

Original Article

Adsorption of Ni (II) and Cd (II) from Aqueous Solutions Using Modified Rice Husk*Soheil Sobhanardakani¹ Raziye Zandipak²

1- Department of the Environment, School of Basic Sciences, Hamedan Branch, Islamic Azad University, Hamedan, Iran
2- Young Researchers and Elite Club, Hamedan Branch, Islamic Azad University, Hamedan, Iran

*s_sobhan@iauh.ac.ir

(Received: 10 Jul 2014; Revised: 5 Sep 2014; Accepted: 9 Feb 2015)

Abstract

Background and purpose: Recently, release of pollutants such as heavy metal ions to the environment becomes one of the most important problems for soil and water. The present study was conducted to introduce modified rice husk (RH) as a new low-cost adsorbent.

Materials and Methods: In this study, tartaric acid modified RH (TARH), was used as an adsorbent for removal of Ni(II) and Cd(II) from water samples. This study was conducted in laboratory scale. Employing batch method, solution pH, adsorbent dose, contact time, and initial metals concentration were optimized.

Results: The optimum pH for removing of both the investigated metal ions from water solutions was found to be 4.0. The process of Ni(II) and Cd(II) adsorption on TARH reached equilibrium within 45 min. The isotherm evaluations revealed that the Langmuir model attained better fits of the experimental equilibrium data than the Freundlich model. In addition, adsorption kinetics data were well-fitted by the pseudo-second-order rate model with high regression coefficients.

Conclusion: It was found that TARH is a highly efficient adsorbent for Ni and Cd from aqueous solution, and the maximum predicted adsorption capacities for Ni(II) and Cd(II) were obtained as 55.5 and 45.5 mg/g, respectively.

[*Sobhanardakani S, Zandipak R. Adsorption of Ni (II) and Cd (II) from Aqueous Solutions Using Modified Rice Husk. *IJHS* 2015; 3(1): 1-9] <http://jhs.mazums.ac.ir>

Key words: Nickel, Cadmium, Tartaric acid modified rice husk, Removal efficiency, Adsorption

1. Introduction

Heavy metals, as a highly toxic pollutant, are widely distributed in the atmosphere, natural water, soil, and food (1). Heavy metal ions are not biodegradable, and they tend to accumulate in the organisms and enter the food chains through various pathways (2). Cadmium (Cd^{2+}) and nickel (Ni^{2+}) ions are of the heavy metal causing environmental pollution specifically in water (3,4). Cadmium and nickel are discharged into the aqueous environment through various sources including electroplating, mining, machinery, and steel making industries (5). Exposure to nickel may cause cancer of lungs, nose, and bones. Moreover, it may cause extreme weakness, dermatitis, headache, dizziness, and respiratory distress. Exposure to cadmium may cause erythrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity (6). The World Health Organization (WHO) has set a maximum guideline concentration of 0.025 and 0.003 mg/L for Ni and Cd in drinking water, respectively (7). At this time, a number of methods have been reported the removal of metals from water, such as precipitation, coagulation, adsorption, ultrafiltration, reverse osmosis, and membrane separation (8). Among them, adsorption is recognized as an effective and economic method for heavy metal removal (9,10). Recently, due to the high cost of adsorbents, there is an increasing interest in the use of low-cost adsorbents, which are able to remove metallic ions from aqueous solutions (11). Agriculture wastes or by-products have been investigated extensively for the removal of heavy metals due to their abundance in nature (12).

Rice is the strategic crop all over the world. Every year, a large amount of rice husk (RH) is produced. Agricultural residues, especially RH, the by-product of the rice milling industry, are produced in large quantities as a waste, creating environmental problems. RH

that mainly consists of crude protein (3%), ash (including silica 17%), lignin (20%), hemicellulose (25%), and cellulose (35%) renders it suitable for metallic cation fixation. RH, an abundant biomaterial, is capable of removing heavy metal ions and can be considered as an efficient and low-cost adsorbent (13,14).

In recent years, attention has been focused on the utilization of unmodified or modified RH as an adsorbent for removal of pollutants. Unmodified RH has been evaluated for their ability to bind metal ions (15,16). Various modifications on RH have been reported in order to enhance sorption capacities for metal ions and other pollutants (17,18). Wong et al. (19,20) reported that tartaric acid modified RH (TARH) has been shown to be a potentially useful material for the removal of Cu and Pb from aqueous solutions.

In the present study, TARH were used for removal of Ni(II) and Cd(II) from aqueous solution. The effect of pH, contact time, and TARH dose were investigated on the removal of Ni(II) and Cd(II). Finally, isotherm and kinetics of adsorption were evaluated

2. Materials and Methods

Ni(II) and Cd(II) concentrations were measured using an inductively coupled plasma-mass spectrometry (Verian710-Es Australia). PH measurements were made with a Metrohm Model 780 pH meter (Metrohm Switzerland). All chemicals and reagents were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments. Stock solutions of Ni(II) and Cd(II) (1000 mg/L) were prepared by dissolving the appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in double-distilled water and diluting in appropriate proportions.

RH was obtained from a rice mill in the north of Iran. It was treated with a diluted NaOH aqueous solution to eliminate trace

organic residues, and then washed several times with double-distilled water at a pH of 7.0. The clean RH was dried at 50°C in a vacuum oven until a constant weight was achieved. RH was ground to pass through a 1 mm sieve. Modification of RH with tartaric acid was carried out using the method reported by Marshall et al. (21). RH was mixed in a ratio of 2 g husk to 14 mL of 1.2 M tartaric acid and the acid/slurry was dried at 50°C overnight. The material was subsequently heated at 90°C for 90 min (20). Table 1 shows the physicochemical characteristics of TARH (22).

Table 1. Physicochemical characteristics of TARH

Characteristics	Values	Unit
Moisture content	9.5	%
Solid density	1.8	g cm ⁻³
Insoluble materials	75	%
Total soluble particles	105	mg/L
Organic materials	82	%
Fe ₂ O ₃	0.16	%
CaO	0.24	%

TARH: Tartaric acid modified rice husk

This experiment was conducted in a laboratory scale using 10 samples. All samples were analyzed three times. Adsorption equilibrium experiments were carried out in 50 mL beakers containing 60 mg/L of metal solution (10 ml Ni(II) and 13 ml Cd(II) solutions) and 0.3 g of TARH. The pH of the solution was adjusted at 4.0, using 0.1 M HCl and/or 0.1 M NaOH solutions. The mixture was shaken at room temperature for 45 min and the metal loaded TARH was separated from the mixture using Whatman filter paper with a diameter of 42 μm. The concentrations of the metals which remained in the solution were determined by inductively coupled plasma-mass spectrometry (Verian710-Es Australia) and the

concentration of the Ni(II) and Cd(II) ions remained in the adsorbent phase (q_e , mg/g) were used to calculate by Eq. (1);

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

where q_e (mg/g) is the equilibrium adsorption capacity, C_e is the metal concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

Finally, the Ni(II) and Cd(II) removal percent ($R\%$) was calculated by the Eq. (2);

$$R(\%) = \frac{\bar{C}_0 - \bar{C}_e}{\bar{C}_0} \times 100 \quad (2)$$

where C_0 and C_e are the initial and final Ni(II) and Cd(II) concentrations(mg/L).

3. Results

The influence of initial solution pH on the adsorption of Ni(II) and Cd(II) was studied in the pH range of 1.0-9.0 for initial metals ion concentration of 60 mg/L (Figure 1b). Furthermore, the zero-point charge (pH_{ZPC}) for the TARH was determined around 3.0 (Figure 1a). As was seen in the figure 2, the removal efficiency increases and reached the maximum and then remained nearly constant at higher pHs.

Figure 2 shows the effect of adsorbent dose on the removal efficiency (%) of Ni(II) and Cd(II) from aqueous solution. It was found that with increasing the dose of adsorbent, the percentage amount of metal removal increased.

Removal of Ni(II) and Cd(II) for different initial concentrations as a function of contact time was studied, and solution pH and adsorbent dose were fixed at their obtained optimum values. It can be seen that after about 45 min, almost all the metals became adsorbed. The results are shown in figure 3. Agitation time of 45 min was selected for further works.

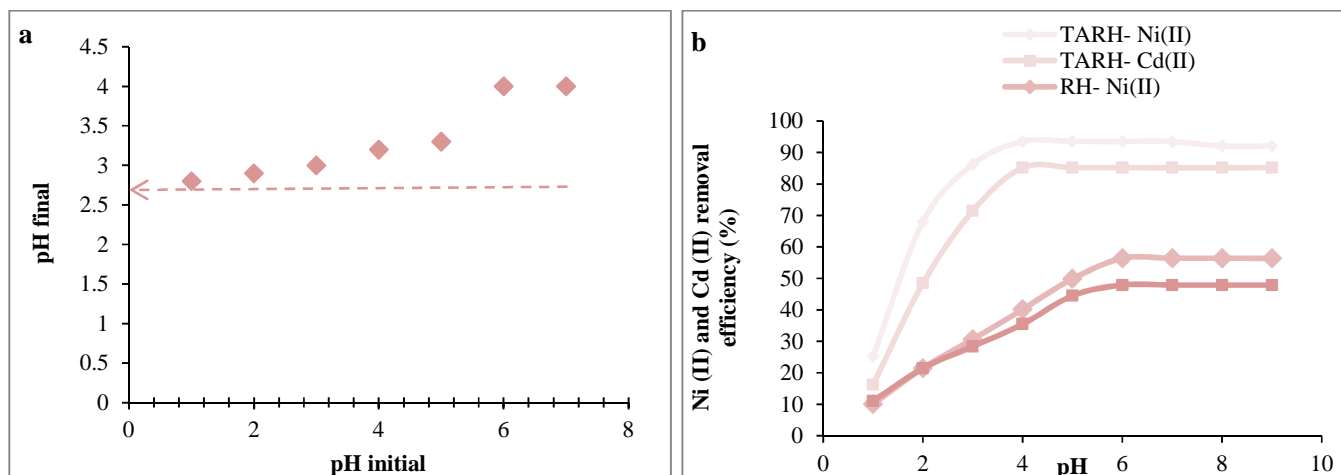


Figure 1. (a) The determination of the point of zero charge of the tartaric acid modified rice husk (TARH). (b) Effect of pH on the removal of Ni(II) and Cd(II) ions from aqueous solution by TARH, ($C_0 = 60$ mg/L, contact time = 45 min, dose of TARH = 0.3 g, temperature = 25°C).

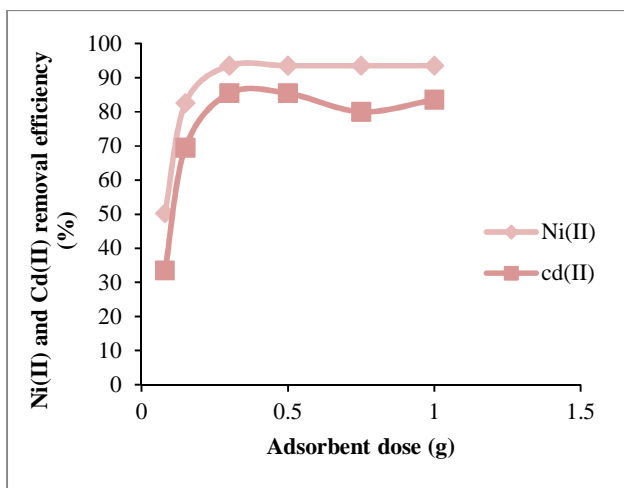


Figure 2. Effect of dose of tartaric acid modified rice husk on the removal of Ni(II) and Cd(II) ions ($C_0 = 60$ mg/L, initial pH = 4.0, contact time = 45 min, temperature = 25°C).

In order to optimize the use of TARH adsorbent, it is important to establish the most appropriate adsorption isotherm. Thus, the correlation of equilibrium data by either theoretical or empirical models is essential to practical operation. Langmuir and Freundlich models were used to analysis the experimental data of the TARH adsorbent for two metals in our work. Figure 4 presents the adsorption isotherms of Ni(II) and Cd(II) on TARH and RH. Table 2 summarizes the models constants and the determination coefficients.

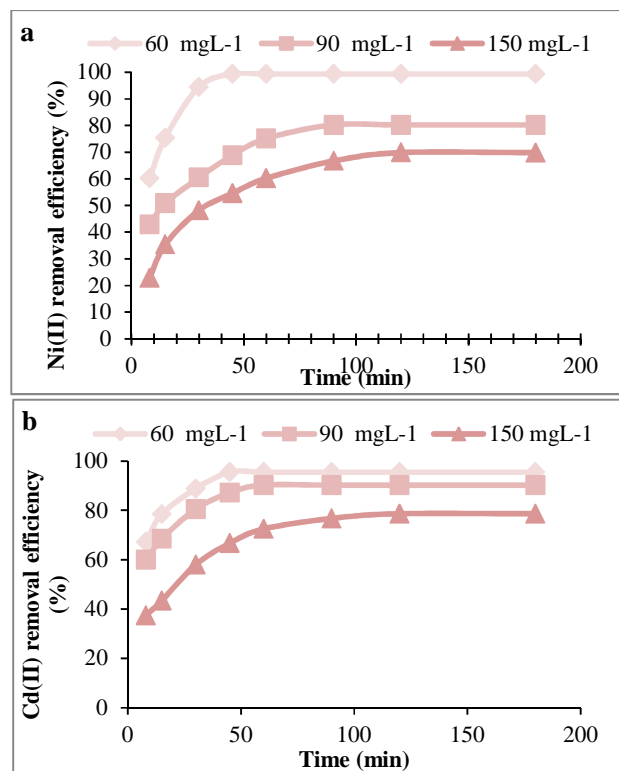


Figure 3. Effect of contact time on the removal of Ni(II) and Cd(II) ions by tartaric acid modified rice husk (TARH) (initial pH = 4.0, dose of TARH = 0.3 g, temperature = 25°C)

In order to analyze the adsorption kinetics of Ni(II) and Cd(II) by TARH, the pseudo-first-order and pseudo-second-order models, were tested. The results of fitting are shown in figures 5 and 6, table 3.

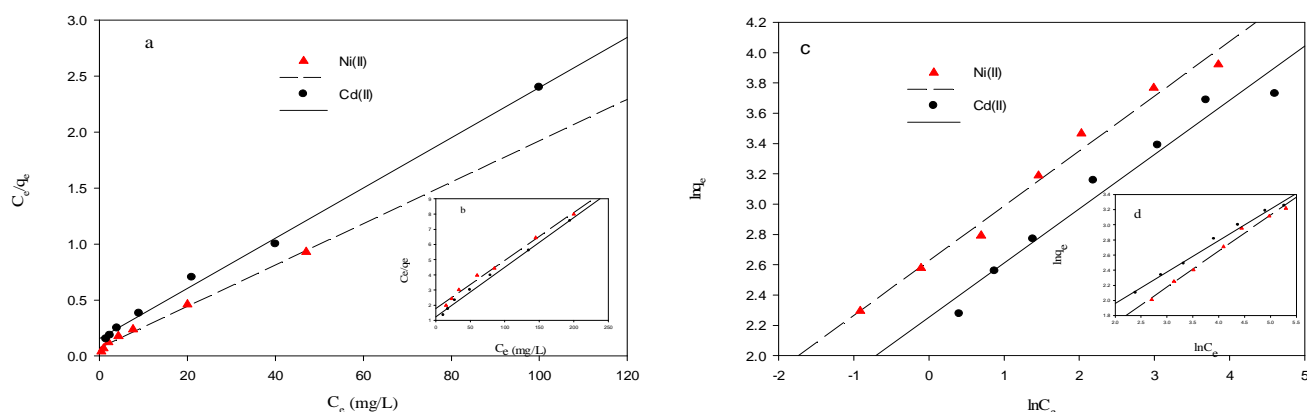


Figure 4. Langmuir isotherms for Ni(II) and Cd(II) ions adsorption onto (a) tartaric acid modified rice husk (TARH) and (b) RH at 25°C, Freundlich isotherms for Ni(II) and Cd(II) ions adsorption onto (c) TARH and (d) RH at 25°C

Table 2. Isotherm parameters of adsorption of metals onto TARH

Isotherm	Linear equation	References	Parameters	Adsorbent			
				Ni-TARH	Cd-TARH	Ni-RH	Cd-RH
Langmuir	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_1}$	(23)	q_m (mg/g)	55.5	45.5	32.2	31.25
			b (L/mg)	0.246	0.143	0.017	0.025
			R^2	0.993	0.997	0.992	0.995
Freundlich	$\ln q_e = \frac{1}{n} \ln C_e + \ln k_f$	(24)	K_f ($\text{mg}^{-1/(1/n)} \text{L}^{1/n} \text{g}^{-1}$)	13.83	9.50	2.11	3.10
			n	2.77	2.80	2.10	2.40
			R^2	0.985	0.960	0.990	0.989

TARH: Tartaric acid modified rice husk

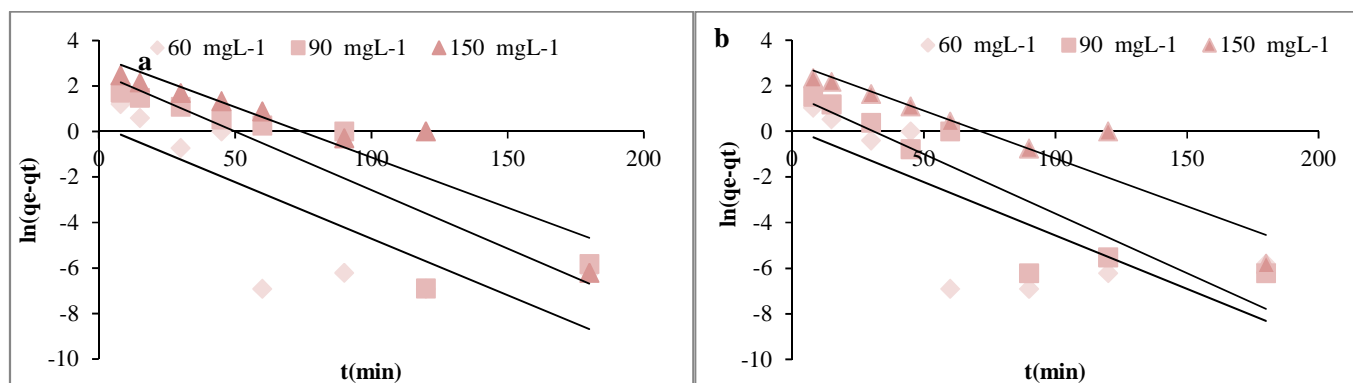


Figure 5. Pseudo-first-order kinetic plot for the adsorption of (a) Ni(II), and (b) Cd(II) onto tartaric acid modified rice husk at 25°C

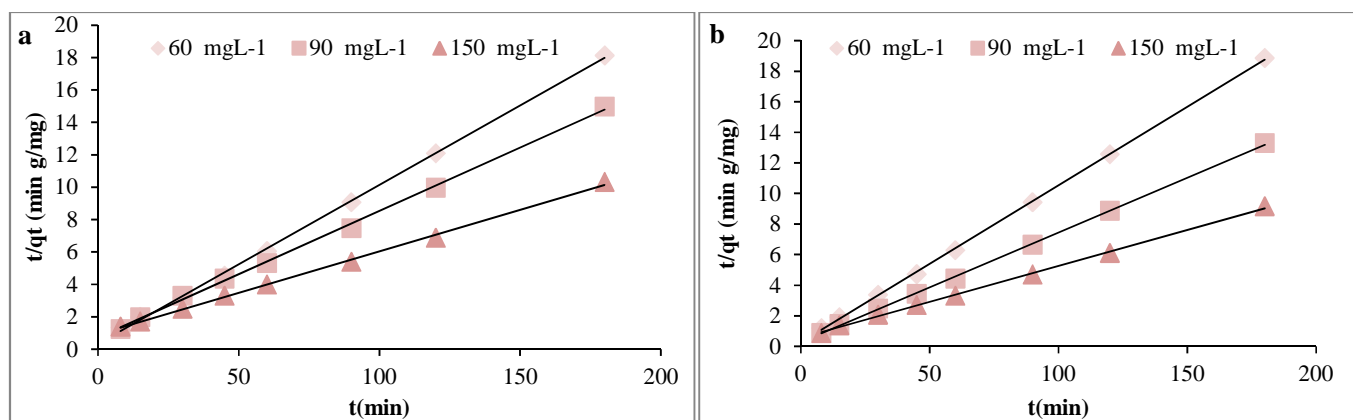


Figure 6. Pseudo-second-order kinetic plot for the adsorption of (a) Ni(II), and (b) Cd(II) onto tartaric acid modified rice husk at 25°C

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Table 3. Pseudo-first-order and pseudo-second order kinetic model parameters for the adsorption of metals onto TARH

Metals	C ₀ (mg/L)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
		q _e exp (mg/g)	q _{e1}	k ₁ (min ⁻¹)	R ²	q _{e2} (mg/g)	k ₂ (g/mg/min)	R ²
Ni(II)	60	9.935	1.28	0.049	0.622	10.20	0.029	0.999
Ni(II)	90	12.36	13.02	0.051	0.791	12.82	0.008	0.998
Ni(II)	150	17.463	26.41	0.044	0.867	19.60	0.051	0.998
Cd(II)	60	9.55	1.135	0.046	0.569	9.80	0.041	0.999
Cd(II)	90	13.54	5.042	0.052	0.808	14.08	0.018	0.999
Cd(II)	150	19.663	15.54	0.041	0.878	21.27	0.003	0.998

TARH: Tartaric acid modified rice husk

4. Discussion

Among all the parameters that might influence the adsorption capacity of adsorbents, pH is one of the most important parameters. It was observed from figure 1 that for TARH, the adsorption percentage of Ni(II) and Cd(II) ions increase from 25 to 93.5% and 16 to 85%, respectively, with increase in the solution pH from 1.0 to 4.0. Also for RH, the adsorption percentage of Ni(II) and Cd(II) ions increased with increasing pH from 1.0 to 6.0. The highest metals removal for Ni(II) and Cd(II) was achieved at pH 4.0 and 6.0 using TARH and RH, respectively.

The increase of Ni(II) and Cd(II) adsorption on TARH with increasing pH is probably attributed to the hydrolysis of Ni(II) and Cd(II). Generally, various Ni(II) and Cd(II) species in aqueous solution are present in the form of Ni²⁺, Ni(OH)⁺, Ni(OH)₂⁰, Ni(OH)₃⁻, Ni(OH)₄²⁻, and Cd²⁺, Cd(OH)⁺, Cd(OH)₂⁰, Cd(OH)₃⁻, Cd(OH)₄²⁻ at different pH values. At pH < 4.0, the predominant specie is Ni²⁺ and Cd²⁺. Therefore, at a lower pH, there exists a competition between H⁺ ions and Ni²⁺ and Cd²⁺ ions for the active surface sites and hence, lesser adsorption was observed. Besides, at lower pH (< p*H*_{zpc}), the number of positively charged on the surface sites of the TARH increases, which does not favor the adsorption of Ni(II) and Cd(II) due to electrostatic repulsion. At higher pH values (> p*H*_{zpc}), the lower concentration of H⁺ lead to greater Ni(II) and Cd(II) adsorption. Thus, pH 4.0 was adopted for further studies. Similar phenomenon has also been shown in the adsorption of Cd (II) ion from water with zinc

oxide nanoparticles (25).

The amount of adsorbent significantly influences the amount of heavy metal adsorption. As in figure 2 was seen, the removal efficiency increases from 50% to 93.5% for Ni(II) and from 33.5 to 85.5% for Cd(II) with an increase in adsorbent dose from 0.08 g to 0.3 g. This is due to an increase in the surface area and availability of more active sites for adsorption. Afterward, the removal efficiency remains unchanged with an increase in adsorbent dose because the Ni(II) and Cd(II) ions become limiting in the system. Therefore, 0.3 g of adsorbent was selected for subsequent work. This phenomenon was also observed by Afkhami and indicated that adsorption percentage increases with increasing adsorbent dose (26).

It was observed that Ni(II) and Cd(II) ions adsorption increased with the increasing of time and reached equilibrium at about 45 min (Figure 3a and b). The rapid adsorption at the initial contact time was due to the availability of more active surface of the adsorbents, which leads to fast adsorption of the metals from the solution. Subsequently, the diminishing availability of the remained active sites and the decrease in the driving force lead to the slow adsorptive process. As shown in figure 3a and b, the removal percent of Ni(II) and Cd(II) ions decreases with the increase in initial concentration from 60 to 150 mg/L. The initial metals concentrations provide an important driving force to overcome the mass transfer resistance of the metal between the aqueous phases and the solid phases, so increasing initial concentrations would

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enhance the adsorption capacity of metal. On the other hand, the metal adsorption process generally involves the first transport of metal molecules from bulk solution through liquid film to the exterior surface of adsorbent and then from the exterior surface to the pores of the adsorbent, which reflects the adsorption of metal onto the adsorbent is relevant to the initial concentration. At the same time, equilibrium time also increased with increasing initial metals concentration. The equilibrium time was 45 min, 90 min and 120 min for Ni(II) and 45 min, 60 min and 90 min for Cd(II), when initial concentration was 60, 90 and 150 mg/L, respectively. Therefore, it was clear that the removal percentage of metals is greater at lower initial concentration but smaller at higher initial concentration and adsorption process was highly dependent on initial metals concentration and contact time. Similar results were observed by Chen who investigated the effect of initial concentration of metal ions on removal of Ni (II) from aqueous solution by multiwall carbon nanotube/iron oxide magnetic composites and indicated that adsorption decreases with increasing initial concentration of metals. Furthermore, similar results have been found by Li et al. (27,28).

An adsorption isotherm describes the relationship between the amount of adsorbate taken up by the adsorbent and the adsorbate concentration remaining in the solution after the system has attained equilibrium. The equilibrium adsorption data of Ni(II) and Cd(II) onto TARH and RH was analyzed using Langmuir and Freundlich models. As shown in table 2, the R^2 of the Langmuir isotherm was greater than that of the Freundlich isotherm for the adsorption of both investigated metals. This indicates that the adsorption of Ni(II) and Cd(II) on TARH and RH is better described by the Langmuir model than the Freundlich model in optimum condition (Figure 4). This explains that the adsorption of Ni(II) and Cd(II) on TARH and RH involves the monolayer

coverage of the metals on the homogenous surface of the adsorbent.

Adsorption kinetic is one of the most important characters which govern the solute uptake rate and represents the adsorption efficiency of the adsorbent and, therefore, determines its potential applications. The adsorption kinetic experiments were carried out in batch mode by three initial concentrations of Ni(II) and Cd(II) at various stirring times and we investigated the adsorption kinetics of metals onto TARH by two kinetic models: the pseudo-first-order and pseudo-second-order models.

The linear form of pseudo-first-order kinetic model was described by Eq (3) (29);

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \quad (3)$$

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min) respectively and k_1 (min^{-1}) is the pseudo-first-order rate constant. Values of k_1 were calculated from the plots of $\log(q_e - q_t)$ versus t (Figure 5 a and b).

The linear form of pseudo-second-order kinetic model was expressed by Eq (4) (30);

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

where k_2 (g/mg/min) is the pseudo-second-order rate constant, and its value was obtained from the plots of t/q_t versus t (Figure 6a and b). The kinetic data from pseudo-first-order and pseudo-second-order models are given in table 3. The correlation coefficients (R^2) for the pseudo-second-order adsorption model were all higher than for the pseudo-first-order model. Thus, the adsorption data may be well-represented by the pseudo-second-order model.

The results of the present study show that Ni(II) and Cd(II) could be effectively adsorbed by TARH in the aqueous solution. The effect of parameters like pH, contact time, amount of adsorbent and adsorbate concentration have been investigated and it is found that the adsorption of Ni(II) and Cd(II) is dependent on these variables and optimum

pH was determined as 4.0. It is also observed that Ni(II) and Cd(II) adsorption decreased with increasing initial metals concentration. The Langmuir and Freundlich adsorption isotherms were used to correlate the equilibrium adsorption data, and the isotherm constants were determined. The Langmuir isotherm provided a better fit than the other. Kinetic studies demonstrated that the mechanism for the adsorption of metal ions followed the pseudo-second-order rate model, which provided the best fit for the experimental data.

Acknowledgement

The authors are very grateful to the Hamedan Branch, Islamic Azad University for providing facilities to conduct and complete this study.

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