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Improving Removal of Nickel from Wastewater using Palm Leaf Ash as a Biosorbent

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Abstract

Nickel (Ni) as a heavy metal due to its toxicity should be removed from wastewater and aquatic environments using efficient technology. The aim of this study was to remove Ni from an aqueous solution using palm leaf ash produced in a furnace. To do so, kinetic and thermodynamic experiments were conducted on the adsorption process. Moreover, the effect of time, pH, adsorbent and initial concentration of Ni was studied on Ni adsorption. The results of the experiment indicated that the Ni adsorption process followed the Freundlich isotherm model. The study of kinetic data also displayed the removal of Ni ions from the pseudo-second-order kinetics. The results showed that the percentage removal of Ni (II) and maximum adsorption capacity of an adsorbent for Ni (II) ions were 94.67% and 40.81 mgg^{-1}, respectively. Furthermore, the enthalpy of the adsorption process (ΔH) was 62706.8 $j.mol^{-1}$.

Keywords: Biosorbent,Nickel Adsorption, Palm Leaf Ash.

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Introduction

Serious problems have been created in life and activities of humans and living organisms with the growth of industry and population, leading to the entry of heavy metal contaminants into the rivers and seas [1-4].Most heavy metals such as oxide or sulfide Nickel (Ni)or Ni salt, sodium, calcium, copper and so on have devastating effects on the environmental balance [5].

The main objective of the removal of heavy metals is to clean the water contaminated with heavy metals. If the level of heavy metals in the contaminated water exceeds the standard level, they should be removed through various physical and chemical processes. Chemical sequestration is one of the most common methods for removal of heavy metals. The disadvantages and problems of this method include incomplete removal of heavy metals, massive sludge production and high expenditure in removal process [6].Other methods such as reverse osmosis, ion exchange [7], solvent extraction and evaporation are also used to remove heavy metals [8]. Biosorption is a non-metabolic process in which the pollutants are trapped in the cellular structure of the adsorbent. In recent years some agricultural wastes have been used as an adsorbent for water purification [9-11]. Numerous studies have been performed on the accumulation of biomass ash to facilitate the potential industrial application [12-16]. Okmanis et al. have suggested that the biomass ash has good adsorption properties and, because of its plenty, is a cost-effective method to remove the heavy metals from wastewater [13].

On the other hand, silica obtained from agricultural wastes like palm ash (silicon dioxide) is considered as valuable and mineral multi-purpose chemical compounds and raw material [10]. Xuet al. evaluated the adsorption properties of copper ions in aqueous solution using biomass ash and its modified products. They modified the biomass ash through mesoporous siliceous material, functionalized using 3-aminopropyltriethoxysilaneand evaluated their potential application to control water pollution [14]. Besides, Ni was removed from wastewater using arumugam and ponnusami through adsorption with amine functionalized sba-15 synthesized using sugarcane leaf ash as a low cost silica source [15]. Mohammadi et al. removed mercury from an aqueous solution using palm ash. They concluded that since the palm leaf had a great reactivity and cross-section to remove the mercury from aqueous solutions; therefore, it might be effective to remove mercury [16].

Hence, according to the previous studies, the aim of this study was to remove or reduce the heavy metals from aqueous environments, to prevent their destructive effects and to absorb the Ni through palm leaf ash (PLA). Kinetic and thermodynamic studies were carried out as well as the optimal conditions for pH, amount of adsorbent, concentration and temperature in contaminated water were investigated. In addition, this method was compared with existing methods and its superiority was studied, too.

Experimental

Materials

Palm leaf used as an adsorbent in the current study belonged to the Phoenix dactylifera and Arecaceae family. Moreover, Ni chloride 97% and sodium hydroxide 97% were purchased from Merck as well as nitric acid 65% was obtained from Scharlu.

Characterization of Sorbent

An X-ray diffraction (XRD) analysis of the powdered samples was performed using a Cu kα radiation (λ= 1.54056 A°) in the range of 10-90° (2θ) at 40Kv and 30Ma. The IR spectra were scanned on a Fourier transform infrared spectroscopy (FTIR) spectrometer (TENSOR 27, BRUKER, Germany) in the wavelength ranged from 400 to 4000 cm^{-1} using KBr pellets. Additionally, the surface morphology of PLA was studied by scanning electron microscope (SEM, Phillips XL30, Holland).

Methods

Adsorbent preparation

Palm leaves were cut into small pieces and powdered after washing and drying. Then, the powder was burnt on an indirect flame and turned into ash in the muffle furnace for 2 hours at a temperature of 600 °C. The obtained ash was used as an adsorbent for the removal of Ni^{2+} in subsequent experiments.

Adsorption studies

Adsorption studies were conducted on pH, amount of adsorbent, concentration, contact time and temperature. To do so, as a sample, a certain amount of Ni solution was added to a certain amount of adsorbent in Erlenmeyer at a t_0 temperature. The adsorption process was performed by stirring the solutions at intervals of 5, 10, 15, 30, 60, 90, 120, 150 and 180 minutes. Then, the adsorbent was removed from the solution using a 0.2μm syringe filter (BIOFIL). Next, the concentrations of Ni cations were collected from the solutions and measured by flame atomic adsorption spectrometer (FAAS) (GBC; Sens AA).

Desorption studies

The experiments were done as follows:

The Ni (II)-loaded PLA (1 gL^{-1}) was accurately weighed and subsequently dissolved in 150 mL of HNO_3 solution at different concentrations.
The mixture was placed on shaker (Jaltahiz, JTFL-2) at various time intervals (5, 10, 15, 30, 60, 90, 120, 150, 180 minute) at 170 rpm.

- After the desorption equilibrium reached the target temperature, the suspensions were filtered by syringe filters (0.2 μm BIOFIL).
- The concentration of collected Ni ions solutions was measured by FAAS.

Equilibrium studies

In the present study, the effect of various concentrations of 50,100,150, 200 and 250 mgL^{-1} was evaluated on the adsorption of Ni ions at optimal pH 8 with adsorbent dosage of 2 gL^{-1}. Samples of Ni solution were analyzed at certain intervals.
The amount of adsorption at equilibrium (q_e) was calculated in the following equation 1:

$$\mathbf{qe = \frac{C_\circ - Ce}{w} V} \qquad (1)$$

Where qe (in *mg/g*) is the *metal* amount *adsorbed by 1 g* of PLA, V is the initial volume of metal solution (L), W (mg) is the amount of PLA added to the tested Erlenmeyer, C0 is the initial concentration of ions in mg L^{-1}, Ce is the equilibrium concentration in mg L^{-1}.
The removal percentage of metal ions was also calculated according to the equation 2 [17]:

$$\mathbf{\%\ Removal = \frac{C_\circ - Ce}{C_\circ} * 100} \ (2)$$

Thermodynamic study

To evaluate the influence of temperature on the adsorption performance through measuring the free energy Gibbs (ΔG^0), 0.2 mg of adsorbent was added to 100 ml solution containing Ni (2 mg L^{-1}) at different temperatures (15, 25, 35, and 45 °C). The ΔH^0 was calculated by the van't Hoff equation:

$$\ln\ Kd = \Delta S/R - \Delta H/RT \qquad (3)$$

ΔH° is the average standard enthalpy change (j mol^{-1}), ΔS^0 is the average standard entropy change (j mol^{-1}) as well as ΔH° and ΔS° areobtained from the slope intercept of the plot ln K versus 1/T. K_d obtained from the following equation is the adsorption equilibrium constant:

$$\mathbf{Kd} = \frac{\mathbf{C_{\circ} - Ce}}{\mathbf{Ce}} \times \mathbf{V/m} \qquad (4)$$

Where V is the *volume* of the solution in *liters*, m is the mass of adsorbent in grams. The equilibrium constant for the adsorption process is thus directly related to ΔG:

$$\mathbf{\Delta G = -RTLnKd} \qquad (5)$$

T is the temperature (K) and R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

Results and discussion

Characterization of PLA

The adsorbent (ash) was obtained from indirect heating of palm leaves in an oven at 600 °C for 30 minutes. The heating of the adsorbent at 600 ° C causes the loss of the C-H, C-C, C-O, C-O-C and C-OH stretching bands [18], confirmed by functional group analysis using FTIR. The characteristics of FTIR bands of PLA are shown in Figure 1. The signals at 400-800 cm^{-1} and 1100–1300 cm^{-1} were assigned to O–Si–O, and the bands at 617 and 875 cm^{-1} were attributed to the stretching and asymmetric bend vibrations of Si–O–Si, respectively [19]. Moreover, a broad band at about 3400 cm^{-1} was assigned to stretching vibrational band of hydroxyl (–OH) group [20].

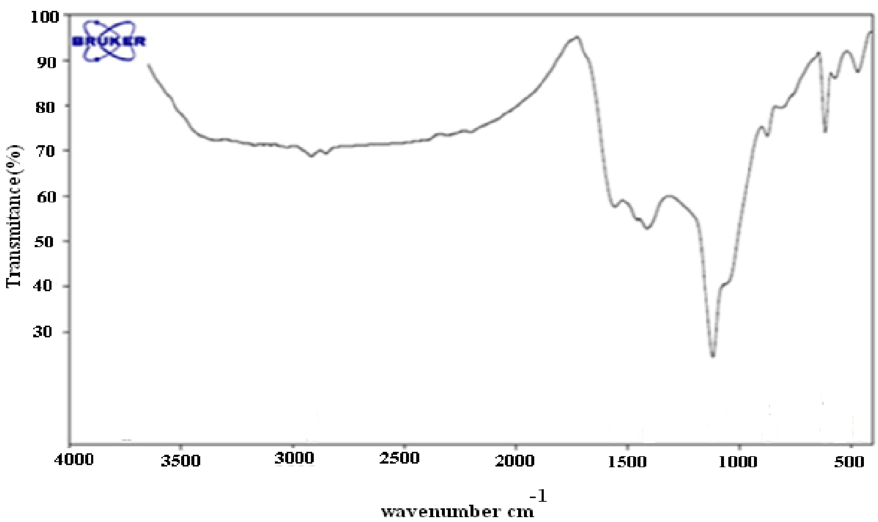

Figure 1. FTIR Spectra of PLA.

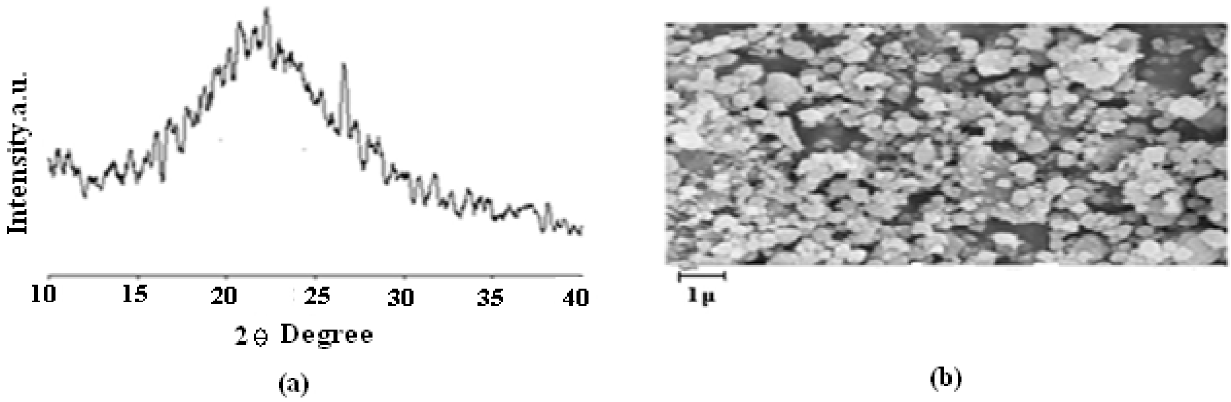

Figure 2. (a) XRD pattern of PLA at 600°C and (b) SEM PLA with leaching at 600°C.

Figure 2a illustrates the XRD pattern of PLA at 600°C. This pattern is similar to the XRD pattern of SiO2 introduced by Kapur who found a widened and strong peak at Bragg angle of 22°-23° [21]. This result indicated that SiO2 product was an amorphous phase. Besides, the morphological and structural characteristics of PLA were studied using field emission SEM. Morphology of the sample composed of almost uniform-sized semi-sphere-like nanoparticles. Figure 2b displays the SEM PLA with leaching at 600°C.

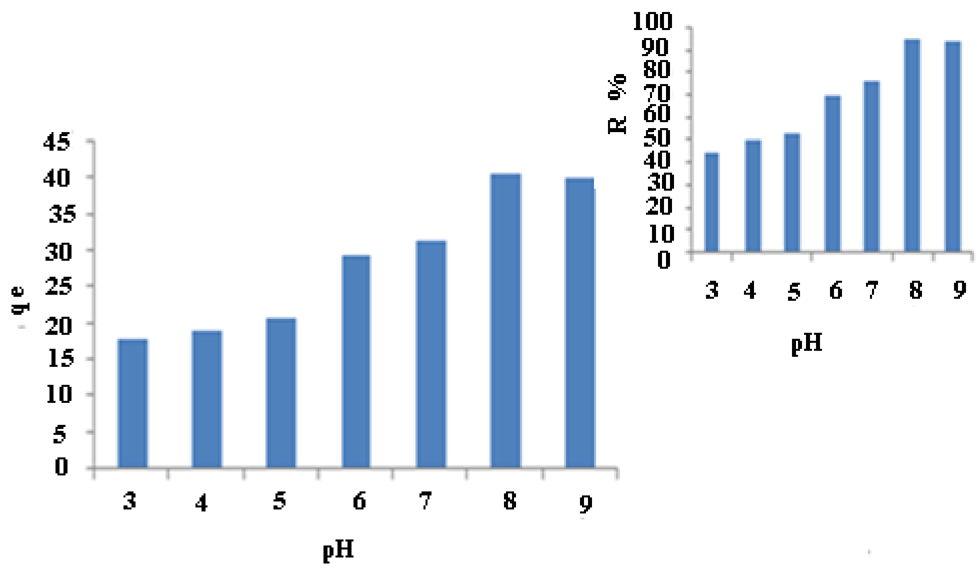

Figure 3. Effect of pH on Ni (II) removal; conditions: adsorbent dose=2 mgl^{-1}, initial concentration=100 mgl^{-1}, agitation time=180 min at 500 rpm and 25 °C.

Evaluation of the pH effect on adsorption

One of the most important parameters controlling the adsorption process of pH is the aqueous solution because it affects the dissolution of metal ions, concentration of ions on the surface functional group of adsorbent and ionization degree of adsorbent during the adsorption process. The effect of pH at levels of 3, 4, 5, 6, 7 and 8 on the adsorption rate at initial concentration of 100 mg/l is shown in Figure 3.According to Figure 3, the optimum pH is 8, the removal percentage and adsorption capacity are accrued from 43.86 to 94.67% and from 17.76 to 40.81mgg^{-1}, respectively.At low pH, Ni^{2+} ions competed with H^+ ions for binding to active adsorbent sites; thus, the ability to absorb was reduced at low pH while at higher pH, the surface of ash attracted the negative loaded particles.

Study the effect of adsorbent amount on Ni^{2+} adsorption process

To study the effect of adsorbent amount on the adsorption process, 5 different amounts of biomass were added to a metal solution with concentration of 100 mgL^{-1} at pH 8 and 25 °C. As illustrated in Figure 4, the removal percentage of metal ion enhances with increasing the amount of adsorbent, in other words, when the adsorbent amount rises from 1 to 3 gL^{-1}, the removal rate increases from 76.93 to 99.7%, and the q_e value decreases from 66.64 to 28.5 mgg^{-1}.

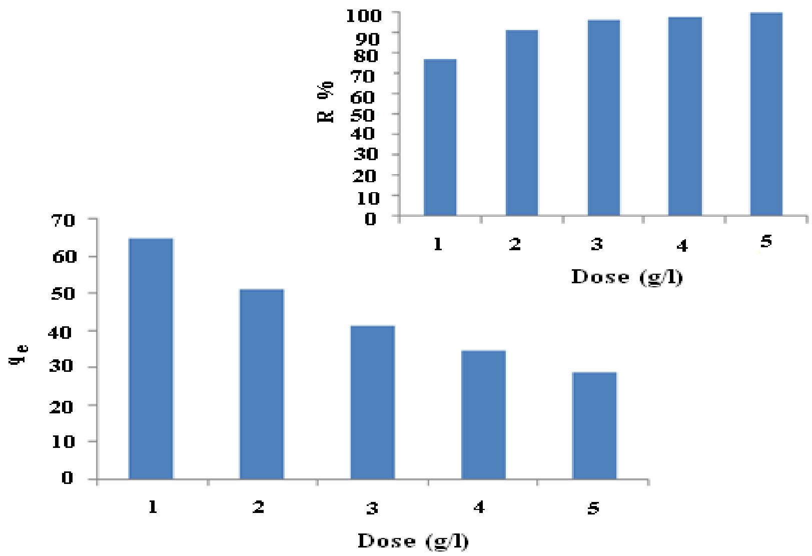

Figure 4. The effect of adsorbent amount, conditions: Ni^{2+} initial concentration=100 mgl^{-1}, pH= 8 and temperature=25 °C.

These results indicated that the number of active adsorption sites was elevated with the increase of adsorbent amount; as a result, the removal percentage was increased, too; because the removal percentage of adsorption depends upon the number of occupied/available active sites [22].

Adsorption thermodynamics

The effect of temperature on the adsorption process of the Ni solution at pH 8 with adsorbent dosage of 1gL^{-1} was investigated at different temperatures of 15, 25, 35, and 45˚C. The study of thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH), entropy change (ΔS) suggested the possibility of carrying out the adsorption process. To obtain the value of these parameters, the van't Hoff equation was used (equation 6) [23].

$$\log\frac{qe}{ce} = \Delta s°/2.303R + (-\Delta H)/2.303R$$

$$(\Delta H) = (\Delta G - T\Delta S) \qquad (6)$$

The obtained values of ΔH°, ΔS° and ΔG° are presented in Table 1. In the present study, the ΔH of Ni adsorption was positive, indicating the endothermic process of adsorption of these ions using PLA adsorbent. Negative values for ΔG at different temperatures demonstrated the possibility of self-sustaining reaction. As illustrated in Table 1, the higher temperature causes the more self-sustaining reaction. The positive amount of entropy indicated the increase of efficiency over time and irregularity at the solid–aqueous solution interface during the adsorption.

Table 1. Thermodynamic parameters for adsorption of Ni ions by PLA.

Ion Concentration (mgL^{-1})	**ΔH° (j mol^{-1})**	**ΔS° (j mol^{-1}K^{-1})**	**ΔG° (j mol^{-1})**			
100	62706.8	237.42	288	298	308	318
			-5670.16	-8044.36	-10418.56	-12792.76

The ΔH can determine the adsorption type. The adsorption process may be physical or chemical. The adsorption heat (ΔH) is not usually more than 10 kcal mol^{-1}in the physical adsorption, but it is 40-400 kcal mol^{-1} (21-420 kjmol^{-1}) in the chemical adsorption. According to the values obtained in table 1, the ΔH is 62706.8 j.mol^{-1}for Ni cation, representing the chemical adsorption of Ni on PLA adsorbent.

Kinetic study of adsorption

In order to predict the adsorption mechanism and delineate the control stage such as mass transfer processes and chemical reactions, the kinetic models are used for in vitro data.

To determine the rate of adsorption of metal ions, the linear form of pseudo-first- and –second-order equations was used. The study on the kinetics of the Ni adsorption process was conducted using PLA at different concentrations of Ni cation, pH=8 and adsorbent dosage=1gL^{-1}. Experimental data showed a significant deviation from the straight line and correlation coefficient (R^2) was low for all studied concentrations. Moreover, the theoretical q_e was significantly different from experimental q_e for a first-order kinetic model. Therefore, the first-order kinetic model was not suitable for the kinetics of the studied adsorption system. The rate constant of the second-order adsorption (k_2), adsorption equilibrium capacity (q_e) and correlation coefficient (R^2) were obtained from the slope and y-intercept of plot (Table 2).

Table 2. Comparison of kinetic constants of pseudo-first- and –second-order kinetic models at different concentrations for Ni.

Initial concentration of the solution (mgL^{-1})	**Pseudo first order kinetic model**			**q_e Experimentl (mgg^{-1})**	**Pseudo second order kinetic model**		
	k_1 (min^{-1})	q_e (mgg^{-1})	R^2		k_2 (mgg^{-1}.min^{-1})	q_e (mgg^{-1})	R^2
50	0.0145	1.77	0.122	38.95	0.00845	38.46	0.996
100	0.0046	12.33	0.446	52.82	0.0231	55.55	0.999
150	0.0138	7.138	0.768	62.61	0.00853	62.5	0.999
200	0.0115	13.39	0.743	64.75	0.00459	66.66	0.999
250	0.0115	32.658	0.924	90.73	0.00149	90.90	0.995

According to the correlation coefficient and proximity of obtained qe to experimental qe, it could be concluded that the adsorption of Ni^{2+} by PLA followed a pseudo-second-order kinetic model.

Adsorption isotherms studies

Adsorption is usually expressed by isotherms related to the concentrations of ion in solution (C_e) and ion adsorbed in the solid phase (q_e). In the current study, the isotherms of Langmuir, Freundlich and Temkin were used to predict the Ni adsorption behavior in the solution by PLA. The Langmuir model is used to determine the maximum adsorption capacity. The q_m parameter in this model is attributed to the maximum adsorbed metal to the total adsorbent saturation as well as b is a constant which refers to the dependence between the adsorbent and adsorbate and whose high value indicates the binding affinity of metal ions, where q_m and b are obtained from the slope and y-intercept of the straight line of the C_e/q_e versus C_e [24].

The Freundlich isotherm model is based on experimental data in nature and can be provided for adsorbing the heterogeneous surfaces or surfaces with different adsorption sites and strengths. K_F and n as the constants of the Freundlich model express the relative biosorption capacity and surface adsorption intensity, respectively [25].

The Tamkin model in addition to other used models is suitable for data descriptions due to a high R^2 value. In the current study, the equations of the table and linear processing method were used to evaluate the experimental data and to determine which isotherm was fit for these data, representing in Table 3.

In Table 3, according to the R^2 value, Freundlich isotherm model provides a better fit to the Ni adsorption process. The high value of K_F represented the ease of adsorption of metal ions from the aqueous medium, and high value of n indicated that the metal ions were well adsorbed by adsorbent, representing that the adsorption was favorable.

In general, the n values ranged from 2 to 10 demonstrate a favorable adsorption. Another Langmuir constant is the separation factor R_L, indicating the favorable adsorption. R_L was 0.02 for Ni and n was 3.33, which were suitable and favorable for this adsorption.

Table 3. Constants of Langmuir, Freundlich and Temkin isotherm models for adsorption of Ni ions by PLA.

Temkin			Freundlich			Langmuir			
R^2	**A**	**B**	**R^2**	**N**	**K_f**	**R_L**	**R^2**	**B (mgL^{-1})**	**q_m (mgg^{-1})**
0.928	-2.22	-0.369	0.977	3.33	18.2	0.02	0.96	0.047	90.9

Desorption studies

The desorption properties of the PLA saturated with adsorbed Ni (II) were studied. In this study, the effect of HNO_3 concentration and desorption time was evaluated on the desorption capacity (Figure 5). The solutions of 1, 0.1, 0.01and 0.001M HNO_3 were used to obtain the desorption amount of ions. The quantity of desorbed Ni enhanced as pH decreased due to the increase of the number of positive charges. Increasing of acid concentration resulted in the accumulation of H^+ in solution, leading to increasing the concentration gradient of Ni (II) and H^+, which could be explained by considering the surface charge. The positive surface charge decreased with the increase of pH.

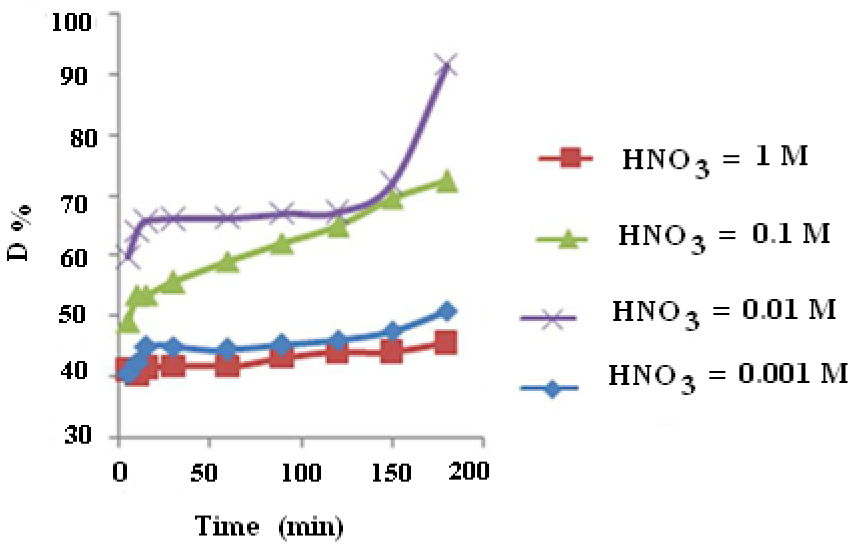

Figure 5. Desorption for Ni ions by PLA adsorbent; conditions: initial Ni^{2+} concentration=1gL^{-1}, pH= 8 and temperature=25 ^{o}C

As exhibited in Figure 5, Ni ion is desorbed at low pH. Ni ion had the highest desorption at the concentration of 0.01M since the adsorption of ions occurred almost in the alkaline environment and returned into the acidic environment.

Conclusion

The current study has indicated that the PLA is an inexpensive and effective adsorbent to remove Ni from aqueous solutions. Optimal conditions for desorption or adsorption of Ni (II) ions were created in the studied systems and the adsorption followed Freundlich model. Moreover, regarding the heat of adsorption for Ni cations, the biosorption process of Ni ions is considered a chemical adsorption process using PLA as an adsorbent. Due to the high efficiency of PLA for removal of Ni from aqueous solutions in addition to the frequency and availability of needed palm leaf to prepare this adsorbent, the studies should be conducted on the use of this adsorbent in industry and should evaluate its effect on other available components including minerals, electrolytes and organic compounds in real wastewater based on kinetic and thermodynamic studies.

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