Nickel (II) Biosorption from Aqueous Solution by Unmodified Eucalyptus Myrtaceae Leaves

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A B S T R A C T

The present work investigated the removal of Ni(II) ions from aqueous solutions onto the surface of Eucalyptus Myrtaceae leaves (EMLs) as a cheap and ecofriendly biomass adsorbent. The plant leaves were used as raw material without any chemical treatments. The parameters impacting Ni(II) adsorption onto EMLs such as contact time, EMLs dose, initial pH, initial Ni(II) concentration and temperature were investigated. Results showed that the removal of Ni(II) cations from aqueous solution are depended on adsorbent dose, time contact, pH and initial ion concentration. The equilibrium data had been fitted very well with Langmuir isotherm (R^2=0.9990) and pseudo-second-order model for kinetic studies (R^2=0.9773). The adsorbed Ni(II) onto EMLs would initialized in 10 min and then the system approached equilibrium within 70 min. The amount of Ni(II) removal was found dependent upon the adsorbent dose and the pH of the initial solution. The optimum pH required for maximum Ni(II) adsorption was 5.5 with the adsorption efficiency equals to 78.1% and adsorption capacity of 7.59 mg/g.

1 Introduction

Duo to the raped development, many industrial products were introduced to our life, discharging many waste materials into water resources. These materials can cause serious harm to the environment and human health, because of their toxic, mutagenic and carcinogenic effects. Heavy metals such Pb, Ni, Cd, Cu, Cr and Hg and their related compounds are one of the environmental pollution M. Ghasemi, *et al.* (2014); Y. Chen, *et al.* (2021); D. Dutta, *et al.* (2021). Nickel is well known to be toxic to the environment, duo to its releases from electroplating industries R. Prabakaran, & S. Rivoli, (2012); N. Mahato, *et al.* (2021). Despite its low concentration in the environment (0.001-0.1 mg.l^{-1}) R. Ramya, *et al.* (2011); G. Yaqub *et al.* (2021) Ni(II) yet has its major concern that pose a risk to human health. Higher concentration of Ni(II) may cause harmful effects such as dry cough, vomiting, chest pain, nausea, etc. Numerous removal processes were used to minimize Ni(II) in the ecosystems, such as ion exchange,

reduction, precipitation, etc. However, these processes are expensive and ineffective to remove Ni(II) and also used harmful chemicals or thermal processes. Among these, the adsorption process by biomass is broadly used to eliminate heavyweight metals from the environment, due to a cheap process and resources like raw waste industrial operation materials. Accordingly, different plant materials such as the Spesia Populnea bark R. Prabakaran, & S. Rivoli, (2012), Delonix regia (Gulmohar) AK Patil, & VS Shrivastava, (2010); SA Razzak *et al.* (2022), and Sphagnum moss peat were used. A comprehensive review by Ioannis *et al.*, I. Anastopoulos, *et al.* (2022) have been reported using a modified and carbonated form of Eucalyptus Myrtaceae (EMLs) as adsorbent material for heavy metals. The current research work describes the removal of Ni(II) from aqueous solutions using Eucalyptus Myrtaceae leaves (EMLs) as a green material without any chemical or physical modification. The adsorption behaviour for Ni(II) onto EMLs was evaluated using isotherm, thermodynamic, and kinetic equations.

2   Materials and Methods

Materials and Methods
All chemicals were purchased from BHD, and Merck companies, and were used without further purification. Commercial-grade solvents and reagents were also used as supplied. Stock Ni(II) solution was prepared by dissolving nickel chloride in deionized water. Working standard solutions of Ni(II) (5 to 25 mg.l^{-1}) were then prepared by proper dilution. Spectrophotometric measurements were conducted using Thermo AA spectroscopy S-series, while pH and conductivity measurements were conducted using a pH-meter (Thermo, Orion 4 star), and conductivity meter (Philips, PW-9527).

Adsorbent.
The green Eucalyptus Myrtsceae leaves (EMLs) used in this present work as zero cost eco-friendly materials were collected from Eucalyptus Myrtsceae trees located in Traghen city, southern region of Libya. The samples were firstly cleaned with cool tap water several times followed by deionized water. EMLs samples were then dried at 25°C for 3 days until no variation in the weight of the sample was observed, grounded to obtain a powder form and then sieved to 125 mm.

Adsorption experiments.
Batch method F. Song, *et al.* (2021); A. Alasadi, *et al.* (2019) was used for the adsorption of Ni(II) into the EMLs surface. Different parameters, including contact time, EMLs dose, pH and Ni(II) concentration were applied. The amount of Ni(II) adsorbed onto the EMLs surface per unit of mass was calculated by the following equation:

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

Where; W (mg) is the mass of adsorbent sample, C_o (mg.l^{-1}) and C_e (mg.l^{-1}) are the initial and final concentration of Ni(II) at equilibrium, respectively. V (ml) is the volume of Ni(II) solution. To calculate the percent sorption of Ni(II), the following equation was used:

$$Removal\% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Adsorption models
Isotherm models
The adsorption described the nature of Ni(II) ions onto the EMLs surface, was calculated using the following equation of Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

Where, C_e is mg.l^{-1} and b is Langmuir equilibrium constant, q_e is the adsorption capacity (mg.g^{-1}) at equilibrium, the maximum of Ni(II) ions is q_{max} uptake per unit mass of EMLs (mg.g^{-1}). A straight line plot of C_e/q_e versus C_e yields a slop of $1/q_e$ and an intercept of $1/q_e b$. The heterogeneous sorption media was evaluated using the Freundlich isotherm model in the liquid phase.

Adsorption kinetic models.
pseudo-second-order (PSO) and Pseudo-first-order (PFO) were used in this study to evaluate the rate and kinetics of Ni(II) adsorption onto EMLs. The mechanisms of the adsorption Ni(II) onto EMLs has been investigated by the use of the pseudo-second-order (PSO) kinetic models MA Mahmoud, (2021).

3   Results and Discussion

Effect of pH
Figure 1 shows the effect of pH on adsorption of Ni(II) onto EMLs. Six different samples of pH values ranging from 2.4 to 7.4 with the initial Ni(II) concentration of 20 mg.l^{-1}, at T = 296K and 0.01g of EMLs were used. Results showed that the percentage removal of Ni(II) ions onto the surface of EMLs was increased sharply in the pH range from 2.4 to 6.4. The extreme removal of Ni(II) ions (about 60%) was reached at a pH of approximately 6.4. this is could be duo to the protonation of the EMLs surface. Which then confirmed by the determination of the final pH, which was found less than the initial pH, meaning that H$^+$ ions were released into solution from the EMLs surface JA Abudaia, *et al.* (2013). Also, at low pH, the charge on the EMLs surface is positively repelling the Ni(II) cation.
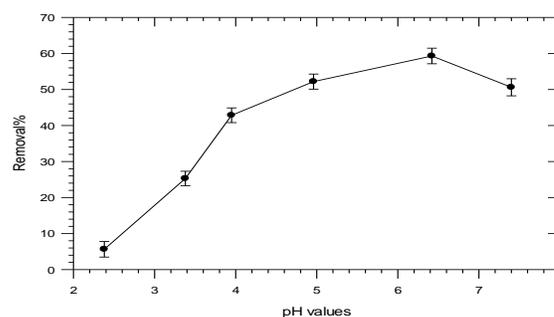

Figure 1. The effect of pH on the adsorption of Ni(II) onto EMLs.

With increasing the pH, the released protons from EML active sites enhanced the removal of H^+ from the EMLs surface due to bio-sorbent surface becoming less positive. This leads to reduce in the adsorption capacity. The decrease in percentage removal of Ni (II) ions by EMLs at high pH could be due to the high number of hydroxyl group, which hindrance to diffusion of Ni(II) ions to form the soluble Ni(II) hydroxylated complexes OO Kehinde, *et al.* (2009). The adsorption process is according to the ion-exchange mechanism Y. Wu, *et al.* (2008); JA Abudaia, *et al.* (2013). In general, Ni(II) ions are better absorbed by the surface of EMLs at low pH. Therefore, further experiments were conducted at pH < 5 to avoid Ni(II) precipitation.

Effect of contact time

Figure 2 shows the adsorption of Ni(II) ions on the EMLs surface as a function of contact time in the range of 1 to 120 min at pH 5, and 0.01 g of EMLs. A rapid interaction between Ni(II) ions and EMLs surface was observed within 20 min. This could be due to a large surface area being available for adsorption, suggesting that the uptake process was mainly dominated by chemisorption rather than physisorption Z. Mohamed Amine, et al. (2012). After 20 min, this interaction was slowed down and the equilibrium was achieved due to quick exhaustion of the adsorption sites. This decrease in removal rate towards the end after 20 min suggests the development of a monolayer of Ni(II) ions on the EMLs surface. Therefore, 120 min were chosen for further experiments.
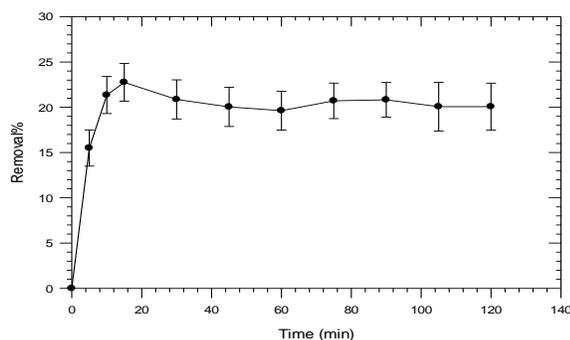

Figure 2. The effect of contact time on the adsorption of Ni(II) ions onto EMLs, [Ni(II)] = 20mg.l^{-1}, and pH = 5.

Effect of adsorbent dosage

The effect of EMLs dosage on the adsorption of Ni(II) ions was investigated by varying the amount of the EMLs adsorbent from 0.01 to 1.0 g. (Figure 3). The equilibrium concentration of Ni(II) ions increased from 38 to 78.1% with increasing EMLs doses from 0.0 to 1.0 g. This is due to the increasing number of adsorption sites on the EMLs surface as the weight of the sorbent increased, resulting in an enhanced percent of removal at a high dose JA Abudaia, *et al.* (2013). Further increase in EMLs dose above 0.05 g did not lead to a substantial increase in the exclusion of Ni(II) ions. This could be due to the combination of adsorption sites resulting in a reduction in total EMLs surface area obtainable to Ni(II) ions OO Kehinde, *et al.* (2009). These results are in good agreement with those found by Abudaia *et al*. JA Abudaia, *et al.* (2013) and Erhayem *et al*. M. Erhayem, *et al*. (2015). Therefore, the best removal efficiency of Ni(II) ions by EMLs surface was gained at 0.05 g.
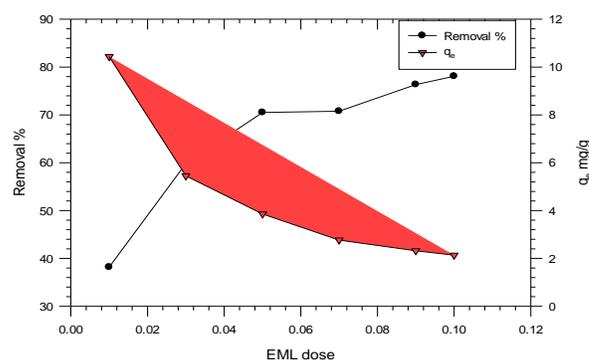

Figure 3. The effect of adsorbent dosage on the removal of Ni(II) ions onto EMLs surface.

Effect of initial Ni(II) ion concentration.

The amount of Ni(II) ions adsorbed onto the EMLs surface was carried out using different concentration of Ni(II), ranging from 5 to 25 mg.l^{-1} (Figure 4). As predictable in the adsorption process, the increase in Ni(II) concentration leads to a decrease in the percentage removal of Ni(II) ions with the increase in the adsorption capacity, q_e mg.g^{-1}. This could be due to the increase in the mass transfer driving force of Ni(II) ions between the aqueous solution and EML surface. EMLs adsorption sites are more quickly adsorb the Ni(II) ions at low concentrations of Ni(II) ions. Increasing Ni(II) concentration could lead to saturating the adsorbed sites on the EML surface, which causes a decrease in the exclusion of Ni(II) adsorption M. Singanan, & E. Peters, (2013).
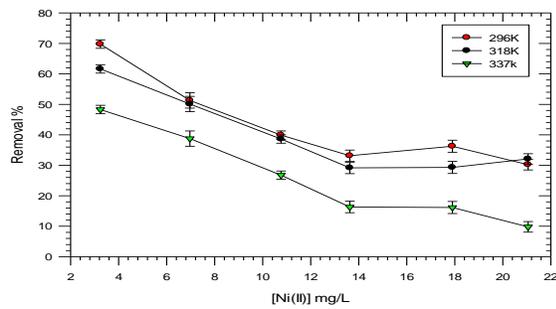
Figure 4. Effect of Ni(II) concentrations and temperature on the adsorption process of Ni(II) ions onto EMLs.

Effect of temperature

At the preliminary stage, the concentration of Ni(II) ions used, were from 3 to 21 mg.l^{-1}, T = 296, 318, 337K, pH= 5 and 0.01g EMLs. It can be seen from Figure 5 that the adsorbed amount of Ni(II) on the EML surface increases as the temperature increases. For instance, when the Ni(II) concentration increases (3 mg.l^{-1}), the percentage of Ni(II) removal increases from 0.979, 1.24 and 1.68% with an increase in the solution temperature from 296, 318 and 337 K, respectively. On the other hand the adsorption equilibrium of Ni(II) ions on EMLs as a function of temperature where found decreases as the solution temperature increases. This is probably due to either the increase in escaping tendency of Ni(II) ions from the surface of EMLs or the Ni(II)-EMLs adsorption process is physical adsorption which the adsorptive force between Ni(II) ions and EMLs surface is weak as Van Der walls. This finding confirm that the present adsorption process of Ni(II) ions on EMLs is exothermic ZA Al-Anber, & MAS Al-Anber (2008).
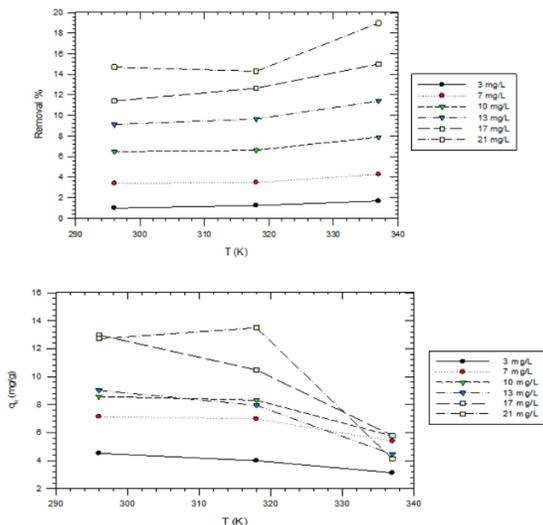

Figure 5. Effect of temperature on the adsorption process of Ni(II) ions on EMLs. pH=5 and 0.05 g EMLs.

Kinetic process

To control the adsorption mechanism of Ni(II) ions onto EMLs surface, intra-particle and liquid film diffusion, pseudo-first and pseudo-second-order HA Ibrahiem, *et al.* (2021) were used to test the experimental data for the best fitting correlation coefficients. Figure 6 and Table 1 showed the result. The squared sum of errors (SSE) was used to evaluate the best fitted kinetic model as well.

Two important steps can control the adsorption processes, i.e. external and internal diffusion. If the q_t versus $t_{0.5}$ gives a straight line passing through the origin, the rate-determining step is internal diffusion. In the present system, two or more linear plots have been noted (Figure 6). The first step is at the original contact of Ni(II) ion and EMLs surface until 15 min. Then, slowly decrease in the rate as the time goes above 15 min was observed. The second step, which might be duo to the saturation on the EMLs surface, took place. After 60 min the stability of the adsorption rate was noticed. This indicated that decreasing in arbitrariness at the solid/liquid interface after 60 min contact time between the Ni(II)-EMLs leading to a stable arrangement of Ni(II) ions onto the surface of EMLs. Experiments for the Ni(II) adsorption onto the EMLs surface were also conducted using external diffusion. The external diffusion of Ni(II) ions from liquid film to the EML surface is the rate-determining step when the linear plot $-\ln(1-F)$ versus t with zero intercepts.
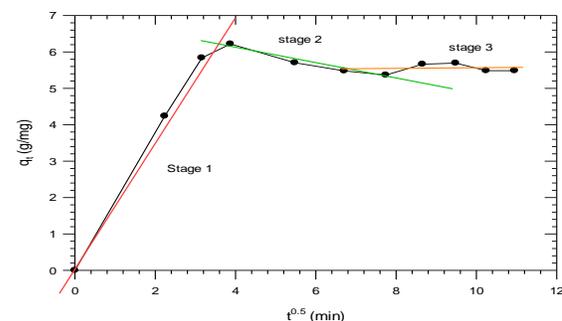

Figure 6: External liquid film diffusion. Ci=25 mg.l^{-1}, 0.05 g EMLs, pH= and 200 rpm.

Figure 6 shows the external diffusion of the adsorption system and doses not exhibit a zero intercept. Therefore, the external diffusion is not the step determining. The R^2 value is 0.9890, but the SSE value is very high suggesting that this model cannot describe the Ni(II)-EML system. Pseudo-second-order equation was also used to test the adsorption process and the rate constant (k_2), q_e and R^2 are listed in Table 1. The $q_{e\,cal}$ value (5.06 mg.g^{-1}) is closer to the experimental data 7.58 mg.g^{-1}. R^2 is higher and SSE was the lowest. Therefore, it can be

Table 2: Adsorption isotherm constants for Ni(II) adsorption on EMLs surface.

T	Freundlich Constant			Longmuir Constant			Temkin Constant				D-R constant			
K	K_F	n	R^2	q_m	K_L	R^2	K_T	q_m	B	R^2	D	q_m	E	R^2
	L.g^{-1}			L.mg^{-1}	L.g^{-1}		J.mol^{-1}	L.g^{-1}			J.mol^{-1}	L.g^{-1}		
298	0.611	2.61	0.913	7.59	0.732	0.9990	9.26	2.07	1.28	0.9969	0.273	10.3	1.35	0.7353
318	0.586	2.37	0.874	4.02	0.261	0.9027	4.37	2.43	1.09	0.9090	0.421	9.78	1.09	0.7727
338	0.402	1.16	1.000	2.23	0.151	0.9324	1.52	3.16	0.837	0.8540	0.454	1.05	1.05	0.6121

concluded that the adsorption kinetics can be better described by the PSO model.

Table 1: Pseudo-first- and pseudo-second-order.

LPFO				PSO				
K1	q_m		R^2	SSE	q_m		K_L	R^2	SSE
min^{-1}	mg.g^{-1}				mg.g^{-1}		L.g^{-1}		
-2.79E-01	0.830		0.9890	4.67	5.06		2.77E-02	0.9919	0.216
Intra-particle diffusion					External diffusion				
KT	q_m	b	R^2	SEE	K_{fd}	q_m		E	R^2	SSE
J.mol^{-1}	mg.g^{-1}				J.mol^{-1}	mg.g^{-1}				
1.06	11.7		0.3592	4.87	1.68E-02	2.96			0.9424	1.71

Internal and external liquid film diffusion rate constants for Ni(II) ions biosorption on EML surface using diverse initial concentrations, Ci=5-25 mg/L, 0.05 g EMLs, 296 K, pH= and 200 rpm

Adsorption isotherm models

The conduction of adsorption isotherm experiments with the early Ni(II) attentions varied from 5 to 25 g.l^{-1} at different temperatures of 296, 318 and 337K. Various equilibrium isotherm models, showed at the experimental part, were employed to find the best fit for the adsorption data in the relationship between adsorption capacity and the initial concentration of Ni(II) ions. Table 2 presented the isotherm coefficients.

The fitted degree for the adsorption of Ni(II) ions onto the EMLs surface follows the sequence: Langmuir>Freundlich> Temkin>D-R isotherms. Therefore, the Ni(II) adsorption onto the surface of EMLs is limited to monolayer and took place at the surface of EMLs consisting of an energetically equivalent distribution. The interaction between Ni(II) ions and EML surface active sites is dependent on the distance between ions and active sites.

Based on the results from Freundlich isotherm, the values of n >1, represent favorable nature adsorption and decrease with rise in temperature which means that the adsorption is favourable at low temperature. Also, the k_F value was decreased with increasing the temperature leading to a decrease in the adsorption capacity of EMLs. The results from the D-R isotherm showed that the values of *E* were found 1.35, 1.09 and 1.05 kJ/mol, which is less than 8 kJ/mol. Therefore, the adsorption of Ni(II) ions onto EMLs is physical adsorption in nature. Table 3 shows the separation factor (R_L) in the dimensionless form of the Langmuir isotherm has been used to predict affinity between the sorbent and sorbate in the biosorption process.

Table 3: The separation factor (RL) of Langmuir isotherm

	3.2398	6.965	10.7619	13.6311	17.9022	21.0548
298	0.296552	0.163946152	0.112618449	0.091072	0.070884518	0.060917
318	0.541491	0.354563923	0.262279937	0.219173	0.176090369	0.153778
338	0.671801	0.487741722	0.381270885	0.327283	0.27030633	0.239527

Thermodynamic studies

The ΔH and ΔS values were determined from the slope and intercept, respectively, using the plot of ln K_D versus 1/T (Figure 7 and Table 4). The negative Gibbs free

energy change, ΔG, means that the Ni(II)-EMLs adsorption is spontaneous of sorption and the spontaneity degree increases with an increase in solution temperature.
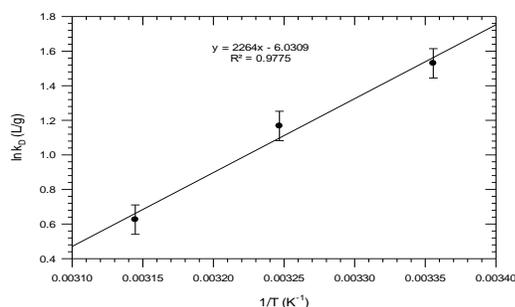

Figure 7: Plot of ln K_D versus 1/T for Ni(II)-EML adsorption.

Table 4: Thermodynamic parameters for Ni(II)-EMLs adsorption.

T (K)	ΔG (KJ/mol)	ΔH (J/mol)	ΔS (J/mol)	R^2
298	-3.79			
318	-3.09	-272	-0.725	0.9775
337	-1.76			

The negative enthalpy, ΔH, indicates an exothermic process, which confirms the previous results in batch results. The negative value of ΔH and the increase in negative values of ΔG with temperature indicates that these adsorption processes are less favorable at higher temperature D Xu, *et al*. (2008). The negative values of ΔS show the decrease in arbitrariness at the solid/liquid interface during the Ni(II)-EML adsorption process and stable arrangement of Ni(II) ions onto the surface of EMLs ZA Al-Anber, & MAS Al-Anber (2008).

Conclusions

These results show that EMLs can be used effectively for the water treatment process to remove Ni(II) ions from an aqueous resolution. The Ni(II)-EML adsorption process follows pseudo-second-order and is fitted Langmuir isotherm. The result for the thermodynamically show that the adsorption processes are spontaneous and unfavorable at high temperatures.

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