



Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes

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ABSTRACT

Adsorption of nickel, copper, zinc and cadmium from aqueous solutions on carbon nanotubes oxidized with concentrated nitric acid was carried out in single, binary, ternary and quaternary systems. TEM and adsorption of nitrogen were used to determine texture and structural parameters, respectively. The surface chemistry was evaluated using the pH at the point of zero charge, FTIR spectroscopy and XPS analysis. The experimental results showed that all isotherms for $\text{Cu}^{2+}(\text{aq})$ fit to Langmuir model in each system. On the other hand, the isotherms for $\text{Ni}^{2+}(\text{aq})$, $\text{Cd}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})$ in multi-component systems reveal the effect of competition for adsorption sites seen as a decrease in the amount adsorbed. The uptakes at the equilibrium concentration of $0\text{--}0.04\text{ mmol L}^{-1}$ in single system and $0\text{--}0.15\text{ mmol L}^{-1}$ in binary system are in the order $\text{Cu}^{2+}(\text{aq}) > \text{Ni}^{2+}(\text{aq}) > \text{Cd}^{2+}(\text{aq}) > \text{Zn}^{2+}(\text{aq})$ while for the ternary and quaternary, the order is $\text{Cu}^{2+}(\text{aq}) > \text{Cd}^{2+}(\text{aq}) > \text{Zn}^{2+}(\text{aq}) > \text{Ni}^{2+}(\text{aq})$. The results indicate that the mechanism of adsorption is governed by the surface features, ion exchange process and electrochemical potential. The latter plays a significant role in multi-component adsorption where redox reactions, not only on the adsorbent surface but also between the adsorbates, are likely to occur.

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1. Introduction

Metal pollution is one of the major environmental concerns of contemporary society. Many natural waters are polluted by metal ions as a result of their release by industrial plants or mining activities. Numerous methods have been proposed for heavy metal removal. Chemical precipitation or electrochemical methods can be used to remove heavy metals present in high concentrations in aqueous phase. On the other hand, at low concentrations, such pollutants can be removed by adsorption on activated carbons and other adsorbents [1–5]. Recently, carbon nanotubes (CNTs), have attracted great interest due to their unique morphologies leading to potential applications. CNTs with functional groups have enhanced surface adsorption properties and have been studied as media for the removal of many organic compounds from both liquid and gas phases [6–8]. Examples are dioxins whose adsorption capacity on CNTs is superior to that of activated carbon [9]. Such behavior was

attributed to the strong interactions between dioxins and CNTs. Li et al. reported that CNTs supported on amorphous alumina had higher fluoride adsorption capacity [10] and that oxidized CNTs exhibit exceptionally high adsorption capacity and efficiency for lead, cadmium, and chromium from water [11–14]. Moreover, CNTs were found as good media for multi-component adsorption of metals [15].

As a result of extensive studies performed to define the interaction phenomena occurring at the solid/water interface surface chemistry was found to play an important role in the adsorption of aqueous heavy metals on carbon adsorbents [12,16–20]. Chemical oxidation, which incorporates oxygen-containing functional groups to the surface of adsorbent, enhances the adsorption of polar species and modifies the selectivity of the adsorbent for these species [21–23]. Aqueous metal ions have different affinities for various functional groups such as carboxylic and phenolic groups present on the carbon surface [24]. Although they are considered to be adsorbed via complex mechanisms [25–27] ion exchange seems to be the predominant mechanism of the removal process [5,24]. Moreover it is well known that several factors including the pH value, initial concentration, the speciation of metal ions and surface charge affect the adsorption of metal species from aqueous solutions [28]. The competitive adsorption of aqueous metal ions is even more complex since the subtle differences in surface interactions start to play a role, depending on the concentration [15].

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The objective of this paper is to evaluate the mechanism of multi-component metal adsorption on oxidized CNTs. In such systems, contrary to activated carbons, the surface can be considered as nonporous and thus adsorption is not limited by diffusion within the pore structure of an adsorbent or by the accessibility of pores [29]. As the adsorption systems, the single, binary, ternary, and quaternary aqueous solutions of $\text{Ni}^{2+}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})$, $\text{Zn}^{2+}(\text{aq})$ and $\text{Cd}^{2+}(\text{aq})$ species were chosen. The pH value of the solution from which the isotherms were measured was not controlled by the addition of buffer to eliminate the interferences of ionic components of the buffer with the metal ion competitive adsorption process. To provide comprehensive analysis of the adsorption mechanism, surface features of CNTs such as surface charge, functional groups, their accessibility along with solution characteristics including ratio of metal concentrations, speciation of metals, and their physico-chemical properties are taken into consideration.

2. Materials and methods

2.1. Materials

CNTs, obtained by chemical vapor deposition method, were purchased from Shenzhen NANO Tech. Port. Co. Ltd. (China). They were refluxed in concentrated HNO_3 at about 120°C for 4 h. The suspension was washed with deionized water to remove excess of the oxidants. Then the oxidized CNTs, denoted as “the CNTs-ox”, were dried at 100°C and stored for further studies.

2.2. Methods

2.2.1. Transmission Electron Microscope (TEM)

The TEM image of the CNTs was obtained on a Philips Technai-G² 20 transmission electron microscope (Philips, The Netherlands). The CNTs were, after ultrasonic treatment in ethanol, dispersed and one drop of the diluted dispersion was placed on a 200-mesh carbon coated copper grid.

2.2.2. Porous structure

The BET surface area, pore specific volume and pore diameter were characterized using adsorption of nitrogen at liquid nitrogen temperature carried out in a Micromeritics ASAP2020 gas sorption analyzer (Micromeritics, USA). The samples were outgassed at 150°C and vacuum condition for 5 h before measurements.

2.2.3. Surface pH

The pH values at the point of zero charge (pH_{PZC}) of the samples were measured using the pH drift method [30]. The pH of a solution of 0.01 M NaCl was adjusted between pH 2.00 and pH 12.00 by adding either HCl or NaOH. Nitrogen was bubbled through the solution at 25°C to remove dissolved carbon dioxide until the initial pH value of the solution stabilized. A total of 0.15 g of CNTs was added to 25 mL of the solution. After the pH had stabilized (typically after 24 h), the final pH was recorded. The graphs of final pH versus initial pH were used to determine the points at which the curves cross the line $\text{pH}(\text{final}) = \text{pH}(\text{initials})$ ($y = x$). These points were taken as the pH_{PZC} of the samples.

2.2.4. Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of the CNTs and the CNTs-ox were examined using an AVATAR 360 E.S.P. FT-IR Spectrometer (Nicolet Instrument Corporation, USA) equipped with a DTGS KBr detector and controlled by EZ OMNIC 5.0 software. All the data was measured in the spectral range $4000\text{--}400\text{ cm}^{-1}$. Sixty-four scans at a resolution of 4 cm^{-1} were averaged. Samples were homogeneously ground with anhydrous potassium bromide in a proportion of 1/20.

The powder is then pressed under 10 t cm^{-2} to form translucent piece.

2.2.5. X-ray Photoelectron Spectroscopy (XPS)

XPS data of the CNTs-ox were acquired using a Kratos Analytical AMICUS XPS instrument (Kratos Analytical Inc., UK). All XPS measurements were made using an Mg K α X-ray source operated at 150 W (10 kV, 15 mA). Energy analysis was performed using the “Dupont” type analyzer, featuring a low-pass/high-pass filter design. The high-resolution scans were performed over the 275–300, 522–547 eV ranges (C 1s and O 1s spectra, respectively). Binding energies (BE) were determined using the C 1s peak at 284.3 eV as a reference to correct charge effect. The tool used for deconvolution of the XPS spectra is the software of peakfit.

2.3. Adsorption from solution

The $\text{Ni}^{2+}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})$, $\text{Zn}^{2+}(\text{aq})$ and $\text{Cd}^{2+}(\text{aq})$ solutions of 1000 mg L^{-1} were prepared by dissolving analytical grade $\text{NiCl}_2 \times 6\text{H}_2\text{O}$, $\text{CuCl}_2 \times 2\text{H}_2\text{O}$, $\text{ZnCl}_2 \times 7\text{H}_2\text{O}$ and $\text{CdCl}_2 \times 2.5\text{H}_2\text{O}$ in 1 L of double-distilled water, respectively. About 0.005 mol HCl was added into each solution in advance in order to avoid hydrolysis process after dilution. The solutions were further diluted before the experiments. Batch experiments were carried out in Erlenmeyer flasks at 298 K. Adsorption isotherms in a single system were studied by adding weighed amounts (0.15 g) of the adsorbent into 100 mL aqueous solutions with different initial concentrations in the range of 1–5 mg L^{-1} . To study the influence of the pH value on adsorption, 0.15 g of the adsorbent was introduced into 100 mL solution containing the same initial concentration of 0.025 mmol L^{-1} . The pH values of the solution were then adjusted from about 2.00 to 12.00 with the diluted nitric acid and the diluted sodium hydroxide. For the binary system, the initial molar concentration ratios of metal ions were 0.5, 1.0, and 2.0. While for the ternary and the quaternary systems, the initial molar concentration ratios of metal ions were 1:1:1 and 1:1:1:1. The flasks with the adsorbent and the solution were mounted on a shaker and shaken for 6 h. The time required to achieve equilibrium was obtained by measuring the adsorbate concentration versus adsorption time. All the initial concentrations were 0.025 mmol L^{-1} . The suspensions were filtered through 0.45 μm membrane filters and then the concentrations of metals in the filtrates were measured by an atomic absorption spectrometer. All the experiments would be paralleled three times. The minimum detection limit was 0.0061 mg L^{-1} of Ni^{2+} , 0.0069 mg L^{-1} of Cu^{2+} , 0.0078 mg L^{-1} of Zn^{2+} and 0.0145 mg L^{-1} of Cd^{2+} , respectively. The standard solution used in the calibration curve was measured ten times. The relative standard deviations were Ni: 0.5%, Cu: 0.4%, Zn: 0.3%, and Cd: 0.2%, respectively. The average values of relative errors were Ni: 1.6%, Cu: 1.7%, Zn: 1.8%, and Cd: 3.8%, respectively. The amount of metal ions adsorbed was determined by the difference between the initial concentration and the equilibrium concentration. In all experiments re-distilled water was used.

3. Results and discussion

Fig. 1 shows the TEM images of the CNTs and the CNTs-ox with ca. 10 nm *i.d.* and 30 nm *o.d.*, and hundreds of nm to μm long. The nanotubes are curved with some open tips. The CNTs-ox sample does not differ significantly from its initial state. This indicates that oxidation treatment with concentrated nitric acid did not alter the nanotube structure.

The BET surface area, pore volume, pore diameter and the pH_{PZC} of the CNTs before and after oxidation are summarized in Table 1. Only a slight increase in the structural parameters is shown after

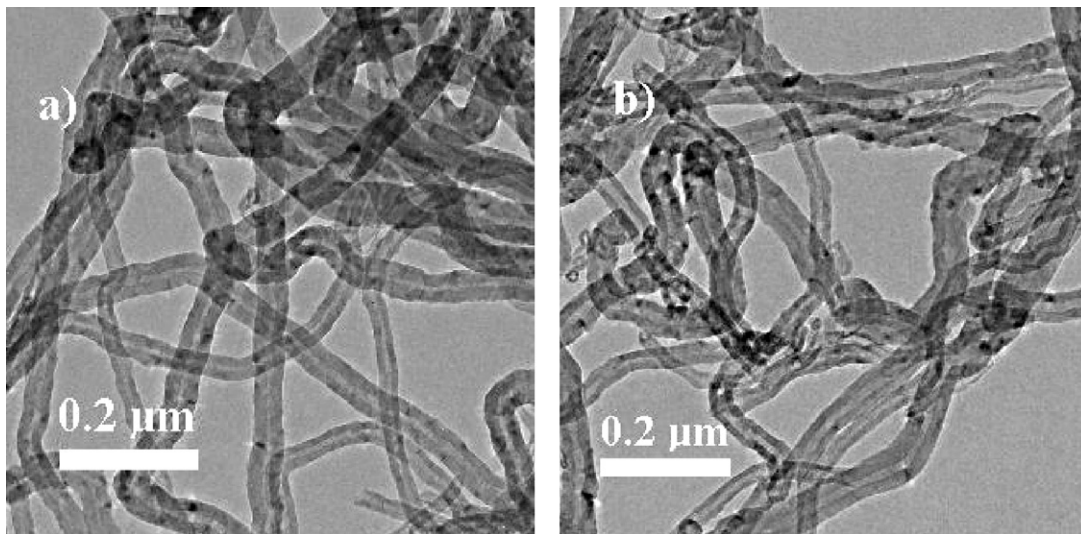


Fig. 1. TEM images of (a) the CNTs and (b) the CNTs-ox.

Table 1
Surface characteristics of the materials studied.

Sample	S_{BET} [$\text{m}^2 \text{g}^{-1}$]	V_p [$\text{cm}^3 \text{g}^{-1}$]	D_p [nm]	pH_{PZC}
CNTs	65	0.18	10.7	6.31
CNTs-ox	77	0.21	10.8	3.10

S_{BET} : BET surface area; V_p : pore specific volume; D_p : pore diameter; pH_{PZC} : point of zero charge.

oxidization. This treatment is known to remove the amorphous carbon and catalyst particles, make better dispersion of the CNTs, break the intertube spaces and even open the tips partially. In our case, a slight increase in the structural parameters can be the result of not only removing a few species mentioned above but also defect formation as a result of the attachment of oxygen functional groups to nanotube walls [31]. The presence of these groups is evident by a decrease in pH_{PZC} of CNTs-ox compared to the initial counterpart. These groups are expected to be strongly acidic, likely carboxylic [22,32], since over 3 pH unit decrease is recorded.

The FTIR spectra for the CNTs are presented in Fig. 2. For both materials, the bands in the spectrum at 1080, 1390, 1730 cm^{-1} are assigned to the stretching vibrations of C–O, –O–H bending deformation in carboxylic acids and phenolic groups, and the stretching

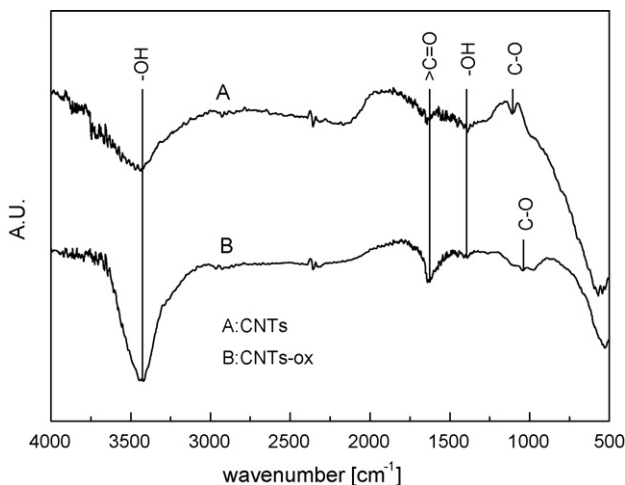


Fig. 2. FTIR spectra for the CNTs and the CNTs-ox.

vibrations of –CO– in saturation ester, respectively [33,34]. The broad band at over 3000 cm^{-1} represents hydroxyl groups. Thus on the surface of our materials oxygen-containing functional groups such as hydroxyl, carboxyl and carbonyl groups are present in detectable quantity, even on the initial CNTs. For this sample the functional groups may come from the acid washing to remove the catalyst when being fabricated or the weak oxidation in air. After oxidative treatment with nitric acid the bands are much more pronounced, especially those representing oxygen in the carboxylic groups arrangement at 1730 and 3000 cm^{-1} , which is consistent with the pH measurements. These groups are expected to be the active centers for metal cation [24,35].

Fig. 3 shows the XPS spectra of the C 1s and O 1s peaks measured at increased resolution. The C 1s peak (Fig. 3A) was deconvoluted into four symmetric peaks of the Gaussian type. Except for a main peak at 284.3 eV due to the graphitic carbon, other three peaks associated with C–C are assigned to C–O bonds of functional groups such as hydroxyl and/or ethers (at 286.1 eV), C=O as in the carbonyl group (at 287.6 eV) and –O–C=O characteristic of carboxylic and/or ester groups (at about 289.1 eV), respectively [34,36,37]. The O 1s XPS spectrum for the CNTs-ox (Fig. 3B) was deconvoluted into four peaks with binding energies of 531.1, 532.3, 533.3 and 534.2 eV which are assigned to the O=C (at 531.1 eV), carbonyl oxygen atoms in esters, anhydrides, hydroxyls or esters (at 532.3 eV), ether oxygen in esters and anhydrides (at 533.3 eV) and the oxygen atom in carboxylic groups (at 534.2 eV) [34,36–37]. As seen based on the peak areas, carboxylic acids seem to be the predominant surface oxygen-containing species which is supported by FTIR study and low pH_{PZC} of the oxidized nanotubes.

In order to study the adsorption from solution, the kinetics of adsorption have to be evaluated to ensure that the isotherms are measured at equilibrium. The examples of the curves showing the dependence of the amount adsorbed at pH 4.5 on the experimental time for four metals are presented in Fig. 4. Although the uptakes differ, depending on the kind of metals, the plateau in concentration is reached very fast after less than half an hour for all species studied. Although the rate of uptake differs, depending on the kind of metal, the plateau in concentration is reached very fast within half an hour for all species studied. This indicates that adsorption, as expected, occurs without the diffusion limitation, owing to the nonporous surface.

It is well known that the pH value is one of the parameters with greatest influence on the adsorption of metallic ions [28]. This is

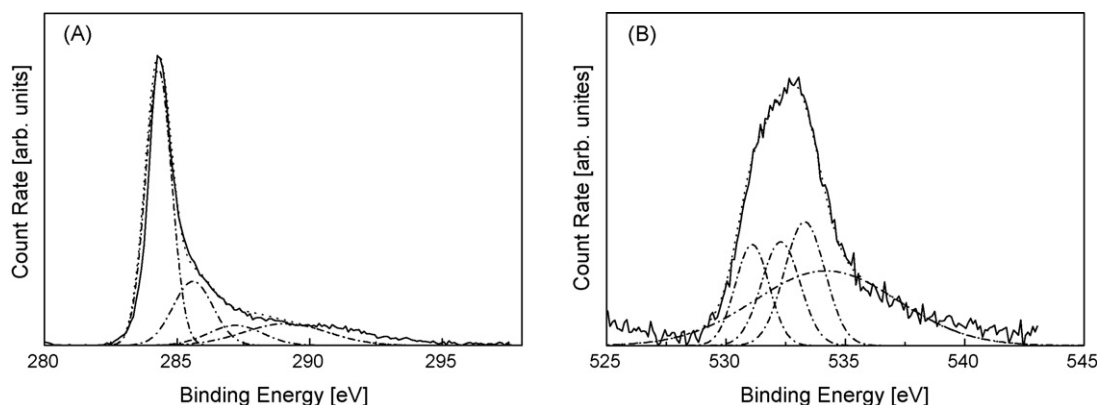


Fig. 3. Deconvolutions of (A) the C 1s and (B) O 1s region XPS spectra corresponding to the CNTs-ox.

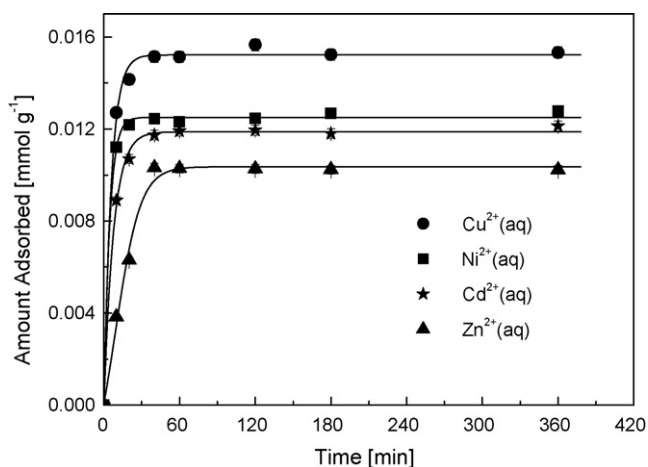


Fig. 4. Amount of M^{2+} adsorbed by CNTs-ox vs. time. pH 4.5, 298 K.

owing to the surface charge density of the adsorbent and to the fact that the charge of the metallic species present depends on the pH [5]. Fig. 5 shows the dependence of the removal percentage of metal ions on the pH values of the solutions. The removal percentage was calculated based on the following equation:

$$\text{Removal percentage \%} = \frac{(C_0 - C_i)}{C_0} \times 100\% \quad (1)$$

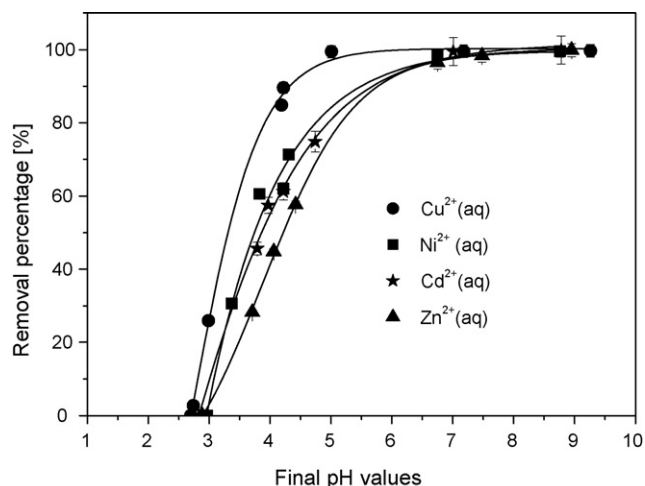


Fig. 5. The pH effect on the Cu^{2+} , Ni^{2+} , Cd^{2+} and Zn^{2+} adsorption by the oxidized CNTs.

where C_0 is the initial concentration. C_i is the final or equilibrium concentration at the effective final pH value. For all metal ions, all species were removed from solution at pH greater than 6. Especially in the basic region, deposition will play the main role in removal. It is interesting that the metal removal percentage increased significantly over a narrow pH range. At this low pH range all metals are expected to exist predominantly in the M^{2+} form [5]. Taking into account that the expected mechanism of adsorption is cation exchange that steep rise in adsorption must be related to the dissociation of surface groups and changes in electrostatic interactions on the surface. If carboxylic groups are in majority, and this is our hypothesis based on surface chemistry studies, they all should dissociate at low pH resulting in an increase in affinity towards metal cations [38]. This is also in agreement with surface complex formation theory (SCF), which states that with an increase in the pH the competition for the adsorption sites between proton and metal species decreases [39]. Moreover, surface positive charge decreases, which leads to less coulombic repulsion of the metal.

Support for the trend presented in Fig. 5 is the pH_{PZC} value of the oxidized nanotube surface. For all metals the adsorption starts at $pH < pH_{PZC}$. When pH is less than pH_{PZC} the surface is positively charged and repulsive interactions take place. This electrostatically repulsive force counteracts the attractive force exactly at $pH = pH_{PZC}$. Thus the $pH > pH_{PZC}$ the negative charge of the surface and thus the attractive electrostatic forces start to govern the adsorption of metals [40].

The adsorption isotherms for the $Ni^{2+}(aq)$, $Cu^{2+}(aq)$, $Zn^{2+}(aq)$ and $Cd^{2+}(aq)$ species on the CNTs-ox are shown in Fig. 6. Since their shapes suggest Langmuir mechanism of adsorption, the data were fitted to linear Langmuir equation:

$$\frac{C_i}{q_i} = \frac{1}{q_{m,i}K_{L,i}} + \frac{1}{q_{m,i}}C_i \quad (2)$$

where C_i is the equilibrium concentration in $mmol L^{-1}$, q_i is the amount adsorbed and $q_{m,i}$ is the maximum amount adsorbed in $mmol g^{-1}$; $K_{L,i}$ is the adsorption constants in $L mmol^{-1}$, and i stands for the metal species; $i = Ni, Cu, Zn$ and Cd .

The parameters derived from Eq. (2) for the isotherms presented in Fig. 6 are reported in Table 2. The fit is included as dotted lines in Fig. 6. The goodness of fit indicated by the high R^2 values indicates

Table 2
Fitting parameters to the Langmuir equation for the single component adsorption.

Metal	q_m [$mmol g^{-1}$]	K_L [$L mmol^{-1}$]	R^2
Cu	0.0404	885	0.9968
Ni	0.0311	1027	0.9951
Cd	0.0260	1180	0.9957
Zn	0.0152	825	0.9996

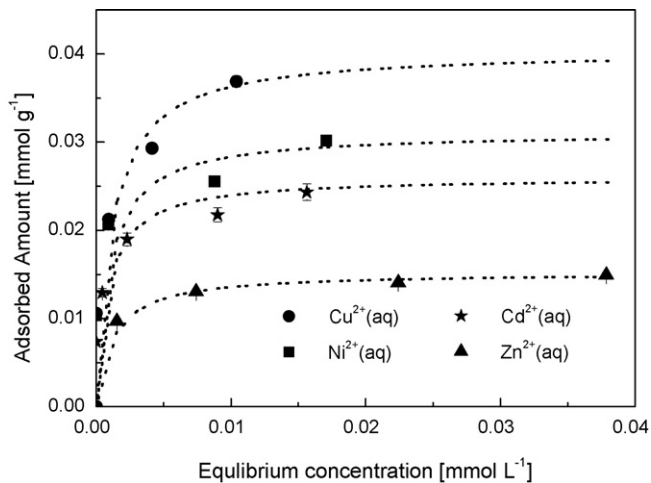


Fig. 6. The isotherms of all adsorbates on the CNTs-ox at final pH 4.50 in single system (adsorbent dosage: 0.15 g per 100 mL). The dotted lines represent the fit to Langmuir equation.

that one active surface center accommodates one metals species. As seen from Fig. 6 and Table 2 the adsorption capacities differ and the surface has higher affinity to copper, than nickel, cadmium and zinc. The amounts adsorbed are very small which must be related to small surface and limited number of adsorption centers. Even though all those metals are bivalent, the differences in the capacity and thus interactions with the adsorption centers exist. They must be related to the properties of these ions in aqueous solution, which may affect the energy of surface binding and interactions. Another factor is the accessibility of centers, which also can be linked to the sizes of species to be adsorbed and their effective charge.

According to Park and Kim [4] and Horsfall and Spiff [41], the adsorption of heavy metal ions should depend on the ionic radius of adsorbate. The large ionic radius should cause a quick saturation of adsorption sites because of steric effects. The order of ionic radius listed in Table 3 is: $\text{Cd}^{2+}(\text{aq})$ (0.97 Å) > $\text{Zn}^{2+}(\text{aq})$ (0.74 Å) > $\text{Cu}^{2+}(\text{aq})$ (0.72 Å) > $\text{Ni}^{2+}(\text{aq})$ (0.69 Å). As shown from our results, this order does not influence the order of the amount adsorbed at the same equilibrium concentration in the single system. Compared to other activated carbons in which adsorption of those metals was studied [20,42], BET surface area of the CNTs-ox is very small, however its number of groups should be significant based on the surface pH. It is well known that surface physical adsorption (related to the surface area), ion exchange (related to functional groups) and redox properties [26] (related to functional groups) can be involved into heavy metal adsorption in solution. In our experiments, it seems that the two latter factors play the main role. It is interesting that the order of the amounts adsorbed at the same equilibrium concentration agrees with that of oxidation ability of ions based on the standard electrode potential data in Table 3. In fact plotting the dependence of the amount adsorbed in mmol g^{-1} against E° reveals a linear trend presented in Fig. 7. No straightforward dependence on other parameters listed in Table 3 was found, although some trends are noticed for electronegativity and ionization energies. Taking into

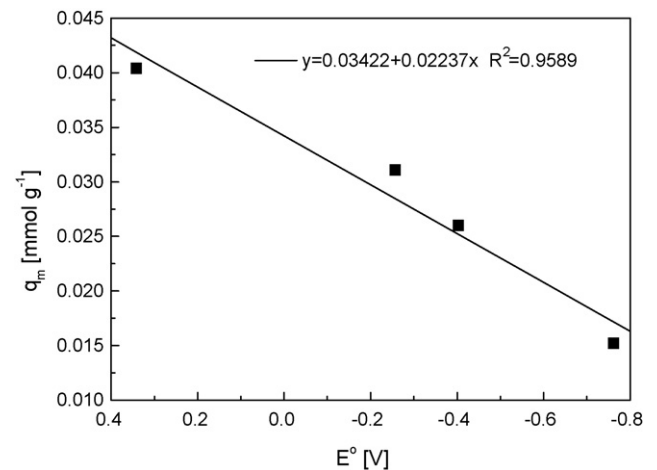


Fig. 7. Dependence of the maximum adsorption capacity at pH 4.5 on the standard electrode potential for the metals studied.

account the above, it is likely that the high copper adsorption is caused by its ability to be reduced by the carbonaceous surface. Copper ions in the close vicinity of the surface are reduced after being attracted to cation exchange center, accommodated on the nanotube surface and then leave the cation exchange site for the adsorption of another ion. With a decrease in E° , the contributions of redox reaction to the mechanism of adsorption decreases and functional groups become the main adsorption sites.

The competitive adsorption of binary aqueous metal cation species in mixtures $\text{Ni}^{2+}(\text{aq})/\text{Cu}^{2+}(\text{aq})$, $\text{Ni}^{2+}(\text{aq})/\text{Zn}^{2+}(\text{aq})$, $\text{Ni}^{2+}(\text{aq})/\text{Cd}^{2+}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})/\text{Zn}^{2+}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})/\text{Cd}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})/\text{Cd}^{2+}(\text{aq})$ on the CNTs-ox was investigated under different initial concentration ratios (0.5, 1.0, and 2.0 mole fraction ratios). Fig. 8A and B show the examples of the isotherms for the metal ion components in the $\text{Ni}^{2+}(\text{aq})/\text{Cu}^{2+}(\text{aq})$ system. A comparison of the isotherms for total ions adsorbed versus total ions in solution is shown in Fig. 8C.

From the analysis of the data it is seen that the adsorption of $\text{Cu}^{2+}(\text{aq})$ increased with increasing $\text{Cu}^{2+}(\text{aq})$ solution equilibrium concentration, while the adsorption of $\text{Ni}^{2+}(\text{aq})$ reached a maximum and then decreased with increasing equilibrium solution concentration. Xiao and Thomas explained that this behavior was caused by the competitive adsorption between $\text{Cu}^{2+}(\text{aq})$ and $\text{Ni}^{2+}(\text{aq})$ [43]. Since $\text{Ni}^{2+}(\text{aq})$ is considered to be more weakly adsorbed species, it is displaced by $\text{Cu}^{2+}(\text{aq})$ as concentration of the solution increases. There is no consensus between the researchers regarding the competitive adsorption of metal ions. Gabaldon et al. found that during multi-component adsorption various metal ions occupy the specific number of surface sites, which decreases the removal efficiency of the adsorbent for the metals of interest [44]. Üçer et al. proposed that the electronegativity plays an important role in competitive adsorption [20]. On the other hand, Allen and Brown interpreted the multi-component isotherm systems as dependent on one or all of the following parameters: ionic radius, electronegativity and ionization energy [45]. Based on our

Table 3
The metal ion properties [34–36].

Metal	Standard electrode potential E° [V]	Ionic radius [Å]	Electro-negativity [Pauling]	Ionization energies [eV]	Polarizability [10^{-24} cm^3]	N	R_H [Å]	N/R_H [Å^{-1}]
Cu	+0.3419	0.72	1.90	20.292	6.10	6.0	2.07	2.90
Ni	−0.257	0.69	1.91	18.168	6.80	6.6	2.06	3.20
Cd	−0.4030	0.97	1.69	16.908	7.20	6.0	2.28	2.63
Zn	−0.7618	0.74	1.65	17.964	7.10	6.0	2.17	2.76

N : the number of water of hydration; R_H : the hydrated radius.

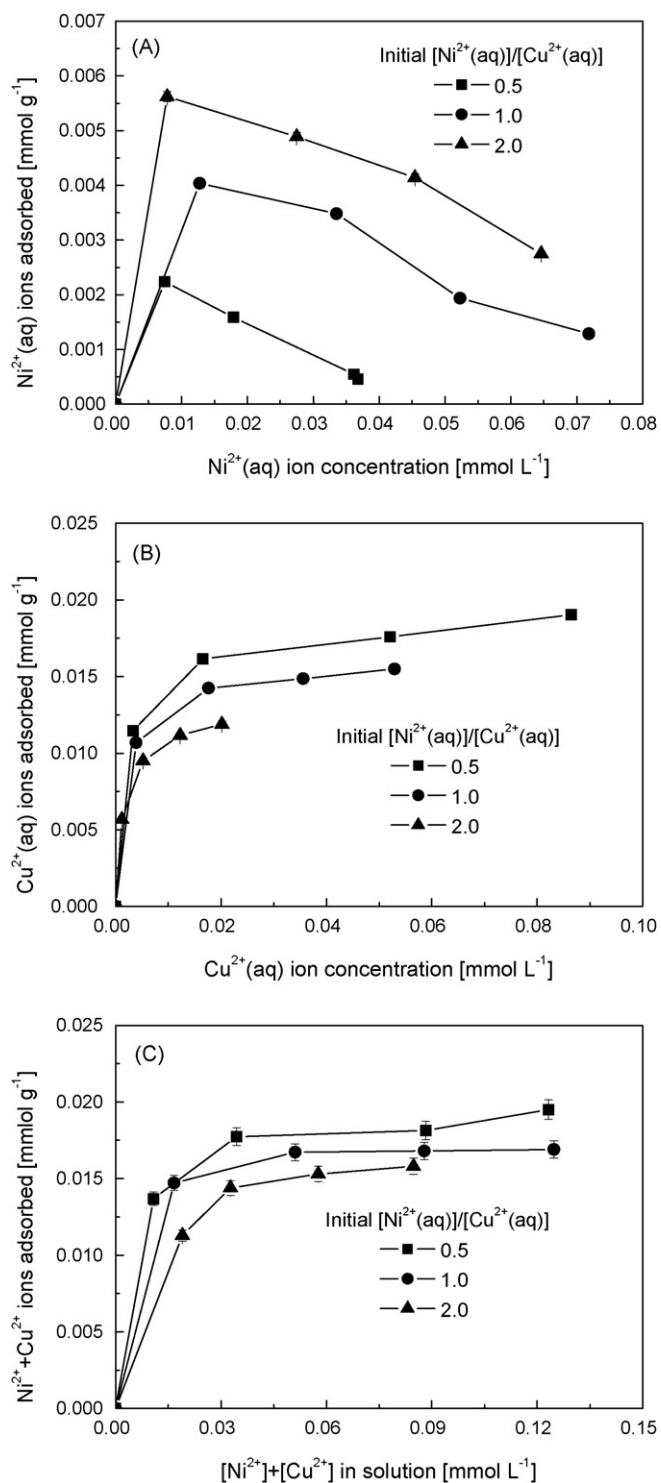


Fig. 8. Adsorption isotherms of Ni²⁺(aq) (A) and Cu²⁺(aq) (B), and Ni²⁺(aq) + Cu²⁺(aq) (C) on the CNTs-ox for binary system of Ni²⁺(aq)/Cu²⁺(aq) with different initial concentration ratios. The effective final pH is 4.50.

results, we hypothesize that this result is mainly related to the ion exchange electrochemical properties of these cations. The CNTs-ox with unique one dimension morphologies have small BET surface area, not large pore volume and abundant functional groups on the surface. Under the experimental conditions, the activated sites on the surface of adsorbent might have powerful attraction to the Cu²⁺ with higher standard oxidation potential compared with Ni²⁺. One has to be aware of that in preparation of our solutions small

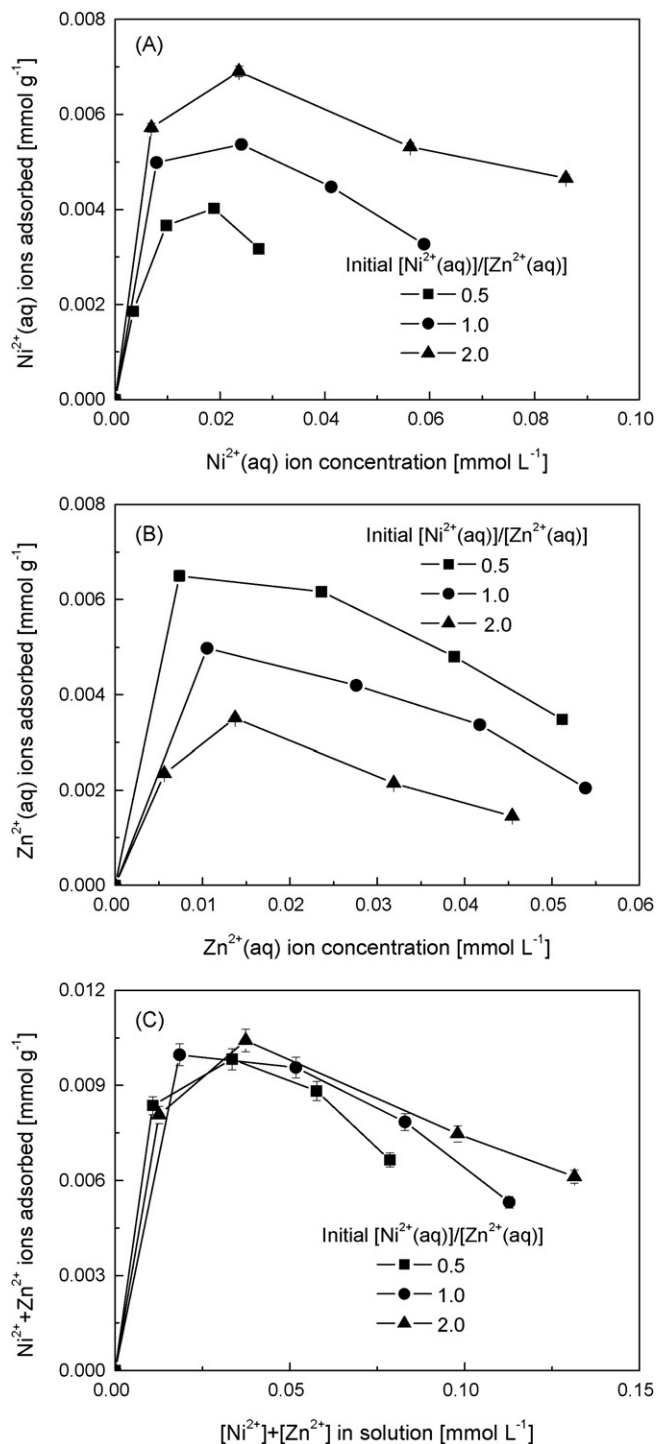


Fig. 9. Adsorption isotherms of Ni²⁺(aq) (A), Zn²⁺(aq) (B) and Ni²⁺(aq) + Zn²⁺(aq) (C) on the CNTs-ox for binary system of Ni²⁺(aq)/Zn²⁺(aq) with different initial concentration ratios. The effective final pH is 4.50.

amounts of H⁺ ions were introduced to the system to avoid hydrolysis. Thus it is likely that part of those hydrogen ions take part in binary system interactions. If nickel can be reduced by carbonaceous surface, H⁺ is able to oxidize it, which may result in returning some nickel ions to the solution. On the other hand, copper, even if reduced to zero state by the adsorbent surface, cannot be affected by the hydrogen ions. Those redox reactions can play a significant part in adsorption on our CNTs. In fact to be reduced, the metal ions have to be first attracted electrostatically and stay in very

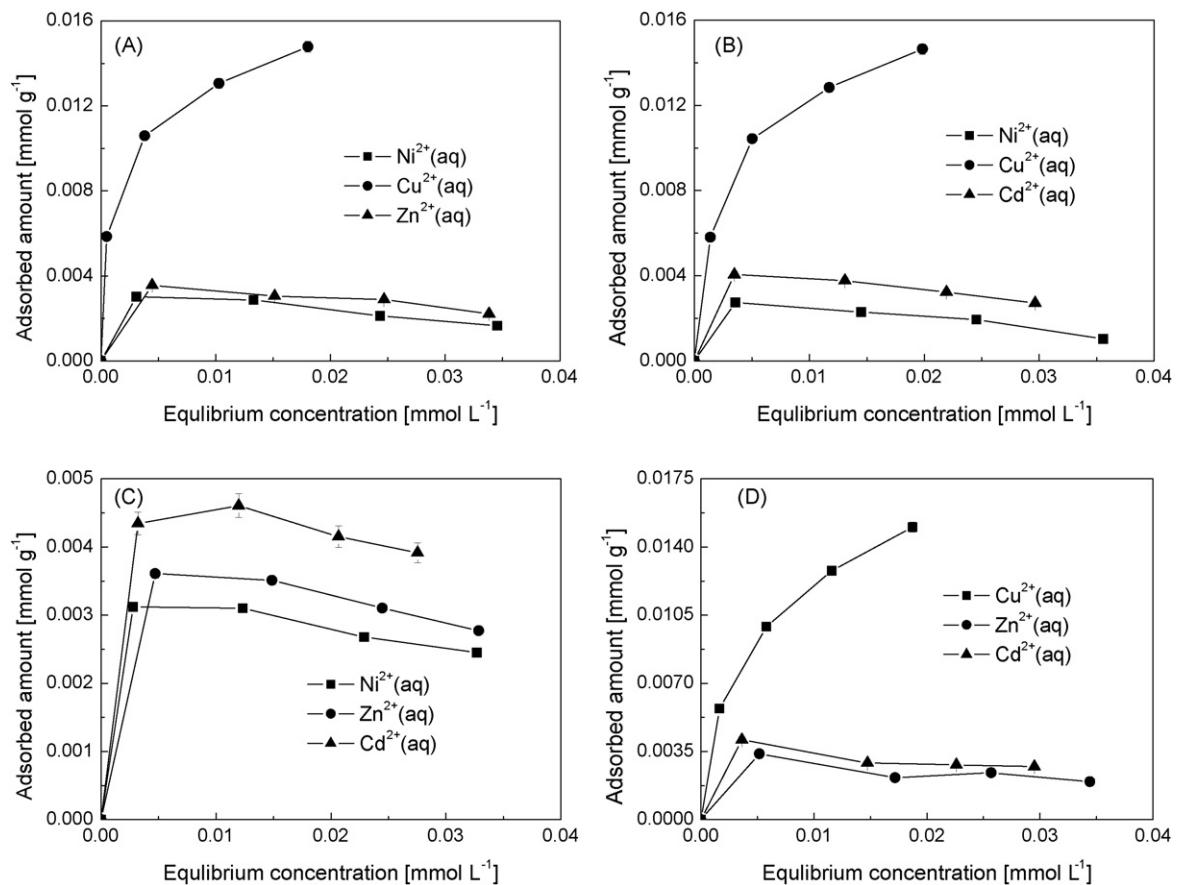


Fig. 10. Adsorption isotherms of Ni²⁺(aq) + Cu²⁺(aq) + Zn²⁺(aq) (A), Ni²⁺(aq) + Cu²⁺(aq) + Cd²⁺(aq) (B), Ni²⁺(aq) + Zn²⁺(aq) + Cd²⁺(aq) (C), and Cu²⁺(aq) + Zn²⁺(aq) + Cd²⁺(aq) (D) on the CNTs-ox in ternary combination systems with initial concentration ratio of 1:1:1 (mole fraction ratios). The effective final pH is 4.30.

close vicinity of the carbonaceous surface. Those attractive sites are oxygen-containing functional groups. As for the binary systems, the isotherms of the total ions adsorbed fitted the isotherm model of Langmuir with all correlation coefficients R^2 higher than 0.995. These characteristics were also found in the other binary systems with Cu(II), for example, Cu²⁺(aq)/Zn²⁺(aq), and Cu²⁺(aq)/Cd²⁺(aq), where Cu²⁺(aq) again were the more strongly adsorbed species. On the other hand, for Ni²⁺(aq)/Zn²⁺(aq), Ni²⁺(aq)/Cd²⁺(aq) and Zn²⁺(aq)/Cd²⁺(aq), all the isotherms showed the maximum value on the uptake curves. Their examples are shown in Fig. 9. Here, as expected the amount of nickel adsorbed is higher than that of zinc. In the absence of cooper the mechanisms of adsorption can be similar to that one hypothesized for nickel since all these metals have negative standard electrochemical potentials and can be oxidized by hydrogen ions. The results obtained here differ from those reported by Xiao and Thomas [43], which we explain by the redox reactions occurring on the surface.

The investigation of all the binary mixture systems showed that the amounts adsorbed were in the order Cu²⁺(aq) > Ni²⁺(aq) > Cd²⁺(aq) > Zn²⁺(aq) at the same equilibrium concentration which is consistent with the trend detected for the single components.

The competitive adsorptions of ternary metal cation mixtures of Ni²⁺(aq), Cu²⁺(aq) and Zn²⁺(aq); Ni²⁺(aq), Cu²⁺(aq) and Cd²⁺(aq); Ni²⁺(aq), Zn²⁺(aq) and Cd²⁺(aq); and Cu²⁺(aq), Zn²⁺(aq) and Cd²⁺(aq) on the CNTs-ox were investigated under the initial concentration ratios of 1:1:1 (mole fraction ratios). The adsorption from quaternary system in mixtures Ni²⁺(aq), Cu²⁺(aq), Zn²⁺(aq) and Cd²⁺(aq) on the CNTs-ox was carried out under the initial concentration ratios of 1:1:1:1 (mole fraction ratios). Figs. 10 and 11 show the isotherms for the metal ion components in the ternary

and quaternary mixture systems, respectively. The same as for the binary system, the data of the Cu²⁺(aq) agreed with the Langmuir model, while other isotherm curves show the maximum amount adsorbed expressed as peaks on the uptake curves. Repeated experiments confirmed that trend. Li et al. obtained similar results in their study of the competitive adsorption isotherms for three ions of Pb²⁺, Cu²⁺ and Cd²⁺ onto CNTs [15]. In their case the decrease in the uptake with an increase in the concentration was found for cadmium while Cu and Pb showed the regular adsorption behavior.

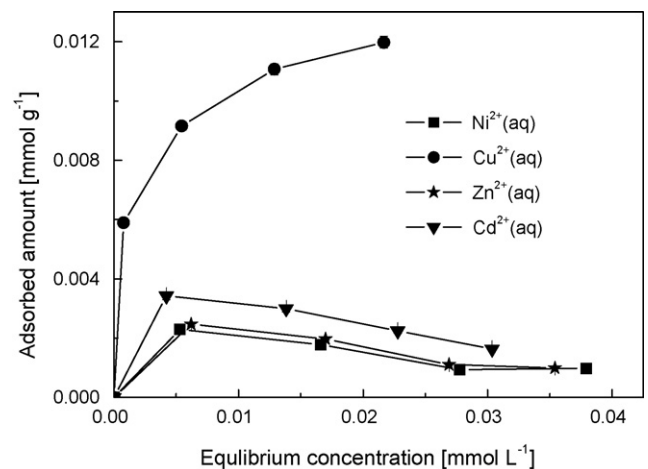


Fig. 11. Adsorption isotherms of Ni²⁺(aq) + Cu²⁺(aq) + Zn²⁺(aq) + Cd²⁺(aq) on the CNTs-ox in quaternary system with initial concentration ratio of 1:1:1:1 (mole fraction ratios). The effective final pH is 4.00.

Although the E^0 for lead is negative (-0.13 V) it is much less negative than that for cadmium or other metals used in our study thus the effect of hydrogen can be less pronounced. That source of hydrogen in the systems studied by Li et al. was in HNO_3 added to adjust the pH for competitive adsorption. Another important fact is that the data in Reference [15] is analyzed based on the number of grams and equilibrium concentrations are compared also in the same units thus the molar concentrations for each species differ. This can affect the amount adsorbed and interactions between ions to different extent than in our experiments. Li et al. attributed the specific behavior of their multi-component systems to the difference in the affinity of metals to the carbons nanotube adsorption sites [15].

As seen from Figs. 10 and 11, the amount of $\text{Cu}^{2+}(\text{aq})$ adsorbed in the various multi-component systems are greater than those of other ions at the same equilibrium concentration. Except for $\text{Cu}^{2+}(\text{aq})$, we still can judge the order of amount adsorbed at the same equilibrium concentration from the peak on the specific isotherms in ternary and quaternary systems. It is: $\text{Cd}^{2+}(\text{aq}) > \text{Zn}^{2+}(\text{aq}) > \text{Ni}^{2+}(\text{aq})$. Obviously, this order is different from that in the single and binary systems and electronegativity and ionization energy seem not to influence directly the competitive adsorption in ternary and quaternary systems. The plausible explanation of this particular behavior once again can be linked to the complex redox properties and ion exchange processes. The higher the polarizability of the ion and smaller the value of N/R_H (N is the number of water of hydration, R_H is the hydrated radius), the greater is the affinity between the ion and functional group [46], such that more can be adsorbed via ion exchange process. This would govern adsorption provided that the effects of electrochemical potential and redox reactions are negligible. This is not a case for our complex mixture system. Even though the metals are adsorbed on the functional groups, some of them get reduced by the carbon surface in the next step, likely leaving the exchange site accessible for another adsorbate species. In the vicinity of those reduced species, besides hydrogen, other metals with different potential exist and thus various oxidation/reduction reactions can occur. Only copper is not affected in this process. In fact supporting evidence for this is that for complex system the amount of copper adsorbed is much higher than those of other metals. For binary systems those differences were not so high. Thus, multi-component adsorption from aqueous solution is much more complex and any factor, which can affect the affinity between adsorbate and adsorbent can influence the adsorption.

4. Summary

The results presented in this paper indicate the complexity of adsorption of metal from multi-component solution on the CNTs-ox. The removal process is related to such factors as the pH value, the surface chemistry of the adsorbent, the initial concentration of ions, the kind and number of components in the adsorption system and the ratio of the metal ion species in solution. For the single and binary systems, it was found that the amount adsorbed on the CNTs-ox followed the order $\text{Cu}^{2+}(\text{aq}) > \text{Ni}^{2+}(\text{aq}) > \text{Cd}^{2+}(\text{aq}) > \text{Zn}^{2+}(\text{aq})$. A good correlation between the amount adsorbed and the standard electrode potential was found indicating the redox process may play a role in the mechanism of adsorption. While for the ternary and the quaternary system, the adsorption was more complex. The order of amount adsorbed at the same concentration was $\text{Cu}^{2+}(\text{aq}) > \text{Cd}^{2+}(\text{aq}) > \text{Zn}^{2+}(\text{aq}) > \text{Ni}^{2+}(\text{aq})$. The isotherms of Cu^{2+} (stronger oxidation ability than hydrogen ion) agreed with the Langmuir model, but isotherms of other metal ion (weaker oxidation ability than hydrogen ion) revealed a maximum value of uptake in multi-component systems. This was explained by the participation of hydrogen ions in competitive adsorption. That hydrogen is

able to oxidize Ni, Cd and Zn but not Cu. In the complex system (three and four components) the polarizability of ion and the value of N/R_H likely affect the adsorption via cation exchange. Moreover, the redox reactions on the carbon surface involving metals might affect negatively the amount adsorbed.

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