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Removal of copper (II) and nickel (II) from aqueous media using silica aerogel modified with amino propyl triethoxysilane as an adsorbent: equilibrium, kinetic, and isotherms study

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Removal of copper (II) and nickel (II) from aqueous media using silica aerogel modified with amino propyl triethoxysilane as an adsorbent: equilibrium, kinetic, and isotherms study

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ABSTRACT

This study focused on the adsorption of copper (II) and nickel (II) from aqueous solutions onto silica aerogel modified with amino propyl triethoxysilane as a compound containing amino functional group. The batch experiments were conducted at various conditions including contact time, pH, adsorbent dose, and adsorbate content. The results showed that the equilibrium time occurred within 5 h for Ni(II) and 24 h for Cu(II) and the maximum adsorption capacity for both the ions happened at a pH of 6. The kinetic and isotherm adsorption of the modified silica aerogel fitted well to pseudo-second order model and Langmuir model, respectively. The Langmuir isotherm model results showed that the maximum adsorption capacity (Q_m) of the modified adsorbent was 47.6 mg/g for Cu(II) and 27.7 mg/g for Ni(II). Experimental data analysis by Dubinin–Radushkevich isotherm also illustrated that the metals adsorption onto the sorbent was physical in nature. With regard to the sorption capacity obtained by the modified silica aerogel, it can be considered as an efficient sorbent in the removal of the metal ions.

Keywords: Adsorption; Modified silica aerogel; Copper; Nickel; Aqueous solution

1. Introduction

Environmental pollution, due to the development of industrial activities, has been considered as one of the major problems in recent years [1]. Heavy metals such as copper, nickel, lead, cadmium, chromium, and zinc are the most inorganic pollutants that have been detected in most of the industrial wastewaters [2]. Heavy metals, because of their characteristics, such as nonbiodegradability and tendency to accumulate in

food chain and then living organisms, cause environmental pollution and various adverse health effects in human [3,4]. Among these, copper and nickel are extensively found in many industrial effluents like metal electroplating, metal cleaning, fertilizers, paints, batteries, and electronics [5,6]. The concentration of them in some industrial effluents (e.g. metal plating process) can reach up to 1,000 mg/L [7]; while based on environmental regulations, the accessible level of copper and nickel in industrial wastewaters for discharge in receiving water bodies have been set as

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0.5 and 1 mg/L, respectively [8,9]. Copper (II) causes Wilson disease and metabolic and mental disorders [3,10]. Nickel (II) can lead to body weakness, cyanosis, headache and dizziness, and be harmful for the respiratory tract [11]. The World Health Organization has considered 2 and 0.07 mg/L as the maximum allowable concentration for Cu(II) and Ni(II) in drinking water, respectively [10]. Because of the harmful effects of Cu(II) and Ni(II), removal of them from water and wastewater is necessary. Many studies including chemical precipitation, ion exchange, electro coagulation, membrane technique, extraction by solvents, and adsorption have been successfully conducted to remove heavy metals from water and wastewater [12,13]. Adsorption process is one of the most attractive alternatives that have been used for higher removal of pollutants over various conditions of solution [14]. Recent studies on the adsorption of copper (II) and nickel (II) by different adsorbents including sawdust [14], kaolinite clay [12], activated carbon [2], limestone [15], Chitosan [16], mine tailing [17], Corn-cobs [15], Lignin [18], Carbon Aerogel [19], and Silica gel [20] have been conducted; their adsorption capacities are presented in Table 1. Silica aerogel is known as a high porous (up to 99%) material with high specific surface area (500–1,000 m²/g) and low density (5 kg/m³). These properties lead to an excellent availability of internal surface via open porous network [21]. The object of this study was to investigate the adsorption of copper and nickel [Cu(II) and Ni(II)] from aqueous solutions by silica aerogel modified with amino propyl

triethoxysilane as a compound containing the amino functional groups. In order to achieve the purpose, the effects of various conditions on the adsorption such as contact time, pH, adsorbent dose, and adsorbate content were investigated.

2. Materials and methods

2.1. Chemicals

All chemicals used in this work [tetraethoxysilane (TEOS) (>98%), 3-amino propyl triethoxysilane (APTES), isopropanol, hexane, HCl, NaOH, Cu(NO₃)₂·3H₂O and Ni(NO₃)₂·6H₂O] were of analytical grade and purchased from Merck Co (Germany). The stock solutions (1,000 mg/L) of Cu(II) and Ni(II) were made by dissolving appropriate quantities of their nitrate salts in deionized water. The working solutions were then prepared by diluting the stock solutions with deionized water. The solution pH was adjusted by HCl (0.1 M) and NaOH (0.1 M).

2.2. Instrument

The surface morphology of the modified and unmodified silica aerogel was specified by a scanning electron microscope (Seron, AIS-2100, South Korea). The FT-IR spectra of the adsorbent were determined by a FT-IR spectrophotometer (JASCO, FT/IR-6300, Japan) in the range of 400–4,000 cm⁻¹. The surface area of the adsorbent was assigned by a single-point N₂ gas adsorption method (model Quanta Chrome Instrument Mono Sorb device). The concentration of the metal ions in the solution was measured by a Perkin-Elmer atomic absorption spectrometer (AAS) (Model AAnalyst300).

2.3. Preparation and modification of the adsorbent

To prepare the sol-gel, 14.7 ml of TEOS and 20.8 ml of isopropanol solvent were mixed with a magnetic stirrer until a clear solution was attained. Then, 19.9 ml of HCl (0.001 M) was drop-wisely added to it while the solution was being stirred and the mixing was continued until its milky color disappeared. The clear sol was incubated at 36 °C for 24 h [23]. For aging, the obtained alcogel was placed into the mixture ratio of 1:1, of water/isopropanol and incubated at 50 °C for 24 h. In order to prevent the reverse reaction during the modification, the isopropanol into the alcogel was replaced by hexane as a nonpolar solvent. For this, the alcogel was maintained in the hexane solution at 36 °C for 48 h [24]. The modification was

Table 1
Various adsorbents for the removal of Cu(II) and Ni(II) from aqueous solutions

Adsorbent	Maximum adsorption capacity (mg/g)		References
	Cu(II)	Ni(II)	
Sawdust	32.051	35.971	[14]
Kaolinite clay	1.22	0.90	[12]
Activated carbon	24.21	27.21	[2]
Limestone	0.0126	0.0165	[15]
Chitosan	16.80	2.40	[16]
Mine tailing	14.96	5.25	[17]
Corn-cobs	7.62	13.5	[22]
Lignin	22.88	5.99	[18]
Carbon aerogel	561.7	12.87	[19]
Silica gel functionalized with 4-phenylacetophynone	0.76	0.82	[20]

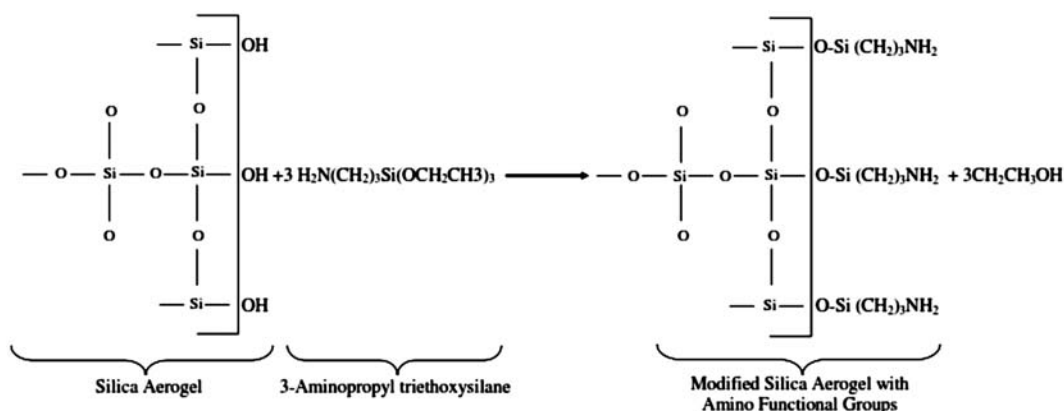


Fig. 1. Modification of silica aerogel with 3-amino propyl triethoxysilane.

then carried out by introducing the alcogel with a molar ratio of 2:1 of TEOS/APTES into the hexane solution containing APTES at 36°C for 24 h. The modified silica aerogel was washed with deionized water, dried at 36 and 56°C for 24 and 48 h, respectively. The obtained modified silica aerogel was then ground to <125 μm. The modification of silica aerogel with APTES is shown in Fig. 1.

2.4. Adsorption experiments

All the batch adsorption experiments were conducted at room temperature (25 ± 0.5°C) on rotary shaker (200 rpm for 48 h) using 150-ml conical flasks containing 50 ml of the metal ion solution and 0.5 g of the adsorbent. The effects of various conditions including contact time (0–48 h), pH (2–12), metal concentration (50–500 mg/L), and adsorbent dose (0.05–1.6 g) on the sorption were examined. Next, the suspension was centrifuged (2,500 rpm for 10 min) and the clear supernatant was analyzed for the metal ions by AAS. The experiments were conducted in duplicates and the average values were considered. Blank

samples (metal ions solution without adsorbent) were also used to determine the value of the metals loss during the experiments and the experimental data were adjusted through the blank sample values. The adsorption capacity of the modified silica aerogel for the metals was determined by Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg/g) is the sorption capacity of adsorbent, C_0 (mg/l) is the initial metal concentration, C_e (mg/L) is the equilibrium concentration of the metal in solution, m (g) is the mass of adsorbent and V (l) is the volume of the solution.

3. Results and discussion

3.1. Characterization of the adsorbent

The surface morphology of the unmodified and modified silica aerogel is presented in Fig. 2(a) and (b). As can be observed, the surface structure of the

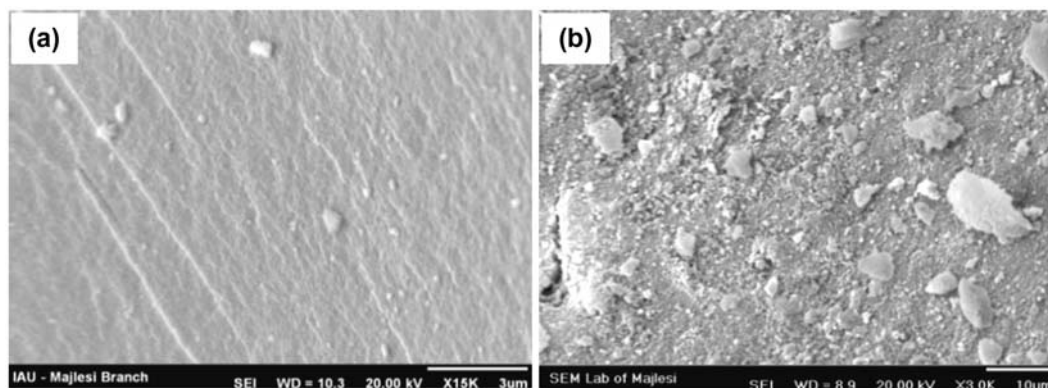


Fig. 2. SEM image of the (a) unmodified and (b) modified silica aerogel.

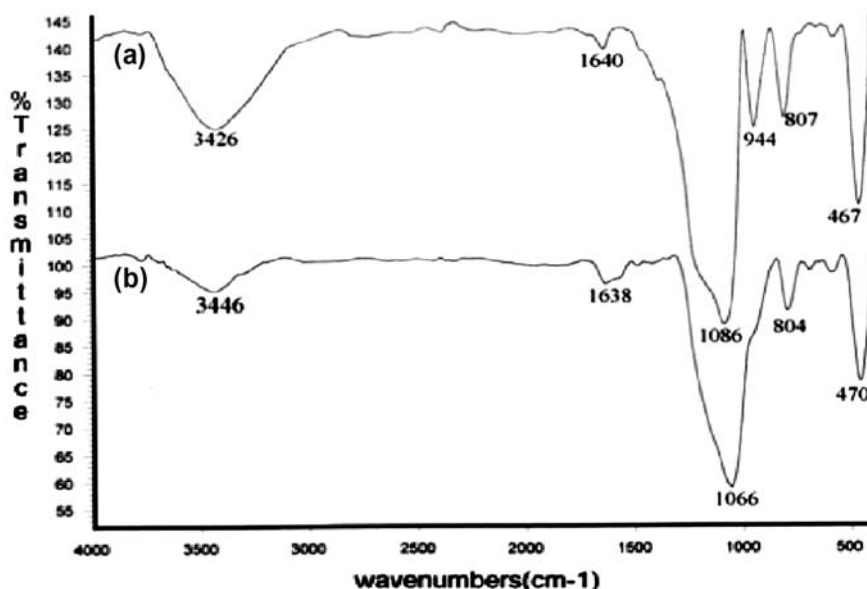


Fig. 3. FT-IR spectra of the (a) unmodified and (b) modified silica aerogel.

unmodified adsorbent is more homogenous than that of the modified type. In other words, the surface of the modified sorbent seems to be jagged and has irregular shapes. The results of BET surface area analysis showed that the modification of the adsorbent resulted in a decrease in the surface area from $940 \pm 23 \text{ m}^2/\text{g}$ to $240 \pm 7 \text{ m}^2/\text{g}$. It can be originated from the insertion of APTES into the pores of the silica aerogel. The FT-IR spectra in the wave numbers of $400\text{--}4,000 \text{ cm}^{-1}$ are illustrated in Fig. 3. In both the adsorbents, the broad bands at $1,638\text{--}1,640 \text{ cm}^{-1}$ and $1,066\text{--}1,086 \text{ cm}^{-1}$ belong to the H–O–H and Si–O–Si bonds, respectively [25]. In the spectra of the unmodified sorbent, the band at 944 cm^{-1} corresponds to the

H–O–H bonds and the band at $3,426 \text{ cm}^{-1}$ is also related to O–H bonds. The broad band at $3,446 \text{ cm}^{-1}$ that overlaps with a band of hydroxyl group ($3,426 \text{ cm}^{-1}$) is attributed to the stretching vibration of N–H bond (amino groups). This indicates that the modification of the adsorbent by APTES has been well conducted.

3.2. Effect of contact time

The effect of contact time in the removal of Cu (II) and Ni(II) using the modified silica aerogel was investigated at the various time intervals (0 to 48 h). As seen from Fig. 4(a), the adsorption rate of the

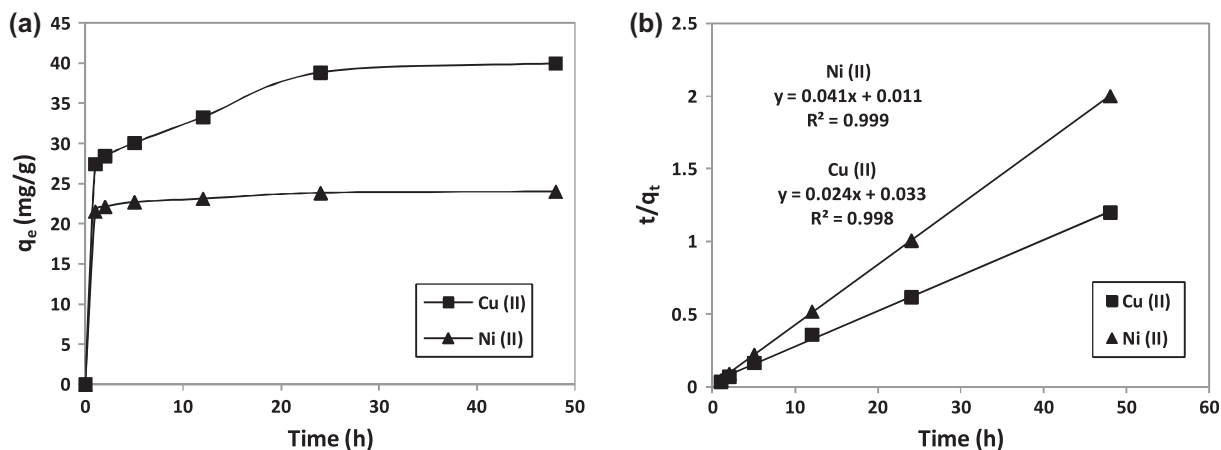


Fig. 4. (a). The effect of contact time on the adsorption of Cu(II) and Ni(II) by the modified silica aerogel (The initial concentration = 400 mg/L , adsorbent dose = 0.5 g and $\text{pH} = 7 \pm 0.5$). (b). The pseudo-second-order kinetic model.

Table 2
Parameters of the pseudo-first- and pseudo-second-order kinetic models from this study

Metals ions	q_e experimental (mg/g)	Pseudo-first order			Pseudo-second order		
		q_e calculated (mg/g)	K_1 (1/h)	R^2	q_e calculated (mg/g)	K_2 (g/mg h)	R^2
Cu(II)	38.9	15.6	0.101	0.950	41.6	0.017	0.998
Ni(II)	22.7	2.57	0.110	0.978	24.4	0.152	0.999

metals ions rapidly increased within the first 1 h of adsorption and then gradually increased as the time went forward. One reason for that was probably due to the more availability adsorption sites at the beginning of the adsorption process and they were slowly saturated as the contact time increased [17]. The equilibrium was acquired in a period of 5 h for Ni(II) and 24 h for Cu(II). In this study, the adsorption capacity of Cu(II), 38.9 mg/g, at the equilibrium time was higher than that of Ni(II), 22.7 mg/g. Similar results have been reported by other researchers [27,16–18,20,26]. The contact times of 5 and 24 h were used for Ni(II) and Cu(II), respectively, in the rest of the experiments.

3.2.1. Adsorption kinetics

Using kinetics models is helpful to determine the nature of adsorption mechanisms and the efficiency of adsorbent in removing pollutants. Two kinetic models including pseudo-first-order and pseudo-second-order were used to analyze the experimental data. The pseudo-first-order kinetic model [27] is obtained as Eq. (2).

$$\ln(q_e - q_t) = (\ln q_e - k_1 t) \quad (2)$$

where q_e (mg/g) and q_t (mg/g) are the quantity of metal adsorbed onto the sorbent at equilibrium and at time (t), respectively. K_1 (1/h) is the rate constant of the pseudo-first order. K_1 and q_e were achieved from the slope and intercept of the plotting $\ln(q_e - q_t)$ against t , respectively [27].

The data were also analyzed by the pseudo-second-order model as presented by Eq. (3).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are same as the pseudo-first-order model parameters. K_2 (g/mg h) is the rate constant of the pseudo-second-order model. k_2 and q_e are obtained by the intercept and slope of linear plot of t/q_t vs. t in the Eq. (3), respectively [28].

The results of the adsorption data using the kinetics models are shown in Fig. 4(b) and listed in Table 2. The linear correlation coefficient of the pseudo-second-order model ($R^2 > 0.997$) is higher than that of the pseudo-first kinetic model. This finding shows that the adsorption data of Cu(II) and Ni(II) by the modified silica aerogel were fitted well by the pseudo-second kinetic model. Furthermore, the q_e calculated (mg/g) using this kinetic model (Table 2) is rationally similar to q_e experimental (mg/g) attained from the experimental data. Many studies reported that the sorption of the heavy metals is followed by pseudo-second kinetic model [14,17].

3.3. Effect of pH

The effect of the solution pH on the removal of Cu(II) and Ni(II) by the modified silica aerogel was investigated at pH 2–12 and the results are presented in Fig. 5. As seen, the adsorption capacity of the sorbent was increased from 14.4 to 40 mg/g for Cu(II) and from 7.6 to 23.7 mg/g for Ni(II) by increasing solution pH from 2 to 6. Then, the capacity of the adsorbent for both the metals ions decreased at the solution pH higher than 6. Rafatullah et al. (2009)

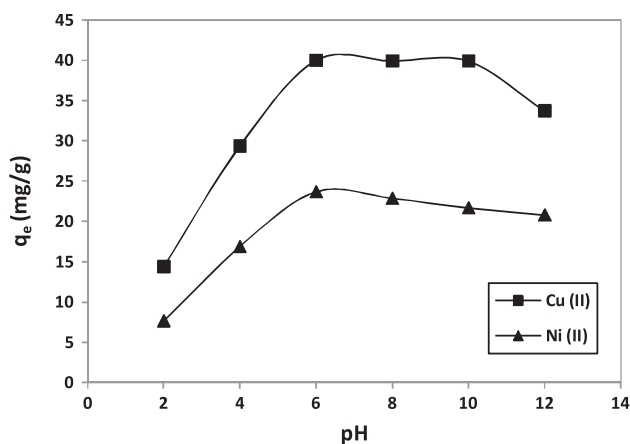


Fig. 5. The effect of pH on the adsorption of the metals ions using the modified silica aerogel (the initial metals ions concentration = 400 mg/L, adsorbent dose = 0.5 g, and contact time = 5 h for Ni(II) and 24 h for Cu(II)).

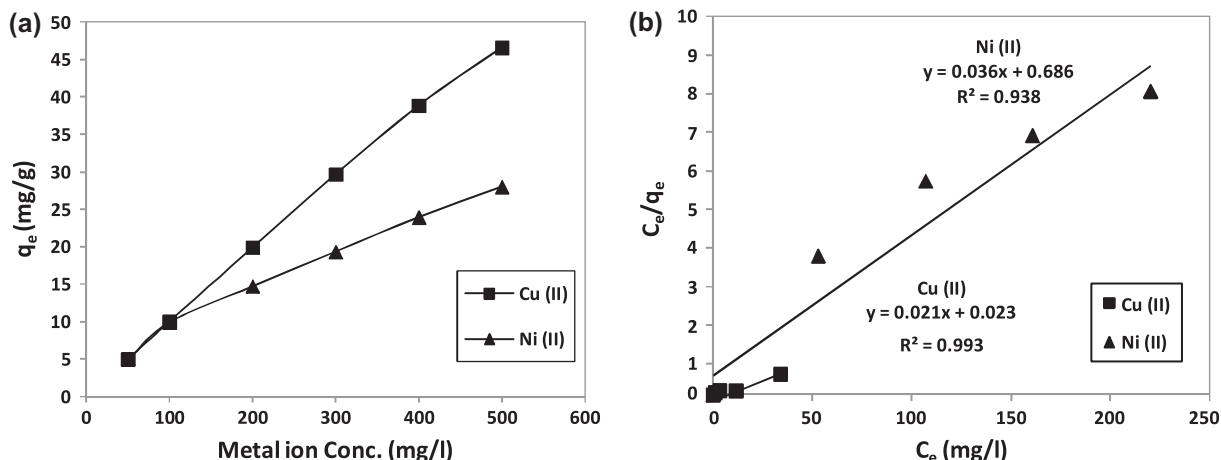
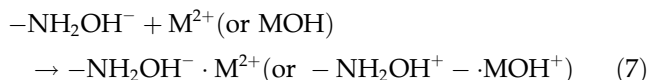
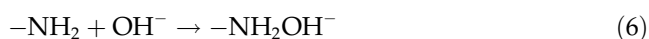
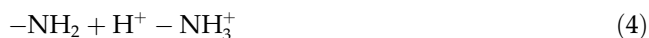


Fig. 6. (a) The effect of metal ion concentration on the adsorption of Cu(II) and Ni(II) by the modified silica aerogel (adsorbent dose = 0.5 g and contact time = 5 h for Ni(II) and 24 h for Cu(II) and pH = 6). (b) The Langmuir isotherm model.

reported that the maximum adsorption of copper (II), chromium (III), nickel (II), and lead (II) ions from aqueous solutions by meranti sawdust occurred at pH 6 [14]. Meena et al. (2005) also showed that the removal efficiency of Cu(II) and Ni(II) by carbon aerogel increased by pH increase up to 6 and it was decreased by further increase in pH [19]. The change in the amount of the metals ions adsorbed by the modified silica aerogel may be explained by the following reactions [29]. The decrease in the adsorption capacity at lower pH may be due to the competitive adsorption between hydrogen ions (H^+), Eq. (4), and the metals ions with amine groups of the adsorbent, Eq. (5), [12,29]. With alteration of more NH_2 groups to NH_3^+ , due to the protonation (Eq. (4)), there were only fewer NH_2 available on the surface of the modified silica aerogel for reaction with the metals ions (Eq. (5)). At higher solution pH ($pH > 6$), the adsorption of hydroxyl ions (OH^-) with the amine groups, Eq. (6), through hydrogen bond can reduce the amount of the metals ions adsorption [29]. At higher pH, as presented in Eq. (7), the product obtained in Eq. (6) can react with the metals ions in the solution through the electrostatic attraction that as a result of it, the adsorption capacity is increased [29].



3.4. Effect of metal ions concentration

As shown in Fig. 6, the adsorption capacity increased rapidly when the concentration of the metal ions increased. As the initial metal ions concentration increased from 50 to 500 mg/L, the adsorption capacity of Cu(II) and Ni(II) onto the modified silica aerogel changed from 5 to 46.6 mg/g and 5 to 28 mg/g, respectively. This indicates that the resistance against metal ions uptake by the adsorbent, because of higher driving force of the metal ions, decreases when there is an increase in the metal ion concentration [30].

3.4.1. Adsorption isotherms

In order to explain the nature of interaction between adsorbent and adsorbate, using adsorption isotherms is essential. Several isotherm models are employed to analyze adsorption data. The Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms are the major conventional models that are used.

The Langmuir isotherm supposes that monolayer adsorption happen on the homogenous sites of the sorbent [14]. It can be written as Eq. (8).

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (8)$$

Table 3
Isotherms parameters for the adsorption of Cu(II) and Ni(II) by the adsorbent

Metals ions	Langmuir isotherm				Freundlich isotherm			D-R isotherm		
	Q_m (mg/g)	b (L/mg)	R^2	R_L	K_f (g/L)	n	R^2	q_e (mg/g)	E (kJ/mol)	R^2
Cu(II)	47.6	0.91	0.993	0.02	0.05	4.08	0.972	39.32	1.33	0.859
Ni(II)	27.7	0.05	0.938	0.28	0.11	5.52	0.867	27.08	1.22	0.658

This isotherm is presented by the unitless constant called equilibrium parameter, R_L , as Eq. (9).

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

where C_0 (mg/L) and C_e (mg/L) are the metal ions concentration at initial and equilibrium time, respectively, b (L/mg) is the equilibrium constant, q_e (mg/g) is the adsorption capacity at equilibrium time, and Q_m (mg/g) is the maximum amounts of the metal ions on the sorbent. The values of Q_m and b are obtained from the intercept and slope by plotting C_e/q_e vs. C_e of Eq. (8), respectively [31]. The values of $R_L > 1$ and $0 < R_L < 1$ indicate unfavorable and favorable adsorption, respectively. $R_L = 0$ represents the irreversible adsorption and $R_L = 1$ is linear adsorption [31].

The Freundlich isotherm is an empirical equation applied to explain the adsorption onto the heterogeneous surface of sorbent as Eq. (10).

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

where q_e and C_e are as mentioned above, K_f (L/mg) is the Freundlich constant, and n is heterogeneity factor. The parameters n and K_f are obtained from the slope and intercept of the linear plot of $\ln q_e$ against C_e , respectively [29].

The D-R isotherm determined the adsorption mechanism type as physical or chemical in nature [28]. This isotherm model can be shown as Eq. (11).

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (11)$$

where q_m (mg/g) is maximum adsorption capacity, β (kJ/mol) is activity coefficient indicated to mean adsorption energy, and ε is Polanyi potential that is equal to $RT \ln(1 + 1/C_e)$. R (kJ/mol k) is the universal gas constant and T (k) is temperature. β and q_m are calculated from the slope and intercept of the plot $\ln q_e$ vs. ε^2 , respectively [28]. The mean adsorption energy, E (kJ/mol), is obtained by Eq. (12).

$$E = \frac{1}{\sqrt{2\beta}} \quad (12)$$

The value of E (kJ/mol) determines the type adsorption process as physical ($E < 8$ kJ/mol) or chemical ($E > 16$ kJ/mol) [31].

The results of the experimental data analysis by the isotherms models showed that the Langmuir isotherm model, as shown in Fig. 6, fitted the data better than other isotherms models ($R^2 = 0.993$ for Cu(II) and $R^2 = 0.938$ for Ni(II)). Table 3 presents the isotherms parameters for the adsorption of Cu(II) and Ni(II) by the modified silica aerogel. The R_L value in the Langmuir model for both the heavy metals is between 0 and 1. This implies that the adsorption of the metal ions is favorable. The values of mean adsorption energies $E = 1.33$ kJ/mol for Cu(II) and $E = 1.22$ kJ/mol for Ni(II) resulted from the D-R isotherm showed that the adsorption process is physical in nature (Table 3).

3.5. Effect of adsorbent dose

Fig. 7 depicts the effect of various adsorbent doses on the removal of the metals. As can be seen, the

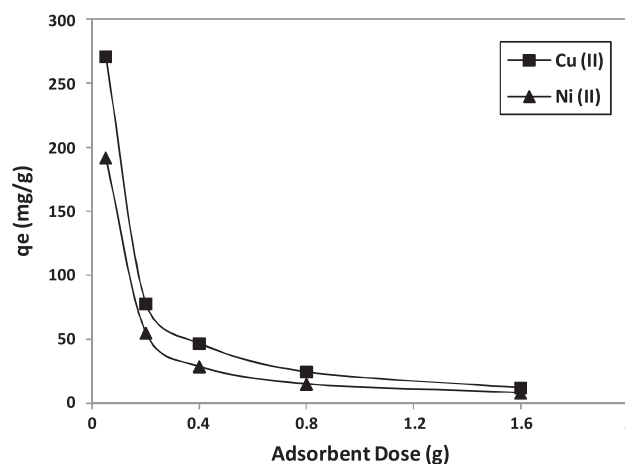


Fig. 7. The effect of different doses of the adsorbent on the removal of Cu(II) and Ni(II) (metals concentration = 400 mg/L, contact time = 5 h for Ni(II) and 24 h for Cu(II) and pH = 6).

adsorption capacity decreased with increasing adsorbent content. The decrease in the sorption capacity of the modified silica aerogel at higher concentration may be due to aggregation of the adsorbent; as a result of it, the specific surface area of the adsorbent decreased [32].

4. Conclusion

The sorption of Cu(II) and Ni(II) from aqueous solutions onto silica aerogel modified with amino functional groups was studied. It was found that the optimum contact time for the removal of Ni(II) and Cu(II) occurred at 5 and 24 h, respectively. High adsorption removal was also observed for both the metals at pH 6. The adsorption capacity of Cu(II) was higher than that of Ni(II). The kinetic and isotherm study showed that the pseudo-second-order kinetic and Langmuir isotherm models fitted the data better than the other models. The results showed that silica aerogel modified with amino functional groups can be used as a competent sorbent to remove these metals. The comparison of the adsorption capacity (mg/g) of the modified silica aerogel with other sorbents (Table 1) illustrated that the removal efficiency of this adsorbent is higher than that of the most adsorbents. However, it is necessary to conduct the economical analysis for using this adsorbent to remove the heavy metals in solutions.

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