

Kinetics and Isotherms Studies for The Removal of Ni(II) From Aqueous Solutions Using Rosa Canina L

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Abstract. Activated carbon prepared from Rosa canina L (RC) was used as an adsorbent for the removal of Ni(II) from aqueous solution. Adsorption was investigated in a batch system with respect to various parameters such as initial metal ion concentration and contact time. Results were analyzed by the Langmuir and Freundlich equations at different temperatures and determined the characteristic parameters for each adsorption isotherm. The kinetics studies were performed by Pseudo first order and Pseudo second order. Maximum monolayer adsorption capacity observed at 25°C (106.04 mg g⁻¹). Kinetic data correlated well with the pseudo second order model, suggesting that the adsorption process might be chemical sorption. The results obtained showed that (RC) could be used as an effective and low-cost adsorbent for removal of Ni(II) from aqueous solutions.

Keywords: adsorption; kinetic; rosa canina l; ni(ii) ; isotherm

1. Introduction

Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development. The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life, besides the facts that these metals kill microorganisms during biological treatment of waste water with a consequent delay of the process of water purification [1]. Nickel is a toxic metal present in wastewaters and more than 40% of the nickel produced is used in steel factories, nickel batteries and in the production of some alloys, which cause increasing of the Ni(II) burden on the ecosystem and deterioration water quality [2]. Its concentrations in industrial wastewaters range from 3.40 to 900 mgL⁻¹ and maximum contaminant limit for nickel in potable water has been fixed as 50 µg l⁻¹ by the European Economic Community[3]. Many conventional methods including oxidation, membrane filtration, coagulation, reverse osmosis, adsorption, ion exchange, precipitation have been reported in the literature to remove heavy metals from waste water. These methods may be ineffective or extremely expensive especially when the waste stream contains relatively low concentration of metal (1-100 mgL⁻¹) dissolved in large volume. However, adsorption can be regarded as one of the most popular method for the removal of heavy metals from the wastewater due to its low cost, easy availability, biodegradability, simplicity of design and high removal efficiency[4]. There are several types of adsorbents that are commonly used, which includes activated carbon, zeolite and the agricultural adsorbents [5]. There have been many studies on the production of low-cost activated carbons from agricultural wastes such as Palm shell, Bamboo and Nettle ash [6-8]. Present research aims to remove Ni (II) by (RC) from aqueous solutions using adsorption technique and to study the effect of different experimental conditions such as contact time and temperature on metal sorption process. The research focuses on adsorption kinetics and isotherm studies of the prepared adsorbent.

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2. Experimental

2.1. Materials and methods

Rosa canina L (RC) was obtained from various regions of Arak-Iran. (RC) was air-dried and washed several times with deionized water to remove the impurities, and then dried in an oven at 105 °C for 24 h. The adsorbent materials was impregnated with concentrated H₂SO₄. Then it was activated in a hot air oven at 150 °C for 24 h. The carbonized material was washed with distilled water to remove the free acid and the activated carbon was then soaked in 1% NaHCO₃ solution to remove any remaining acid. Then it was washed with distilled water until the pH of the activated carbon reached 6.25, dried at 105 °C, and sieved to the particle size 120µm.

All the reagents used were of analytical reagent grade and doubly distilled deionized water was used in sample preparation. Stock solution of Ni (II) was prepared by dissolving Ni(NO₃)₂.6H₂O in distilled deionized water. Further working solutions were prepared by diluting this stock solution. Initial pH was adjusted using 0.1N H₂SO₄ or 0.1N NaOH.

2.2. Batch mode adsorption studies

Adsorption experiments were carried out in 100 mL Erlenmeyer flasks containing 50 ml deionized water and 0.1gr of carbon prepared previously and 10 mL solution with known concentration, pH value and temperature. The flasks were stirred, the agitator stirring speed was 200 rpm. After a preset contact time, the samples were separated from the solution by filtration through the filter paper. The exact concentration of the residual metal ion in the filtrate was analyzed by an atomic absorption spectrometer (Shimadzu AA-680, Japan).

The equilibrium adsorption amount (q_e) is calculated according to Eq. 1:

$$q_e = \left(\frac{C_o - C_e}{m} \right) V \quad (1)$$

where q_e is the amount of Ni(II) adsorbed (mg g⁻¹ carbon) at equilibrium contact time, C_o is the initial Ni(II) concentration (mgL⁻¹), C_e is the Ni(II) concentration at equilibrium time in the solution (mgL⁻¹), V is the volume of the Ni(II) solution (L), and m is the weight of carbon added into the solution (g).

2.3. Adsorption isotherms

The salient features of isotherm studies are essential for the adsorption process to be interpreted adequately. Many models have been proposed by the researchers to explain adsorption equilibrium. The most commonly used isotherm models for solid-liquid adsorption are the Langmuir and Freundlich isotherms. The Langmuir isotherm is based on monolayer adsorption (constant heat of adsorption for all sites) on the active sites of the adsorbent and it is expressed by following equation. The linear form of the Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} k_L} + \frac{1}{q_{\max}} C_e \quad (2)$$

When $\frac{C_e}{q_e}$ is plotted against C_e , a straight line with slope $\frac{1}{q_{\max}}$ and intercept of $\frac{1}{q_{\max} k_L}$ is obtained.

The linear plot of Langmuir Isotherm is shown on Fig. 1 at 25 ,45 and 60 °C and the model parameters are listed in Table 1.

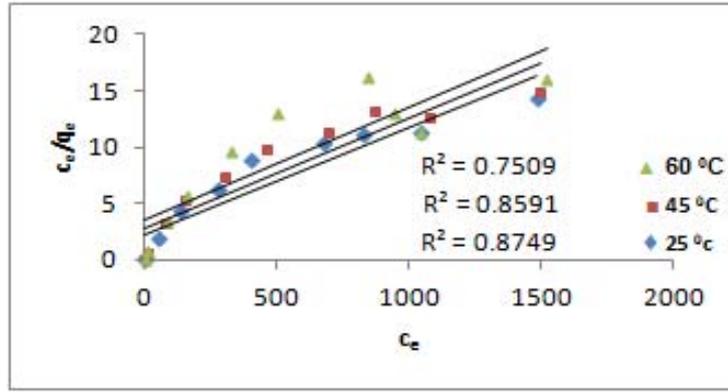


Fig. 1. Langmuir isotherm for adsorption of Ni(II) by activated carbon Rosa canina L(RC)

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface) properties. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \quad (3)$$

where, K_f (mg g^{-1}) and $\frac{1}{n}$ relates the multilayer adsorption capacity and intensity of adsorption.

The Freundlich plot for the adsorption of Ni (II) is shown in Fig. 2 and the model parameters are listed in Table 1.

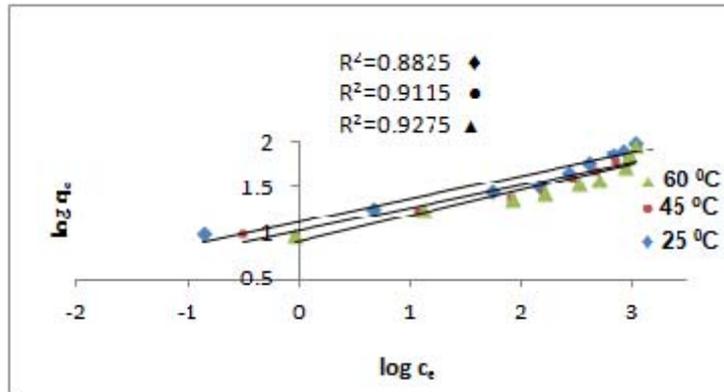


Fig. 2. Freundlich isotherm for adsorption of Ni(II) by activated carbon Rosa canina L(RC)

2.4. Kinetic studies

To design the sorption systems, chemical kinetics is very important as it explains how slow and fast the rate of chemical reaction occurs and the factors which affect the reaction rate. In order to gain some insight into the sorption process of Ni (II) ions onto the surface activated (RC), pseudo first order and pseudo second order kinetic models were implemented. The pseudo first order equation based on equilibrium adsorption is expressed as[9]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

Where k_1 is the first order rate constant (min^{-1}). The plot of $\log(q_e - q_t)$ versus t gave the slope k_1 and intercept of $\log q_e$. Pseudo second order equation can be given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (5)$$

Table 1: Isotherm model parameters and correlation coefficient at different temperatures

Isotherm model	Parameters	values		
		25 °C	45 °C	60 °C
Langmuir	q_{\max} (mg g^{-1})	106.04	102.04	100.00
	K_L	0.0041	0.0035	0.0029
	R^2	0.8749	0.8591	0.7509
Freundlich	K_F (mg.g^{-1})	8.400	10.334	13.332
	n	3.5881	3.7679	3.9479
	R^2	0.8825	0.9009	0.9275

Where k_2 is the rate constant of second order adsorption.

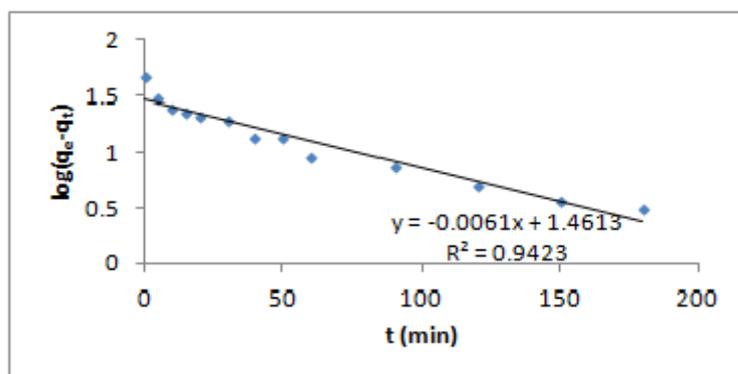


Fig. 3: Pseudo first order Kinetics for adsorption of Ni(II) by activated carbon Rosa canina L(RC)

Table 2: The kinetic parameters evaluated for Ni (II) ion adsorption.

Kinetic model	Parameter	Ni(II) Concentration (100 mg.L^{-1})
Pseudo-first order	K_1 (min^{-1})	0.014
	q_e (mg.g^{-1})	28.926
	R^2	0.942
Pseudo-second order	K_2 ($\text{g.mg}^{-1}.\text{min}^{-1}$)	0.0013
	q_e (mg.g^{-1})	48.780
	R^2	0.984

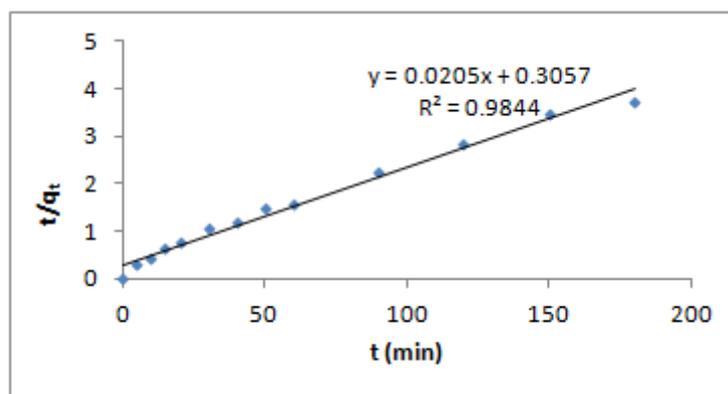


Fig. 4 : Pseudo second order Kinetics for adsorption of Ni(II) by activated carbon Rosa canina L(RC)

The parameters obtained from these models, pseudo first order Fig. 3 and pseudo second order Fig. 4 plots for Ni(II) were compared in Table 2. The results show that pseudo second order kinetic model better represented the adsorption process in comparison to the pseudo first order kinetic model.

3. Conclusion

The results from the experiments described in this study show that nickel ions can be adsorbed efficiently on activated carbon *Rosa canina* L (RC). Results were analyzed by the Langmuir and Freundlich equations and determined the characteristic parameters for each adsorption isotherm. The maximum sorption capacity q_m was found to be almost 106.04, 102.04 and 100.00, as evaluated using Langmuir isotherms at 25°C, 45°C and 60 °C, respectively. Pseudo second order gave better R^2 values confirming chemisorptions onto the surface. The result indicates that, (RC) is environmentally friendly and promising material which can be used successfully for separation of Ni(II) from aqueous solution.

4. References

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