International Journal of Engineering and Applied Sciences (IJEAS)
ISSN: 2394-3661, Volume-4, Issue-10, October 2017

Investigation of the Ni(II) Adsorption, in Respect to Kinetics and Thermodynamics, by Carbonized Walnut Shell from Aqueous Solution

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Abstract— **The objective in this study was to investigate the adsorption, in terms of reaction speed and thermodynamics, of the Ni(II) from aqueus solution. Carbonized walnut shell was used as an adsorbent. The effect of contact time (0-90min) and temperatures (26-45°C) on the adsorption properties have been studied. The adsorption process follows the pseudo-second-order kinetic model very well. The thermodynamic parameters, such as Gibb's free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were also evaluated. The thermodynamic parameters (ΔG° < 0, ΔS = -17.37 J/mol/K, ΔH° = -5.72 kJ/mol) indicated that it was a spontaneously exothermic reaction.**

Index Terms— **Adsorption, Kinetics, Ni (II), Thermodynamics, Walnut Shell.**

I. INTRODUCTION

Agricultural and industrial developments have been increased with scientific and technological progress throughout the world in recent years. These developments have caused the release of various pollutants especially heavy metals into the watersource, which threaten and hazard for all living organisms in the ecosystem. Heavy metals such as lead, copper, cadmium, zinc and nickel are among the most common pollutants in the water[1]. Among these metals, nickel is in wide demand in different industries such as batteries, mineral processing, electroplating, smelting, coin, paint formulation etc. [2],[3]. Nickel is among the non-biodegradable toxic heavy metals and at high concentrations Ni(II) is known to cause different types of diseases such as headache, pulmonary fibrosis, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis, renal edema and skin dermatitis and extreme weakness [4-7]. Therefore, it is necessary to remove Ni(II) from the water. For this purpose, there are various methods to solve this problem such as chemical precipitation, ionic exchange, filtration, electrochemical treatment, membrane techniques, recovery by evaporation and adsorption [8], [9]. The adsorption methods is used commonly because it is both economically favorable and technically applicable than other methods[10]. In this study the adsorption of Ni(II) on the adsorbent prepeared from walnut shell has been investigated under different environmental conditions. Kinetic data have been analyzed by pseudo-first and pseudo-second order models to obtain the kinetic constants and also thermodynamic study of Ni(II) removal has been conducted.

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II. MATERIAL AND METHOD

A. *Preperation of Adsorbent*

The adsorbent was prepeared from walnut shell. The plant was first broken and then carbonized in the oven which was heated from the ambient temperature to the 500°C with the heating rate of 10°C/min for 90 minutes. During the carbonization process nitrogen was fed to furnace at a flow rate of 58 L/h. After the carbonization was completed, sample removed from the oven was first grinded and then sieved down to 0.092-0.063 mm.

B. *Experimental*

Adsorption studies were carried out by 200 mL solutions prepared at the desired concentration that obtained by diluting from the 1000 mg/L Ni(II) stock. In the experiments a thermostatic incubator shaker with a shaking speed of 200 rpm was used. During the experiments initial Ni(II) concentration 20 mg/L, adsorbent dosage 0.4 g/L and pH of 6 were selected as constant while temperatures selected varied between 26, 37, 45°C. Samples obtained between 1-90 min. were filtered to obtain clear solutions. The concentration of the residual Ni(II) in the solution was measured by Atomic Absorption spectrophotometer (Shimadzu AA-670).

III. RESULTS AND DISCUSSION

A. *Kinetic studies*

In order to determine the rate of Ni(II) removal from the solutions, kinetic studies were evaluated. Kinetic models were examined to explain the kinetics of Ni(II) adsorption on the CWS by using pseudo first-order and pseudo second-order [9]. The correlation coefficient (R^2) was selected for expressing the conformity between experimental data and the model predicted. The R^2 values approaching to 1 indicates the best fitting between the data obtained from the kinetic model and by the experimentally.

B. *The pseudo first-order model*

The pseudo first-order equation is generally presented as follows;

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption capacity at equilibrium and at time t (min), respectively, k_1 is the rate coefficient of pseudo first-order adsorption (L min^{-1}). The plot of log (q_e - q_t) vs. t was shown in Figure 1. From the Figure 1, k_1 can be determined from the slope of linear line and also qe can be determined from the intercept of the plot [11].

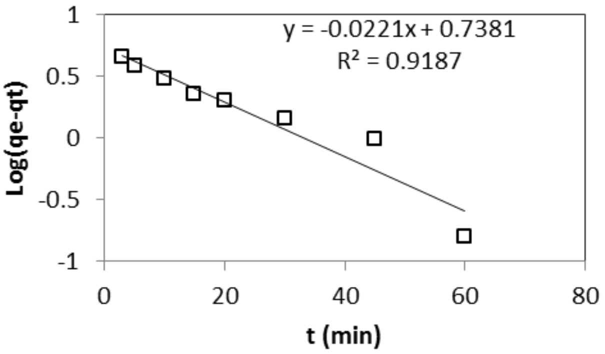

Figure 1. Pseudo first order kinetics model of Ni(II) removal by CWS

C. The pseudo second-order model

The pseudo second-order adsorption kinetic rate equation is expressed as:

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

where k_2 is the rate coefficient of pseudo second-order adsorption (g mg^{-1} min^{-1}). The plot of t/qt vs t illustrated in Figure 2. From the Figure 2, qe can be determined from the slope of linear line and also k_2 can be determined from the intercept of the plot [11].

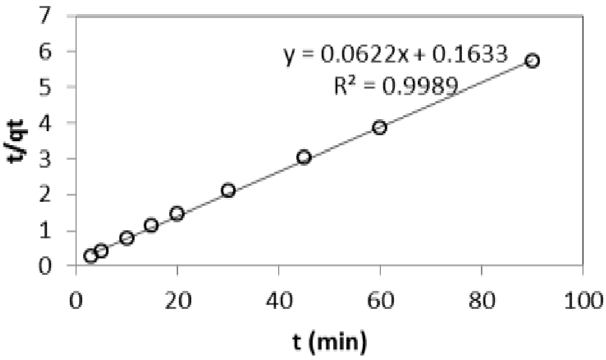

Figure 2. Pseudo second order kinetics model of Ni(II) removal by CWS

Kinetic model parameters obtained were given in Table 1. The obtained correlation coefficient values of R^2 for pseudo second-order expression, and pseudo-first order were 0.999, 0.919 respectively. It is obvious that the correlation coefficient R^2 of pseudo second-order expression was higher than that of pseudo-first order expression. The adsorption of Ni(II) onto CWS was represented by the pseudo-second-order kinetic model. Similar results have been reported by Wang and Li, 2009 for nonliving biomass of the marine brown alga laminaria japonica, by [12] for calcium alginate, by [13] for blank alginate beads.

Table 1. Adsorption rate constants associated with pseudo first and second order kinetic models.

	$q_{e.experimental}$ (mg g^{-1})	R^2	$q_{e.calculated}$ (mg g^{-1})	k_1 1 min^{-1}
Pseudo first-order kinetic model	15.748	0.968	5.471	0.051
	$q_{e.experimental}$ (mg g^{-1})	R^2	$q_{e.calculated}$ (mg g^{-1})	k_2 g mg^{-1} min^{-1}
Pseudo second-order kinetic model	15.748	0.999	16.088	0.025

D. Thermodynamic study

The effect of temperature on Ni(II) adsorption was investigated at the temperature range of 26-45°C and was illustrated in Figure 3. It was seen from the Figure that percentage removal of Ni(II) increased with increasing temperature from 26–45°C, which indicates that adsorption of Ni(II) onto the surface of CWS was exothermic.

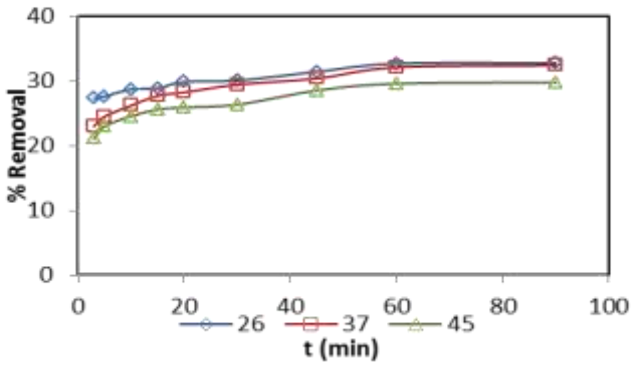

Figure 3. Effect of temperature on removal of Ni(II) (adsorbent dosage 0.4 g/L, initial concentration 20 mg/L, pH 6)

Thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy, (ΔG°) for Ni(II) adsorption onto CWS were obtained. These parameters describe whether the adsorption is endothermic or exothermic, and also spontaneously of the adsorption process. The Gibbs free energy (ΔG°) of the adsorption is given by the following equation:

$$\Delta G^\circ = -RT\ln K_d \quad (3)$$

where K_d is the distribution coefficient, R(8.314 j mol^{-1} $\mathbf{K}^{-1}$) is the gas constant and T is the absolute temperature (K) (Ding et al. 2013). The adsorption distribution coefficient (K_d) can be calculated from:

$$K_d = \frac{q_e}{c_e} \quad (4)$$

where q_e is adsorption capacity at equilibrium, and is obtained by the following equation

$$q_e = \frac{(c_0 - c_e) \times V}{m} \quad (5)$$

where C_0 and C_e are the initial and equilibrium concentrations of Ni(II) ion in solution (mg/L). m is the mass of carbon sample (g), V is the volume of adsorption solution (L).The value of the distribution coefficient (K_d) for the adsorption of Ni(II) ion on the adsorbent were calculated at different temperature and at equilibrium time using Eqs. (4) and (5). The amounts of ΔH°and ΔS° can be determined from the slope and intercept of the straight line obtained from plotting $\ln K_d$ vs 1/T using Eq (6) which was shown in Figure 4 [14].

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

After obtaining ΔH° and ΔS° values of the adsorption, ΔG° for the examined temperature was calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

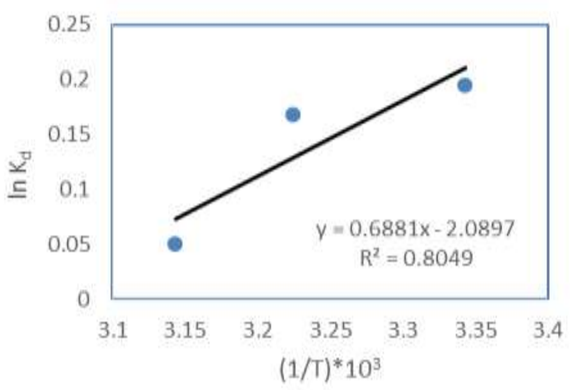

Figure 4. Adsorption thermodynamics.

Table 2. Thermodynamic parameters for the adsorption of Ni(II)

T°C	K_d	ΔG° kj mol^{-1}	ΔS° jmol^{-1} K^{-1}	ΔH° kj mol^{-1}
26	1.22	-0.52		
37	1.18	-0.33	-17.37	-5.72
45	1.05	-0.19		

All the thermodynamic parameters were listed in Table 2. As the ΔG values were negative it can be said that the adsorption process of Ni(II) was spontaneous under the studied conditions. The values of ΔG° increased from -0.52 to -0.19 kJ/mol in the temperature range of 26–45°C. The negative value of enthalpy change (ΔH°) obtained for Ni(II) adsorption, illustrates the exothermic nature of the reaction. Some authors such as [15-17] have reported similar results.

IV. Conclusions

This study highlights the potential of CWS usage as an adsorbent for the removal of Ni(II) from solutions. The adsorption of Ni(II) on CWS was represented by the pseudo-second-order kinetic model. Adsorption thermodynamic showed that the adsorption process was exothermic and spontaneous.

ACKNOWLEDGMENT

This work was supported by the Atatürk University Research Foundation (BAP, 2013/108)

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