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Diplocyclos palmatus Seed powder: An ecofriendly sorbent for the uptake of Ni (II) from aqueous solution

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Abstract
Ni (II) is one of most hazardous heavy metal present in industrial effluents the study was carried to test the use of *Diplocyclos palmatus* seed as adsorbent for Ni (II) removal from aqueous solution. Batch adsorption method was used and the concentration of Ni (II) measured using an ultraviolet-visible (UV-Vis) spectrophotometry. The effect of contact time, adsorbent dosage, pH, initial metal ion concentration was studied. The data showed that adsorption on *Diplocyclos palmatus* seed fitted well to Langmuir isotherm. Pseudo-second order model explains the nickel kinetics more effectively. Reusability of the adsorbent was examined by desorption in which HCl eluted 93 % nickel. The results revealed that nickel is considerably adsorbed on *Diplocyclos palmatus* seed and it could be an economic method for the removal of nickel from aqueous solutions.

Keywords: diplocyclos palmatus, nickel, adsorption isotherms

1. Introduction
Heavy metal pollution caused by industrial activities and technological development is posing significant threats to the environment and public health because of its toxicity, non-biodegradability, bioaccumulation and persistent tendency through the food chain [1-3].

The process of adsorption is considered one of the most suitable methods for the removal of contaminants from water and a number of low cost adsorbents have been reported for the removal of heavy metals (ions) from aqueous solutions. Activated charcoal is very efficient in removal of metal ions, but is readily soluble under very low and high pH conditions. There are a quite large number of studies regarding the preparation of activated carbons from agriculture wastes, fruit stones, hard shell of fruit stones, bagasse, manure compost, oil palm waste, agriculture residue from sugarcane, saw dust, sewage sludge [4]. Most of activated carbons are prepared by a two stage process carbonization followed by activation. The first step is to enrich the carbon content and to create an initial porosity and activation process helps in enhancing the pore structure. The activation can be carried by two different processes, physical and chemical. Chemical activation has two important advantages as compared to physical activation. One is a lower temperature in which the process is accomplished. The other is that the global yield to the chemical activation tends to be greater since burn off char is not required [5]. Among the numerous dehydrating agents, sulphuric acid is the widely used chemical agent in the preparation of activated carbon.

In this study, activated carbon prepared from Diplocyclos palmatus seed have been used for the removal of Ni (II) ions from aqueous solution since it is readily available and can be used as a viable adsorbent for the removal of heavy metals. The effect of pH, contact time, sorbent dose and initial metal ion concentration on the uptake of nickel have been studied.

2. Materials and Methods
2.1 Preparation of adsorbent
Diplocyclos palmatus seeds were first washed with tap water then with distilled water and dried in an oven at 110 °C for 12 hours. The dried seeds were crushed into small particles. In order to have sufficient quantity of seed for systematic studies of Nickel removal, several 50g lots of seed were carbonized using 20ml of concentrated sulphuric acid in each instance. After mixing thoroughly, the samples were let stand in an oven at 140 ℃ -160 ℃ for 24 hours. They were then washed with tap water. Finally, they were washed with distilled water, dried in an air oven at 110℃ for 8 hours. After 24 hours, the carbon was taken out from the oven and washed with tap water and tested for sulphate. When it was found to be sulphate free, it was

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filtered, washed well with double distilled water, dried, sieved to different sizes and kept in airtight glass containers.

2.2 Chemicals
All chemicals and reagents used were of analytical grade. Stock solutions of Ni (II) were prepared from nickel sulphate in deionized water. Digital pH meter was used to measure the pH values of the solutions. Solutions of 0.1M NaOH and 0.1 HCl were used for pH adjustment. All the working solutions were prepared by diluting the stock solutions with deionized water.

2.3 Batch adsorption experiments
Batch adsorption experiments were carried out in a series of stoppered reagent bottles. A weighed amount (1 g) of adsorbent was introduced into the reagent bottles (100 ml) containing various concentration of nickel. The total volume of the aqueous solution is equal to 50 ml. The solution pH was adjusted to the desired value by adding 0.1M HCl and 0.1M NaOH. The bottles were then shaken at room temperature using an electric shaker for a prescribed time to attain the equilibrium.

The solutions were filtered and final Nickel (II) concentrations of metal ions were determined by using an ultraviolet-visible (UV-Vis) spectrophotometry The instrument calibration was checked by using standard metal solutions. The amount of Nickel (II) adsorbed was calculated by the following mass balance equation.

$$C_e = \frac{(C_o - C_e) * V}{W}$$

Where C_o and C_e are initial and equilibrium concentration of metal ion (mg/L) respectively, m is the mass of adsorbent in gram (g) and V is the volume of the solution in liter (L).

3. Results and Discussion
3.1 Effect of pH
In order to establish the effect of pH on the adsorption of Ni (II) onto adsorbent, the batch adsorption studies at different pH values were carried out (Fig. 1). From results it is evidence that maximum adsorption of Ni (II) was 83.40 % at pH 5.0. pH of the solution plays a very important role in the metal uptake. Both adsorbent surface metal binding sites as well as metal chemistry in solution are influenced by solution pH. At low pH values, metal cations and protons compete for binding sites on adsorbent surface which results in lower uptake of metal. It has been suggested that at highly acidic condition, adsorbent surface ligands would be closely associated with H_3O^+ that restricts access to ligands by metal ions as a result of repulsive forces. It is to be expected that with increase in pH values, more and more ligands having negative charge would be exposed which result in increase in attraction of positively charged metal ions [9]. In addition, at higher pH the lower binding is attributed to reduced solubility of the metal and its precipitation [10].
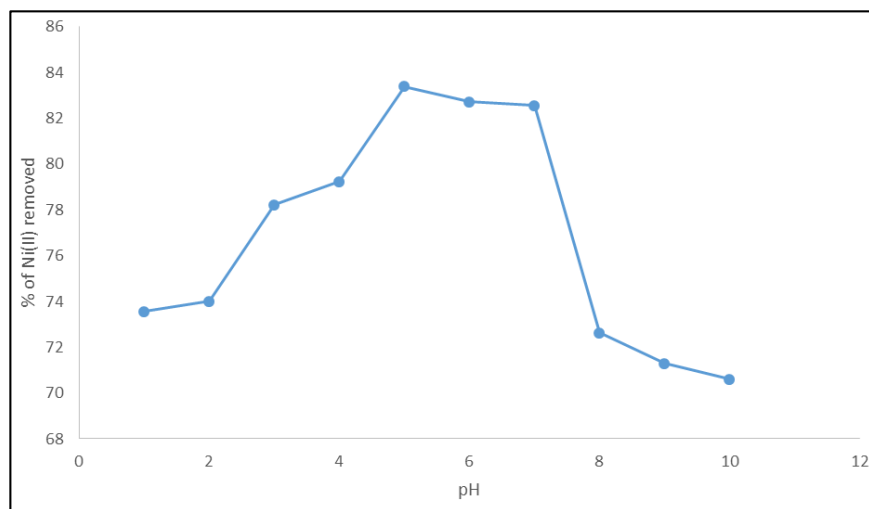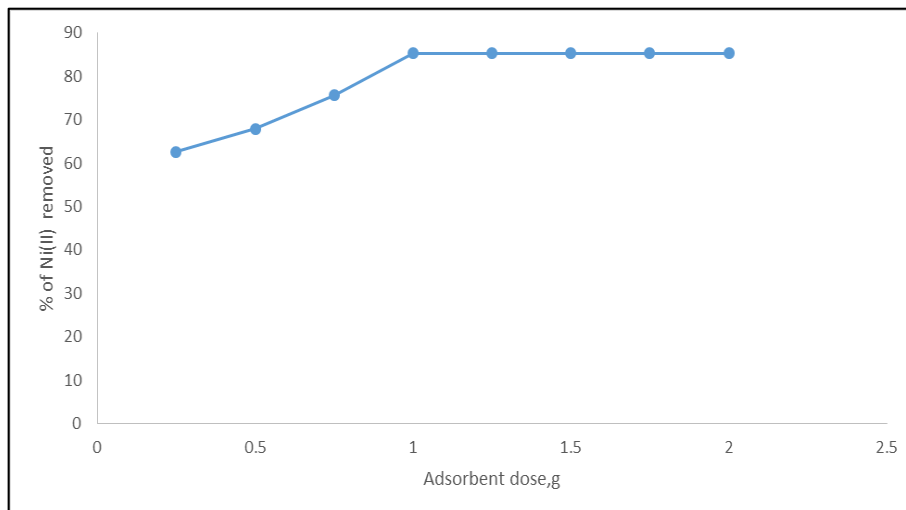

Fig 1: Effect of pH on Ni (II) removal [Ni (II) concentration = 100 mgL-1; adsorbent dose = 1.00 g; contact time = 60 min; stirring speed =100 rpm; temp = 32 ºC]

3.2 Effect of adsorbent dose
Effect of adsorbents dosage on percentage removal of Ni (II) was investigated by varying adsorbents dosage in the range of 0.5g to 2.00 g. It was observed that the percentage removal of Ni (II) increases with the increase in the adsorbent dosage (Fig. 2). The maximum percentage removal of Ni (II) was 85.35% at 1.00 g of adsorbents dose and constant initial metal ion concentration of 100 mg L-1. The phenomenon of increase in percentage removal of Ni (II) with increase in adsorbent dose may be explained as with increase in adsorbent dose, more and more surface becomes available for metal ion to adsorb and this increase the rate of adsorption [11].
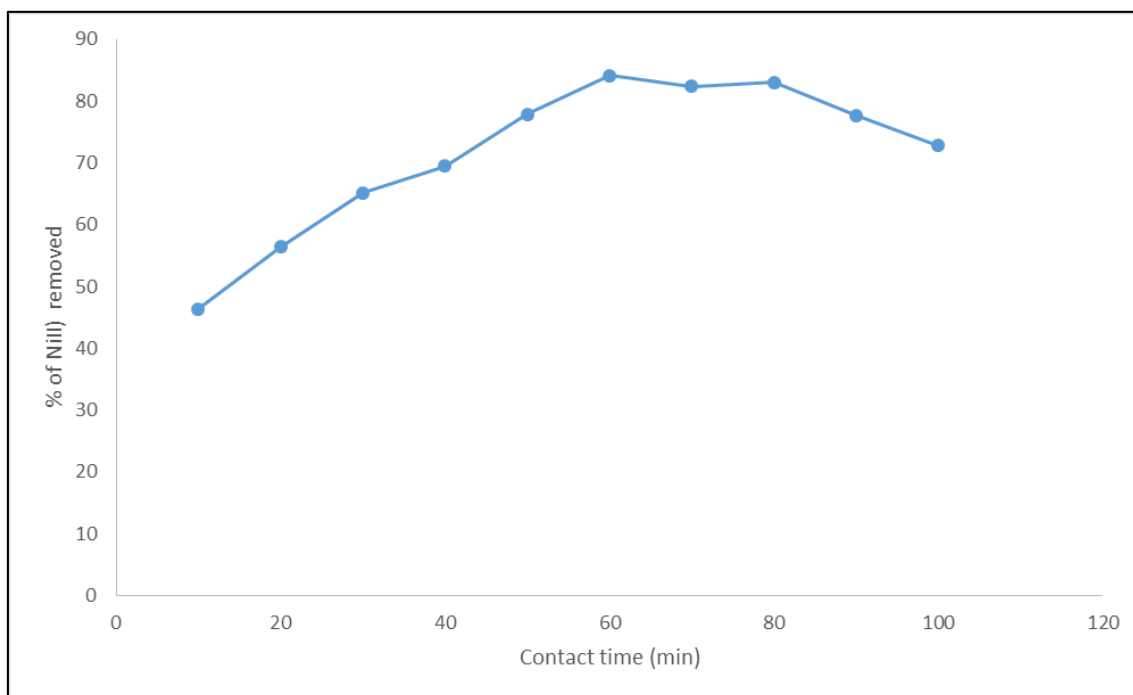
Fig 2: Effect of adsorbent dose on Ni(II) removal [Ni(II) concentration = 100mg L-1; pH= 6.0; contact time= 60 min; stirring speed= 100 rpm; temp= 32 ºC]

3.3 Effect of contact time

Fig. 3 shows the effect of contact time on the extent of adsorption of Ni (II). It has been observed that adsorption rate increased from 46.38 % to 84.10% with increased in contact time from 10 to 100 min. Maximum Ni (II) removal was achieved within 60 min after which Ni (II) concentration in the test solution became constant. It may be explained by the fact that initially for adsorption large number of vacant sites was available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase [12].
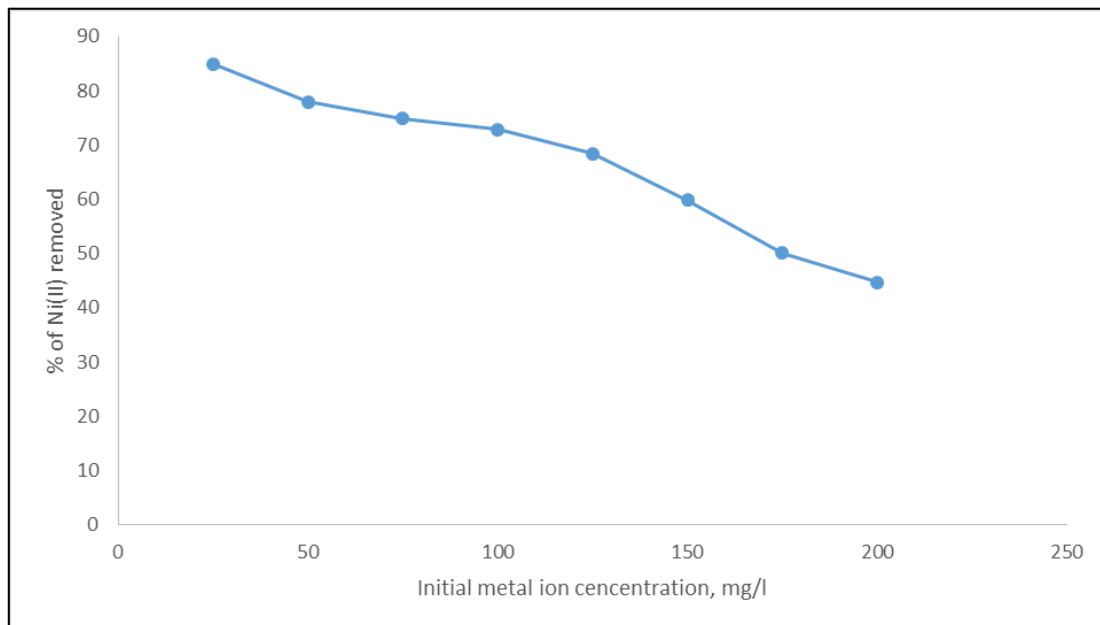

Fig 3: Effect of contact time on Ni (II) removal [Ni (II) concentration = 100 mgL-1; pH = 6.0; adsorbent dose = 1.00; stirring speed = 100 rpm; temp = 32 ºC]

3.4 Effect of initial metal ion concentration

Fig. 4 shows the effect of initial metal concentration on the adsorption experiment. It was observed that adsorption of Ni (II) decreased from 84.90% to 44.67 % with increased in metal concentration from 25 – 200ppm. At higher concentration, most of the Ni (II) are left unabsorbed due to saturation of adsorption sites. As the ratio of sorptive surface to ion concentration decreased with increasing metal ion concentration and so metal ion removal was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding sites in the biomass increased [13].

Fig 4: Effect of initial metal ion concentration on Ni (II) removal [Adsorbent dose = 1.00g; pH = 6.0; contact time = 60 min; stirring speed = 100 rpm; temp = 32 °C]

3.5 Equilibrium Isotherms

There are several models that express a relation between the amounts of sorption and the residual solute concentration. The most frequent models are the Langmuir, Freundlich and Temkin isotherm models. An isotherm describes the relationship of the concentrations of a solute between two separate phases at equilibrium at a constant temperature. A sorption isotherm, then would express the relation between the amount of solute or vapor adsorbed as a function of the equilibrium concentration of the solute or vapor in the solution. A sorption isotherm describes the process without reference to the mechanism [14]. The equilibrium sorption isotherm points to how the sorbate molecule or ions are distributed between the solid phase and the liquid phase. To find out the suitable isotherm models, analysis of isotherm data by adapting to different isotherm models is an important step that can be used for design purpose. In the present research, the sorption equilibrium data of Ni^{2+} by Diplocyclos palmatus seed was analyzed in terms of Langmuir, Freundlich and Temkin, isotherm models [15].

3.5.1 Langmuir isotherm

The Langmuir isotherm model is based on ideal assumption of a total monolayer sorption on sorbent surface [16]. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. The isotherm is based on three assumptions, namely, sorption is limited to monolayer coverage, all surface sites are alike and can only accommodate one sorbed atom, and the ability of a molecule to be sorbed on a given site is independent of its neighboring site's occupancy [16, 17]. The Langmuir model suggests that sorption occurs on homogenous surfaces by monolayer sorption (sorption onto a surface with a finite number of identical sites), without interaction between sorbed molecules. The equation (1) describes the model:

$$\frac{q_e = q_m \; bc \; C_e}{1 + b \; C_e} \quad \dots\dots\dots\dots \text{(1)}$$

Where: b= is constant related to the affinity of the binding site (L mg-1), qe = the sorbed metal ions on the biomass (mg g-1), Ce = metal ions concentration in the solution at equilibrium (mg L-1), and qm = maximum sorption capacity for a monolayer coverage (mg g-1).

The maximum sorption amount of the metal ion per unit weight of biomass needed to form a complete monolayer on the surface. qm represents a practical limiting sorption capacity when the surfaces fully covered with metal ions and assists in the comparison of sorption performances. The sorption parameters (qm, b) can be determined from the linearized plotting 1/qe vs. 1/Ce as shown in figure (5) according to equation (2) and Table (1) show this parameter.

$$\frac{C_e}{q_e} = \frac{1+}{q_m b} \quad \frac{C_e}{q_m} \quad \dots\dots\dots\dots \text{(2)}$$

Probably the Langmuir isotherm model is the most widely applied model because it allows obtaining the maximum sorption capacity (qm) for given sorbent/sorbate system, at constant temperature [18].
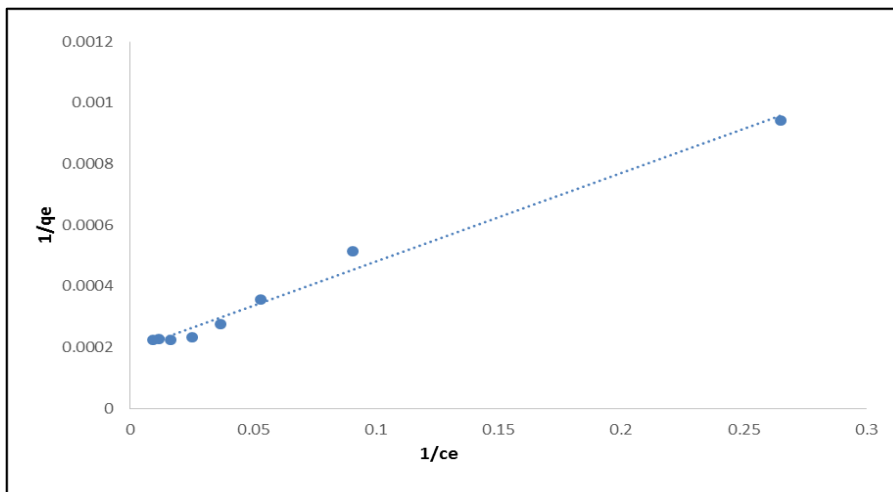
Fig 5: Langmuir isotherm for adsorption of Ni (II) [Adsorbent dose = 1.00g; pH = 6.0; contact time = 60 min; stirring speed = 100 rpm; temp = 32 ºC]

3.5.2 Freundlich isotherm:

The Freundlich isotherm model is based on heterogeneous surface assumption, expressed by equation as [19]:

$$q_e = K_F \, C_e^{1/n} \qquad\qquad\qquad ………….\ (3)$$

Where: K_F and n = the Freundlich constants, K_F related to the sorption capacity, (mg g-1)

The Freundlich isotherm describes equilibrium on heterogeneous surfaces and hence doesn't assume monolayer capacity. The larger its value, the higher capacity, n is the sorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. If 1/n approaches 1, the equation becomes linear. If 1/n value within 0.1 and 1 there is a favorable sorption of the sorbate on the given sorbent. The Freundlich relation is an exponential equation that assumes that the concentration of sorbate on the

sorbent surface increases by increasing the sorbate concentration in the liquid phase. Equation (4) can be linearized in logarithmic form and the Freundlich constants can be determined.

$$\text{Log } q_e = (1/n) \log C_e + \log K_F \qquad ………….\ (4)$$

The values KF and n can be estimated respectively from the intercept and slope of a linear plot of experimental data of logqe versus logCe as shown in Figure (6) and Table (1). Freundlich isotherm provides no information on the monolayer sorption capacity in comparison with the Langmuir model. This isotherm is widely recommended due to its accuracy. If gives more accurate results, then the Langmuir isotherm for a heterogeneous sorption system [14, 18, 20].
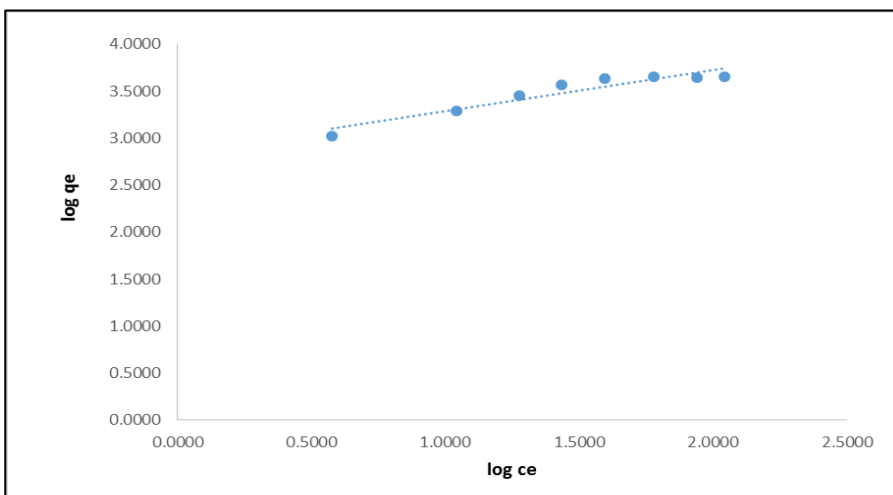
Fig 6: Freundlich isotherm for adsorption of Ni (II) [Adsorbent dose = 1.00g; pH = 6.0; contact time = 60 min; stirring speed = 100 rpm; temp = 32 ºC]
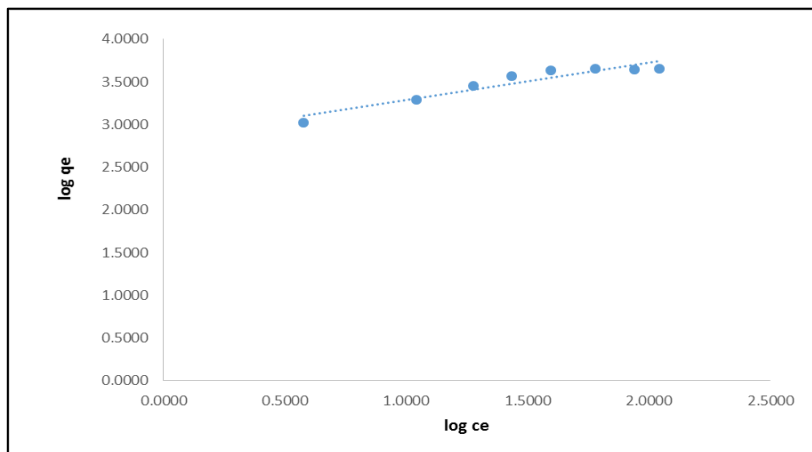
3.5.3 Temkin isotherm

Another empirical equation is the Temkin equation proposed originally by Temkin 1935. Temkin and Pyzhev were considered the effects of indirect sorbate/sorbent interactions on sorption isotherms. The heat of sorption of all molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions [21]. The linear form of the Temkin isotherm equations are given as [22]:

$$q_e = BT \ln K_T + B_T \ln C_e \qquad\qquad ------------------(5)$$

$$b_T = RT/B_T \qquad\qquad\qquad ------------------(6)$$

Where: KT is Temkin sorption potential (L/mg), BT & bT are Temkin constants. When qe was plotted against ln Ce, a straight line with the slope of BT must be obtained. The values KT and BT can be estimated respectively from the intercept and slope of a linear plot of experimental data of qe versus ln Ce as shown in Figure (7) and parameters listed in Table (1).

Fig 7: Temkin isotherm for adsorption of Ni (II) [Adsorbent dose = 1.00g; pH = 6.0; contact time = 60 min; stirring speed = 100 rpm; temp = 32 °C]

Table 1: Parameters of Langmuir, Freundlich and Temkin isotherm for sorption of Ni (II) on Diplocyclos palmatus seed

Parameters	Value
Langmuir Isotherm	
q_e (mg g^{-1})	500
b (L mg $^{-1}$)	0.6897
R^2	0.9867
Freundlich Isotherm	
K$_F$ (mg g^{-1})	703.55
n (L mg $^{-1}$)	2.2826
R^2	0.9033
Temkin Isotherm	
B$_T$ (J/mol)	1119
K$_T$ (L/mol)	0.7096
R^2	0.9285

3.6 Sorption kinetics

Kinetics of sorption describing the solute uptake rate, which is turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption. Several researchers have used different kinetic models to predict the mechanism involved in the sorption process. In which Pseudo first-order and pseudo second-order kinetic models are widely used [17, 23]. To investigate their action-based model, pseudo-first-order and pseudo-second-order models were employed.

3.8.1. Pseudo first-order kinetic model

Lagergren (1898) s presented a first-order rate equation to escribe the kinetic process of liquid-solid phase sorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the sorption rate based on the sorption capacity. It can be presented as follows:

$$\frac{qt}{dt} = k1 \, (qe - qt) \qquad \ldots\ldots\ldots\ldots (7)$$

Where: qe and qt (mg/g) are the sorption capacities at equilibrium and time t (min), respectively. k1 (min−1) is the pseudo-first-order rate constant for the kinetic model. Integrating equation (7) with the boundary conditions of qt=0 at t=0 and qt=qt at t=t, yields.

$$Ln \, (qe/qe-qt) = K1 \, t \qquad \ldots\ldots\ldots\ldots (8)$$

Which: can be re-arranged to:

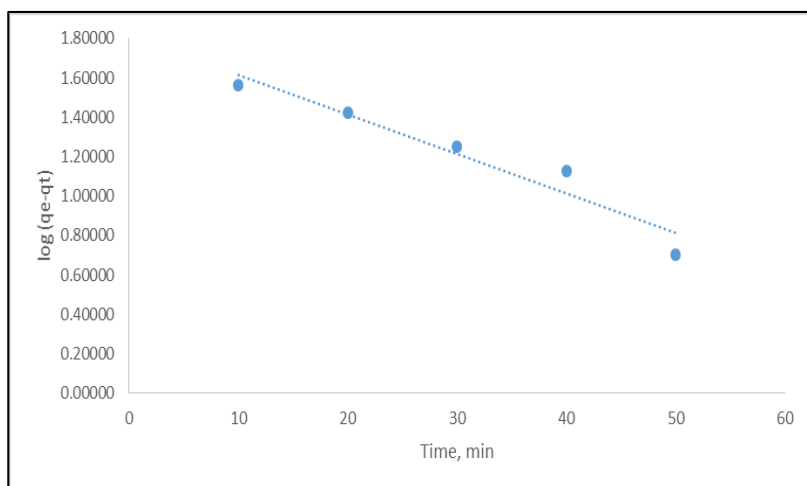$$Log \, (qe - qt) = log \, qe - k1/2.303 * t \qquad \ldots.. (9)$$

To distinguish kinetic equations based on sorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order [24]. In recent years, it has been widely used to describe the sorption of pollutants from wastewater in different fields.

Fig 11: Test of pseudo first order equation for sorption of Ni (II) [Adsorbent dose = 1.00g; pH = 6.0; contact time = 60 min; stirring speed = 100 rpm; temp = 32 °C]

3.6.2 Pseudo-second order kinetic model

In 1995, Ho described a kinetic process of the sorption of divalent metal ions onto natural sorbents [25], in which the chemical bonding among divalent metal ions and polar functional groups such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity. The rate of sorption described by equation. (8) is dependent upon the amount of divalent metal ions on the surface of sorbents at time t and that sorbed at equilibrium. The driving force, (qe−qt), is proportional to the available fraction of active sites [26]. Then, it yields

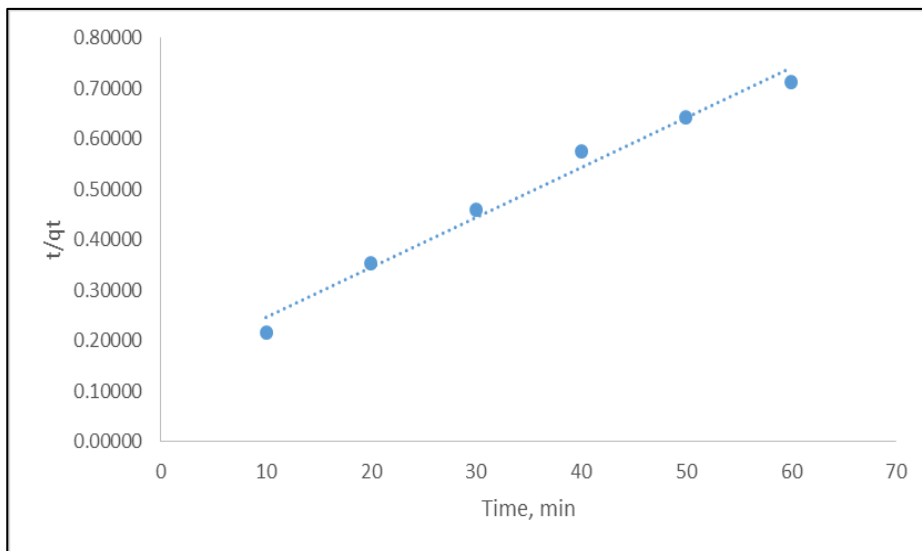$$Dqt/dt = k_2 (qe - qt)^2 \qquad \dots\dots\dots\dots(10)$$

Eq. (16) can be re-arranged as follows:

$$Dqt / (qe - qt)^2 = K_2\, dt \qquad \dots\dots\dots\dots\dots (11)$$

Integrating equation (11) with the boundary conditions of qt=0 at t=0 and qt=qt at t=t, yields

$$1/qt = 1/qe + K_2\, t \qquad \dots\dots\dots\dots (12)$$

Plotting t/qt against t at different sorbate concentrations provided second order sorption rate constant (k2) and qe values from the slopes and intercepts as showing in Figure (12).

Fig 12: Test of pseudo second order equation for sorption of Ni (II) [Adsorbent dose = 1.00g; pH = 6.0; contact time = 60 min; stirring speed = 100 rpm; temp = 32 °C]

The values of correlation coefficient indicate a good fit of Lagergren second order model with the experimental data. In many cases the first order kinetic process was used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second order kinetic model assumes that the rate limiting step may be chemical sorption [27].

Table 2: The Kinetic Parameters from the Pseudo-first-order and Pseudo-second-order model for the biosorption of Ni (II) on Diplocyclos palmatus seed.

Parameters	Value
Pseudo-first-order	
qe (mg g^{-1})	65.72
K_1*10^{-2} (min^{-1})	0.04629
R^2	0.9332
Pseudo-second-order	
qe (mg g^{-1})	101.01
K_2*10^{-2} (g mg^{-1} min^{-1})	0.667
R^2	0.9823

4. Conclusion

According to the experimental results, the Diplocyclos palmatus seed as an effective sorbent, low cost, and alternative sorbent precursor for the removal of nickel (II) from wastewater. The equilibrium conditions were attained equilibrium within 60 min. The sorption capacity first increased with increases in contact time due to the availability of the uncovered surface area of the sorbents, then remains almost constant, which reflects the maximum sorption capacity of the sorbent under operating conditions. It has been found that the sorption increased with increasing in pH until the optimum pH is reached, because the surface of sorbent becomes negative at higher pH values. The amount of heavy metal ions removal was increased with increasing temperature, While the removal percentage of heavy metal ions does not have same behavior with the increasing concentration. The sorption capacity increased with increasing sorbent dosage due to great surface area. The linear Langmuir, Freundlich, and Temkin were used to represent the experimental data, and the data could by relatively well interpreted by Langmuir isotherm model and it was found that the sorption of nickel (II) followed Pseudo-second-order kinetics.

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