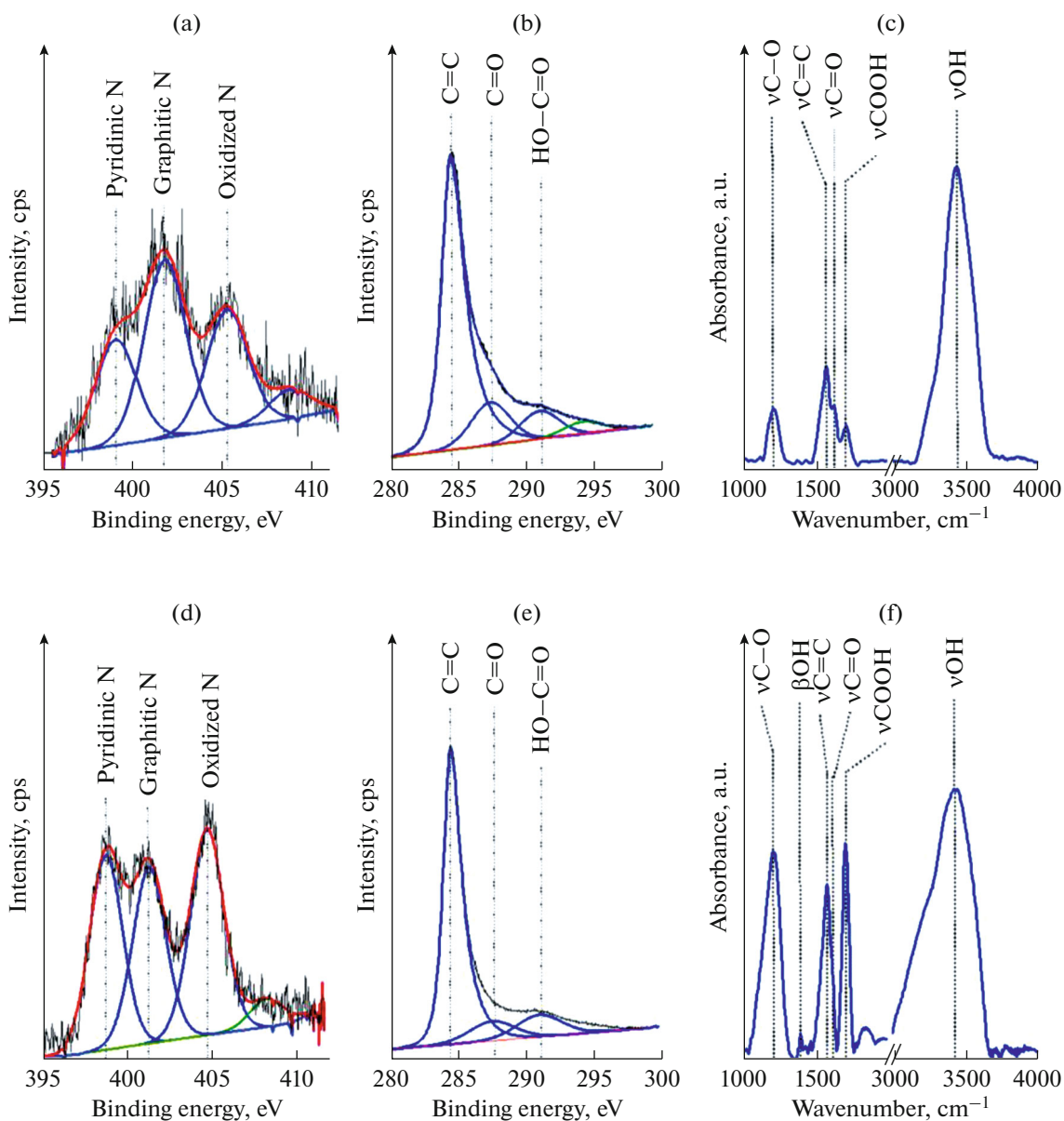


Fig. 2. XPS spectra with deconvoluted N 1s band of (a) the non-oxidized and (d) oxidized N-CNTs and C 1s band of (b) non-oxidized and (e) oxidized N-CNTs. FTIR spectra of the (c) non-oxidized and (f) oxidized CNTs.

was observed. A further increase in the contact time up to 24 hours did not give a noticeable change in the adsorbed amount of metal ions. For the oxidized sample, an insignificant decrease in the adsorbed amount (about 5%) was observed at a contact time longer than 20 hours. Similar results were obtained for Cr(III) ions adsorbing on the CNTs surface [4]. A contact time of 60 min was selected to measure the equilibrium adsorption isotherms. The data in Fig. 6 show that this time is enough to establish adsorption equilibrium.

Adsorption Isotherms

Figure 7 demonstrates the adsorption isotherms of Cu(II) ions onto as-prepared and oxidized N-CNTs measured at the non-adjusted pH. The shape of adsorption isotherms gives similar picture. A stepwise rise in adsorption with an increase of the equilibrium concentration of the copper ions shows a tendency to reach a plateau value of the adsorbed amount (Langmuir type isotherm). The maximum adsorbed amounts slightly increases from as-prepared (28 mg/g) to oxidized (36 mg/g) samples.

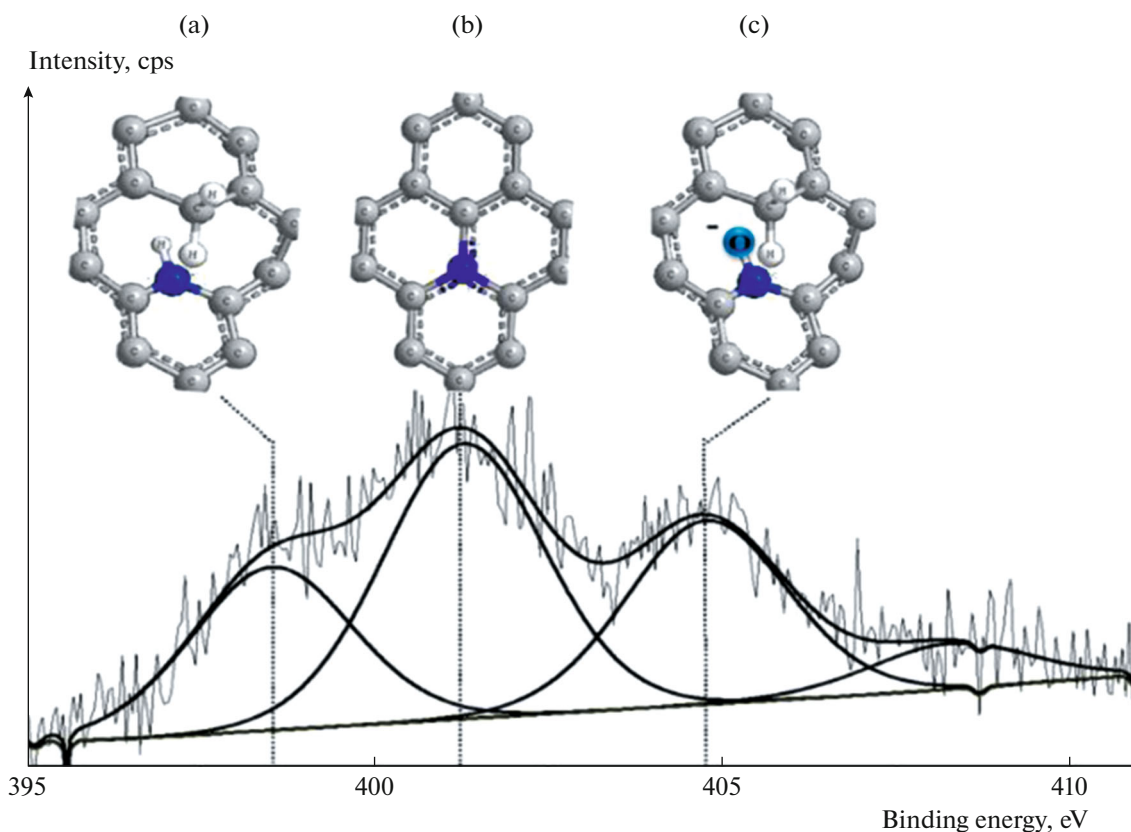


Fig. 3. XPS spectra of the N-doped carbon nanotubes with schematic illustration of positions/states of the N atom in the CNT lattice, with corresponding binding energies.

The adsorption of Cu(II) gives a moderate lowering in the solution pH for pristine N-CNTs (up to 1.5 pH unit) and a remarkable drop for the oxidized sample (about 2.5 pH unit) as a result of the ion exchange of surface H^+ ions by adsorbing copper ions (see Table 1).

Effect of pH on Adsorption

While studying the effect of pH on the adsorption of Cu(II) ions by carbon nanotubes, several different effects should be considered:

(i) Cu(II) ions in aqueous solutions are hydrated by six water molecules, possessing moderate resistance to

Table 1. Effect of Cu(II) adsorption (mg/g) on changes of the equilibrium pH of 0.1% N-CNTs suspension at various initial/adjusted pH of the system

Suspension of N-CNT			Suspension of oxidized N-CNT		
pH adjusted	pH equilibrium	adsorption	pH adjusted	pH equilibrium	adsorption
2.02	2.08	6.13	2.03	2.09	12.1
2.93	3.18	9.71	2.43	2.99	22.4
4.20	5.64	25.4	4.84	3.72	32.5
5.76	5.73	33.3	5.95	3.96	31.5
6.71	5.86	34.7	6.58	5.00	54.6
8.96	6.62	59.9	8.86	6.45	60.9

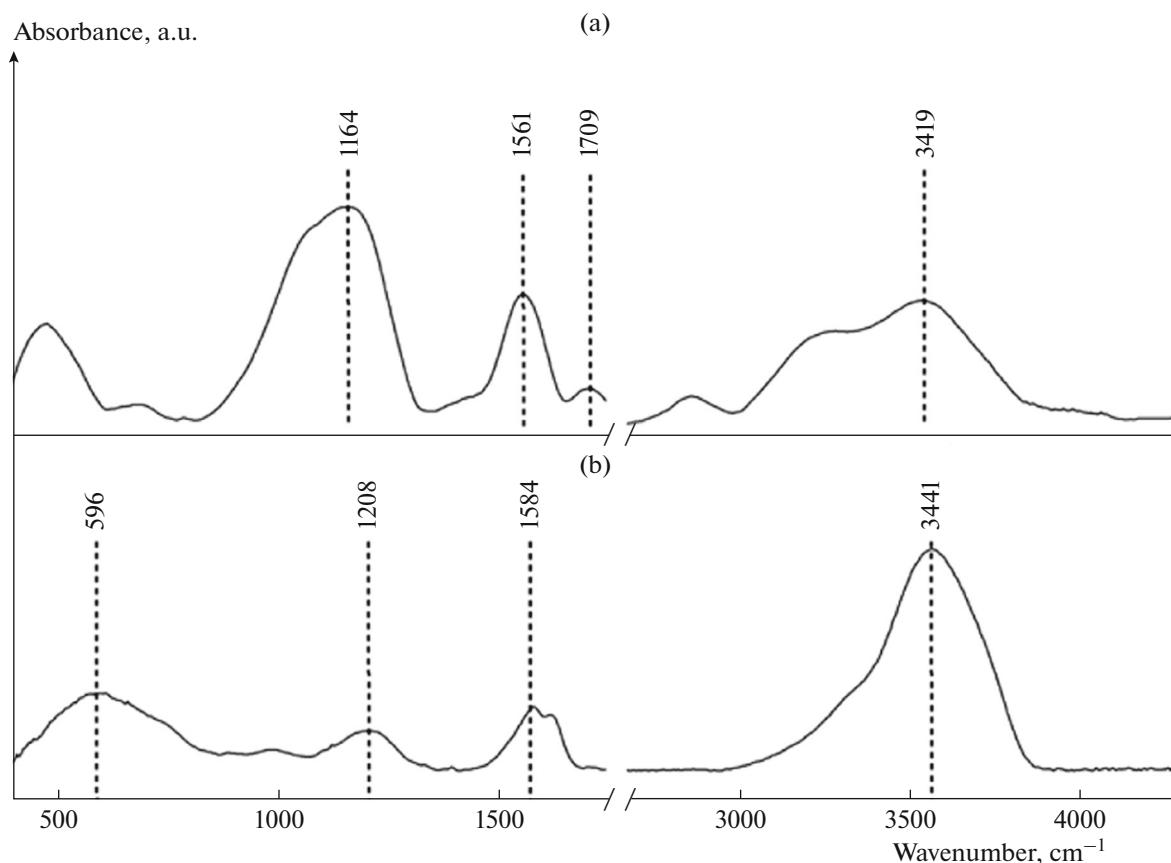


Fig. 4. FTIR spectrum of the oxidized N-CNTs (a) before and (b) after adsorption of Cu(II) ions.

hydrolysis. At low concentrations, Cu^{2+} is the predominantly existing copper form at low pH values up to pH 7.5. At higher pH values, copper hydroxide, $\text{Cu}(\text{OH})_2$, is the dominant species up to pH 12.3, at which the copper ion $\text{Cu}(\text{OH})_3^-$ is formed. At higher copper concentrations, solid $\text{Cu}(\text{OH})_2$ precipitates at copper concentrations above the solubility product of copper hydroxide at 1×10^{-8} M. The domain of stability of solid $\text{Cu}(\text{OH})_2$ is expanding to lower and higher pH values with an increase of copper concentration. A small but significant amount of an important Cu(II) complex $\text{Cu}(\text{OH})^+$ is formed at low pH (3–7) [21]. Obviously, a hydrolysis of copper salt with a release of H^+ ions results in a change of the surface charge of N-CNTs (see above) and possibly the adsorption of Cu(II) ions.

(ii) Increasing the system pH gives a rise to the negative surface charge density of N-CNTs and to the adsorption of positively charged copper ions via electrostatic mechanism.

(iii) At pH 6.5 the process of precipitation of $\text{Cu}(\text{OH})_2$ occurs [22] which leads to a pseudo-adsorption of the metal ion on the CNTs surface.

The dependencies of Cu(II) adsorption on the adjusted pH values by N-CNTs are shown on Fig. 8. In acidic media (pH 2–4) a marked rise in adsorption with an increase in pH was observed. Then, a constant value of adsorption was measured in the interval of pH 4.0–6.5. After that, a sharp increase in the Cu(II) adsorption occurred due to precipitation of copper hydroxide on the surface. The changes of the equilibrium pH of N-CNT suspensions as a result of Cu(II) adsorption will be discussed below.

To estimate the role of ion-exchange processes in the mechanism of adsorption of Cu(II) ions by N-CNTs, it is useful to examine the changes in the suspension pH as a result of adsorption of different amounts of copper ions. Selected results of these experiments are presented in the Table 1.

The results suggest different changes in the equilibrium pH of the N-CNT suspensions having various adjusted pH values and different adsorbed amounts of Cu(II) ions. The adding of N-CNTs to the acidic

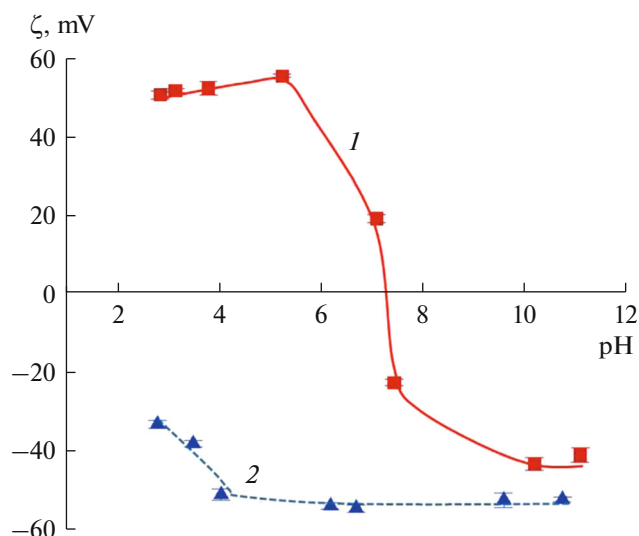


Fig. 5. Plots of the pH-dependence of zeta-potential for as-prepared (1) and oxidized (2) N-CNTs in 0.1% suspension.

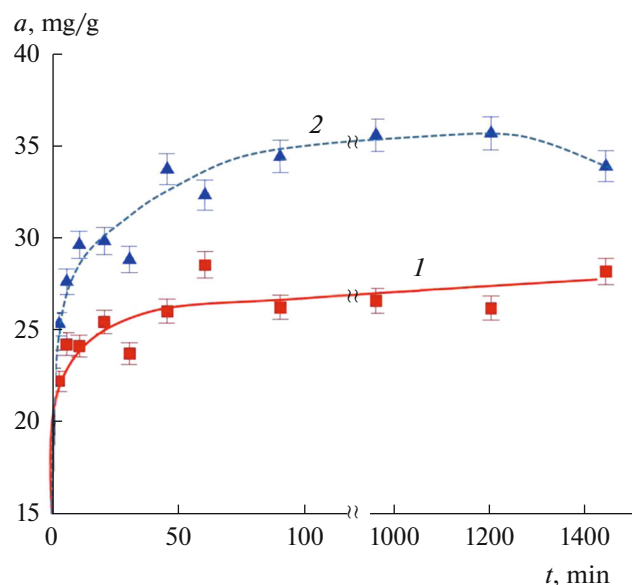


Fig. 6. Time dependencies of Cu(II) adsorption by as-prepared (1) and oxidized (2) N-doped CNTs at pH 5.5. The initial concentration of $\text{Cu}(\text{NO}_3)_2$ in the system was 50 mg/dm^3 .

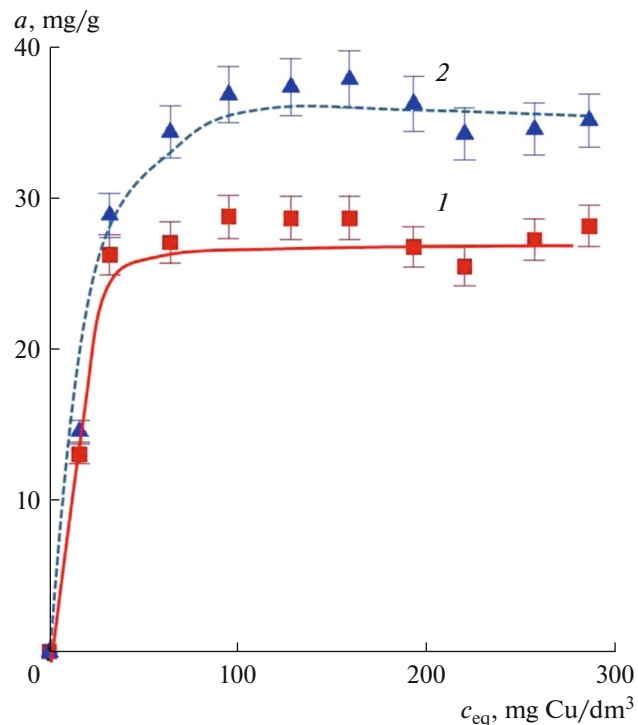


Fig. 7. Adsorption isotherms of Cu(II) ions by as-prepared (1) and oxidized (2) N-CNTs.

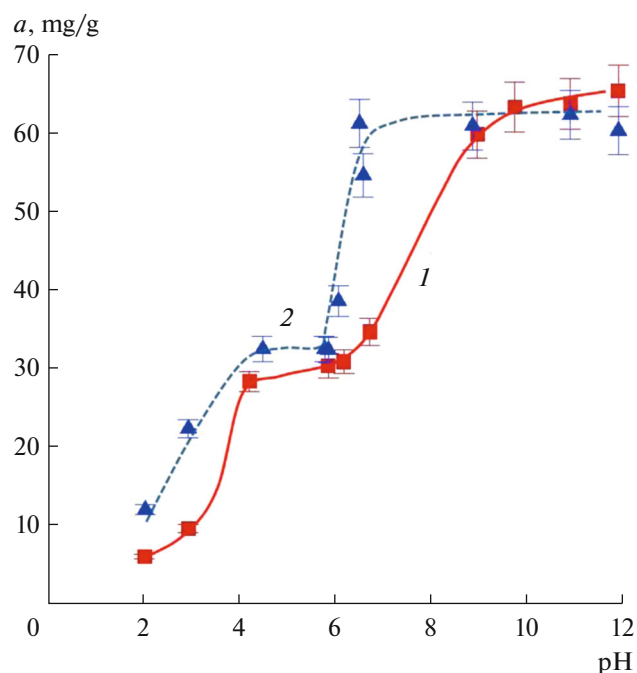


Fig. 8. Plots of the pH-dependence of Cu(II) ions adsorption by as-prepared (1) and oxidized (2) N-CNTs.

Cu(II) solutions with the adjusted pH (approximately pH 2–5 for pristine and pH 2–4 for oxidized samples) led to a measurable increase of the suspension pH value. We attribute this pH rise to the transfer of H^+

ions from the solution to pyridine N-atoms on the N-CNTs surface, because the substitution of surface hydrogen ions by adsorbing copper ions in the presence of excess H^+ ions is much less probable. At higher

pH values this effect is overcompensated by the ion-exchange of Cu(II) with surface H⁺ ions which gives a moderate decrease of pH for pristine N-CNTs and a much larger one (up to 2.5 pH unit) for the oxidized samples. Finally, an additional release of H⁺ ions occurs as a result of hydrolysis and precipitation of Cu(II) ions in the form of hydroxides in the alkaline media.

Obviously, different mechanisms are guiding the adsorption of Cu(II) ions by N-CNTs. A release of H⁺ ions from the oxidized N-CNTs confirms the essential role of the ion-exchange in binding copper ions for this adsorbent. This mechanism is also supported by FTIR data (Fig. 4). To estimate the contribution of this factor, we compared the adsorbed amounts with changes of the solution pH, i.e., the concentration of substituted H⁺ ions by copper ions from the surface. For example, the adsorption of 31.5 mg/g or 4.9×10^{-4} mol/g Cu(II) by oxidized N-CNTs resulted in a decrease of the solution pH from 5.95 to 3.96, which corresponds to an appearance of roughly 10^{-4} M ions in the suspension with concentration 1.0 g CNT/dm³. This decrease implies, that approximately 20% of Cu(II) ions is adsorbed via ion-exchange with H⁺ ions of the surface. At the same time, the majority of copper ions are bound to the CNTs as a result of other interactions, most probably, donor-acceptor interaction between the free electron pair of N-atoms of the surface and vacant *d* orbitals of the adsorbing ions. Similar results were obtained with other Cu(II) concentrations. It is remarkable that the value at which the adsorption dependencies reach the plateau regions do not differ substantially for the pristine and oxidized samples.

CONCLUSIONS

It was demonstrated that the N-doped multi-walled carbon nanotubes (N-CNTs) can serve for extraction of Cu(II) ions from aqueous solution. The specific adsorption values (28–36 mg/g) and degree of extraction (10–99% from solutions of equilibrium concentration of 580–5.0 mg/dm³) of this ion is comparable with those for non-oxidized and oxidized carbon nanotubes, i.e. without incorporated N atoms, described in the literature [1, 3, 11, 12].

The main laws of the studied adsorption can be summarized as follows: (i) the adsorption of Cu(II) reaches equilibrium value within 60 min; (ii) the degree of extraction of copper ions sharply increases with a decrease in their concentration, (iii) the adsorption of Cu(II) by as-prepared N-CNTs results in a moderate decrease in the pH value of the solution (1.5 pH unit) and in a considerable lowering the pH for oxidized sample (up to 2.5 pH unit); (iv) the adsorption isotherms of Cu(II) can be described by the Langmuir equation; (v) at pH 6.5 and higher a sharp increase in adsorption took place.

These observations can be explained by accounting three types of binding the Cu(II) ions to the N-CNTs surface. First, it is an ion exchange between Cu(II) ions and H⁺ of surface functional groups. This effect is more pronounced for the oxidized N-CNTs sample but does not make a key contribution into adsorption process. Second, these are donor-acceptor interaction between the vacant *d* orbital of adsorbing transition metal ions and N-atoms of the nanotubes matrix. This effect seems to play major role in the binding of Cu(II) ions to the surface of both as-prepared and oxidized samples. Finally, it is a precipitation of Cu(OH)₂ onto carbon nanotubes surface at relatively high pH values (pH > 6.5).

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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