



## Equilibrium, Kinetic and Thermodynamic Studies on Biosorption of Ni(II) and Cu(II) by using *Nyctanthes arbor-tristis* leaf Powder

K. Subbarayudu<sup>1</sup>, R. Prathibha<sup>1</sup>, C. Narasimha Rao<sup>1</sup>, K. Sivakumar<sup>2</sup>, P. Venkateswarlu<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, S. V. University, Tirupati - 517 502, Andhra Pradesh, India. <sup>2</sup>Department of Chemistry, S. V. Arts College, Tirupati - 517 502, Andhra Pradesh, India.

Received 28<sup>th</sup> January 2017; Revised 03<sup>rd</sup> March 2017; Accepted 05<sup>th</sup> March 2017

### ABSTRACT

The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing metal ions from aqueous solution. The influence of various parameters on biosorption was established to optimize Ni(II) and Cu(II) ions removal from aqueous solutions using *Nyctanthes arbor-tristis* leaf powder. The pH value for maximum metal ion adsorption was determined as 6.0 and 5.0 for Ni(II) and Cu(II) ions, respectively. The adsorption follows pseudo-second order model and rate constants were calculated. The metal ion adsorption equilibrium was satisfactorily described by the Langmuir isotherm model than Freundlich model. The thermodynamic parameters such as standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ), and standard entropy ( $\Delta S^\circ$ ) changes were evaluated and concluded that this system was spontaneous and endothermic in nature.

**Key words:** *Nyctanthes arbor-tristis* leaf powder, Adsorption, Nickel, Copper, Kinetics, Thermodynamics.

### 1. INTRODUCTION

Heavy metals are emitted from wastewater produced by industries such as metal-plating, dyeing operations, mining and metallurgical engineering, electroplating, nuclear power plants, aerospace industries, and battery manufacturing processes. Atmospheric pollution resulting from industrial and vehicular emissions is a major environmental risk factor for the onset of various diseases, ranging from common cold to cancer [1]. The rate at which effluents are discharged into the environment, especially water bodies is increasing as a result of urbanization. The presence of heavy metals in the environment is of major concern because of their bioaccumulating tendency, threat to human life and the environment.

Various wastewater treatment technologies such as filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process, biosorption and adsorption have been developed for removing toxic metal ions [2-5]. A number of low-cost adsorbents have been examined for removal of metal ions, including some agricultural by-products, sawdust [6], clay [7], zeolite [8], microorganisms [9], and other low-cost adsorbents.

In this study, *Nyctanthes arbor-tristis* (Night Jasmine, Coral Jasmine) leaves were utilized as a cheap and

environmentally friendly biosorbent for the biosorption of nickel and copper from aqueous solutions.

### 2. EXPERIMENTAL

#### 2.1. Preparation of *N. arbor-tristis* Leaf Powder (NALP)

The *N. arbor-tristis* leaves were separated from the plant and washed thoroughly with tap water followed by deionized water to remove the dust particles. Then, the leaves were sun dried for 72 h and ground to fine powder. A weighed amount of NALP was transferred into round-bottomed flask and added deionized water. The resulting mixture was stirred for 1 h using magnetic stirrer at room temperature. Then, the biosorbent was separated from the solution by filtration, washed with distilled water several times until no color was detected in the filtrate. Afterward, it was dried in an oven and kept in a desiccator for further studies. The resulting biomass was designated as NALP for further representation.

#### 2.2. Preparation of Solutions

All the chemicals used in this study were of analytical grade. The stock solutions (1000 mg/L) for nickel and copper ions were prepared by dissolving a predetermined amount of nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) and copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in ultrapure deionized water and working solutions of desired

\*Corresponding Author:

E-mail: pvprofvenkat51@gmail.com

concentration used in the adsorption experiments were prepared by the dilution of the stock solution. The pH of the solutions was adjusted to a given initial pH using 0.1 N HCl and 0.1 N NaOH.

### 2.3. Batch Adsorption Experiments

Adsorption experiments were conducted in 250 ml conical flasks containing 100 ml solution in the concentration range of 50-125 mg/L of Ni(II) and Cu(II) solutions to which a weighed amount of the biosorbent was added. The solutions were stirred in a thermostatic shaking incubator at 160 rpm at the desired temperature. The thermodynamic parameters were studied at 303, 308 and 313 K. The samples were filtered and the supernatant was analyzed for equilibrium concentration by atomic absorption spectrometer.

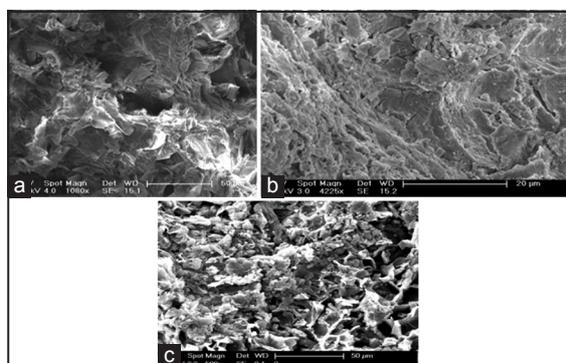
## 3. RESULTS AND DISCUSSION

### 3.1. Scanning Electron Microscope (SEM) Analysis

Figure 1 shows the SEM micrographs of NALP before and after adsorption. It is clear that the biosorbent has porous and rough surface texture, where there is a good possibility for the adsorption of nickel and copper on NALP. In the SEM images, it is clearly shown that the surface of NALP is covered with a layer of nickel and copper.

### 3.2. Effect of Agitation Time and pH

The adsorption capacity of nickel and copper increased with the increase in agitation time, and equilibrium was attained at an agitation time of 120 min. It was observed that with the increase of initial pH, the removal efficiency of Ni(II) and Cu(II) increased first but decreased after attaining a pH of 6.0 and 5.0, respectively. Adsorption increased with increasing solution pH since more metal binding sites could be exposed with negative charges, with subsequent attraction of metal ions with positive charges [10]. This phenomenon is also attributed



**Figure 1:** (a) Scanning electron microscope (SEM) image of *Nyctanthes arbor-tristis* leaf powder (NALP) before adsorption, (b) SEM image of NALP after adsorption of Ni(II), (c) SEM image of NALP after adsorption of Cu(II).

to the fact that substantial hydrogen ions compete for vacant adsorption sites of adsorbent at lower pH values. With an increase of initial pH, there are more amounts of negative ions and the Ni(II) and Cu(II) ions were surrounded by them. Beyond the pH of 6.0 and 5.0 for nickel and copper ions respectively metal precipitation occurred. Hence for the further studies, the experiments were carried out at pH values of 6.0 and 5.0 for nickel and copper ions, respectively, with an agitation time of 120 min.

### 3.3. Effect of Biomass Concentration

The biosorption efficiency for Ni(II) and Cu(II) ions as a function of biomass concentration was investigated at pH 6.0 and 5.0, respectively, by varying the adsorbent doses from 0.1 to 0.6 g for different initial metal ion concentrations. The biosorption yield steeply increased with concentration as the biomass concentration was increased from 0.1 to 0.4 g/100 ml for both the metal ions. This result can be explained by the fact that for optimum biosorption, extra sites must be available for biosorption, whereas by increasing the biomass concentration number of sites available for biosorption increases. A further increase in biomass concentration did not lead to a significant improvement in biosorption yield due to the saturation of the biosorbent surface with the metal ions. This trend can be explained as a consequence of partial aggregation of biomass at higher biomass concentration, which results in the decrease in effective surface area for the biosorption [11]. Therefore, the optimum biomass concentration was taken as 0.4 g/100 ml for Ni(II) and Cu(II) biosorption onto NALP in further studies.

### 3.4. Kinetic Studies

For evaluating the adsorption kinetics of nickel and copper, pseudo-first order, pseudo-second order, and intraparticle diffusion models were applied to find fit the experimental data. The Lagergren pseudo-first order model [12] postulates that the rate of change of solute uptake is proportional to the difference in the saturation concentration and the amount of solid uptake with time.

The general form of this equation is given as,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (1)$$

Where,  $q_e$  and  $q_t$  are the amount of metal ion adsorbed on adsorbent (mg/g) at equilibrium and at “t” time, respectively, and  $K_1$  is the rate constant of pseudo-first order adsorption ( $\text{min}^{-1}$ ). If equation 1 applies, a plot of  $\log(q_e - q_t)$  versus t should give a straight line.

The kinetics of adsorption process may also be described by pseudo-second order rate equation

proposed by Ho and McKay [13,14]. The linearized form of the equation is expressed as,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Where  $K_2$  is the rate constant of pseudo-second order adsorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The rate constant  $K_2$  is obtained from the linear plot of  $t/q_t$  versus  $t$  (Figures 2 and 3). The  $R^2$  values are close to unity for all Ni(II) and Cu(II) concentrations indicating the applicability of the pseudo-second order kinetic model for the present biosorption process.

In the model developed by Weber and Morris [15], Poots and McKay [16], the initial rate of intraparticle diffusion is calculated using the equation,

$$q_t = K_{id} t^{0.5} + C \quad (3)$$

Where  $K_{id}$  is the intraparticle diffusion rate constant ( $\text{mg/g min}^{-1/2}$ ) and  $C$  is the intercept that gives an idea about the thickness of the boundary layer [17]. If the Weber-Morris plot of  $q_t$  versus  $t^{0.5}$  gives straight line, and pass through origin, the adsorption process is controlled by intraparticle diffusion only. The plots in the figure are multi-linear with three distinct

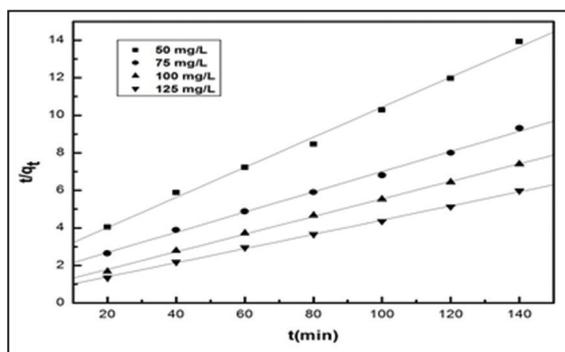


Figure 2: Pseudo-second order kinetic plots at different initial concentrations of Ni(II) onto *Nyctanthes arbor-tristis* leaf powder.

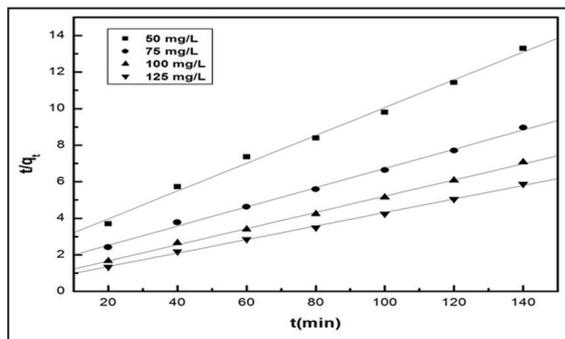


Figure 3: Pseudo-second order kinetic plots at different initial concentrations of Cu(II) onto *Nyctanthes arbor-tristis* leaf powder.

regions. Figures 4 and 5 show the initial covered region corresponding to the surface adsorption, second region relate the gradual uptake indicating intraparticle diffusion, and final region indicates the equilibrium uptake. The values of rate constants and correlation coefficients of kinetic studies are shown in Table 1.

Compared to pseudo-first order and intraparticle diffusion kinetic models, a good correlation coefficient was obtained for pseudo-second order, which indicate that the nickel and copper adsorption on the NALP follows pseudo-second order rate expression.

### 3.5. Equilibrium Studies

The data of Ni(II) and Cu(II) biosorption onto NALP were analyzed with the Freundlich and Langmuir isotherms which are widely used.

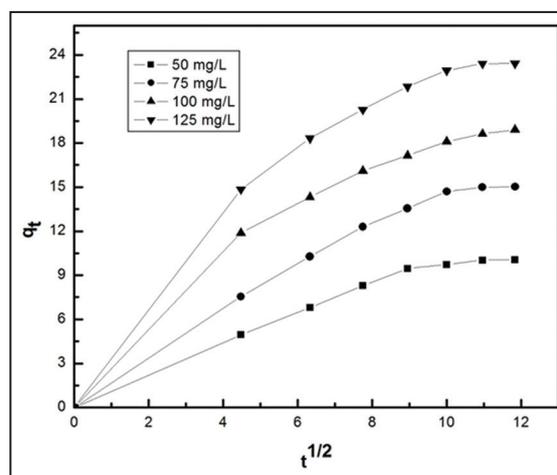


Figure 4: Weber-Morris plots at different initial concentrations of Ni(II) onto *Nyctanthes arbor-tristis* leaf powder.

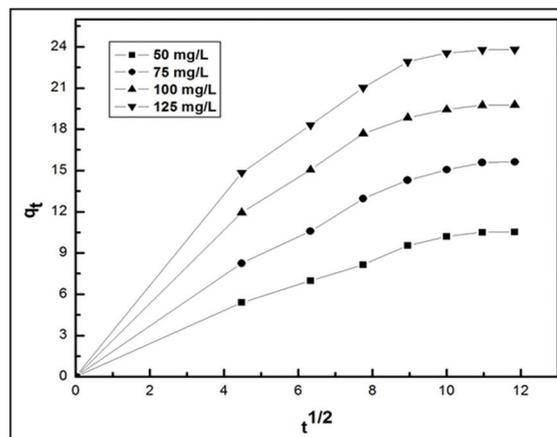


Figure 5: Weber-Morris plots at different initial concentrations of Cu(II) onto *Nyctanthes arbor-tristis* leaf powder.

Freundlich isotherm [18] is used for modeling the biosorption of metal ions on heterogeneous surfaces. The general form of Freundlich equation is given as

$$q_e = K_F (C_e)^{1/n} \tag{4}$$

Where  $K_f$  (mg/g)(L/mg)<sup>1/n</sup> is the Freundlich constant related to the adsorption capacity and 1/n is a dimensionless parameter. Equation 4 can be linearized in logarithmic form as given below.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

The Langmuir isotherm [19] assumes that the surface of any adsorbent material contains a number of active sites where the adsorbate attaches itself and the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The Langmuir equation in general form can be presented as:

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \frac{1}{C_e} + \frac{1}{q_m} \tag{6}$$

Where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  the equilibrium concentration (mg/L).  $q_m$  (mg/g) and  $K_L$  (L/mg) are Langmuir parameters indicating adsorption capacity and energy, respectively. The parameters  $q_m$  and  $K_L$  were calculated from the graph

plotted by  $1/q_e$  on Y-axis and  $1/C_e$  on X-axis, and the values are presented in Table 2.

Examination of correlation coefficient suggests that Langmuir isotherm is a better model for the sorption of Ni(II) and Cu(II) ions onto NALP.

### 3.6. Thermodynamic Studies

The thermodynamic parameters such as Gibbs free energy change  $\Delta G^\circ$ , enthalpy change  $\Delta H^\circ$ , and entropy change  $\Delta S^\circ$ , for the adsorption process were calculated using the following equations for the temperature range of 303-313 K.

$$\Delta G^\circ = -RT \ln K_c \tag{7}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \tag{8}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

Where T is the temperature in Kelvin, R is the gas constant (8.314 J/mol.K),  $K_c$  is the equilibrium constant. Table 2 shows the values of thermodynamic parameters of nickel and copper adsorption onto NALP. The negative values of  $\Delta G^\circ$  confirm the spontaneity of adsorption process, and the positive value of  $\Delta H^\circ$  suggested that the adsorption is endothermic in nature. The positive value of  $\Delta S^\circ$  shows the increasing randomness at the solid/liquid

**Table 1:** Adsorption rate constants of pseudo-first order, pseudo-second order and Weber-Morris model for Ni(II) and Cu(II) onto NALP.

Initial concentration of metal ion(mg/L)	Pseudo-first order model				Pseudo-second order model				Weber-Morris model			
	Ni(II)		Cu(II)		Ni(II)		Cu(II)		Ni(II)		Cu(II)	
	$K_1$	$R^2$	$K_1$	$R^2$	$K_2$	$R^2$	$K_2$	$R^2$	$K_{id}$	$R^2$	$K_{id}$	$R^2$
50	0.0494	0.952	0.0495	0.933	0.0023	0.998	0.0022	0.996	0.7153	0.962	0.7445	0.98
75	0.0531	0.936	0.046	0.943	0.0016	0.999	0.0017	0.998	1.052	0.973	1.0489	0.974
100	0.0313	0.982	0.0534	0.955	0.0026	0.999	0.0023	0.999	0.9658	0.984	1.0763	0.95
125	0.0529	0.926	0.0569	0.965	0.0021	0.999	0.002	0.999	1.1855	0.971	1.2509	0.954

NALP=*Nyctanthes arbor-tristis* leaf powder

**Table 2:** Parameters of Freundlich and Langmuir isotherms and thermodynamic parameters of Ni(II) and Cu(II) adsorption onto NALP.

Metal ion	Temperature (K)	Freundlich constants			Langmuir constants			$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (KJ/mol.K)
		$K_F$	1/n	$R^2$	$q_m$	$K_L$	$R^2$			
Ni(II)	303	2.152	0.6922	0.989	55.13	0.0232	0.993	-32.08	14.64	0.154
	308	2.236	0.6853	0.987	54.53	0.0242	0.991	-32.72		
	313	2.406	0.6672	0.988	50.59	0.028	0.992	-33.62		
Cu(II)	303	3.208	0.598	0.989	44.39	0.0402	0.995	-33.33	13.06	0.153
	308	3.396	0.5882	0.986	44.36	0.0424	0.994	-34.01		
	313	3.624	0.5701	0.987	42.24	0.0474	0.994	-34.86		

NALP=*Nyctanthes arbor-tristis* leaf powder

interface during the adsorption of nickel and copper onto NALP.

#### 4. CONCLUSION

This study emphasizes on the ability of NALP to adsorb Ni(II) and Cu(II) ions from aqueous solutions. The experimental data were found to fit better with the pseudo-second order model. Biosorption equilibrium was better described by Langmuir isotherm model than by Freundlich isotherm model. The values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  show the endothermic and spontaneous nature of adsorption process on the surface of NALP. This study concludes that this adsorbent is inexpensive, easily available material and effective in removing Ni(II) and Cu(II) ions from aqueous solutions.

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#### \*Bibliographical Sketch



Professor P. Venkateswarlu has more than 30 years of teaching and research experience in the Department of Chemistry, S. V. University, Tirupati. He guided 15 Ph. D. students. He has more than 115 publications in internationally reputed journals which are indexed in science citation index. He is the reviewer for many Elsevier journals.