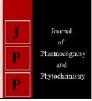


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## Adsorption of nickel (II) by low cost *Hopea* parviflora Saw dust

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#### Abstract

This work has been carried out to check the ability of *Hopea parviflora* saw dust, to remove Ni(II) ions from aqueous solution. The effect of pH, contact time, and initial adsorbent dosage on the metal ion adsorption capacity were investigated. The obtained results indicate that the adsorption amount of heavy metal ions increased with the increase of shaking time, adsorbent dose and pH of the media, which revealed that the optimum pH and adsorbent dosage for Ni(II) was found to be pH 6 and 1.00 g. The optimum contact time for nickel metal ion was observed to be around 60 minutes. The experimental results were examined using the Langmuir and Freundlich isotherms to obtain the appropriate model. The observed results indicate that the Langmuir equation was the best model for the adsorption of Ni(II) from aqueous solution. The results of the kinetic investigations indicated that the pseudo second order model fitted better the adsorption kinetics of Ni<sup>2+</sup> on *Hopea parviflora*. From the above results it was concluded that the *Hopea parviflora* saw dust, carbon found to be low cost efficient adsorbent Nickel (II) under optimum conditions.

Keywords: adsorption, Hopea parviflora, Ni (II) and adsorption isotherms

#### 1. Introduction

Water is an essential raw material in almost all manufacturing plants, though only a small amount of it may appear in the final product. The remainder becomes a waste material contaminant to a smaller or larger degree, depending on its usage in the plant. After entering the natural water resources it contaminates them <sup>[1]</sup>. Industrial waste water pollutants which include heavy metals and toxic pollutants are very important because they are not biodegradable and can be accumulated in living tissues causing various diseases and disorders. Contaminated waste waters commonly include Ni, As, Cu, Cd, Cr and Pb. Nickel is a toxic heavy metal that its ions is frequently met in wastewater of various industries such as electroplating, non-ferrous metal, mineral processing and battery manufacturing <sup>[2-3]</sup>. Ni exposure may cause noxious effects such as carcinogens and damage skin, lungs, nervous system and mucous membranes <sup>[4]</sup>. The maximum permissible concentration of nickel in wastewater systems is usually up to 5 mg L<sup>-1</sup> while the amounts greater than 0.1 mg L<sup>-1</sup>is prohibited for drinking water <sup>[5-6].</sup> A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption <sup>[7]</sup>. Most of these methods suffer from drawbacks such as high capital and operational cost or the disposal of the residual metal sludge.

Adsorption onto solid adsorbents can effectively remove pollutants from both aqueous and gaseous streams and therefore has considerable environmental significance. Activated carbon, the most popular adsorbent, has been traditionally used for the removal of odour, taste and color, which are designated as trace pollutants. Other commercial adsorbents, having increased reversibility, have been reviewed <sup>[8]</sup> and although their versatility and adsorption capacity are generally less than those of activated carbon, they are advantageous for certain applications. Such low cost adsorbents <sup>[9-10]</sup> have found use in laboratory scale for the treatment of various pollutants from water and wastewater.

#### 2 Experimental

#### 2.1 Preparation of adsorbent and adsorbate

In order to get sufficient amount of carbon for the systematic adsorption studies of nickel removal, several 50g lots of saw dust of *Hopea parviflora* was carbonized using 20ml of concentrated sulphuric acid in each instance. After mixing thoroughly, the samples were allowed to stand in a hot air oven at  $110^{\circ}$ C for 4 hours to facilitate charring of the material.

The charred carbon was washed with tap water and distilled water dried in a hot air oven at  $110^{\circ}$ C for 60 minutes. This carbon was abbreviated as HPC

Batch adsorption experiments were carried out in aqueous solutions with controlled initial Ni<sup>2+</sup> concentrations (25-200 mg/L) and pH values. An aqueous solution of different concentrations was prepared by dissolving of appropriate amounts of Nickel sulphate (NiSO<sub>4</sub>.7H<sub>2</sub>O), in double distilled water, and 0.1 mol/L HCl or 0.1 mol/L ammonia solutions were used for pH adjustment. All the experiments were performed by agitating of the nickel solution at the desired concentration and temperature. Samples were taken at appropriate time intervals and then filtered through Whatman No. 40 filter paper and the amount of Nickel ions was determined in the liquid phase using

UV visible spectrophotometer. All experiments were carried out twice.

#### The percent removal of Ni(II) was calculated as follows

% Removal of Ni (II) = 
$$\frac{C_{initial} - C_{final}}{C_{final}} \times 100$$
 ..... (1)

Where  $C_{initial}$  and  $C_{final}$  are the initial and final Ni(II) concentrations, respectively.

Adsorption experiments for the effect of pH were conducted by using a solution having 100 mg/L of Ni (II) concentration with an adsorbent dosage of 1.00 g/L and stirring the same for a contact time of 60 minutes. The effect of adsorbent dosage level on percent removal of Ni(II) was studied for Ni(II) concentration of 100 mg/L, pH adjusted to

6. In this study, the contact time was varied from 10 to 100 min, the pH of the solution from 1 to 10, the initial nickel concentration from 25 to 200 mg/L and the amount of adsorbent from 0.25 to 2 g/L.

## **3. Results and Discussions**

## 3.1 Effect of adsorbent dose

The dependence of Ni(II) adsorption on *Hopea parviflora* was studied at room temperature and fixed pH values by varying the adsorbent amount from 0.25 to 2.0 g/L keeping the adsorbate volume of 50 ml and the Ni (II) concentration of 100 mg/L. The results are shown in Figure 1. The percentage removal of Ni(II) increases rapidly with the increase in the amount of the adsorbents used in this study, which may be due to the greater availability of the exchangeable sites at higher amounts of the adsorbents. This decrease in adsorption capacity with increase in the adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process<sup>[11]</sup>.

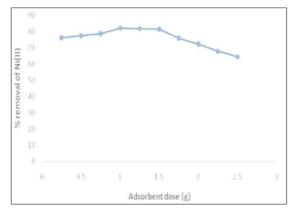


Fig 1 shows the Effect of adsorbent dose on removal of Nickel ions by HPC

## 3.2 Effect of pH

Metal adsorption from aqueous solutions is critically related to pH. It has also been reported that biosorption capacities for heavy metals are strongly pH sensitive and that adsorption increases as solution pH increases <sup>[12-13]</sup>. To find out the effect of solution pH for the removal efficiency of HPC, experiments were conducted with metal ion solutions having different pH values. pH of the solution was varied from 1 to 10, keeping all other variables constant, 60 minutes equilibration time, 100 mg/L Ni(II)ion concentration and 1.00 g of adsorbent. The effect of pH on the adsorption of Ni(II) was shown in Figure 2 in terms of the percentage of Ni (II) ions adsorbed.

Initial investigation of adsorption capability (Figure 2) showed that all the adsorbents possessed maximum sorption capacity for the cationic metal ion at around pH 6. This may be due to the fact that, at these pH values, there was a net negative charge on the surface components of the adsorbents and the ionic state of ligands such as carboxyl, hydroxyl and amino groups will be such as to promote a reaction with metal cations. Overall surface charge on the surface of the adsorbents became positive at lower pH and the presence of  $H^+$  ions hinders the access of metal ions by repulsive forces to the surface functional groups, which resulted in a decrease of the percentage of metal adsorption <sup>[14]</sup>.

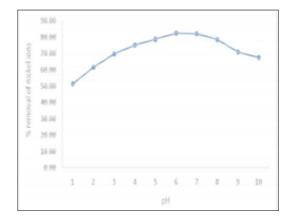
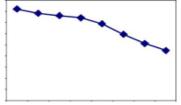


Fig 2: Shows the Effect of pH on the uptake of Nickel ions by HPC

#### 3.3 Effect of initial metal ion concentration

The amount of Ni(II) adsorbed per gram of the adsorbent( $q_e$ ) was observed at different metal ion concentrations (25–200 mg/L). It was observed that adsorption of Ni(II) decreased from 84.11% to 44.97% with increased in metal concentration from 25 to 200 ppm. 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 <sup>[15]</sup>.



initial metal ion concentaration in ppm

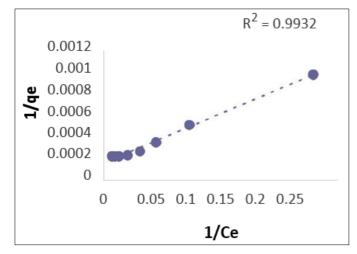
Fig 3: Effect on initial concentration of the removal of Ni(II) ion by HPC

#### 3.4 Langmuir adsorption isotherm

Attempt was carried out to investigate biosorption isotherms and kinetics of Ni(II) by the saw dust of *Hopea parviflora* carbon. Data used was obtained from effects of initial concentration and contact time. Langmuir isotherm model can be written in linear form as <sup>[16]</sup>.

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm max}} K_{\rm L} + \frac{1}{q_{\rm max}} \times C_{\rm e} \qquad \dots (2)$$

Where,  $q_{\text{max}}$  = The monolayer adsorption capacity of the adsorbent (mg g<sup>-1</sup>) is the (maximum amount adsorbed)  $K_{\text{L}}$  = The Langmuir adsorption constant (L mg<sup>-1</sup>)  $C_{\text{e}}$  = The equilibrium metal ion concentration in the solution (mg L<sup>-1</sup>)  $q_{\text{e}}$  = The equilibrium metal ion concentration on the adsorbent (mg g<sup>-1</sup>).



**Fig 4:** Langmuir isotherm plot for the adsorption of Ni(II) [initial Ni(II) conc = 25-200 mg  $L^{-1}$ ] pH = 6.0; adsorbents dose = 1.00 g  $L^{-1}$ 

#### 3.5 Freundlich Adsorption Isotherm

This is commonly used to describe the adsorption characteristics for the heterogeneous surface <sup>[17]</sup>. These data often fit the empirical equation proposed by Freundlich:

$$q = K C^{\frac{1}{n}} \qquad \dots (3)$$

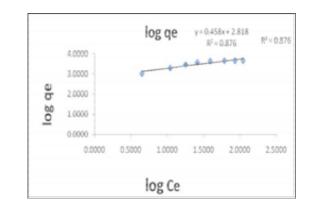
Where,

 $K_{F}$ = Freundlioch isotherm constant (mg/g) n = adsorption intensity

 $C_{\rm e}$  = the equilibrium concentration of adsorbate (mg/L) q<sub>e</sub> = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation 3, we have

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \dots (4)$$

The constant  $K_{\rm F}$  is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process <sup>[18]</sup>. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption However,  $K_{\rm F}$  and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models <sup>[20]</sup>. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where 1/n is a heterogeneity parameter, the smaller 1/n, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/n =1. If *n* lies between one and ten, this indicates a favorable sorption process <sup>[21]</sup>. From the data in Table 1, that value of 1/n = 0.4587 while n = 2.18 indicating that the sorption of Ni<sup>2+</sup> unto HPC is favourable and the  $R^2$  value is 0.876. The model parameters along with non linear correlation coefficient (R<sup>2</sup>) are summarized in Table 1. It was observed from the correlation coefficient values that the Langmuir isotherm fitted the experimental data better than the Freundlich model which indicates the homogenous distribution of active sites on adsorbent surface.



**Table 1:** Adsorption isotherm model constants and correlation coefficients for the adsorption of metal ions on *Hopea parviflora* carbon at room temperature °C.

Adsorption isotherms	Isotherm constants	
Langmuir isotherm	Qmax (mg/g)	500
	$K_L(L mg^{-1})$	0.56
	R <sup>2</sup>	0.993
Ensue dii ah	$k_F(mg g^- 1)$	658.87
Freundlich isotherm	n	2.18
	$\mathbb{R}^2$	0.876

#### 3.6 Biosorption kinetic model

To describe the kinetics of the biosorption of Ni(II) by the HPC. Pseudo-second-order kinetic model was applied.

The pseudo second-order model <sup>[22]</sup> is presented by the following equation (5):

$$\frac{T}{q_{t}} = \frac{1}{K_{2} \times q^{2}} + \frac{1}{q_{e}} \times t \qquad ...(5)$$

-

where,  $K_2$ = The Second order constant

 $q_e$  = The equilibrium metal ion concentration on the adsorbent (mg g<sup>-1</sup>)

 $q_t$  = The metal ion concentration on the adsorbent in time t (mg g<sup>-1</sup>). Pseudo - second-order model is in good agreement with experimental  $q_e$  value. This suggests that the sorption system followed the pseudo second-order model. The values of kinetic constants and  $q_e$  values of nickel sorption onto adsorbent are given in Table

2. It can be concluded from the very high correlation coefficients ( $R^2 = 0.996$ ) that the pseudo-second-order adsorption model is highly suitable to describe the adsorption kinetics of HPC onto Ni(II). These results imply that the adsorption system sticks to the pseudo second-order kinetics which further suggests that biosorption is the rate-controlling step <sup>[22]</sup>.

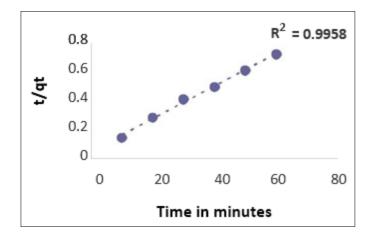


Table 2: Kinetic Parameters for the Removal of Nickel

Pseudo-Second	q <sub>e</sub> (mg g <sup>-1</sup> )	K <sub>2</sub> *10 <sup>-3</sup> (mg g min <sup>-1</sup> )	<sub>R</sub> 2
order kinetic model	88.4956	2.455	0.9958

## Conclusion

A low-cost activated carbon was derived from the saw dust Hopea parviflora by activation with sulphuric acid and utilized for Nickel (II) ions removal from aqueous solution in a batch system. It was found that the adsorbent dosage, initial Ni(II) concentration, pH of solution, and contact time influenced on the adsorption capacity of the prepared adsorbent significantly. The removal efficiency decreased with increase in metal ion concentration. The maximum metal uptake capacity of prepared adsorbent occurred at the optimum condition of adsorbent dosage of 1.00 g, pH 6.0, initial Ni(II) concentration of 100 ppm and contact time of 60 minutes. The equilibrium adsorption capacity was tested by using Langmuir and Freundlich isotherm models. The Langmuir isotherm indicated better fit compared to Freundlich isotherm model. The Ni(II) adsorption onto prepared activated carbon of TPC followed pseudo-second order kinetic model. The results of the present study showed that the prepared adsorbent from Hopea parviflora saw dust could be appraised as potential adsorbent in order to remove Ni(II) ions from aqueous solutions.

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