Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20246

71 (2017) 107–115
April

Continuous removal of toxic nickel from industrial wastewater by flotation-adsorption with multi-walled carbon nanotubes: kinetic and adsorption isotherms

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Received 18 July 2016; Accepted 30 September 2016

ABSTRACT

Nickel is a toxic metal ion present in industrial wastewater. In this study, ion flotation combined with multi-walled carbon nanotubes (MWCNTs) adsorbent experiments was performed to investigate the removal of nickel ions from aqueous solution. Various parameters such as aeration time, sodium dodecyl sulfate and MWCNTs concentrations, pH, surfactant, frother concentrations and airflow rate were tested to determine the optimum flotation conditions. Sodium dodecyl sulfate was used as collectors. Ethanol was used as frother. In the airflow of 150 mL/min and after 5, 15, 30, 60, 90 and 120 min of ion flotation with MWCNTs adsorbent, the efficiency of nickel removal was 14%, 24%, 33%, 38%, 44% and 48%, respectively. The maximum reduction in the concentration of nickel occurs at 30 mg/L concentration (with removal efficiency of 71.7%). This method reduces the time to reach equilibrium point and increases the minimum concentration to adsorb. The results show that the combination of ion flotation method and adsorption with MWCNT works well for reduction in the concentrations of compounds such heavy metal ions.

Keywords: Multi-walled carbon nanotubes; Industrial wastewater; Nickel; Ion flotation

1. Introduction

Industrial effluents loaded with heavy metals are hazardous to humans and other forms of life [1]. The presence of heavy metals in the aquatic environment has been of a great concern because of an increase in discharge, their toxic effects, and other adverse effects on receiving water [2]. Heavy metals like cadmium, zinc, lead, and nickel may have general toxic effects on the human organism and plant metabolism even in the presence of low concentrations [3]. Nickel is a toxic metal ion present in wastewater, which can cause vomiting, chest pain, and shortness of breath, damage to lungs and kidneys, gastrointestinal distress, pulmonary fibrosis, renal edema, and skin dermatitis [4]. Epidemiological studies have associated exposure to nickel compounds to elevated incidence of cancer in the respiratory tract, such as nasal and lung cancer [5]. Ni^{2+} can be found mainly in wastewater from electroplating, electronics, and metal cleaning industries and widely used chemical for the preparation of industrial and household products, but inhalation or ingestion of nickel(II) induces multiple toxic effects in both humans and animals. Nickel compounds can enter the body through inhalation, ingestion, and dermal adsorption [6].

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Various techniques have been employed for the treatment of heavy metals, including precipitation, solvent extraction, reverse osmosis, ultrafiltration, adsorption, biosorption, ion exchange, electrodialysis, membrane separation, and adsorption gas bobble separation [7–10].

Ion flotation may be an alternative method to remove heavy metal ions from wastewaters. The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surface active agents (surfactants) and subsequent removal of these hydrophobic species by air bubbles [11]. A typical surfactant molecule such as those used in this study consists of a polar ionic head and non-polar hydrocarbon chain. Attachment of the polar head group to a metal ion exposes the non-polar, hydrophobic section of the surfactant into the solution. When air bubbles are introduced into the flotation cell, the metal ion-surfactant assemblies are collected by the air bubbles due to the favored interactions between the exposed hydrocarbon chains and the air bubbles [12]. Therefore, these surfactant molecules are also called collectors in the flotation terminology. The air bubbles laden with the metal ions float to the surface and are removed as a froth, which is rich in metal content [13]. The size of the air bubbles in a flotation cell should be fine (in the order of a few hundred micrometers) to present sufficient surface area for collection. The reagents that control the size of the bubbles by reducing the air/water interfacial tension are called frothers. Some common flotation frothers are methyl isobutyl carbinol (MIBC), ethanol, methyl ethers, and polypropylene glycol. Some commercial frothers may have both frothing and collecting properties [11–13].

Ion flotation has been used in order to recover numerous heavy metal ions such as precious metals from leaching liquors. Nevertheless, these techniques present serious problems when treating great volumes of effluents in relatively short periods, making it necessary to develop a highly efficient and selective system, with low investment costs. An innovative technique could help in solving this problem [11–14].

Carbon nanotubes (CNTs) are a novel and interesting carbon material that combined with ion flotation process, first found in 1991 by Iijima. CNTs are formed by rolling sheets of graphite-like carbon, creating hollow tubes. They are categorized based on the number of carbon layers assembled together: single-walled (SW), double-walled (DW), and multi-walled (MW). Because of its large specific surface area and small, hollow, and layered structures, multi-walled carbon nanotubes (MWCNTs) have been investigated as promising adsorbents for various metal ions and can easily be modified by chemical treatment to increase their adsorption capacity [15–20].

The objective of the present study was to investigate the adsorption capability of MWCNTs combined with ion flotation process for the removal of nickel ions from aqueous solutions under different experimental conditions. In addition, investigate the parameters that influence the separation efficiency, such as contact time, pH, and dose of MWCNTs, surfactant, and initial metal concentrations. Also, this study aims at determining isotherm model and kinetic models for this system.

2. Materials and methods

2.1. Materials

Sodium dodecyl sulfate (SDS), C_2H_5OH, and nickel standard stock solution were used as the surfactant, frother, and the source of nickel ion, respectively. The nickel standard stock solution, SDS, H_2SO_4, and NaOH were purchased from Merck, Germany.

2.2. Preparation of materials

Atomic adsorption spectroscopy grade metal solution of Ni concentration 1,000 ± 2 mg/l (Merck) were diluted in ion-free double distilled water to obtain standard solutions with concentrations ranging from 10 to 50 mg/L. MWCNTs (20–40 nm) of 95% purity, length 1–10 μm, and number of walls 3–15 were purchased from Research Institute of Petroleum Industry (Tehran, Iran). Raw MWCNTs were soaked in concentrated nitric acid at 120°C for 2 h and then washed with distilled water until the filtrate's pH value reached 7.0. The aim of this procedure was not only to purify the MWCNTs but also to modify the surface of MWCNTs with functional groups. Due to the intermolecular force, the MWCNTs of different sizes and directions form an aggregated structure.

2.3. Procedure section

Nickel removal was done by three processes: MWCNTs adsorption, ion flotation, and ion flotation with MWCNTs adsorption. The ion flotation experiments have been performed using a home-built flotation vessel as visualized in Fig. 1. The flotation vessel was built up with an inner diameter of 10 cm and a height of 90 cm; a glass frit has been used to obtain a homogeneous dispersion of the gas feed from the bottom of the glass vessel. The airflow rate was 150 mL/min in most experiments. The MWCNTs dosage effects on nickel ion adsorption were carried out by adding 0.5–3 g of treated MWCNTs to solution. Each test solution was prepared by combining the required amount of nickel stock solution, SDS stock solution, MWCNTs, and the necessary frother or sodium sulfate stock solution with distilled water to make up 0.7 L of solution volume, filling approximately half of the column.

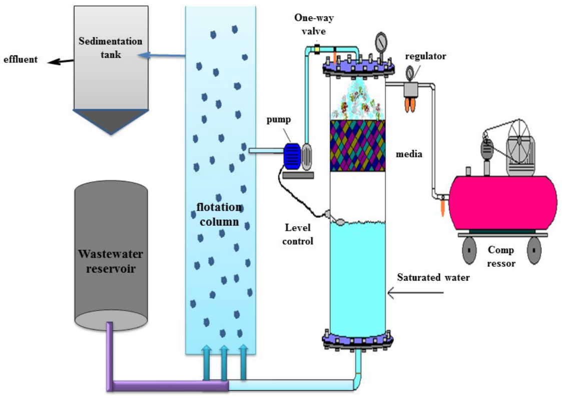

Fig. 1. Schematic of ion flotation system combined with MWCNTs adsorbent process.

The solution was stirred for approximately 15 min to ensure consistent mixing of all reagents, and pH values were adjusted by the addition of diluted NaOH (1 N TitriPUR, Merck) under stirring; the pH was measured using a pH meter (WTW microprocessor pH meter). To assess the effect of parameters, several series of experiments were planed by variation of: (a) aeration time (5–60 min); (b) nickel ion concentration (10, 15, 20, 30, and 50 mg/L); (c) pH (2–12); (d) SDS concentrations (1.47, 4.41, 5.88, and 7.35 g/L); (d) MWCNTs concentrations (0.5, 1, 2, and 3 g/L); and (e) addition of ethanol (0.8%).

Concentration of nickel, remaining in solution as the residual metal after ion flotation combined with MWCNT, was determined using atomic adsorption spectrophotometer (Varian- AA240, USA). The limit of detection for this method was 0.1 mg/L. Analyses were done on triplicate samples. The average uncertainties were about 5%. Controls comprised adsorbent in double-distilled water blank and adsorbent-free nickel solutions.

2.4. Characterization of MWCNTs

The morphology of these products was investigated by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), fourier transform infrared (FTIR) spectroscopy, and their X-ray diffraction (XRD) patterns that were taking place on a Panalytical X'pert PRO XRD using Cu Kα radiation.

3. Results and discussion

3.1. MWCNTs characterization

Figs. 2(A) and (B) display the SEM and TEM images of oxidized MWCNTs. As can be observed, the oxidized MWCNTs have very smooth surfaces and cylindrical shapes with an external diameter of 10–25 nm. The structure of MWCNTs is further confirmed by the XRD tests. The results are showed in Fig. 2(C). The pattern of the MWCNTs shows a high intense peak at 25.2° and 2θ = 44.0°; these peaks show a downward shift, which is attributed to an increase in the sp 2 C=C layers spacing. Fig. 2(D) shows the typical FTIR spectra of oxidized MWCNTs. The spectra indicate intensive bands at wave number 3,400 cm^{-1}.

3.2. Effect of aeration time and Ni^{2+} concentration on Ni^{2+} removal by ion flotation with MWCNTs

This study investigates the efficiency of nickel removal from contaminated water using ion flotation combined with MWCNT as adsorbent. At every stage of this study, 700 mL

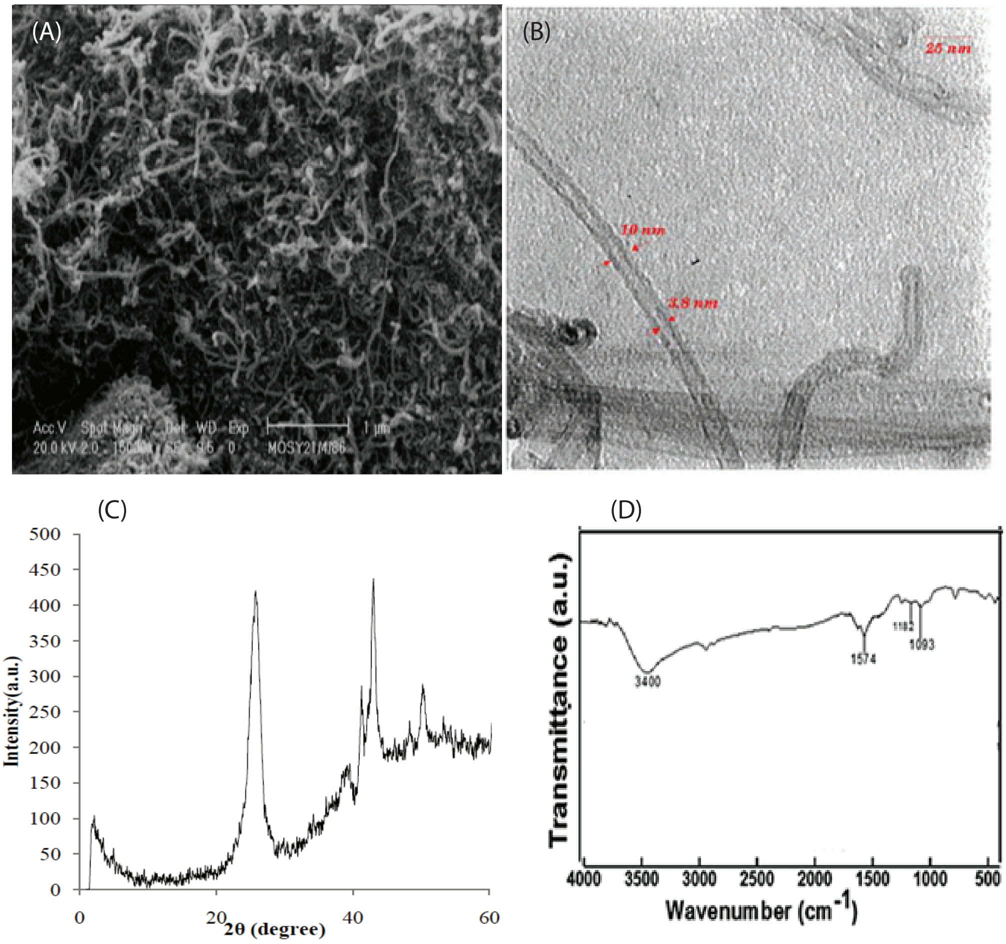

Fig. 2. (A) SEM micrographs of MWCNTs, (B) TEM micrographs of MWCNTs, (C) XRD of MWCNTs, and (D) FTIR of MWCNTs.

artificial wastewater containing nickel in concentrations of 10, 15, 20, 30, and 50 mg/L was prepared. According to other studies as well as the initial study, SDS at a concentration of 3 times the molar concentration of nickel as the collector and ethanol at a concentration of 0.8% were added to the solutions above; then, aeration was performed for 60 min with 150 mL/min flow, and MWCNTs adsorbent was 2 g/L in concentration and pH 8. Fig. 3 shows the removal of nickel at pH 8 and air pressure of 1.1 atm. As seen in Fig. 1, the maximum reduction in the concentration of nickel occurs at 30 mg/L concentration (with removal efficiency of 71.7%). In the airflow of 150 mL/min and after 5, 15, 30, 60, 90, and 120 min of ion flotation with MWCNTs adsorbent, the efficiency of nickel removal was 14%, 24%, 33%, 38%, 44%, and 48%, respectively.

Increasing the initial concentration of nickel raised its concentration at the output, but the removal efficiency was also increased, so that the highest concentration and thus the highest removal efficiency 71.5% were achieved at the concentration of 30 mg/L of nickel ions. In a study by Ulewicz et al. [21] on the effect of concentration on the flotation process of Cd^{2+} and Zn^{2+}, it was observed that increasing the metal ions concentration from 0.3×10^{-4} to 2×10^{-4} mol/L improved ion flotation efficiency and reduced the concentrations of zinc and cadmium in the effluent, means that increased concentration leads to an increase in removal efficiency. The impact of this process on the removal of zinc was more than cadmium Basically, as the atomic diameter of a metal increases, ion contact of anionic detergent with heavy metal is also increased; thus, the efficiency of ion flotation is improved. The results show that this method is more efficient for removing high concentrations of heavy metals with more atomic diameter.

Tavallali et al. [22] in a study on the floatation of metal cations with anionic detergents concluded that increasing initial concentration of metal ion up to a certain level will increase the removal efficiency of metal and explain it as a principle in ion flotation process. However, increased concentration of given ion doesn't mean to increased demand for collector material (anionic detergent) that leads to the production and waste of froth and increase in costs. Therefore, it has been suggested that it is better using ion floatation method to remove medium to low concentrations of metal ions [23]. Therefore, in this study, ion flotation method combined with MWCNTs adsorbent was used to increase the efficiency of nickel removal at higher concentrations (up to 30 mg/L). With increasing the initial concentration of metal ions, the time to reach equilibrium in the adsorption of ions on the surface of MWCNTs was increase. Over time, unoccupied active adsorption sites on the adsorbent surface would gradually decrease, and it continues to reach equilibrium. After reaching equilibrium, adsorption level has not changed over time, and thus, adsorption and desorption level will be equal.

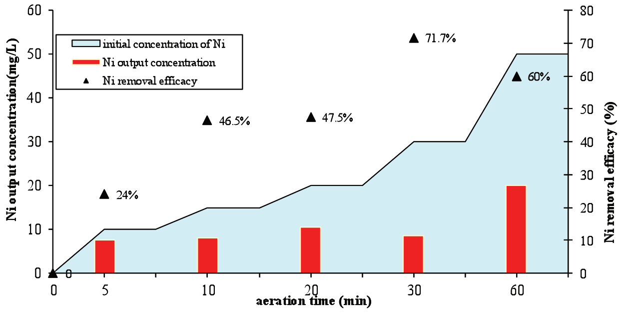

Fig. 3. Effect of aeration time and initial nickel concentration on removal efficacy.

Increased concentration of nickel has two considerable effects on adsorption. Increased concentration of nickel, on one hand, increases the possibility of collision between ions and active adsorption sites and, on the other hand, provides sufficient propulsion force for the penetration of nickel ions into the adsorption sites on nanotubes. Both above effects lead to increased adsorption by increasing the concentration of ions [24]. With increasing concentration of metal ions, active sites on the CNT saturate and thus decrease the adsorption capacity of Ni^{2+}. On the other hand, increased retention time until 30 min increases the removal efficiency of nickel, and then removal efficiency starts to decline. It indicates increased adsorption speed during initial minutes, but over time and saturation of active sites, the time of equilibrium between adsorption and nickel ion arrives, and then the output concentration will increase. Fig. 3 shows the effect of active sites' saturation after 30 min. In a study carried out by Gupta et al. [25], the time of equilibrium between active adsorbent sites and nickel ions was determined at 50 min. This time point came to 30 min by simultaneous application of ion flotation process with MWCNTs adsorbent. This method reduces the time to reach equilibrium point and increases the minimum concentration to adsorb.

3.3. Effect of pH on Ni(II) removal by ion flotation process combined with MWCNTs

Another parameter affecting the ion flotation process control and nickel adsorption by the MWCNTs is pH of the solution. In this study, the effect of pH 2, 4, 6, 8, 10, and 12 on the ion flotation process by MWCNTs was studied at different concentrations and different types. According to Fig. 4, efficiency of nickel removal by ion flotation process at pH 10 was 72%, and also at pH 2, 4, 6, 8, and 12, the removal efficiencies were 20%, 33.5%, 52%, 76%, 74.5%, and 69%, respectively. The removal efficiency of ion flotation process using MWCNTs at pH within 2–12 was 30%–89%, where the removal efficiency of ion flotation system using SDS detergent was improved by increasing the pH.

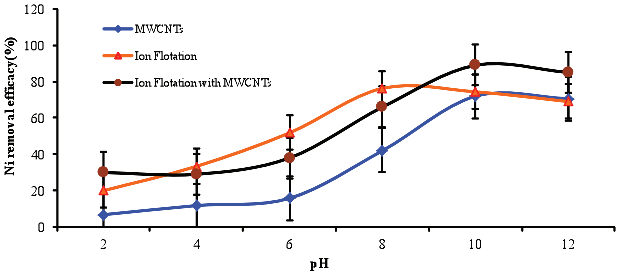

Fig. 4. Effect of pH on adsorption of Ni(II) on oxidized MWCNTs by ion flotation process.

As can be seen in Fig. 4, nickel adsorption is dependent on pH values. Adsorption is well done at pH higher than 6 and less than 11. It is while, within very acidic (2–6) and alkaline (10–12) pH, removal efficiency of the metal was not favorable. According to Fig. 4, the maximum efficiency of nickel removal by ion flotation method was obtained at pH 8. It is despite the fact that ion flotation method alone has the highest efficiency (76%) at pH 8. Nickel adsorption at pH 3–7 rises slowly. By increasing the pH from 7 to 10, the adsorption level shows a sudden sharp rise.

In this pH, both precipitation and adsorption process interfere in nickel removal. So that the maximum adsorption occurred at pH 10, because H^+ value decreases at higher pH and most of Ni^{2+} are precipitated as hydroxide or adsorbed by MWCNTs. According to the study of Liu and Doyle [26], the adsorption of Ni^{2+} and Zn^{2+} increases with increasing pH in the range of 2–8, and it reaches to its maximum value in the range of 8–11 and then decreases at pH 12 [27].

The effect of increasing pH leads to the increased efficiency of nickel removal for three reasons: (1) change in surface charge of MWCNTs and increase in its ionization level; (2) production of different species of nickel at different pH; and (3) effect on the SDS and frother material. Increase in pH to a range of 8–10 adds on the surface ionization of MWCNTs. At higher pH, MWCNTs' surface will have a greater negative surface charge, thus increasing the electrostatic attraction increase the remove of nickel. Therefore, it is expected the highest removal of Ni^{2+} to occur at a pH between 8 and 10 [28]. pH 8–10 leads to increase the number of negatively charged sites such as SO^- and hydrolyzed cationic sites such as ($-COOH^{+2}$) groups, carboxylic group, phenolic ($-OH^{+2}$), and chromic on MWCNT and thus increase the adsorption of cationic compounds and growth affinity to Ni^{2+}. Additionally, the surface of active CNT at alkaline pH has agent groups from oxygenated compounds such as COOH, –OH, and –C=O that not only increase dispersion level of nanotubes but also increase nickel adsorption on the surface of these agent groups. Also, the presence of these agent groups increases the negative electric charge on MWCNTs surface and connects oxygen atoms to the metal ions resulting in the increased cationic exchange capacity. At high pH, various species of nickel are produced [29,30]. On the other hand, the amount of proton (H^+) production in SDS frother material decreases by increasing the pH and then facilitates the binding of air bubbles metal ions such as Ni^{2+} to them and finally increases the removal efficiency of ion flotation [31].

In a study by Ulewicz et al. [21], both zinc and cadmium was removed to a greater amount by increasing the pH from 4 to 8; so that up to 90% Zn^{2+}, 10% $[Zn(OH)]^+$, up to 35.15% Cd^{2+}, and 5% $[Cd(OH)]^+$ are produced from the hydrolysis of Zn^{2+} at pH 8.

According to the study of Rujirawanich et al. [29], it was revealed that nickel ion can exist in solution in the form of Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$, and $Ni(OH)_3^-$. In pH < 8, Ni^{2+} is the dominant species of nickel in the solution. At pH < 8, adsorption of metal ions might be increased due to the formation of hydrolysis products such as $Ni(OH)^+$ and $Ni(OH)_2$. Thus, increasing the adsorption of nickel at higher pH could be due to reduced competition between H^+ and Ni^{2+} in adsorption sites on MWCNTs. As the solubility of these compounds reaches its minimum at this state, therefore, Ni^{2+} removal will be maximum. However, metal ions such as Ni^{2+} at pH 12 are often in the form of $Ni(OH)_3^-$. This compound would greatly compete with OH^- to be adsorbed on a particular position of the CNT, so it will reduce removal efficiency. In addition, creating a strong negative charge on CNTs increases the electrostatic repulsion of $M(OH)_3^-$ [30] .

In general, increase in the pH of the solution leads to the increased adsorption of metal cations, such as Cd^{2+}, Pb^{2+}, Ni^{2+}, and Cu^{2+} on the adsorbent anionic sites, and on the other hand, increased pH will decrease surface positive charge in MWCNTs and thus reduce the repulsion of cationic compounds [32]. Conversely, at acidic pH (less than 6), the maximum adsorption capacity of cationic compounds is reduced.

3.4. Effect of SDS on Ni(II) removal by ion flotation combined with MWCNTs

The use of surfactants such as SDS helps the formation of dispersed colloids of CNTs in a non-covalent approach. The repulsive force applied by surfactants on the surface of nanotubes dominates the van der Waals gravity force between carbon layers and then causes their stable dispersion and eventually increases the adsorption efficiency. In this study, the SDS was used to remove nickel at the concentrations of 1.47, 4.41, 5.88, and 7.35 g/L during the process of ion flotation with MWCNTs adsorbent, which were, respectively, equal with a ratio of SDS/Ni, 1: 1, 3: 1, 4: 1, and 5: 1. For this purpose, 700 cc solutions containing nickel at the concentration of 30 mg/l were supplied and entered into the ion flotation reactor with MWCNTs adsorbent with 2 g/l concentration, 150 mL/min airflow, and pH 8.

As seen in Fig. 5, if the aeration of synthetic wastewater containing 5.88 g/L SDS is done, then the removal efficiency of nickel after 5, 15, 30, 60, 90, and 120 min would be 35.5%, 50%, 70%, 78%, 80%, and 86%, respectively. In the above circumstances, and with the increasing concentration of SDS in the 7.35 g/L, removal of nickel would be 26%, 48%, 65%, 74%, 77%, and 79%, respectively. With the concentration 4.41 g/L SDS, removal of nickel would be 29%, 45%, 61%, 70%, 75%, and 77%, respectively. According to Fig. 5, with increasing SDS concentration ratio of 4 to 1 SDS/Ni, Ni removal efficiency increases. As the same condition after 120 min of flotation, nickel removal efficiency of 74% at a concentration 1.47 g/L SDS (SDS to Ni^{2+} 1:1) to 77% at a concentration

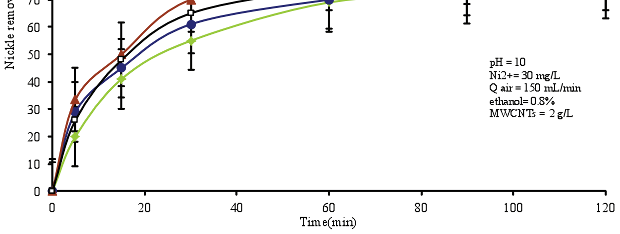

Fig. 5. Nickel removal efficiency by oxidized MWCNTs as a function of contact time and SDS concentration.

4.41 g/L SDS (SDS to Ni^{2+} 3:1) and 79% at a concentration 7.35 g/L SDS (SDS to Ni^{2+} 5:1) and 86% at a concentration 5.88 g/L (SDS ratio of Ni^{2+} 4:1) SDS increases. The maximum removal of nickel was obtained in concentration 5.88 g/L SDS at a retention time of 120 min.

According to the study Zamboulis et al. [23], the maximum removal efficiency of metal ions occurs when the ratio of the collector to the ion is more than stoichiometric level (1:1). The results of Zamboulis et al. [23] showed in the 3:1 ratio of SDS to Ni^{2+}; the maximum removal of nickel is 99%, but the foam production was also very high.

Yuan et al. [33] obtained removal efficiency of lead, copper, and nickel ions (cadmium, 1×10^{-2} mol/L; copper, 8×10^{-2} mol/L; and lead 2×10^{-2} mol/L) in 3:1 ratio of biosurfactant to metal to be 90%, 81%, and 71%, respectively. The reason for metal ions separation was divalent metal ion binding to the carboxylate groups. In the study of Ulewicz and Walkowiak [34], at 10:1 ratio of surfactant to the metal ion, removal efficiency was 89% for Cd and 92% for Zn.

Another study by Maciejewski and Walkowiak [35] on the removal of cesium, strontium, and barium from synthetic wastewater used ethers compounds as the collector and the results showed that Sr was removed about 98% at 5:1 molar ratio of metal ion to collector. Yamashita et al. [36] used diethyl dithio phosphoric acid (Edtp) and diphenyl dithio phosphoric acid (Pdtp) for flotation of metal ions. The results showed that the highest removal efficiency was obtained at 3:1 ratio of Edtp to Cd. However, if the collector Pdtp is used, then the highest Cd^{2+} removal efficiency was obtained at 2:1 ratio of collector to metal. The results of all these studies are similar to the present study.

The presence of benzene rings in MWCNTs molecule is among the main reasons for dispersion of adsorbent molecules in aqueous environment and increase in nickel removal process. Under such circumstances, the active surface of MWCNTs sorbent was increased. Finally, the presence of surfactant inhibit the adsorption and accumulation of MWCNTs on each other so that its colloidal stability in the suspension increase in the long term [36,39].

It should be noted that values higher than 30 mg/L of nickel and concentrations over 5.88 g/L of SDS are restricting. Adding ethanol as the frother material in concentrations of 0.8% to the above reactor increases the removal efficiency of nickel up to 92%. Adding this compound on the right combination, values can appropriately fix Ni–SDS and increase the ability of flotation. Getting smaller and stability of air bubbles in the solution are among other positive effects of frother materials on ion flotation process. Adding excessive alcohols in flotation process leads to the excess fixation of collector species of metal ions, so that their connection to the air bubbles will be disrupted. Also, frother materials tend to stick to the gas–liquid interface, so if their concentration increases, then they would occupy the adsorption sites of Ni–DS to the bubbles and prevent from flotation of desired metal ion [36–39].

3.5. Effect of MWCNTs concentrations on Ni(II) removal by ion flotation method

Fig. 6 demonstrates the effect of different concentrations of MWCNT on the ion flotation process with MWCNTs adsorbent. In a study by Pyrzyńska and Bystrzejewski [38] on the adsorption of copper and chrome ions from aqueous environments, it was found that the efficiency of CNTs to remove metal ions are significantly higher than active carbon, and their adsorption capacity is also higher [38]. Therefore, MWCNT activated by nitric acid was used in this study. El-Sheikh [39] studied the effects of MW nanotubes oxidation using nitric acid and their application in the removal of heavy metals from aquatic environments.

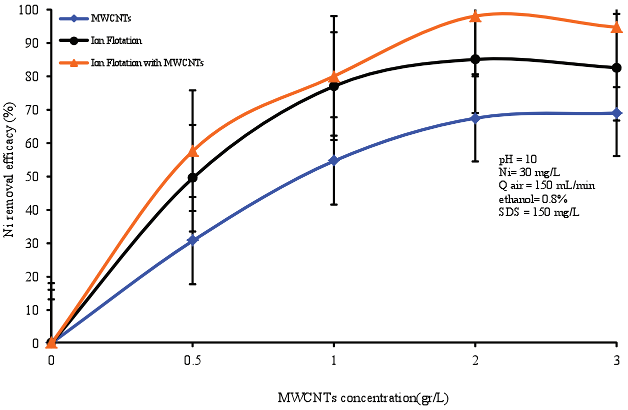

Fig. 6. Effect of different concentrations of MWCNT on Ni removal efficacy.

The results of his study showed that the oxidized nanotubes are much more efficient in removing heavy metals rather than its not-reduced form. So we can say that oxidation of CNTs by nitric acid can have a dramatic impact on their performance. Chemical interaction between the metal ions and the surface functional groups of CNTs is the major sorption mechanism.

Use of oxidizing agents leads to open the pores and fractures in five- and seven-sided structures of CNTs; therefore, it will improve their dispersion and increase the oxygenated agent groups such as –COOH and –OH on the surface of CNTs. These groups increase negative charge on the carbon's surface, and oxygen atoms of agent groups give their sole electron pairs to metal ions, thus increase their cation exchange capacity. Investigating the effect of the amount of sorbent used to adsorb the pollutant showed that increasing the sorbent mass from 0.5 to 3 g will increase the removal of color from 30.7% to 98% [37]. The highest removal percentage was related to the concentration.

3.6. Adsorption kinetic of nickel by ion flotation combined with MWCNTs

The results of adsorption-time study for nickel ions are shown in Fig. 7. To determine the reaction speed constant, pseudo-first-order and pseudo-second-order equations within the range of 10–250 min were used. Pseudo-first-order equation is as follows:

$$dp/dt = k_1(q_e - q_t) \tag{1}$$

where q_e and q_t are the amounts of nickel ions adsorbed per unit mass of adsorbent MWCNTs in equilibrium state and at time t (mg/g dry weight of adsorbent), and k_1 is the reaction

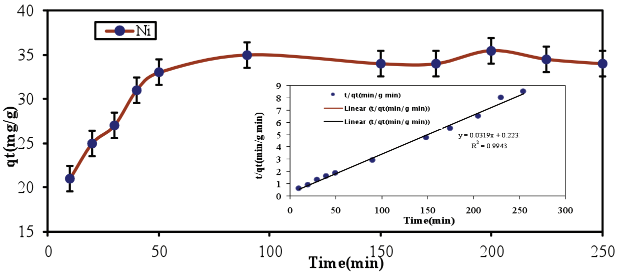

Fig. 7. Pseudo-second-order kinetics plots for nickel adsorption by ion flotation with MWCNTs at pH 8.

speed constant from first-degree equation (min^{-1}). In the boundary conditions for $t = 0$ and $q = 0$, Eq. (2) can be true:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \tag{2}$$

There is a linear direct relationship between $\log(q_e - q_t)$ and t in the adsorption process with first-degree equation. The pseudo-second-order equation assumes that the adsorption mechanism is a chemical process and the occupation of adsorption sites is proportional to the square number of unoccupied sites. Chemical reaction rate constant in the quadratic adsorption mechanism is as the following equation (Eqs. (3) and (4)).

k_2 is the speed constant of the quadratic equation (g/mg.min). Considering the boundary conditions for $t = 0$ and $q = 0$, the equation becomes as below:

$$dp/dt = k_2(q_e - q_t)^2 \tag{3}$$

k_2 reaction speed constant can be obtained from the intercept point of the quadratic equation:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \tag{4}$$

There is a linear relationship between t/q_t and t in the quadratic equation. The relationship between $\log(q_e - q_t)$ vs. time t during the studied times is not linear, indicating the existence of more than one adsorption mechanism. While the plot of t/q_t vs. t follows a linear pattern, Fig. 8 shows the adsorption process by the quadratic equation ($R^2 = 0.999$, $p < 0.0001$).

q_e and k_2 for Ni(II) from the linear regression curve of t/q vs. t are equal to 6.80 mg/g and 0.0071 g/mg, respectively.

To determine the adsorption capacity of MWCNTs in the removal of nickel ions during the ion flotation process, the initial concentration of 20–400 mg/L nickel was used. Maximum adsorption capacity of MWCNTs have been studied by adsorption isotherm. Two different models of isotherms (Langmuir and Freundlich) were used. The Langmuir model assumes that all adsorption sites have equal bond energy, and each adsorption site is necessarily bond to one ion. Langmuir isotherm equation is as follows:

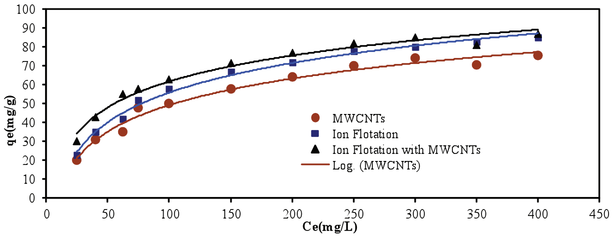

Fig. 8. Adsorption isotherms of Ni(II) by ion flotation with MWCNTs at pH 8.

$$q_e = (q_m bC_e)/1 + bC_e \tag{5}$$

The linearized form of Langmuir isotherm is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{mb}} + \frac{C_e}{q_m} \tag{6}$$

where q_e is the equilibrium adsorption capacity in mg (metal ion) to g (adsorbent); C_e the equilibrium concentration of metal ions in mg/L; q_m the maximum amount of adsorbed metal ions in mg (adsorbed metal ion) to g (adsorbent); and b is a constant reference to the bond energy in L/mg. Constants b and q_m, respectively, come from the intercept point and slope of the linear curve of C_e/q_e vs. C_e.

Freundlich model is based on the reversibility of the heterogeneous adsorption process. Freundlich isotherm equation is as follows:

$$q_e = K_f C^{1/n} \tag{7}$$

The linearized form of Freundlich isotherm is:

$$\log q_e = \log K_f + 1/n \log C_e \tag{8}$$

where q_e is the equilibrium adsorption capacity in mg (metal ion) to g (adsorbent); C_e the equilibrium concentration of metal ions in mg/L; k_f is a constant implying to the adsorption capacity in mg/L; and n is constant related to the adsorption intensity.

Constants n and k_f, respectively, come from the linear curve of $\ln q_e$ vs. $\ln C_e$.

The relationship between the initial concentration of nickel and adsorption capacity was examined by the above two models. Adsorption coefficients (b, q_m, n and K_f) and linear regression coefficient (R^2) for both Freundlich and Langmuir modules are in Table 1.

Table 1
The parameters for Langmuir and Freundlich isotherm models of Ni(II) adsorption by ion flotation with MWCNTs

Modules		MWCNTs	Ion flotation	Ion flotation with MWCNTs
Langmuir	q_m (mg/g)	60.6	86.2	94.33
	b (L/mg)	0.035	0.025	0.054
	R^2	0.993	0.996	0.988
Freundlich	K_f	6.38	8.12	12.5
	n	2.35	2.42	2.85
	R^2	0.962	0.969	0.966

The results show that the correlation coefficients for nickel ions adsorption, for MWCNTs, ion flotation, and ion flotation with MWCNT adsorbent are, respectively, 0.993, 0.996, and 0.988 which represents that Langmuir model is desirable. As can be seen, the maximum adsorption of Ni^{+2} ions is obtained by ion flotation method with MWCNT adsorbent and detergent SDS. The presence of MWCNTs adsorbent together with the detergent SDS increases the collision between detergents SDS and overcome the resistance to mass transfer (acceleration of mass transfer). These conditions increase the removal of nickel by adsorbent and eventually increased adsorption capacity. This could be due to the particle size distribution, surface area, morphology, surface structure etc. Langmuir equation is true for the study of dynamic balance on homogeneous surfaces. But Freundlich equation is often applicable to heterogeneous surfaces. Liu et al. [27] showed that Pb^{2+} adsorption on unmodified CNTs is proportional to Freundlich equation. Also, nickel adsorption on oxidized MWCNT followed the Langmuir equation. Note that the value of regression coefficient (R^2) for Langmuir isotherm is closer to 1, the adsorption of nickel by MWCNTs using Langmuir isotherm estimates better than Freundlich isotherm. Langmuir model assumes that adsorbing materials are connected to a certain points on the adsorbent surface and a single-layer adsorption process occurs and there will be no reaction between adsorbing molecules. It is known that the adsorption isotherm coefficients for nickel in the presence of SDS are much higher than without SDS. According to Table 1, the maximum adsorption capacity of nickel on MWCNTs with bonded SDS is greater than the adsorption capacity of MWCNTs alone. The adsorption capacity of MWCNTs in the presence of SDS will be higher than other cases [26].

4. Conclusions

The MWCNT/ion flotation processes were used for continuous nickel removal. The results can be summarized as follows:

- Increasing the concentration of nickel metal has increased its concentration at the outlet of the ion flotation reactor, but the removal efficiency of nickel rose.
- The highest efficiency of nickel concentration reduction 71.1% occurred at concentration 30 mg/L.
- At the lowest concentration of Ni^{2+} (10 mg/L), the effect of changing pH on the removal efficiency is not high. But at high concentrations (50 mg/L), pH has a significant impact on the removal of Ni^{2+} from the solution. When the pH is increased from 2 to 10, the removal will be increased regularly. Generally, increasing the pH up to 10 leads to better results in the removal of nickel ions and thus increases the adsorption capacity.
- Surfactants such as SDS at molar concentration of 0.0204 mM, which is equivalent to 4:1 SDS to Ni^{2+} (5.88 g/L), help the better formation of dispersed colloids of CNTs and the efficiency of ion flotation reaches to 86%.
- The concentration 2 g/L of MWCNT adsorbent increases the removal efficiency to 98%.
- Langmuir isotherm well indicated the effect of MWCNT adsorbent on the improvement of ion flotation process and nickel adsorption ($R^2 = 0.996$). Experimental data to study the reaction kinetics indicated that the process of removing nickel follows pseudo second order.

The results show that the combination of ion flotation method and adsorption with MWCNT works well for reduction in the concentrations of compounds such heavy metal ions. The combination of ion floating and adsorption by MWNTs was very easy and simple, and it can be used for environmental samples such as natural water. It can be stated that the method can be used to remove heavy metals and trace elements in environmental samples with satisfactory results.

Acknowledgments

This article is approved by Arak University of Medical Sciences coded 766. I appreciate the research deputy of university, and management of research projects for project funding and all those who without their cooperation, this study was not possible.

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