

# Removal of Cu (II) Ions from Aqueous Solutions with Modified Carbon Nanotubes

Azizi, Reza; Ghadi, Arezou<sup>\*+</sup>

Department of Chemical Engineering, Islamic Azad University, Ayatollah Amoli Branch, Amol, I.R. IRAN

Mahjoub, Soleiman<sup>•</sup>

Cellular and Molecular Biology Research Center, Health Research Institute, Babol University of Medical Sciences, Ganjafrooz Avenue, Babol, I.R. IRAN

**ABSTRACT:** Heavy metals such as copper are known as environmental pollutants and lead to irreversible damage to human health and other living organisms. This study aims to remove copper ions from aqueous solutions using a new adsorbent that includes the carboxylated Multi-Wall Carbon NanoTube (COOH-MWCNT) functionalized with 3-amino-dihydroxy benzo-indeno-furan (MWCNT-f) and in a discontinuous adsorption system. The results showed that MWCNT-f adsorbent can act as an effective adsorbent for the removal of copper ions so the maximum removal efficiency was 90.2% (pH 6, adsorbent mass: 0.3 g, and contact time: 45 min). The kinetic process of copper adsorption onto the mentioned adsorbent was found to fit the Morris-Weber kinetic model. Moreover, the equilibrium adsorption data indicated that Langmuir isotherm covers the equilibrium data with a maximum adsorption capacity of 16.78 mg/g for MWCNT-f. It was found the temperature increase possesses a positive effect on the removal efficiency of ions and it was achieved 95.76% at 50°C. The thermodynamic parameters demonstrated that the adsorption of copper on MWCNT-f, in the studied conditions, was spontaneous and thermosetting. The present study provides a new recyclable and efficient adsorbent for the removal of Cu (II) ions from aqueous solutions.

**KEYWORDS:** Removal efficiency; Copper; Carbon nanotubes; Amino-dihydroxy benzo indeno-furan, Isotherm; Kinetics.

## INTRODUCTION

Nowadays, heavy metal toxicity has become a global problem and it seriously threatens the environment and human health. High concentrations of heavy metals exhibit toxicities and can be lethal for all life forms [1]. These heavy metals which flow into the environment (directly/indirectly) via the process of industrial production and evacuation of urban sewage sludge, in

many parts of the world, have been considered pollutants even at very low concentrations [2]. These materials pollute drinking water resources and lead to biological aggregation of the mentioned elements in the body and consequently genetic mutations, fetal deficiencies, severe poisoning, skin disorders, inflammation of the digestive system, etc [3,4].

---

\*To whom correspondence should be addressed.

+ E-mail: arezoo.ghadi@gmail.com ; a.ghadi@iauamol.ac.ir

Other address: Department of Clinical Biochemistry, School of Medicine, Babol University of Medical Sciences, Babol, I.R. IRAN.

1021-9986/2023/10/3224-3234

11/\$/6.01

Therefore, the removal of such elements from water and wastewater solutions to prevent their aggregation in the body, and decrease environmental pollution is the main goal in this field.

In this regard, different methods exist, including chemical precipitation, ultrafiltration, ion exchange, vacuum-evaporation, membrane technologies, electro-dialysis, reverse osmosis, etc. but, the adsorption method is known as one of the main methods in this field, due to the simpler treatment of large volumes of ion solutions and low cost [5, 6].

In recent years, the adsorbents used to treat wastewater and water resources involve activated carbon, zeolite, bentonite, charcoal ashes, clay, algae, carbon nanotubes, biological materials, etc. [3, 8–10]. Among them, carbon nanotubes (CNTs) possess unique properties. The arrangement of carbon atoms in the wall of these cylindrical structures is exactly the same as the arrangement of hexagonal arrays of carbon in graphite sheets which leads to strong interactions with other molecules/atoms (due to each layer have connected to the underlying layer through weak bonds of van der Waals). Multi-wall carbon nanotubes functionalized with 3-Amino-5a, 10a-dihydroxy benzo [b] indeno [2,1-d]furan-10-one (ADIF), (MWCNT-ADIF), are the sample of these adsorbents that can be used for removing lead ions from aqueous solutions. In this field, *Eyni et al.* showed that lead ions can be desorbed from MWCNT-ADIF up to 92% at pH=3 and the recycled MWCNT-ADIF could be reused for 5 regeneration cycles [11].

Carboxylated multi-walled carbon nanotube (MWCNT-COOH) functionalized with 1-isatin-3-thiosemicarbazone (MWCNT-f) is another sample in this field fabricated by *Jahangiri et al.* to remove lead ions from aqueous solutions. In this study, they applied an orthogonal array design with four factors to assign the significant factors affecting the Pb<sup>+2</sup> uptakes. Based on the results of this study, sorption kinetics was well described by a pseudo-second-order kinetic model for the designed adsorbents (i.e. MWCNT-COOH and MWCNT-f). Moreover, the Langmuir isotherm for MWCNT-COOH and Freundlich model for MWCNT-f was found to best represent the measured sorption data [12].

Nowadays, many theoretical and practical studies have focused on the structure and adsorption ability of carbon nanotubes and nanocomposites [13,14].

Hence, this study aimed to investigate the process of copper adsorption from an aqueous solution by a carbon nanotube treated with HNO<sub>3</sub> and functionalized with 3-amino-dihydroxy benzo-indeno-furan (MWCNT-f). Notably, the experiment was performed in a discontinuous system, so that, the effect of experimental parameters such as pH value, contact time, adsorbent mass, the concentration of ions, and temperature was studied on the adsorption performance. Afterward, the isotherms of Langmuir, Freundlich, Dubinin Radushkevich, and Weber–Morris adsorption kinetics, pseudo-first-order, and pseudo-second-order were used to study adsorption efficiency. Finally, the thermodynamics of the copper adsorption process from an aqueous solution by MWCNT-f was evaluated. Given that, heavy metals such as copper can be absorbed by the carbon nanotubes whether on the surface or inside the holes. Here, Cu (II) ions have been selected to remove from aqueous solutions.

## EXPERIMENTAL SECTION

### Materials

All materials and solvents such as ninhydrin, 3-aminophenol, acetonitrile, thionyl chloride (SOCl<sub>2</sub>), acetone, dichloromethane, and dimethylformamide (DMF) were purchased from Merck Chemical Company. Carboxylated multi-wall carbon nanotubes (COOH-MWCNT) with 10-20nm in outer diameter, 30 micrometers in length, and 95% purity was purchased from the Neturino company. Moreover, Copper (II) nitrate salt (Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O) was purchased from the Mercury chemical company to prepare the copper aqueous solution.

### Preparation of adsorbent

#### Preparation of MWCNT-COOH

200 mg of MWCNT is mixed with 50 mL of HNO<sub>3</sub> on the stirrer (120 °C, 24 h). Afterward, the nanotubes are rinsed with water to reach a pH of 7. Finally, the HNO<sub>3</sub>-treated MWCNT was dried in a vacuum oven at 80-70 °C for 24 h.

#### Preparation of 3-amino dihydroxy benzo-indeno-furan

Ninhydrin and 3-aminophenol (amount of each element: 5.6 mmoles) were dissolved in 100 ml of distilled water (under stirring conditions, 25 °C, 16 h). As follow, the needle-shaped crystals of the 3-amino dihydroxy benzo-

indeno-furan was filtered and then purified by a crystallization process in acetonitrile solvent along with some water [15].

#### Preparation of MWCNT-f

To prepare MWCNT-f, 200 mg of MWCNT-COOH was solved in  $\text{SOCl}_2$  (30 ml) and DMF (1 ml). The mentioned solution was then mixed at 70 °C for 24 h. Afterward, to form the chlorinated acrylate nanotube (MWCNT-COCl), the remaining thionyl chloride was removed by vacuum distillation. Moreover, the 3-amino-dihydroxy benzo indeno-furan solution with a weight fraction of 2.5% in DMF was prepared, then add to the reaction mixture and mixed at 120 °C for 72 h. This mixture was washed several times with solvents of acetone and dichloromethane (at room temperature). Finally, the formed solid black material was dried at 25 °C, for 8 h under vacuum conditions.

#### Adsorption characterization

The Scanning Electron Microscope (SEM, XL30 ESEM, Philips, Germany) was employed to study the morphology and pores size of the adsorbent. Before SEM evaluation, the surface of the adsorbent was coated with a thin layer of gold (Au).

Fourier-transform infrared spectroscopy (FTIR) analysis was also performed by FTIR (Model-ALPHA, Bruker, Germany) spectrometer, to identify functional groups of the adsorbent. Briefly, the sample was prepared in KBr (1 mg in 1g of KBr) and pressed under the pressure of 200 kg/cm<sup>2</sup> for 5 min. Then, the adsorbent was scanned in the wavenumber range of 400–4000 cm<sup>-1</sup>.

To find the thermal stability of the adsorbent, the thermal analysis of the sample was performed by thermogravimetric analysis (TGA) device (PerkinElmer, Inc., UK) with heating the sample from 25 °C to 725 °C under a nitrogen atmosphere and heating rate of 10 °C min<sup>-1</sup> [16].

#### Adsorption experiments

The adsorption studies were performed in discontinuous experiments according to the following procedure.

Step 1) Preparation of 1000 ppm solution containing copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) and distilled water (as mater solution) and then dilution of the prepared solution to obtain copper solutions with different concentrations (50-120 ppm). Step 2) Nitric acid ( $\text{HNO}_3$ , 1M) and sodium hydroxide (NaOH, 1M) were used to adjust pH in the range

of 2-6 (SP21 pH meter). Step 3) The mentioned adsorption systems were stirred to evaluate the effects of contact time (at different time intervals: 5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 min), different values of adsorbent (0.05-0.4 g) and temperatures studied (20, 30, 40, 50 °C). Step 4) The adsorbent and solution were separated by centrifuging the solutions (8000 rpm, 30 min). Step 5) The concentration of the remained copper in the solutions was measured by the atomic absorption spectrometer (Varian, model AA240). Step 6) The adsorption kinetic and isotherm modeling, the study of the effect of temperature and thermodynamics.

Equation (1) was employed to study the removal efficiency (%) of copper by the adsorbent. Equation (2) was also used to study the adsorption capacity of the adsorbent.

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

$C_i$  (mg/L) and  $C_f$  (mg/L) are the initial and final metal concentrations in the solution, respectively.

$$q_t \text{ (or } q_e) = (C_i - C_t \text{ (or } C_e)) \times \frac{V}{m} \quad (2)$$

where:  $q_t$  and  $q_e$  are the adsorption capacity of the adsorbent at a specific time and the state of equilibrium (mg/g) respectively. Likewise,  $C_i$ ,  $C_t$ , and  $C_e$  are the initial, specific time, and equilibrium metal concentrations of metal ions in solution (mg/L).  $V$  and  $m$  are the volumes of the solution (L) and dry weight of the adsorbent (g) respectively.

#### Adsorption kinetics and isotherm modeling

##### Adsorption kinetics

Three kinetic models of Weber–Morris (intra-particle diffusion), pseudo-first-order, and pseudo-second-order, were used to fit the experimental data, study the adsorbate rate, and obtain an insight into the possible reaction pathways of the adsorption process. The non-linear equation and parameters of the mentioned kinetic models were provided in Table 1.

##### Adsorption isotherm

To analyze the experimental equilibrium data and assess the maximum adsorption capacity of the adsorbent, as well as to identify the better adsorption mechanism, the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models were studied. The non-linear and linear mathematical expressions and parameters of the three applied models were given in Table 2.

**Table 1: Adsorption kinetic models studied**

Kinetic model	Equation	Parameters of the kinetic model
Morris-Weber	$q_t = K_{id}(t)^{0.5}$	$K_{id}$ = Intra-particle diffusion rate constant (mg. (g. min) <sup>0.5</sup> )
pseudo-first-order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$ $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	$K_1$ = Pseudo-first order rate constant (min <sup>-1</sup> ) $q_e$ = Equilibrium capacity (mg/g)
pseudo-second-order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	$K_2$ = pseudo-second-order rate constant (g.mg <sup>-1</sup> .min <sup>-1</sup> ) $q_e$ = Equilibrium capacity (mg/g)

$q_t$  (mg/g) = amount adsorbed [at the time (t)]

**Table 2: Adsorption isotherm models studied**

Isotherm model	Non-linear equation	Linear equation	Parameters of the isotherm model
Langmuir	$q_e = \frac{q_m k_L c_e}{1 + k_L c_e}$ $R_L = \frac{1}{1 + k_L c_0}$	$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m}$	$q_m$ = Maximum adsorption capacity (mg/g) $k_L$ = Langmuir constant (L/mg) $R_L$ = Langmuir separation factor (dimensionless)
Freundlich	$q_e = k_F c_e^{\frac{1}{n}}$	$\log(q_e) = \log(k_F) + \frac{1}{n} \log(c_e)$	$k_F$ = Empirical Freundlich constant (min <sup>-1</sup> ) $n$ = Freundlich's exponent which demonstrates severity of adsorption
Dubinin–Radushkevich	$q_e = q_d^{-K_{DR} RT \ln(1 + \frac{1}{C_e})}$ $E_a = \frac{1}{\sqrt{2K_{DR}}}$	$\ln(q_e) = \ln(q_d) - K_{DR} \varepsilon^2$ $\varepsilon = RT \ln[1 + \frac{1}{C_e}]$	$q_d$ = Maximum adsorption capacity (mg/g) $K_{DR}$ = Dubinin–Radushkevich constant related to $E_a$ (mol <sup>2</sup> /kJ <sup>2</sup> ) $E_a$ = The mean of free adsorption energy (kJ/mol)

$c_0$  (ppm) = initial metal concentration

$c_e$  (ppm) = final metal concentration

## RESULTS AND DISCUSSIONS

### Adsorption characterization

#### Morphology of adsorbent

The SEM images of carboxylated and functionalized carbon nanotubes (MWCNT-COOH and MWCNT-f) were shown in Fig. 1 As can be clearly observed in the SEM images, there are many pores throughout MWCNT-f compared with MWCNT-COOH that can lead to increased functionality of this material in the adsorption process. Absorbent particles with an average size of 200 to 500 nm can be seen. Also, the nanoparticles of this absorbent with dimensions less than 10 nm were observed on the surface of the modified absorbents.

#### FTIR spectrum

The FTIR spectra of MWCNT-COOH and MWCNT-f have presented in Fig. 2a The spectra analysis indicated that the absorption band at 1400 cm<sup>-1</sup> (in both spectra), is related to O-H (hydroxyl) groups of acid or alcohol. Moreover, peaks at 1600 and 1740 cm<sup>-1</sup> in the MWCNT-COOH spectrum are related to C-O and C=O of bonded carboxylic on the surface of the MWCNT [17]. The peak in the range of 1600 cm<sup>-1</sup>- 1680 cm<sup>-1</sup>, as well as the new

peak of 3135 cm<sup>-1</sup> for the MWCNT-f spectrum, are also attributed to C=C, C=N, and N-H groups, which confirm the successful attachment of 3-amino-dihydroxy benzo indeno-furan onto the surface of MWCNT-COOH. Fig. 2b shows the structure of the modification route of the MWCNT-COOH and MWCNT-f.

To check the thermal stability of the MWCNT-F, TGA analysis was carried out and compared with MWCNT-COOH and 3-amino-dihydroxy benzo indeno-furan which are shown in Fig. 3. Since MWCNT-COOH is relatively stable in terms of heat, higher weight loss MWCNT-f is related to the elimination of the group attached to the carbon nanotube. As was found from the MWCNT-f thermogram, the bonding of 3-amino-dihydroxy benzo indeno-furan into the MWCNT-COOH has significantly impacted the thermal stability of MWCNT-COOH. Such that, ~30% of the weight loss of MWCNT-f at the temperature of 200 °C to ~540 °C is attributed to the degradation of side-chains of 3-amino-dihydroxy benzo indeno-furan. Observed weight loss from 550 °C to 600 °C is also assigned to the loss of MWCN main chains. It is notable that, weight loss before 100 °C was attributed to the loss of adsorbed water into adsorbent [18,19].

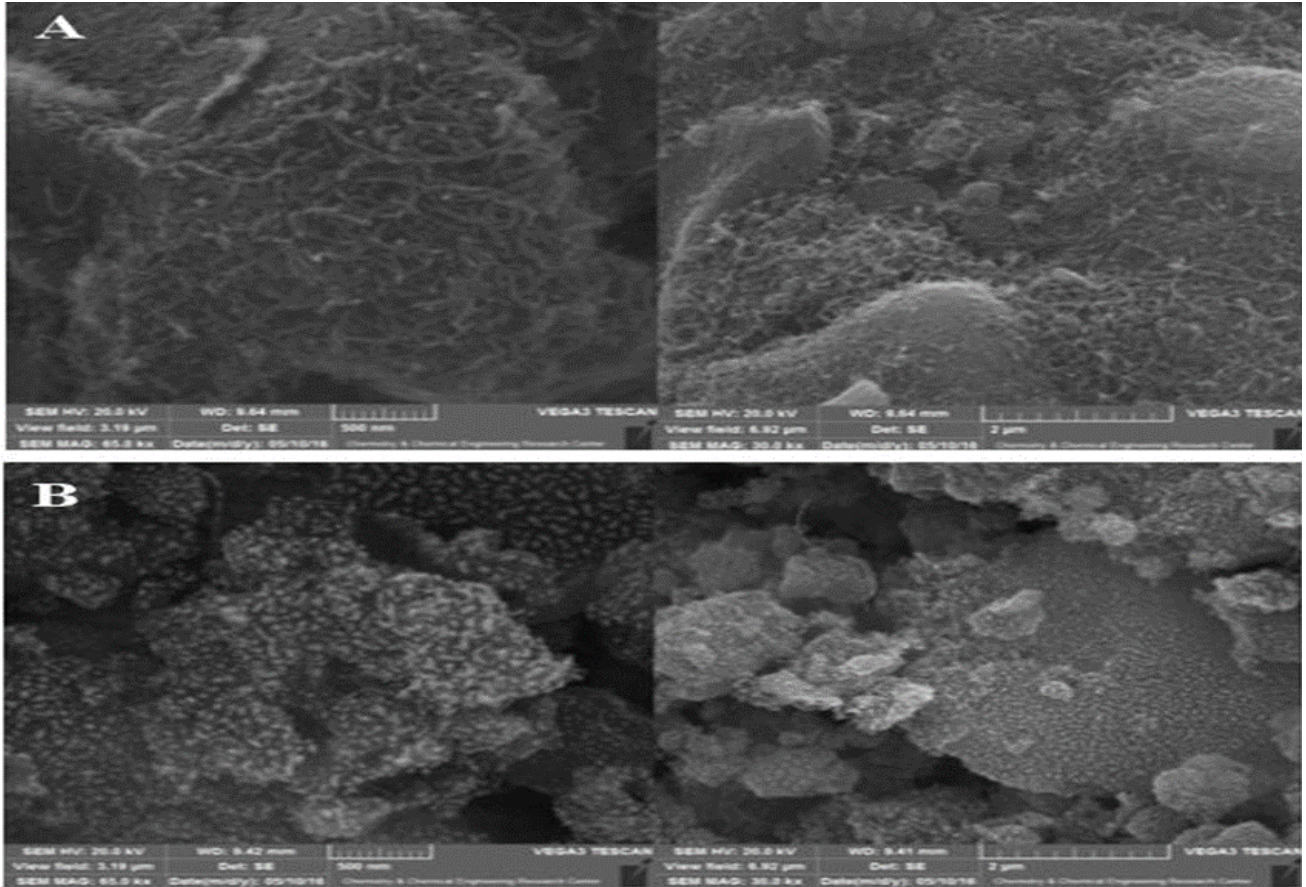


Fig. 1: The SEM images of (A) MWCNT-COOH and (B) MWCNT-f

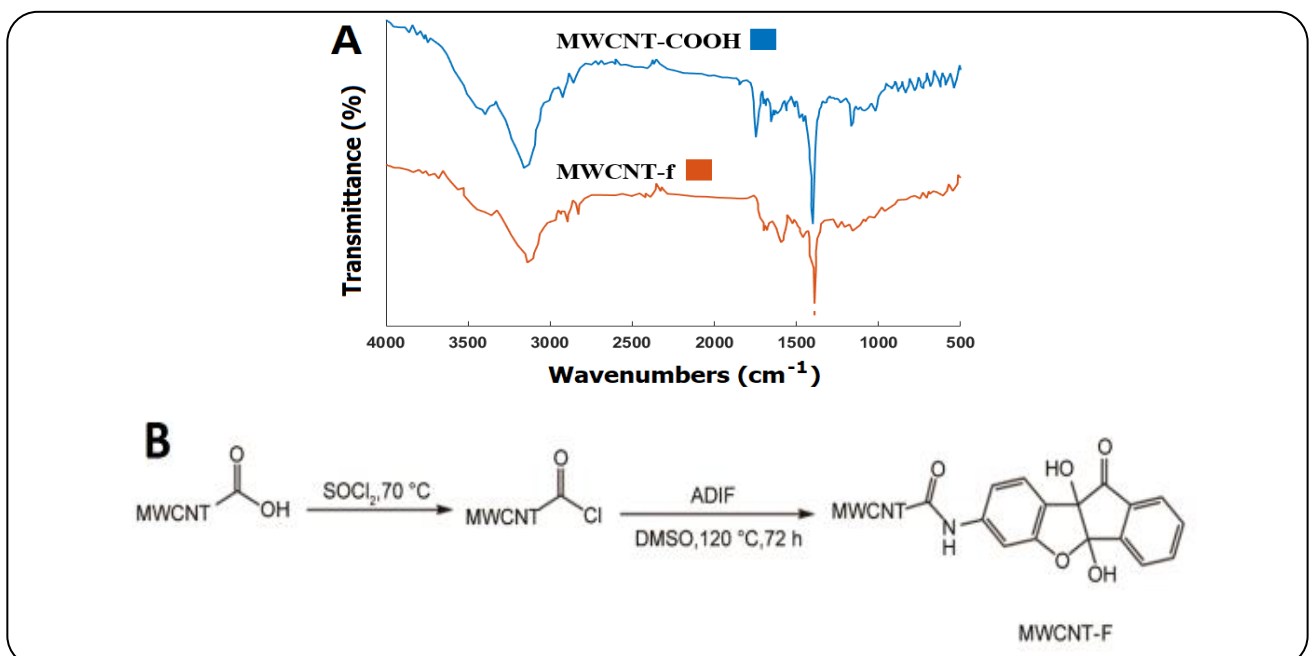


Fig. 2: (a) The FT-IR spectra of MWCNT-COOH (green) and MWCNT-f (blue), (b) Structure of the modification route of the MWCNT-COOH and MWCNT-f. Thermo Gravimetric Analysis (TGA)

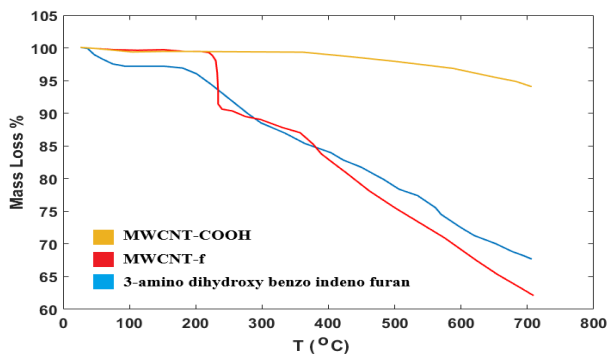


Fig. 3: The TGA curve of MWCNT-COOH, MWCNT-f, and 3-amino dihydroxy benzo indeno furan Effect of pH

The pH plays a crucial role in the adsorption of metal ions onto the adsorbent. Indeed, the pH affects the adsorption process through the degree of ionization, the surface charge of the adsorbent, or the speciation of the adsorbate. Here, the influence of solution pH for the removal of copper ions, by MWCNT-f, is illustrated in Fig. 4A. For this experiment, the initial concentration of Cu (II) ions and the adsorbent content were 50 ppm and 0.5 g per 100 ml, respectively. Since pH values higher than 6 lead to the formation of copper deposits and copper hydroxide, the pH was selected in the range of 2-6 [20–22].

As apparent from Fig. 4A, the removal of Cu (II) ions was highly pH-dependent so the maximum removal occurred at pH 6. At this pH, the MWCNT-f can acquire a negatively charged surface which leads to an increase in the electrostatic attraction between the adsorbent surface and copper ions [19,23,24]. As PH is decreased, the removal of copper ions was also reduced which can be due to an increase in  $H^+$  ion concentration and limitation of the number of available sites for the adsorption of ions. It leads to the surface ionization of adsorbent and results in the reluctance for adsorption of metal cations on MWCNT-f. Therefore, the optimum pH to promote adsorption efficiency was found at pH 6.

#### Effect of contact time

The influence of contact time on the removal of copper ions, by MWCNT-f is shown in Fig. 4B. For this experiment, the initial concentration of copper in the aqueous solution, the pH, and the adsorbent content were 50 ppm, 6, and 0.5 g per 100 ml, respectively.

As can be seen in this Fig., the rate of Cu (II) removal during the 30 min was about 73%, afterward, the system gradually approached the equilibrium state. This

equilibrium for Cu (II) was reached in less than 50 min, so that, the copper removal efficiency from the aqueous solution, at 45 min, was reported 90.19% and followed by, very little change in removal efficiency was observed. It indicates that the copper adsorption is controlled by the interactions taking place on the studied adsorbent surface at 45 min [25, 26]. Therefore, the contact time of 45 min was determined as the optimum time to carry out the subsequent experiments.

#### Effect of adsorbent dosage

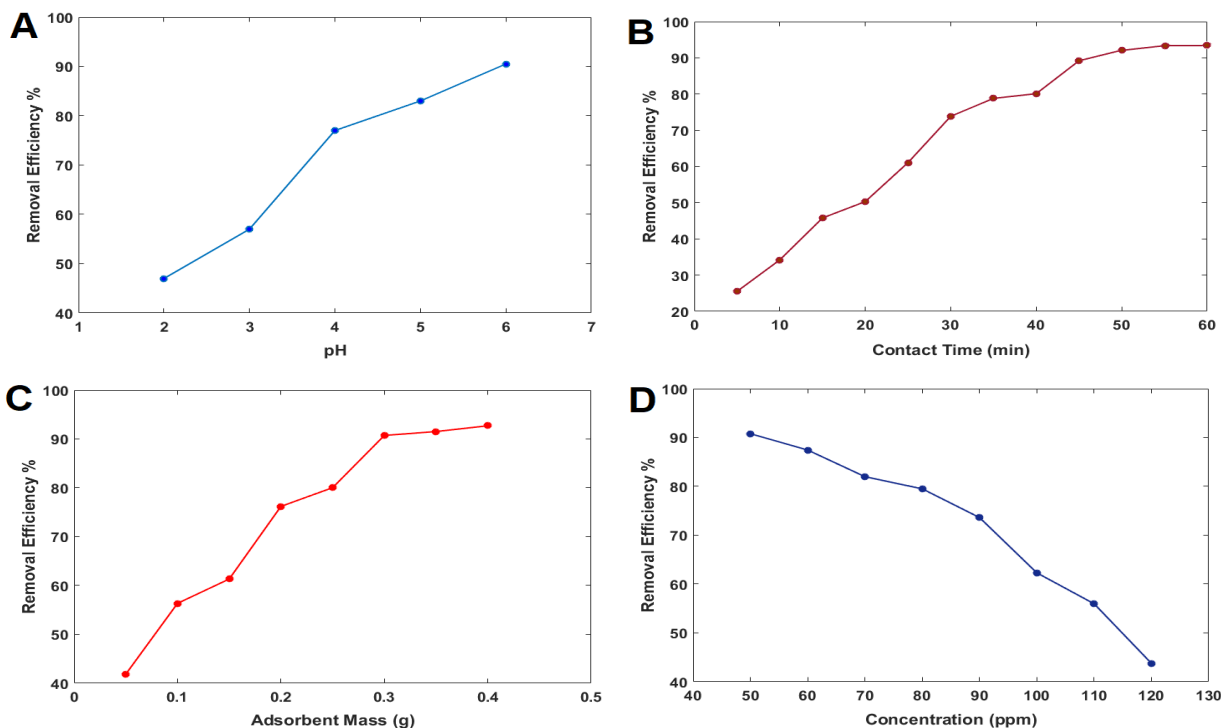
Fig. 4C illustrates the effect of adsorbent dosage on the removal efficiency of copper ions. For this experiment, the different amounts of MWCNT-f (0.05-0.4 g) were evaluated into 100 ml of the copper aqueous solution with an initial concentration of 50 ppm, pH of 6, and contact time of 45 min.

As was apparent from the mentioned Fig., the removal efficiency of Cu (II) ions has enhanced with an increase in the amount of adsorbent. In this field, a similar trend was reported for the removal of metal ions using the MWCNTs [27]. It can be explained by the increasing number of sites available for the adsorption of Cu (II) ions on the adsorbent. So, the removal of Cu (II) increased from 41.12 to 90.43 %, when the amount of MWCNT-f was increased from 0.05 to 0.3 g. With increasing the amount of adsorbent (0.4 g) no significant difference was observed in the adsorption efficiency. It can be due to the constant concentration of metal ions in the solution which despite the increase in sorption sites, due to the increase of MWCNT-f dosage, the amount of adsorption has not increased. Hence, 0.3 g dosage was selected as the optimum amount of adsorbent.

#### Effect of initial concentration of the metal ions

The removal of metal ions by adsorbent affected by the initial concentration of Cu(II) (in the range of 50–120 mg/L) was evaluated at a pH of 6 and the mass of adsorbent of 0.3 g of MWCNT-f.

Fig. 4D indicates the effect of the initial concentration of copper ions vs. the removal efficiency (%). An increase in the initial concentration of metal ions leads to a reduction of removal efficiency; so the highest removal percentages by MWCNT-f at the concentration of 50 mg/L of copper was recorded at 90.43%. In this concentration, the copper ions react to active adsorption sites of MWCNT-f, quickly. While, at the high concentrations of Cu(II), due to the existence of a constant number of adsorbent



**Fig. 4:** (A) The effect of pH, (B) The effect of contact time, (C) Effect of adsorbent, (D) The effect of initial copper concentration on the removal efficiency of copper by the MWCNT-f adsorber

sites available and an increased ratio of an initial number of moles of Cu(II), each of the mentioned sites is surrounded by several Cu(II) ions, which lead to a decrease in removal efficiency (%) of metal ions.

Notably, at the higher concentrations of metal, adsorption capacity is almost constant which is related to saturated adsorption sites of adsorbent. Many studies confirm the mentioned results [7,28].

#### Adsorption kinetics

Many adsorption processes are dependent on time, so, knowing the kinetic of these processes is very important to understand the dynamics of the reaction and predict the adsorption rate with time. There are numerous kinetic models, applied for adsorption in discontinuous processes. Although, they cannot be easily applied due to their mathematical complexity, however, Morris-Weber's pseudo-kinetic model, first-order and pseudo-second-order models are simple kinetic models which widely used to study adsorption capacity ( $q_t$ ) at the time ( $t$ ).

It is notable that in first-order and pseudo-second-order equations, it is assumed that  $(q_e - q_t)$  is the main factor for the adsorption action, and the adsorption rate is proportional to this factor, while Weber-Morris model is

intra-particle diffusion and used for investigation of the influence of penetration in the process kinetic. Indeed, the adsorption process of heavy metals from an aqueous solution onto an adsorbent occurs in several steps and total adsorption may be controlled by one or more of these steps. The first step involves the adsorbate penetration on the external surface of the adsorbent. The intra-particle diffusion is the second stage of the adsorption process, if this step controls the process, can be used the Morris-Weber equation. The third stage is related to penetration at the adsorbent surface. In this stage, the final equilibrium is created by the very low concentration of adsorbate in solution and the decrease of active sites on the adsorbent. Hence, the investigation of adsorption kinetic was carried out utilizing the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, and the best fit kinetic model was chosen based on the correlation coefficient value obtained through Morris-Weber equation. The studied parameters were listed in Table 3.

The experimental data showed very good compliance with the Morris-Weber model ( $R^2 = 0.98$ ), hence, it can be claimed that the adsorption process is controlled by the penetration step. However, this stage is not the only

**Table 3: Kinetic stability parameters for copper adsorption on MWCNT-f adsorbents**

Morris-Weber equation	$K_{id} (\text{min}^{-1})$		$R^2$
		2.4674	
Pseudo First Order Kinetic Model	$K_1 (\text{min}^{-1})$	$q_e (\text{mg/g})$	$R^2$
	0.091	30.4719	0.7536
Pseudo Second Order Kinetic Model	$K_2 (\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$q_e (\text{mg/g})$	$R^2$
	0.0014	24.0385	0.9253

**Table 4: Isotherm constant values for copper adsorption on adsorbent MWCNT-f**

Langmuir Equation	$K_L (\text{min}^{-1})$	$q_m (\text{mg/g})$	$R^2$
		0.209	16.78
Freundlich Equation	$K_F (\text{min}^{-1})$	N	$R^2$
	15.164	13.21	0.30
Dubinin Radushkevich Equation	$K_{DR}$	$q_d$	$R^2$
	0.000001	20.25	0.66

stage-controlling in the adsorption process because the line has not passed through the origin. Moreover, the pseudo-second-order model led to a linear curve with  $R^2=0.92$ , which that shows, the pseudo-second-order equation can be also a relatively suitable model for describing the copper adsorption kinetics on MWCNT-f.

It is notable that, in the pseudo-first-order equation, the adsorption intensity of metal ions in the adsorbent sites fits with the number of empty sites and linear propulsion forces, so the adsorption process follows the pseudo-first-order mode when the adsorbate concentration into the aqueous solution is high. Here, the correlation coefficients for the pseudo-first-order kinetic model are low indicating this model is a poor fit for the experimental data ( $R^2=0.75$ ).

Accordingly, it was found that one of the steps-limiting in this adsorption process is the intra-penetration stage (intra-particle diffusion), due to the high correlation coefficient for the Morris-Weber equation. Moreover, the experimental data demonstrate that the adsorption of Cu(II) ions by MWCNT-f may follow the pseudo-second-order kinetic model ( $R^2 > 0.91$ ). It relies on the assumption that chemisorption can be the rate-limiting step. In this type of sorption, the metal ions attach to the adsorbent surface via forming chemical bonds (like covalent) and tend to find sites that increase the number of their coordination with the adsorbent surface [29].

### Modeling adsorption isotherm

Adsorption isotherms play an important role in the design of the adsorption system and provide the maximum

adsorption capacity for adsorbents to remove metal ions from an aqueous solution. In this field, there are various isotherm models, however, isotherm models of Langmuir, Freundlich, and Dubinin–Radushkevich widely employ to describe the equilibrium process of adsorption [18]. Here, the experimental data were analyzed using the mentioned models to describe the adsorption of copper on the MWCNT-f. The curves resulting from all three models along with the parameters of these functions are shown in Table 4.

The comparison of the results showed that the experimental data are well correlated with Langmuir's linear isotherm due to the high correlation coefficient (Table 4). It can be attributed to the homogeneous distribution of activating sites which resulted in the surface of homogeneous, and monolayer adsorption on MWCNT-f. Moreover, the amount of free adsorption energy ( $E_a$ ), calculated using the Dubinin–Radushkevich model, was smaller than 8 kJ/mol ( $E_a=707/11 \text{ j/mol}$ ). It implies that the physical interactions, as opposed to ion-exchange and chemical bonds formation, control the studied system, because the adsorption process is physical, ion-exchange or chemical type when  $E_a < 8 \text{ kJ/mol}$ ,  $8 \text{ kJ/mol} < E_a < 16 \text{ kJ/mol}$ ,  $E_a > 16 \text{ kJ/mol}$ , respectively [30]. This finding is consistent with the reached results by non-linear modeling of the kinetic data. Hence, Langmuir isotherm is a suitable model for describing the adsorption process of copper ions on MWCNT-f.

### Effect of temperature on the removal efficiency

The temperature effect on removal of copper ion by



**Table 5: Effect of temperature on copper adsorption efficiency on MWCNT-f**

Temperature (°C)	Removal Efficiency (%)
20	90.31
30	92.45
40	94.63
50	95.76

**Table 6: Thermodynamic parameters for copper adsorption on MWCNT-f**

	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	T (°C)	$\Delta G$ (kJ/mol)	R <sup>2</sup>
Cu (II) adsorption onto MWCNT-f	25.50	0.105	20	-5.437	0.98
			30	-6.31	
			40	-7.46	
			50	-8.37	

MWCNT-f was studied within the range of 20-50 °C (under optimum conditions of pH, contact time, the dose of adsorbent, and initial metal ions). Table 5 indicates the effect of temperature on the adsorption capacity of copper, according to which, the temperature rising was led to an increase in removal efficiency of copper from aqueous solution, by MWCNT-f adsorbent, although a minor difference was observed at the temperatures of 40 °C and 50 °C. Indeed, the temperature rising leads to a decrease in the thickness of the boundary layer, in the adsorbent surface, resulting in the improvement of the adsorbate transfer, from the solution to the adsorbent active sites. The increase of this parameter not only can lead to an increase in the number of active sites available for the adsorption process but also promotes the driving force of adsorption between adsorbate and adsorbent, as well as adjacent adsorbed molecules. The positive effect of the temperature in the removal efficiency confirms the endothermic nature of the adsorption process of the copper by MWCNT-f.

In the study of *Xu et al.*, which used Poly(ethyleneimine)-Functionalized Silica for the adsorption of copper ions from electroplating wastewater, the removal efficiency of Cu(II) ions was 92.6% [31]. In our study, the removal efficiency of copper ions after 45 min was 90.2%. We found the temperature increase positively affected the removal efficiency of ions and achieved 95.76% at 50°C.

#### Thermodynamic study

Based on the results provided in Table 3, the values of thermodynamic parameters of the adsorption process [i.e. free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ),

and entropy change ( $\Delta S$ )] were calculated by equations 3-5 [21].

$$K_c = \frac{F_e}{1-F_e} \quad (3)$$

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (4)$$

$$\Delta G = -RT \ln K_c \quad (5)$$

Where  $F_e$  is the fraction of copper ions that adsorbed in equilibrium status,  $K_c$  is the sorption distribution coefficient,  $R$  (8.314 J/mol.K) is the universal gas constant, and  $T$  (K) is the temperature. The values of  $\Delta H$  and  $\Delta S$  can be obtained from the slope and the intercept of the plot of the  $\log K_c$  line vs.  $1/T$ . The calculated values for  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  are listed in Table 6.

Based on the results, the negative values of  $\Delta G$  show that the removal of Cu(II) ions by MWCNT-f is a spontaneous adsorption process. Likewise, the positive value of  $\Delta H$  confirms the endothermic nature of the adsorption process. Moreover, many reports indicate the  $\Delta H$  values provide useful information about the type of adsorption process so that  $\Delta H$  values for physisorption and chemisorption have been reported in the range of 2.1-20.9 kJ/mol and 20.9-418.4 kJ/mol, respectively [18, 21, 32]. Therefore, the  $\Delta H$  value obtained in this study demonstrates that chemisorption can be contributed to the removal of copper ions by MWCNT-f.

Furthermore, the positive value of  $\Delta S$  indicates the possibility of increased randomness at the solid-liquid interface during the copper ions adsorption onto MWCNT-f.

## CONCLUSIONS

Removal of Copper ions from aqueous solutions was evaluated using a new adsorbent of the carboxylated multi-wall carbon nanotube (COOH-MWCNT) functionalized with 3-amino-dihydroxy benzo-indeno-furan (MWCNT-f), and in a discontinuous adsorption system. The designed MWCNT-f was the effective adsorbent for the removal of Cu (II) from an aqueous solution. It was found that the increase in pH led to the promotion of adsorption capacity, which could be due to the decreased competition between H<sup>+</sup> and Cu<sup>2+</sup> in the available adsorbent sites. Notably, the higher adsorption capacity was related to pH 6. Moreover, in the early minutes, the adsorption of copper was rapidly carried out due to a large number of active sorption sites on the surface of adsorption. Followed by, with increasing contact time, the available adsorption sites gradually reduced, due to their filling by Cu ions, which resulted in the decrease of adsorption rate. It is notable that, the optimum amount of adsorbent was determined 0.3 g/ 100 ml, also the copper adsorption efficiency was reported 90.31%. The adsorption process of copper followed the Morris-Weber kinetic model and the adsorption isotherm studies demonstrated, the results possess more in accordance with the Langmuir model. The effect of temperature evaluation on the copper adsorption process, by MWCNT-f, showed that the temperature rise has a positive effect on copper removal efficiency. Furthermore, the calculated values of the thermodynamic parameters in the adsorption reaction on the adsorbent showed that the copper adsorption on MWCNT-f is a spontaneous and endothermic process. Our study provides a new recyclable adsorbent for the efficient treatment of Cu (II) ions from aqueous solutions.

## Acknowledgments

We would like to express our deep appreciation to Dr. Aliakbar Seif Kurdi for his guidance.

Received : Dec. 08, 2022 ; Accepted : May. 22, 2023

## REFERENCES

- [1] Riyazuddin R., Nisha N., Ejaz B., Khan M.I.R., Kumar M., Ramteke P.W., Gupta R. *A Comprehensive Review on the Heavy Metal Toxicity and Sequestration in Plants*, *Biomolecules*, **12**(1): 43 (2022).
- [2] Sun W., Wu H., Xu Z., Li C., Qian X., Chen L., *Adsorption of Heavy Metal Ions by Carbon-Nanofibers-Blended Carbon Nanotubes*, *ChemistrySelect*, **3**: 12410–12414 (2018).
- [3] Wei B., Yang L., *A Review of Heavy Metal Contaminations in Urban Soils, Urban Road Dusts and Agricultural Soils from China*, *Microchem. J.*, **94**: 99–107 (2010).
- [4] Jain R., Jordan N., Schild D., Van Hullebusch E.D., Weiss S., Franzen C., Farges F., Hübner R., Lens P.N.L., *Adsorption of Zinc by Biogenic Elemental Selenium Nanoparticles*. *Chem. Eng. J.* **260**: 855–863 (2015).
- [5] Wang Z., Xu W., Jie F., Zhao Z, Zhou K., Liu H. *The Selective Adsorption Performance and Mechanism of Multiwall Magnetic Carbon Nanotubes for Heavy Metals in Wastewater*, *Scientific Reports*, **11**: 16878 (2021).
- [6] Eyni H., Tahermansouri H., Kiani F., Jahangiri M., *Kinetics, Equilibrium and Isotherms of Pb<sup>2+</sup> Adsorption from Aqueous Solutions on Carbon Nanotubes Functionalized with 3-Amino 5a,10a Dihydroxybenzo[B] Indeno [2,1 -d] Furan-10-One*, *New Carbon Materials*, **34**: 512-523 (2019).
- [7] Seyedmohammadi J., Motavassel M., Maddahi M.H., Nikmanesh S., *Application of Nanochitosan and Chitosan Particles for Adsorption of Zn(II) Ions Pollutant from Aqueous Solution to Protect Environment*, *Model. Earth Syst. Environ.*, **2**: 165 (2016).
- [8] Ting C., Chen C., Rong T., Cheng-H H., Yuan T., *Competitive Adsorption of Cu, Ni, Pb, and Cd from Aqueous Solution Onto Fly Ash-Based Linde F(K) Zeolite*, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **37**(1): 61-72 (2018).
- [9] Wan Ngah W.S., Teong L.C., Hanafiah M.A.K.M., *Adsorption of Dyes and Heavy Metal Ions by Chitosan Composites: A Review*, *Carbohydr. Polym.*, **83**: 1446–1456 (2011).
- [10] Vasconcelos P.N.M., Lima W.S., Silva M.L.P., Brito A.L.F., Laborde H.M., Rodrigues M.G.F., *Adsorption of Zinc from Aqueous Solutions Using Modified Brazilian Gray Clay*, *Am. J. Anal. Chem.*, **4**: 510–519 (2013).
- [11] Eyni H., Tahermansouri H., Kiani F., Jahangiri M., *Kinetics, Equilibrium and Isotherms of Pb<sup>2+</sup> Adsorption from Aqueous Solutions on Carbon Nanotubes Functionalized with 3-Amino-5a,10a-Dihydroxybenzo[b] Indeno [2,1-d]Furan-10-One*, *New Carbon Materials*, **34**: 512–523 (2019).

- [12] Jahangiri M., Kiani F., Tahermansouri H., Rajabalinezhad A., The Removal of Lead Ions from Aqueous Solutions by Modified Multi-Walled Carbon Nanotubes with 1-Isatin-3-Thiosemicarbazone, *Journal of Molecular Liquids*, **212**: 219–226 (2015).
- [13] Stafiej A., Pyrzyńska K., Adsorption of Heavy Metal Ions with Carbon Nanotubes, *Sep. Purif. Technol*, **58**: 49–52 (2007).
- [14] Barmaki Z., Aghaie H., Seif A., Monajjemi M., Kinetic and Thermodynamic Study of Chromium Picolinate Removing from Aqueous Solution onto the Functionalized Multi-Walled Carbon Nano Tubes, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **40(3)**: 765-779 (2021).
- [15] Bullington J.L., Dodd J.H., Synthesis of Tetrahydroindeno[1,2-B]Indol-10-Ones and their Rearrangement to [2]Benzopyrano[4,3-b]Indol-5-Ones, *J. Org. Chem.* **58**: 4833–4836 (1993).
- [16] Hsieh Y.-C., Chou Y.-C., Lin C.-P., Hsieh T.-F., Shu C.-M., Thermal Analysis of Multi-walled Carbon Nanotubes by Kissinger's Corrected Kinetic Equation, *Aerosol Air Qual. Res.* **10**, p. 212–218 (2010).
- [17] Wepasnick K.A., Smith B.A., Bitter J.L., Howard Fairbrother D., Chemical and Structural Characterization of carbon Nanotube Surfaces, *Anal. Bioanal. Chem.* **396**: 1003–1014(2010).
- [18] Karthik R., Meenakshi S., Facile Synthesis of Cross Linked-Chitosan–Grafted-Polyaniline Composite and its Cr(VI) Uptake Studies, *Int. J. Biol. Macromol.* **67**: 210–219 (2014).
- [19] Yavuz A.G., Uygun A., Bhethanabotla V.R., Substituted Polyaniline/Chitosan Composites: Synthesis and Characterization, *Carbohydr. Polym.* **75**: 448–453 (2009).
- [20] Heidari A., Younesi H., Mehraban Z., Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous Solution by Amino Functionalized Mesoporous and Nano Mesoporous Silica, *Chem. Eng. J.* **153**: 70–79 (2009).
- [21] Karthik R., Meenakshi S., Removal of Pb(II) and Cd(II) Ions from Aqueous Solution Using Polyaniline Grafted Chitosan, *Chem. Eng. J.* **263**: 168–177 (2015).
- [22] Cimino G., Removal of Toxic Cations and Cr(VI) from Aqueous Solution by Hazelnut Shell, *Water Res.* **34**: 2955–2962 (2000).
- [23] Sankararamakrishnan N., Jaiswal M., Verma N., Composite Nanofloral Clusters of Carbon Nanotubes and Activated Alumina: An Efficient Sorbent for Heavy Metal Removal, *Chem. Eng. J.* **235**: 1–9 (2014).
- [24] Maliyekkal S.M., Lisha K.P., Pradeep T., A Novel Cellulose–Manganese Oxide Hybrid Material by in Situ Soft Chemical Synthesis and its Application for the Removal of Pb(II) from Water, *J. Hazard. Mater.* **181**: 986–995 (2010).
- [25] Abdel Salam M., Removal of Heavy Metal Ions from Aqueous Solutions with Multi-Walled Carbon Nanotubes: Kinetic and Thermodynamic Studies, *Int. J. Environ. Sci. Technol.* **10**: 677–688 (2013).
- [26] Hu J., Chen C., Zhu X., Wang X., Removal of Chromium from Aqueous Solution by Using Oxidized Multiwalled Carbon Nanotubes, *J. Hazard. Mater.* **162**: 1542–1550 (2009).
- [27] Xiong L., Chen C., Chen Q., Ni J., Adsorption of Pb(II) and Cd(II) from Aqueous Solutions Using Titanate Nanotubes Prepared via Hydrothermal Method, *J. Hazard. Mater.* **189**: 741–748 (2011).
- [28] Navaei Diva T., Zare K., Taleshi F., Yousefi M., Removal of Cd<sup>2+</sup> from Aqueous Solution by Nickel Oxide/CNT Nanocomposites, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **38(1)**: 141-154 (2019).
- [29] Senthil Kumar P., Vincent C., Kirthika K., Sathish Kumar K., Kinetics and Equilibrium Studies of Pb<sup>2+</sup> Ion Removal from Aqueous Solutions by Use of Nano-Silversol-Coated Activated Carbon, *Brazilian J. Chem. Eng.* **27**: 339–346 (2010).
- [30] Šolíc M., Maletic S., Isakovski M.K., Nikic J., Watson M., Kónya Z., Trickovic J., Comparing the Adsorption Performance of Multiwalled Carbon Nanotubes Oxidized by Varying Degrees for Removal of Low Levels of Copper, Nickel and Chromium(VI) from Aqueous Solutions, *Water (Switzerland)*, **12**: 1–18(2020).
- [31] Xu H., Liu D., He L., Liu N., Ning G., Adsorption of Copper(II) from a Wastewater Effluent of Electroplating Industry by Poly(Ethyleneimine)-Functionalized Silica, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **34(2)**: 73-81 (2015).
- [32] Karthik R., Meenakshi S., Removal of Hexavalent Chromium Ions from Aqueous Solution Using Chitosan/Polypyrrole Composite, *Desalin, Water Treat.* **56**: 1587–1600 (2015).