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Characterization of multi-walled carbon nanotubes and application for Ni^{2+} adsorption from aqueous solutions

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were used to remove Ni^{2+} from aqueous solutions. Batch experiments performed to examine the effects of initial Ni^{2+} solution concentrations, pH, and contact time on Ni^{2+} sorption process. MWCNTs were characterized by scanning electron microscopy, transmission electron microscopy, atomic force microscopy, micro-Raman spectroscopy, thermogravimetric analysis, and specific surface area (BET) techniques. The tested MWCNTs exhibit purity >95%, average diameter 20–30 nm, and specific surface area >150 m^2/g. The results showed that 60–95% of Ni^{2+} was absorbed depending on the initial solution concentrations. As it is suggested by the distribution coefficient (k_d) values, increased initial Ni^{2+} solution concentrations resulted to lower Ni^{2+} adsorption intensity onto MWCNTs, while the total amount of Ni^{2+} that removed from the equilibrating solutions increased. The adsorption of nickel onto MWCNTs was significantly affected by the solution pH; higher Ni^{2+} adsorption was observed at $pH > 6.0$. According to the contact time experiments, the sorption process reached equilibrium at 60 min. This study suggests that MWCNTs can be utilized for the removal of nickel ions from aqueous solutions and that they can be a promising candidate adsorbent for environmental applications and wastewater treatment.

Keywords: Multi-walled carbon nanotubes (MWCNTs); Nickel; Adsorption; Electron microscopy (SEM—TEM); Atomic force microscopy (AFM); Micro-Raman spectroscopy; Thermogravimetric analysis (TGA)

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1. Introduction

Removal of heavy metal ions from wastewaters and industrial wastes has received considerable attention in the recent years due to the toxicity and environmental issues that can be raised. Nickel (Ni) is a non-biodegradable toxic heavy metal present in wastewater derived from industrial production processes such as galvanization, smelting, mining, batteries production, and metal finishing [1]. According to the European Union regulations, the maximum permissible limit of nickel in drinking water is 0.02 mg L^{-1}, while in wastewaters, nickel concentration must not exceed 1 mg L^{-1} [2]. Thus, the removal of nickel from aquatic media to prevent environmental degradation resulted to the development of treatment processes, such as chemical precipitation, ion exchange, filtration, and reverse osmosis [3]. Among these methods, absorption is considered as a promising technique and is widely applied mostly due to its relatively low operational cost.

Carbon nanotubes (CNTs) since their discovery by Iijima [4] have gained high attention by the scientific community due to their unique structural, electronic, mechanical, chemical, and physical properties. CNTs are built from sp^2 carbon units in hexagonal networks as in a graphene sheet [5]. CNTs are classified as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). SWCNTs contain one-layered graphitic cylinders with diameter around 0.4–3 nm and several μm in length [6]. On the other hand, MWCNTs consist of 2–30 concentric cylinders, with diameters 10–50 nm and a distance between the sheets or inter layer spacing of approximately 0.34 nm.

As it was expected, CNTs have been considered as novel nanomaterials for many commercial and industrial applications such as in material science, energy management, and electronics. Among their applications, the potential use of CNTs to prevent environmental degradation has gained the attention of academic and industrial community during the last few decades [7]. The CNTs exhibit significant adsorption capacity for many kinds of inorganic and organic pollutants, such as heavy metals, radionuclides, and herbicides [8]. The high adsorption capacity of CNTs is mainly attributed to their highly porous and hollow structure, their large surface area and the presence of surface functional groups [9,10]. Rao et al. [11] summarized the removal of divalent metal ions from aqueous solutions by various kinds of CNTs and suggest that the CNTs are efficient sorbents for environmental protection applications. According to Ren et al. [12], the adsorption of heavy metal ions on CNTs is strongly dependent on pH values, and the adsorption capacity of CNTs is higher than that of other adsorbents under similar conditions.

The use of MWCNTs for the efficient removal of nickel ions from aqueous media was suggested by Abdel-Ghani et al. [13], Tofighy and Mohammadi [14], and Adolph et al. [15]. The effects of the ionic strength of the equilibrating solutions and of the adsorbent mass as well as the effect of competing ions on Ni^{2+} adsorption by CNTs was thoroughly studied by Lu and Liu [9] and Yang et al. [16], respectively. Yet, [17] supports, that nickel removal from aqueous solutions by MWCNTs was not so intensively studied as for other metal ions.

Since commercial CNTs greatly differ in their physicochemical and structural properties, mainly due to the followed production procedures and the catalyst content [18], it is essential to fully characterize any new CNTs product prior to its utilization for specific applications. Thus, the purposes of this work were to study: (a) the morphological and structural characteristics of ONEX MW1000 C1 MWCNTs and (b) the ability of these MWCNTs to remove nickel ions from aqueous solutions under different experimental conditions as pH, initial Ni^{2+} concentration, and contact time.

2. Materials and methods

2.1. Multi-walled carbon nanotubes

The multi-walled carbon nanotubes (MWCNTs-ONEX MW1000 C1) produced by chemical vapor deposition (CVD) and provided by Glonatech S.A. (Greece).

2.2. Analytical methods

The morphology of MWCNTs was analyzed by scanning electron microscopy—(SEM) (JEOL FEG 7401F), a transmission electron microscopy—(TEM) (Philips CM20), and an atomic force microscopy—(AFM) (Scan Fast microscope- Bruker).

Micro-Raman spectra were obtained in backscattering configuration on a Renishaw inVia Reflex microscope using an Ar^+ ion laser ($\lambda = 514.5$ nm) and a high-power near-infrared diode laser ($\lambda = 785$ nm) as excitation sources.

For the thermogravimetric analysis (TGA) of the MWCNTs, a TGA SETARAM SETSYS Evolution 18 instrument was used. The specific surface area of MWCNTs was determined by N_2-BET method (NOVA 2200).

2.3. Batch sorption experiments

Batch experiments were adopted to study the Ni^{2+} sorption behavior on MWCNTs. MWCNTs subsamples of 0.2 g in 20-mL solution containing the appropriate Ni^{2+} concentration and 0.01 M $NaNO_3$ as a background electrolyte were shaken at 180 rpm for 48 h at room temperature (20°C). Four initial Ni^{2+}concentrations (1, 5, 10, and 20 mg L^{-1}) were used and the pH of the solutions was adjusted at near neutrality by 0.1 M HNO_3 or 0.1 M NaOH.

To test the effect of the solution pH on Ni^{2+}sorption onto MWCNTs two initial Ni^{2+} concentrations (7.5 and 20 mg L^{-1}) were selected. The pH of the equilibrating solutions was adjusted at 4, 5, 6, 7, and 8 by adding 0.1 M HNO_3 or 0.1 M NaOH. Other conditions such as temperature, stripping rate, equilibrium time, background electrolyte, and ratio mass of MWCNTs to volume of solution were kept the same.

To assess the effect of contact time, 5 mg L^{-1} of initial Ni^{2+} solution concentration was used and the selected contact times were 15 min, 30 min, 60 min, 150 min, 24 h, and 48 h. Other conditions such as temperature, stripping rate, pH, background electrolyte, and ratio mass of MWCNTs to volume of solution were kept the same.

After equilibration, the aqueous phase was immediately separated from the suspensions by centrifuging for 15 min. The supernatant solutions filtered through a Whatman No 42 filter paper and analyzed for Ni^{2+} in a Varian SpectrAA-300 atomic absorption spectrophotometer. All the experiments were performed in triplicate, and the mean values are reported; the standard deviation was <5%.

The amount of sorbed Ni^{2+} was calculated as follows:

$$q = (C_0 - C) \times \frac{V}{m} \tag{1}$$

where q is the amount of Ni^{2+} sorbed onto MWCNTs (mg kg^{-1}); C_0 is the initial Ni^{2+} concentration (mg L^{-1}); C is the absorbed Ni^{2+} concentration (mg $L^{-1)}$; V is the initial solution volume (L); and m is the MWCNTs mass (kg).

To characterize Ni^{2+} sorption, the equilibrium distribution coefficient (k_d) [16] was calculated according to the following equation:

$$k_d = \frac{q}{C} \tag{2}$$

The extent of sorption was expressed as the percentage sorption, $A\%$ [19], and calculated from the k_d values, as follows:

$$\%\, A = \frac{100 * k_d}{k_d + \frac{v}{m}} \tag{3}$$

3. Results and discussion

3.1. Morphological and structural characteristics of MWCNTs

To interpret the adsorption properties of MWCNTs, it is essential to study their physicochemical

Table 1
Physicochemical properties of MWCNTs

	MWCNTs
Production method	CVD
Diameter	20–30 nm
Length	≥5 μm
Purity	≥95%
Catalyst	4.5%
Amorphous carbon	<0.5%
Specific surface area	>150 $m^2\ g^{-1}$

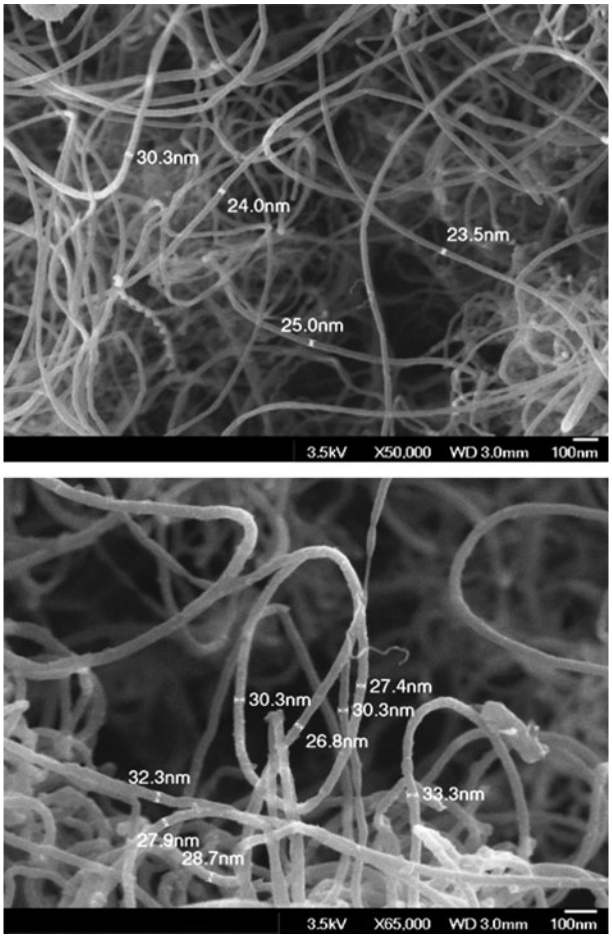

Fig. 1. SEM images of the studied MWCNTs.

characteristics, morphology, and structure at an atomic level. In this paper, various analytical methods have been utilized for the structural characterization of MWCNTs (Table 1). SEM, TEM, and AFM provide quantitative analysis and determine the size and the shape of nanomaterials with high spatial resolution, while TGA and Raman spectroscopy fulfill the structural analysis of MWCNTs.

The SEM micrographs are presented in Fig. 1 and show that the MWCNTs samples appear free of impurities and consist of bundled CNTs, highly curved and randomly oriented (MWCNTs). The average diameter of the MWCNTs ranges from 20 to 30 nm, while their length is ≥5 µm. Relatively longer tubes were bent and grew in random directions as previously suggested by Shukrullah et al. [20]. Diameters of approximately 30 nm were also observed with TEM, confirming the SEM findings (Fig. 2). An inner diameter of 8 nm and an outer average of 30 nm were also measured for the MWCNTs (Fig. 2). On the AFM image in Fig. 3, the presence of an isolated CNT with a length >5 µm can be distinguished.

TGA determines the thermal stability of MWCNTs and the purity of the sample. Due to their fully aromatic nature, these materials present excellent thermal stability (i.e. high degradation temperature). CNTs have a different oxidation temperature than the other carbonaceous products and MWCNTs are oxidized between 500 and 800˚C in air [21]. According to Fig. 4, MWCNTs present high stability as they are able to withstand oxidation temperatures as high as 500˚C and started to burn at 550˚C. The residual verified purity higher than 95%.

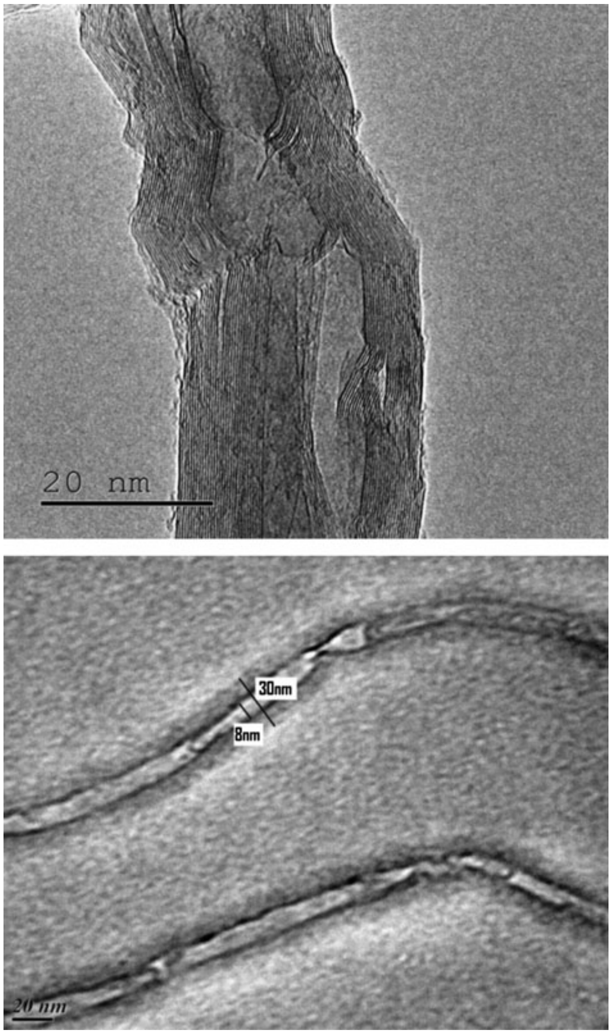

Fig. 2. TEM images of the studied MWCNTs.

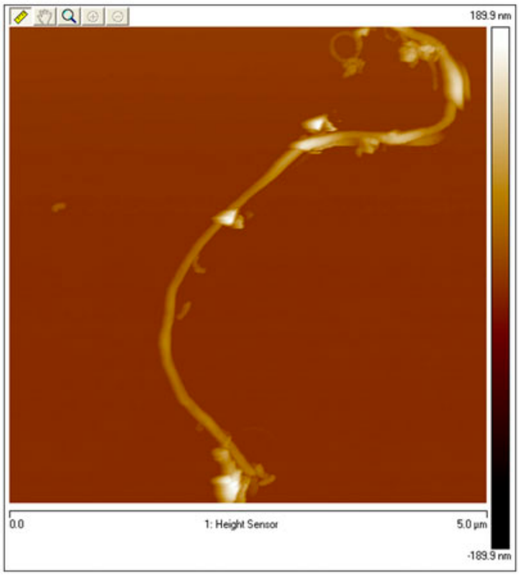

Fig. 3. AFM image of the studied MWCNTs.

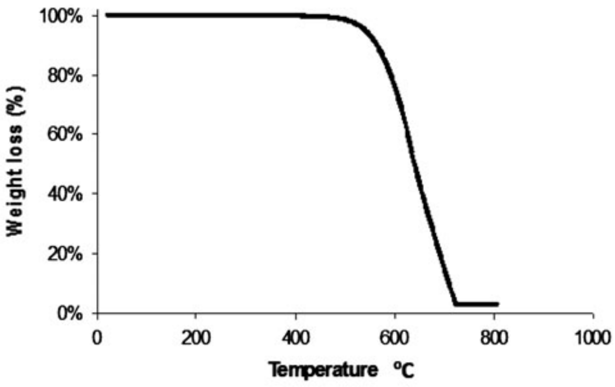

Fig. 4. TGA analysis of MWCNTs.

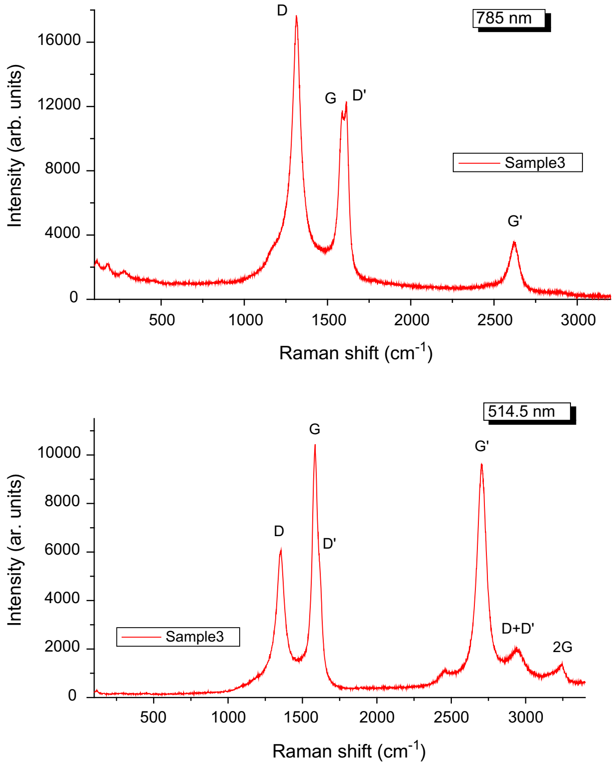

Fig. 5. Raman analysis of MWCNTs.

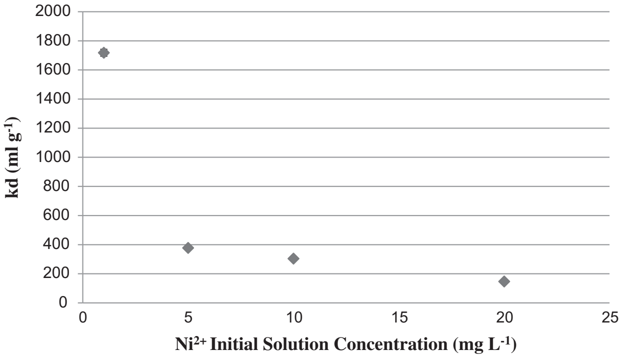

Fig. 6. Effect of initial solution concentration on the k_d values.

Raman spectroscopy is one of the most powerful tools for the characterization of CNTs [22]. According to Raman analysis, two main peaks appeared at 785 and 514.5 nm for the tested MWCNTs, the D band (1,300 cm^{-1}) and the G band (1,600 cm^{-1}) (Fig. 5). The G band corresponds to planar vibrations of carbon atoms and is present in most graphite-like materials, while the D band is present in all graphite-like carbons and originates from structural defects in the graphitic sp^2 network typical of carbonaceous impurities, as amorphous carbon particles. Nevertheless, the intensity ratio of G band to D band (I_D/I_G ratio) reflects both the purity and the defect density of MWCNTs. The results indicated the absence of major defects as well as the crystallinity of the graphitic planes (Fig. 5).

3.2. *Effect of initial Ni^{2+} concentration*

Nickel ions in contaminated aqueous media exist in different concentrations depending on the sources of contamination [23]. Thus, Ni^{2+} adsorption on pure MWCNTs was studied for initial Ni^{2+} concentrations that ranged between 1.0 and 20 mg L^{-1}. A very high k_d value was observed at the lowest Ni^{2+} solution concentration that decreased as the metal concentrations in the solution increased (Fig. 6). This pattern of adsorption points to a highly selective Ni^{2+} sorption on MWCNTs at low concentrations and suggests a complex sorption mechanism. Indeed, Rao et al. [11] and Ren et al. [12] concluded that the mechanisms of heavy metal ion adsorption onto CNTs are ion specific, very complicated, and appear attributable to physical adsorption, electrostatic attraction, precipitation, and chemical interaction between the heavy metal ions and the surface functional groups of CNTs. Hence, at low Ni^{2+}concentrations, Ni^{2+} adsorption on MWCNTs preferably occurs at sites of high selectivity for heavy metal ions. This indicates that, at low initial concentration, the adsorption of Ni^{2+} onto pure MWCNTs is mainly dominated by sorption involving valence forces through sharing or exchanging electrons between sorbate and sorbent. In this case, the adsorption capacity is directly proportional to the number of active sites occupied on the adsorbent's surface. At higher Ni^{2+} concentrations, as the specific sites progressively saturate with Ni^{2+}, the lower k_d values suggest that less-favorable sites were involved in Ni^{2+} adsorption process.

However, as it is indicated by the percentage sorption values ($A\%$), the amount of Ni^{2+} removed from the solution increased as the Ni^{2+} initial solution concentration increased. At low concentrations (i.e., 1.0 mg L^{-1}), 95% of the nickel ions were adsorbed onto MWCNTs, while further gradual increase in the metal ion concentration up to 20 mg L^{-1} resulted into 60% sorption (Fig. 7). A similar trend is also reported by Kandah and Meunier [1].

3.3. *Effect of pH*

The solution pH is a very important factor for the sorption process of metal ions as it affects the surface charge, the degree of ionization and the speciation of

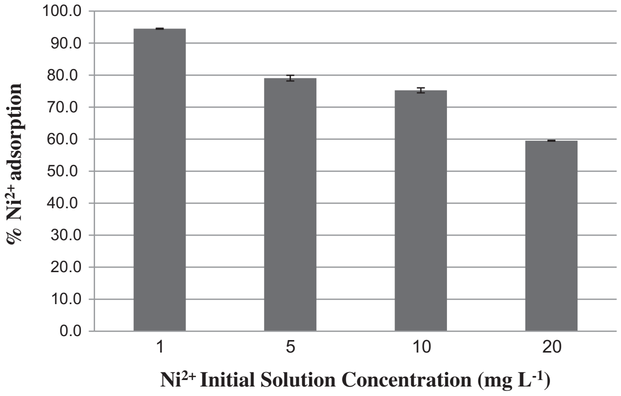

Fig. 7. Effect of initial solution concentration on the % adsorption of Ni^{2+} by MWCNTs.

sorbents. As it is presented in Fig. 8, the adsorption capacity of the tested MWCNTs increased as the pH of the solution increased (Fig. 8). Low Ni^{2+} adsorption observed at low solution pH values that greatly increased for pH solution values higher than 5.0, especially for the lowest Ni^{2+} concentration. At this concentration, Ni^{2+} adsorption involves the high energy sites that progressively saturate as the Ni^{2+} concentration increases. Accordingly, at higher Ni^{2+} solution concentrations adsorption begins on lower energy sites, resulting to decreasing adsorption efficiencies as previously reported by Kadirvelu et al. [24]. At different pH solution values, nickel is present as Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$, $Ni(OH)_3^-$, and $Ni(OH)_4^{2-}$ [25]. At $pH < 8$, Ni^{2+} dominates and its removal from the solution is mainly accomplished by sorption. At acidic pH values below 5.0, the positive surface charge of MWCNTs increases and the competition between H^+ and Ni^{2+} ions for the same sorption sites reduces the absorption uptake of Ni^{2+} by MWCNTs. As the pH increases, this competition progressively fades, the surface of MWCNTs is more negatively charged; thus, enhancing the electrostatic attractive forces between OH^- and Ni^{2+} and the Ni^{2+} sorption percentage increases rapidly. According to Li et al. [26], Wang et al. [27], and Sheng et al. [28], the pHzpc of MWCNTs is ~5. Below the pHpzc, the surface charge of MWCNTs is positive and Ni^{2+} is hardly adsorbed on the surface of MWCNTs. Above the pHpzc, the negatively charged surface of MWCNTs increases generating electrostatic attraction forces with Ni^{2+} (Fig. 8). Similar results reported by Lu and Liu [18], who observed that Ni^{2+} removal by CNTs quickly increased when the solution pH increased from 1 to 8, slightly fluctuated and reached a maximum in the pH range of 8–11, and steeply decreased at pH 12.

3.4. *Effect of contact time*

The sorption percentage of Ni^{2+} onto MWCNTs as a function of contact time was determined from 15 min to 48 h and for an initial Ni^{2+} concentration of 5 mg L^{-1} (Fig. 9). Even at the 15-min contact time, the Ni^{2+} sorption percentage on MWCNTs was high and kept increasing up to 60 min, showing a maximum of 80% sorption. Afterwards, the percentage removal of Ni^{2+} reached a plateau and the sorption capacity of MWCNTs remained rather constant by further increase in contact time. Such behavior implies that the sorption of nickel ions occurs rapidly at specific available sorption sites on the surface of MWCNTs. The short equilibrium time also indicates that MWCNTs have a strong potential for nickel ion sorption applications [1]. Short equilibrium contact times of 60 and 120 min for 10 and 60 mg Ls^{-1}initial Ni^{2+}

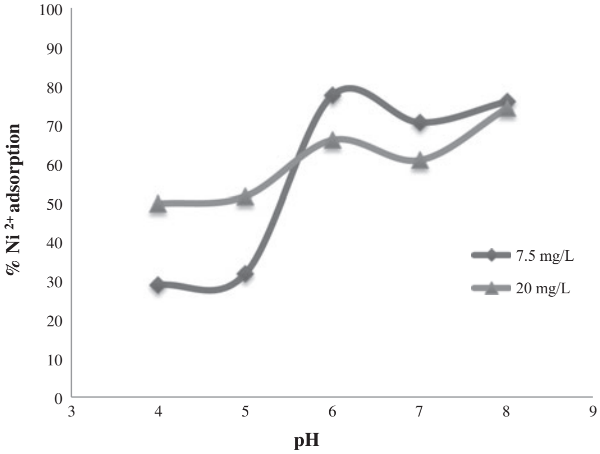

Fig. 8. Effect of solution pH on the adsorption of Ni^{2+} by MWCNTs.

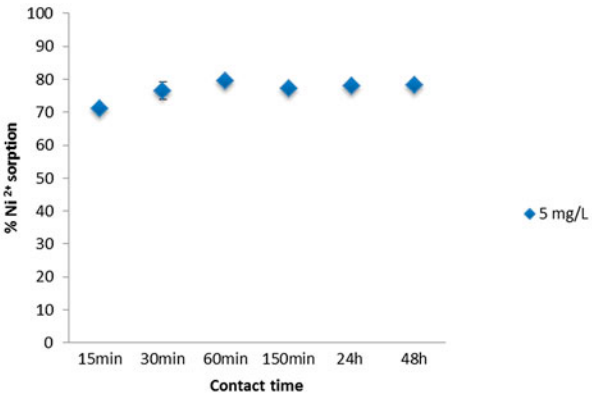

Fig. 9. Effect of contact time on the adsorption of Ni^{2+} by MWCNTs.

concentrations were also reported by Lu and Liu [9], while 120 min were needed for the system to reach equilibrium according to Yang. et al. [16].

4. Conclusions

The tested MWCNTs showed high ability for the removal of nickel ions from aqueous solutions. Depending on the solution pH value and the initial Ni^{2+} concentration, up to 95% of the Ni^{2+} present in the solution adsorbed onto the MWCNTs. The short contact time of 60 min for the system to reach equilibrium, further supports the application of MWCNTs as effective sorbents. However, the adsorptive capacity of MWCNTs must be checked for multi-metal solutions and real wastewater effluents and desorption studies are needed to investigate the possibility of MWCNTs reuse. Overall, the globally growing consideration to protect and improve the quality of the environment and to secure the functionality of nature deserves the scientific effort for the development and the assessment of technologically leading materials as the MWCNTs.

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