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Adsorption of Ni (II) from aqueous solution on *Delonix regia* (Gulmohar) tree bark

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Abstract

The potential to remove Ni (II) from aqueous solutions through adsorption using Delonix regia (Gulmohar) tree bark was investigated. The effects of pH, contact time, initial concentration and adsorbent dosage on the adsorption of Ni (II) were studied. The different experimental conditions were investigated in this study. It was observed that the amount of Ni (II) adsorbed increases rapidly initially, then system approaches equilibrium within 90 minutes. The extent of Ni (II) removal increased with increase in time and adsorbent dosage. The reaction kinetics was studied using different models. Langmuir and Freundlich adsorption model is used for the mathematical description of the adsorption equilibrium and isotherm constants are evaluated. Equilibrium data fitted very well to the Langmuir and Freundlich model. The Langmuir adsorption capacity was found to be 4.81 mg/g. The Freundlich constants K_f and n were 0.4315 and 1.5715, respectively. The pseudo first- and second-order kinetic models were also applied to the experimental data. The data agreed very well with the pseudo second-order kinetic model.

Keywords: Adsorption**,** *Delonix regia*, Ni (II) removal, Isotherms.

INTRODUCTION

Nickel is comparatively a rare metal in nature, but its widespread use in many industrial applications leads to relatively high concentrations in aquatic environment. Nickel is widely used in stainless steel, electroplating, batteries manufacturing, the manufacturing of magnetic tape, jewelry and coinage, in welding rods, as a catalyst in oil hydrogenation and coal gasification, dental procedures, electric storage batteries, pigments and so on [1]. Ni (II) is present in small quantities (0.1- 0.6 ppm) in plants, animals and occurs in trace amounts in sea water. [2] The main symptoms of nickel exposure causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness[3]. Due to this, World Health Organization (W.H.O) has prescribed standards for desirable nickel concentration in drinking water as 0.1 mg/L and industrial effluents as 3.0 mg/L. Therefore, it is necessary to bring the nickel concentration below the prescribed limits [4].

There are numerous methods currently employed to removal of metals from aqueous environment. Some of these methods are chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment, evaporation and adsorption [5]. Among all these, adsorption is the most promising technique and economically feasible alternative for metal removal. [6]. Adsorption method offers the advantages of low operating cost and minimizing secondary pollution. Plant material is easily available and relatively; inexpensive an investigation of its use as a adsorbent seems most appropriate Earlier researchers used different plant materials such as Sawdust of *Dalbergia sissoo*[1], babhul Bark [2], *Mangifera indica* (mango), coconut fibers and *Madicago sativa* (alfalfa) for metal removal from wastewater.

In the present work, the Ni (II) ions adsorption capacity of *Delonix regia* (Gulmohar) tree bark (DRTB) was studied by a batch technique. The effect of pH, concentration of Ni (II) ions, contact time and adsorbent dose on percentage of adsorption has also been investigated.

MATERIALS AND METHODS

Preparation of Adsorbent

Delonix regia (Gulmohar) tree bark (DRTB) was collected from a local farm. It was cut in to small segment and dried in sunlight until almost all the moisture evaporated. Then it was ground to get desired particle size of 100 to 200 μm. It was then soaked 2 hours in 0.1M NaOH solution to remove the lignin content. Excess alkalinity was then removed by neutralizing with 0.1 N HCl. The DRTB was then washed several times with distilled water till the washings are free from color and turbidity. The washed DRTB was oven dried at 50^0 C for 24 hrs and stored for the study.

Preparation of solutions

All the reagents used were of AR grade.

Ni (II) solution

Stock Ni (II) ions solution (1000 mg/L) was prepared by dissolving 4.479 gm of A.R. grade $NiSO_4$, $6H_2O$ in 1000 ml distilled water. The solutions of lower concentrations were prepared by dilution of appropriate volume of stock solution.

Dimethylglyoxime

Dissolve 1 gm of dimethylglyoxime in 100 ml of ethanol.

Batch Adsorption Studies

Batch adsorption experiments were carried out by shaking 50 ml of 10 and 20 mg/L of Ni (II) ions solution concentration and 5 g/L of adsorbent dose at room temperature. The initial pH values of the solution were previously adjusted with 0.1 M HCl or NaOH using pH meter

(Equiptonics EQ-610). At the end of the predetermined time interval, the adsorbent was removed by centrifugation. The amount of nickel was estimated by the dimethylglyoxime method [7]. The absorbance was measured on UV-VIS spectrophotometer (Systronics model-118) at 445 nm.

RESULTS AND DISCUSSION

Effect of pH

The effect of pH on the adsorption process is shown in Fig 1. These experiments were undertaken at initial nickel concentration of 20 mg/L with adsorbent dose of 5 g/L and contact time 90 minutes. The pH of feed solution was examined from solutions at different pH, covering a range of 2.0–7.0. There was continuous increase in percentage removal with increase in pH and reached 51.5 % at pH 7. The increase in percentage removal may be attributed to higher degree of ionization of metal ion at higher pH and the reduced competition of H^+ ions with the metal ions for adsorption sites. The removal of Ni (II) ions decreases rapidly bellow pH 4. At pH < 4.0, H^+ ions compete with Ni (II) ions for the surface of the adsorbent which would hinder Ni (II) ions from reaching the binding sites of the adsorbent caused by the repulsive forces. At pH grater than 5, the Ni (II) ions get precipitated due to hydroxide ion forming a nickel hydroxide precipitate [8]. For this reason the maximum pH value was selected to be 5.

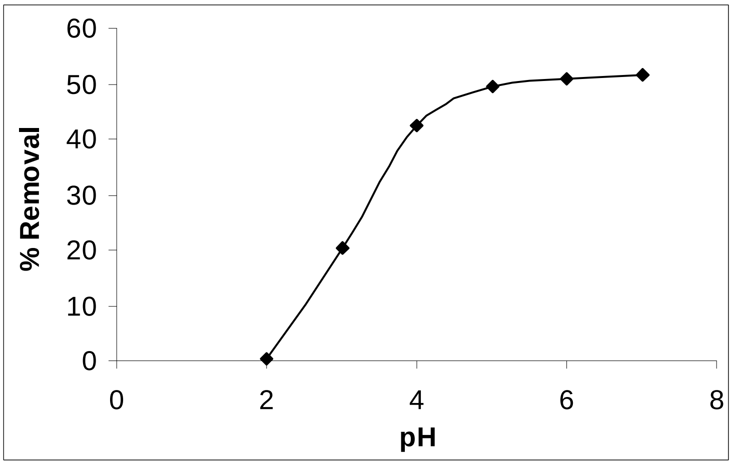

Fig 1 Effect of pH on adsorption of Ni (II) ions on DRTB; (Ni (II) ions concentration: 20 mg/L, adsorbent: 5 g/L, agitation time: 90 min)

Effect of contact time

The effect of contact time on the amount of Ni (II) ions adsorbed was investigated using 10 and 20 mg/L initial concentration o Ni (II) ions with 5 and 8 gm/L DRTB at pH 5. The effect of contact time and metal concentration on the percent removal of Ni (II) ions by DRTB is presented in Fig 2. The results indicate removal of Ni (II) ions increases with increase in contact time and equilibrium was attained in about 90 min. The extent of removal of Ni (II) by DRTB was found to increase, reach a maximum value with increase in contact time. The percentage of Ni (II) ions removal increases at equilibrium from 50 to 59 % as Ni (II) ions concentration decreases from 20 to 10 mg/L for 5 gm/L of a DRTB.

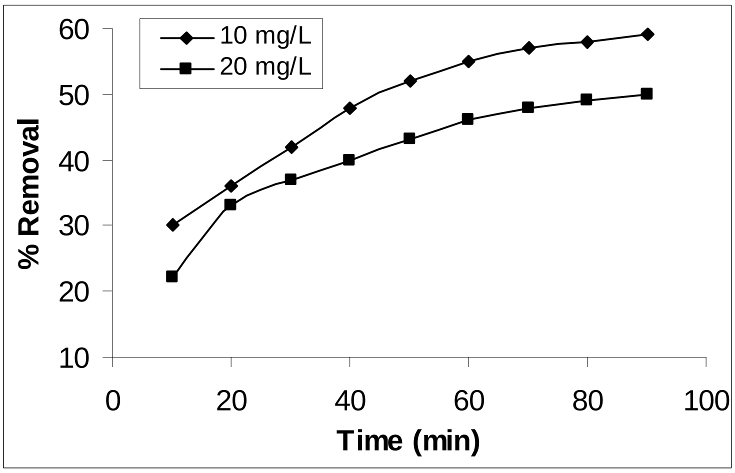

Fig 2 Effect of contact time on adsorption of Ni (II) ions by DRTB; (Ni (II) ions concentration: 10 and 20 mg/L, adsorbent: 5 g/L, pH: 5)

Effect of adsorbent dose

The effect of adsorbent dosage on the adsorption of Ni (II) ions process is shown in Fig 3. The effect of adsorbent dose on the removal of Ni (II) ions was investigated using 20 mg/L of initial Ni (II) concentration at initial pH 5.0. The adsorbent dose was varied from 2 to 12 g/L. It is observed that the removal of Ni (II) ions increases with an increase in the adsorbent dose. Removal of Ni (II) ions increases with increase of adsorbent dosage. The percentage removal increases from 24 to 72.5% by increasing the adsorbent dosage from 2 to 12 g/L.

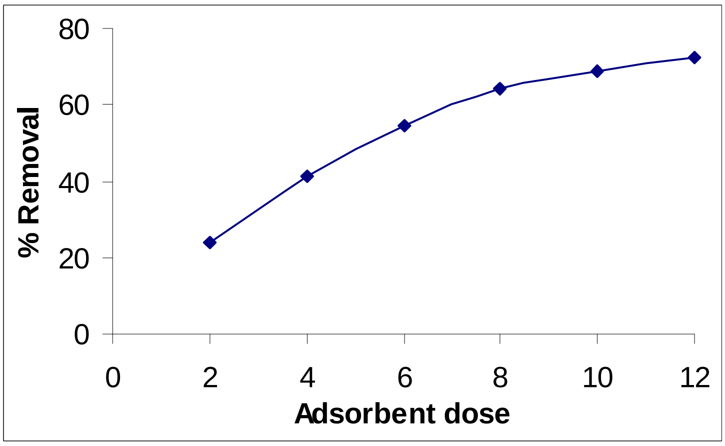

Fig 3 Effect of adsorbent dose on adsorption of Ni (II) ions by DRTB; (Ni (II) ions concentration: 20 mg/L, pH: 5, agitation time: 90 min)

Adsorption Isotherms

Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir and Freundlich isotherm equations. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Freundlich isotherm

The sorption data of nickel ions sorption onto DRTB was also fitted to Freundlich isotherm, in the following linear form [9]:

$$\log q_e = \log K_f + 1/n \log Ce \qquad (1)$$

Where, q_e is the amount of metal ion adsorbed per gram of adsorbent (mg/g). Ce is the equilibrium concentration of metal ion in solution (mg/L). K_f and $1/n$ are Freundlich constants, indicating the adsorption capacity and adsorption intensity, respectively.

Straight lines were obtained by plotting $\log q_e$ against $\log Ce$ (Fig 4), which show that sorption of nickel ions obeys Freundlich isotherm well. The K_f and $1/n$ values were calculated from intercept and slop of the plot respectively and presented in Table 1. The correlation coefficient R^2 > 0.9887 and the values of n were higher than 1.0, indicating that adsorption of Ni (II) ions on DRTB follows the Freundlich isotherm [10].

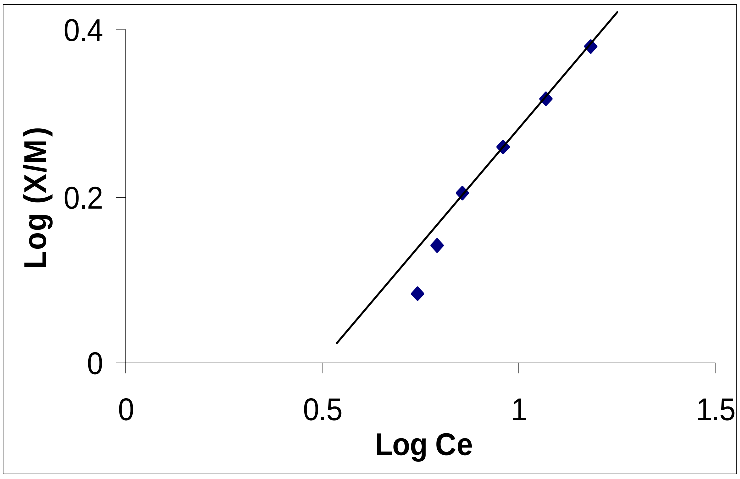

Fig 4 Freundlich adsorption isotherm of Ni(II) ions adsorption by DRTB; (Ni (II) ions concentration: 20 mg/l, pH: 5, agitation time: 90 min)

Langmuir isotherm

The Langmuir isotherm [11] is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented in the linear form as:

$$Ce / q_e = 1/ b\, Q_0 + Ce / Q_0 \qquad (2)$$

Q_0 and b *is* Langmuir constants related to the capacity and energy of sorption respectively. A plot of $Ce/\,q_e$ versus Ce should indicate a straight line of slope $1/\,Q_0$ and an intercept of $1/\,(b\,Q_0)$ (Fig 5). The values of Qo and b and correlation coefficient obtained from the Langmuir model are shown in Table 1. The correlation coefficient $R^2 > 0.99$ suggests that adsorption of Ni (II) ions onto DRTB follows the Langmuir isotherm. The maximum monolayer capacity Q_0 obtained from the Langmuir is 4.81 mg/g.

Separation factor

A dimensionless constant, separation factor (R_L) can be used to predict whether a sorption system is favorable or unfavorable in batch adsorption process [12]. R_L was calculated from Langmuir isotherm based equation [13]:

$$R_L = 1\,/\,(1 + b\,Co) \qquad (3)$$

Where, b is the Langmuir constant (L/mg) and Co is the initial Ni (II) ions concentration (mg/L). The value of R_L indicates the type of the isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). Value of R_L was found to be 0.4642 and confirmed that the DRTB is favorable for adsorption of Ni (II) ions under conditions used in this study [14].

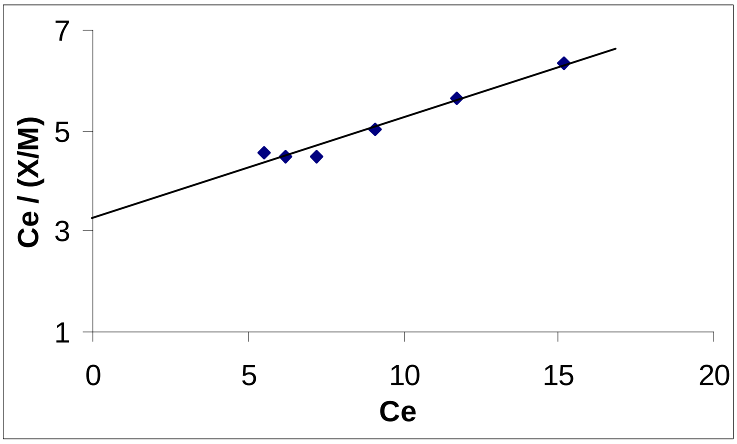

Fig 5 Langmuir adsorption isotherm of Ni(II) ions adsorption by DRTB; (Ni (II) ions concentration: 20 mg/l, pH: 5, agitation time: 90 min)

Table 1 Langmuir and Freundlich isotherm parameters for Ni (II) ions uptake by DRTB

Ni(II)	Freundlich Constants			Langmuir Constants		
Conc.	*K*	*1/n*	R^2	Q_0 (mg/g)	*b* (l/mg)	R^2
20 mg/l	0.4315	0.6363	0.9887	4.8146	0.05770	0.9900

Adsorption kinetic study

The kinetics of Ni (II) ions adsorption onto DRTB was analyzed using pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients

(R^2, values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of Ni (II) ions adsorption onto DRTB.

Pseudo-first-order model

In order to analyze the adsorption kinetics of nickel ions, the first-order kinetic model was applied to the experimental data. The first-order rate expression of Lagergren can be expressed as [15]**:**

$$\log (q_e - q_t) = \log q_e - K_1 t/2.303 \qquad (4)$$

Where, q_e and q_t are the amounts of Ni (II) ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 the rate constant of pseudo first order adsorption (min^{-1}). Straight lines were obtained by plotting log ($q_e - q_t$) against t, as shown in Fig 6. The calculated q_e, K_1 and regression correlation coefficient R^2 values are summarized in Table 2. It was observed that, calculated q_e values and experimental q_e values does not shows good agreement between them. This shows that the adsorption of Ni (II) ions on DRTB is not a first order reaction.

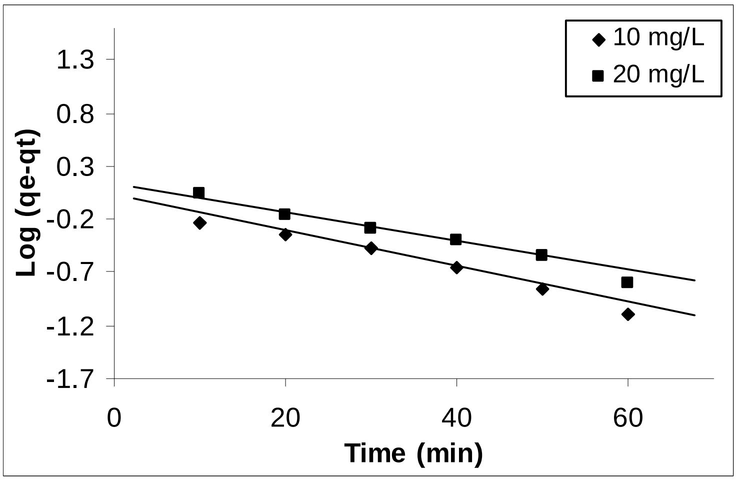

Fig 6 Lagergren plots for the adsorption of Ni (II) ions on DRTB; (Ni (II) ions concentration: 10 and 20 mg/l, adsorbent: 5 g/l, pH: 5)

Pseudo-second-order model

The adsorption kinetic may be described by the pseudo-second order model [16]:

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \qquad (5)$$

Where, K_2 (g/mg min) is the rates constant of second-order adsorption. The second-order rate constants were used to calculate the initial sorption rate, h (mg/ g. min), given by the following equation:

$$h = K_2 q_e^2 \qquad (6)$$

The plot of t/q_t *versus* t shown in Fig 7. Values of K_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plots respectively. The values of the calculated q_e,

K_2, *h* and correlation coefficients R^2 are also presented in Table 2. The linear plots of *t/qt* versus *t* show good agreement between experimental and calculated q_e values. The correlation coefficients for the second-order kinetic model are greater than 0.9951. This shows that the model can be applied for the adsorption process and confirms that the sorption of Ni (II) ions onto DRTB follows the pseudo-second-order kinetic model.

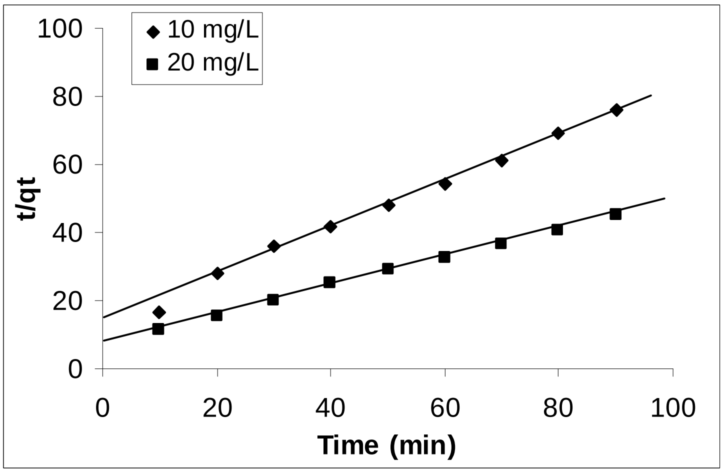

Fig 7 Pseudo second-order adsorption of Ni (II) ions on DRTB (Ni (II) ions concentration: 10 and 20 mg/l, adsorbent: 5 g/l, pH: 5)

Table 2: Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo first order and to pseudo second order kinetic models

Ni (II) ions Conc. mg/l	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic model			Pseudo second order kinetic model			
		K_1,ads (min−1)	$q_{e,cal}$ (mg/g)	R^2	K_2,ads (g/mg min)	$q_{e,cal}$ (mg/g)	*H* (mg/g min)	R^2
Adsorbent dose 5 g/l								
10	1.18	5.373 X 10^{-2}	1.820	0.9711	2.1193 X 10^{-2}	1.666	0.0588	0.9951
20	2	5.264 X 10^{-2}	4.074	0.9663	2 X 10^{-2}	2.5	0.125	0.9983
Adsorbent dose 8 g/l								
20	2.62	4.350 X 10^{-2}	1.479	0.9598	6.2718 X 10^{-2}	2.8235	0.4999	0.9997

Desorption studies:

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Ni (II) ions. In this research desorption of Ni (II) ions was carried out using distilled water, 0.1N HCl , 0.1N HNO_3 and 0.1 N H_2SO_4. Table 3 shows the percent desorption of Ni (II) ions in various desorbing media.

The desorption studies indicate that 0.1 N hydrochloric acid, nitric acid and sulphuric acid is a better reagent for desorption of Ni (II) ions, because we could get more than 99.66, 84.06 and 94 % desorption, respectively. Desorption of Ni (II) ions by mineral acids indicates that the nickel ions was adsorbed on DRTB by physisorption mechanisms. The adsorbed nickel ion can be desorbed 26% using water, indicates some nickel ion attached to adsorbent is by weak bonds

Table 3 Desorption of Ni (II) ions from DRTB

% Desorption of Ni(II) ions with			
water	0.1 N HCl	0.1 N HNO_3	0.1 N H_2SO_4
26%	99.66%	84.06%	94%

CONCLUSION

Adsorption of Ni (II) ions, from aqueous solutions using DRTB studied. The following results were obtained:

- These studies show that *Delonix regia* (Gulmohar) tree bark is an inexpensive adsorbent for Ni (II) removal from aqueous solutions.
- The adsorption of Ni (II) ions on DRTB was dependent on the pH, initial Ni (II) ions concentration, quantity adsorbent dose and contact time.
- pH 5 was used as the optimum pH.
- The equilibrium time for the adsorption of Ni (II) ions on DRTB from aqueous solutions is estimated 90 minutes.
- The adsorption process of Ni (II) ions can be described by Langmuir isotherm and Freundlich isotherm model
- The amount of Ni (II) ions adsorbed increased with increase initial Ni (II) ions concentration.
- Kinetic of Ni (II) ions adsorption obeyed the pseudo-second-order model.

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