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## Biosorption of Cu(II) from wastewater using *Azadirachta indica* (neem leaves)

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## BIOSORPTION OF Cu(II) FROM WASTE WATER USING *Azadirachta indica* (NEEM LEAVES)

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### ABSTRACT

This study concerns the development of *Azadirachta indica* (neem leaf) based biosorbents for the low-cost and high-capacity removal of Cu(II) ions from waste waters. Batch adsorption experiments were performed with varying process parameters such as agitation time and adsorbent dosage. The neem leaves were dried and ground to neem leaf powder (NLP) of size 80  $\mu\text{m}$  and below. Known dosages of NLP (0.4, 0.6, 0.8, 1.0, 1.2 g/L) and metal ion concentration of 100 mg/L were mixed and agitated for 4 hours at a constant temperature of 298 K with pH between 4.5 to 5.5. From the study, it was found that with lower NLP dosage, the amount of metal ions adsorbed was higher. A dosage of 0.4 g/L of NLP sorbents could remove as much as 40 % of Cu(II) ions in 120 min from a metal solution of concentration 100 mg/L and temperature 298 K. The adsorption capacity at these conditions was found to be an impressive 100 mg Cu(II)/g NLP used. The adsorption favourably fit a Freundlich isotherm, indicating a multilayer adsorption process. Results obtained from this study indicate that NLP is a very promising candidate for the low-cost and high-capacity removal of Cu(II) ions from waste water.

**Key Words** : Biosorption, Neem leaf powder, Copper(II) ions, Heavy metals, Waste water.

### INTRODUCTION

Industries which generate waste waters containing heavy metals such as the metal plating, mining, manufacturing, textile and semiconductor industries are seeking more efficient and cost effective metal removal methods. This is due to the rise in more stringent waste water discharge regulations as well the growing awareness in the field of eco-friendly and sustainable technologies. There are various methods available to remove heavy metals from waste waters.

The most popular ones are chemical precipitation (for highly polluted waters), ion exchange (for water pollution of variable strengths) and carbon adsorption (for mildly polluted waters). These technologies are very effective in removing heavy metals, but they however, have some disadvantages, either in respects of their costs or efficiencies.

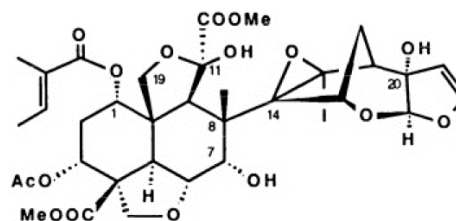
Chemical precipitation for instance, utilises chemicals and produces large amounts of sludge, primarily in the form of metal hydroxides. Metal hydroxide sludges

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fall under the hazardous waste category and needs to be disposed off in a proper manner, which costs a lot of money. Thus, this method has become an unattractive option to most industries. Carbon adsorption and ion exchange on the other hand, is getting less popular due to the rise of their raw material, installation and operational costs. Therefore, many industries today are seeking alternative metal removal technologies which can replace these conventional technologies. One such technology which is becoming popular and widely accepted today is biosorption.

Biosorption technology uses biomass-based adsorbents called "biosorbents". The biosorbent material is comprised of dead biological matter which has active groups on its surface for the purpose of metal binding. The advantages of biosorbents are their high versatility, high metal selectivity, minimal concentration dependence, high uptake, and cost-effectiveness. Moreover, these natural materials are abundantly available and most of the time can be disposed off without expensive regeneration due to their low cost<sup>1</sup>. Waste materials or materials that can be regenerated are the best options. Some examples of biosorbents include agricultural wastes, wood residues, sawdust, activated sludge, plant materials, bacteria, crustacean shells and natural minerals.

For the present study, a biosorbent based on neem leaves was developed. Neem is a tree native to South Asia, which is also found in countries like India, Malaysia, Thailand and Indonesia. It is an evergreen tree that can grow to a height of up to 30 m and 2.5 m in girth. Neem leaves have been traditionally used for various human ailments, as a pesticide as well as an air purifier. Neem has certain powerful chemical ingredients which exhibit these curative properties. They are azadirachtin (**Fig. 1**), salannin, meliantriol, nimbin and nimbidin<sup>2</sup>.



azadirachtin

**Fig. 1** : Azadirachtin compound

These compounds are structurally related to one another and belong to the "limonoid" group of natural products.

Recently, research has been carried out especially in Asia, pertaining to neem's metal binding capacity. This is because the chemical compounds in neem, besides having medicinal properties, were found to have the capacity to reversibly bind metallic ions. The binding of metallic ions take place on active groups (carboxyl and hydroxyl) of the chemical compounds in neem. The binding mechanism is an area that is still at research stage, but however, generally it is agreed that metallic ions bind through ion-exchange, chelation, complexation or precipitation mechanisms<sup>3</sup>.

Therefore, in view of the importance of metal recovery and recycling, an attempt has been made to study the removal of a common heavy metal ion from an aqueous phase, using the developed neem leaf powder (NLP) biosorbents. Copper ions were chosen for the study, because it is not only toxic to living organisms, but its value is getting dearer by the day, as they are becoming scarce due to the large amounts being wastefully dispersed in the environment after their industrial usage. Moreover, limited studies have been carried out on copper biosorption, and so far none using NLP. Therefore, its removal and recycling from waste waters is timely will prove beneficial in terms of research and findings for metal-based industries. The

results obtained may be compared with other biosorbents in terms of performance and metal binding efficiencies.

## MATERIAL AND METHODS

Fresh neem leaves were collected from a local tree, washed and dried in an oven at temperature about 60°C until 80% of the moisture was removed. For the drying of neem leaves, it is important that the temperature remain below 70°C, as beyond this temperature value, the active groups on neem may be destroyed. The dried neem leaves were then ground and the powder of size 80 µm and below were separated to be used in the experiments. The NLP was then stored in a dessicator. Storage of NLP must be moisture-free at all times because if moisture is present, it encourages the growth of mould.

Cu(II) ion solution of 100 mg/L was prepared by diluting from a concentrated Cu(NO<sub>3</sub>)<sub>2</sub> standard solution. Its concentration was verified using the AAS. The solution was stored in volumetric flasks for experimental usage. The presence of NO<sub>3</sub><sup>-</sup> ions in the solution did not matter, as it is a cationic adsorption process which takes place in the NLP.

Batch adsorption experiments were carried out by varying the NLP dosages and contact time. NLP dosages used were 0.4, 0.6, 0.8, 1.0 and 1.2 g/L. The NLP was mixed with 100 mL of Cu(II) ion solution and agitated on a water bath shaker at a speed of 200 rpm for 4 hours. Temperature was kept constant at 298 K by adjusting the dial on the water bath shaker. pH was measured to be between 4.5 to 5. Every 40 minutes, solutions were drawn out for metal analysis with the AAS. Metal analysis enabled the calculation of the total amount of Cu(II) ions adsorbed on the NLP via the formula in equation (1).

$$q = \frac{C_o - C_e}{m_a} \dots\dots\dots(1)$$

Where,

q – adsorption capacity (mg/g)

C<sub>o</sub> – initial concentration of metal in the solution (mg/L)

C<sub>e</sub> – equilibrium concentration of metal in the solution (mg/L)

m<sub>a</sub> – adsorbent dosage (g/L)

Adsorption isotherms are very important in the design of an adsorption system. They provide information on the pollutant removal capacity of a particular adsorbent at specified system conditions. In this study, the Langmuir and Freundlich isotherms were used to describe the equilibrium characteristics of Cu(II) adsorption onto NLP. The Langmuir isotherm is given in equation (2) below<sup>4</sup>.

$$q_e = q_m \frac{bC_e}{1 + bC_e} \dots\dots\dots(2)$$

Where:

q<sub>e</sub> – equilibrium adsorption capacity (mg/g)

q<sub>m</sub> – maximum adsorption capacity (mg/g)

b – Langmuir constant

C<sub>e</sub> – equilibrium concentration (mg/L)

Its linearised form is given in equation (3). By plotting C<sub>e</sub>/q<sub>e</sub> vs C<sub>e</sub>, the Langmuir constants can be obtained. The constants give an indication of the adsorption capacity and efficiency.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \dots\dots\dots(3)$$

There is also another constant for the Langmuir isotherm called the equilibrium or separation parameter, R<sub>L</sub>, which is defined as in equation (4). R<sub>L</sub> is a dimensionless constant.

$$R_L = \frac{1}{1 + bC_o} \dots\dots\dots(4)$$

Where:

$C_o$  – initial concentration (mg/L)

The  $R_L$  value indicates the nature of the Langmuir adsorption, where unfavourable adsorption gives a value of  $R_L > 1$ ; linear adsorption a value of  $R_L = 1$ ; favourable adsorption a value of  $0 < R_L < 1$  and irreversible adsorption a value of  $R_L = 0$ . The Langmuir isotherm fulfills a monolayer adsorption process.

For multilayer adsorption, the Freundlich isotherm is used<sup>5</sup>. It is given in equation (5) below. The linearised form is given in equation (6).

$$q_e = k_f C_e^{1/n} \dots\dots\dots(5)$$

Where:

$k_f$  – Freundlich constant that indicates adsorption capacity

$n$  – Freundlich constant that indicates adsorption intensity

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \dots\dots\dots(6)$$

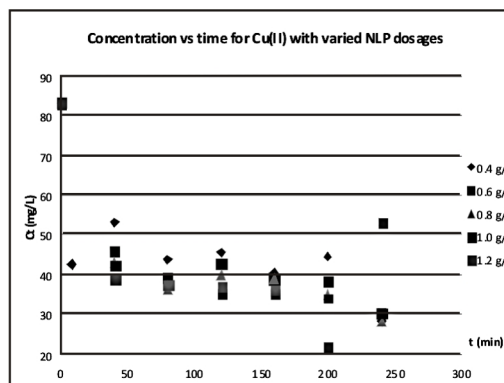
For favourable adsorption, the fulfilling condition is  $0 < n < 1$ .

## RESULTS AND DISCUSSION

To study the adsorption characteristics of Cu(II) ions on NLP, some graphs were plotted. They are: (i) the concentration versus time graph ( $C_t$  vs  $t$ ), which depicts the concentration of the Cu(II) ions in the solution after the completion of the adsorption process. It enables the determination of the equilibrium concentration,  $C_e$ , and time taken to reach equilibrium,  $t_e$ ; (ii) the adsorption capacity versus time graph ( $q_t$  vs  $t$ ), which depicts the amount of Cu(II) adsorbed per gram of NLP used. This graph gives the equilibrium

adsorption capacity value,  $q_e$  at time  $t_e$ ; (iii) the adsorption isotherms, which include both Langmuir and Freundlich, to study the nature and type of adsorption process as well as its favourability.

**Fig. 2** shows the concentration versus time ( $C_t$  vs  $t$ ) plot for the adsorption of Cu(II) with varied NLP dosages. From **Fig. 2**, it is observed that as the contact time increased, the amount of Cu(II) ions adsorbed increased for all NLP dosages used. The concentration values reach equilibrium between times 80 and 200 min. A straight line, parallel to the time-axis was drawn to obtain the equilibrium concentration and time values for each NLP dosage. They are tabulated in **Table 1**.



**Fig. 2 :** Cu(II) concentration versus time plot with varied NLP dosages

The equilibrium time,  $t_e$ , for all the NLP dosages used was found to be approximately 120 min. At this point of time, it is assumed that the rate of adsorption is equal to the rate of desorption. When compared to work carried out by other researchers (for copper removal but with other types of biosorbents), an equilibrium time of 10 minutes with sericite sorbents<sup>6</sup> while equilibrium time of 20 minutes for copper concentration of 3 mg/L and 60 minutes for copper concentrations of 5 and 10 mg/L using rubber leaf powder<sup>7</sup>. Using NLP but with other types of metallic ions, an

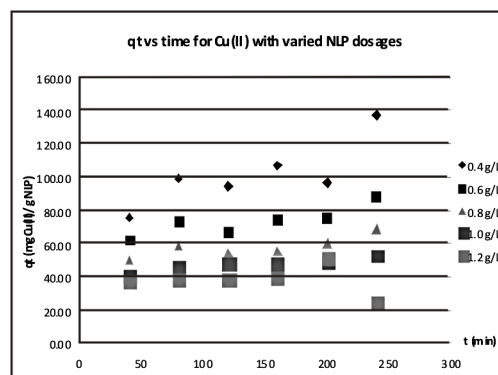
equilibrium time of 300 minutes was obtained for the maximum removal of chromium (95%)<sup>1</sup> and lead (93%)<sup>2</sup>. Thus, copper seemed to adsorb relatively quickly compared to other types of heavy metals. This may be due to greater affinity of the active groups in the bisorbents towards copper ions.

**Table 1 : Equilibrium concentration and time for the NLP dosage experiments**

NLP dosage (g/L)	Equilibrium concentration, $C_e$ (mg/L)
0.4	44
0.6	40
0.8	37
1.0	35
1.2	36
Equilibrium time, $t_e$ (min)	Percent Cu(II) removal (%) [a]
120	56
120	60
120	63
120	65
120	64

The percentage of Cu(II) ion removal from the solution is given in **Table 1**. With the increase in adsorbent dosage, the metal removal percentage increased. This is theoretically true as well, because when the amount of NLP increases, the available active sites for metal binding increases. However, it is not a very good representation of metal adsorption process, as there may have been other chemical processes taken place in the solution which removed ions, for instance precipitation. Therefore, in this context, the adsorption capacity (mg/g) would be a better representation of the metal adsorption process. The adsorption capacity can be calculated using equation (1).

The adsorption capacity versus time curves were plotted and represented in **Fig. 3**. Highest adsorption capacity was found to be for an NLP dosage of 0.4 g/L, followed by 0.6, 0.8, 1.0 and 1.2 g/L. Similar results have been obtained by other researchers, where the lower the dosage of adsorbents used, the higher the adsorption capacity<sup>7</sup>. The decrease in adsorption capacity (mg/g) with increase of adsorbent dosage is due to the high number of unsaturated adsorption sites through the adsorption reaction<sup>8</sup>. Another reason may be due to adsorbent particle interaction and aggregation due to the high dosage used. Such aggregation may reduce the available surface area for metal adsorption<sup>9</sup>.



**Fig. 3 :** Amount of Cu(II) adsorbed per gram of NLP used

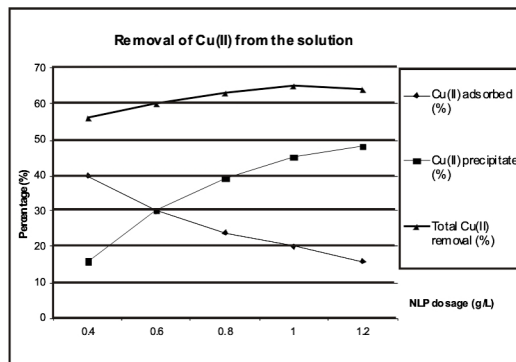
Highest adsorption capacity from **Fig. 3** was found to be 140 mg/g of copper when a dosage of 0.4 g/L of NLP was used. The equilibrium adsorption capacity ( $q_e$ ) was determined by drawing a parallel line along the time-axis on the NLP curves and the values obtained are given in **Table 2**. The equilibrium adsorption capacity for 0.4 g/L of NLP was found to be 100 mg/g. This equates to an adsorption percentage of 40%. Similarly, for the other NLP dosages (0.6, 0.8, 1.0, 1.2 g/L), the copper adsorption capacity was found to be 30, 24, 20 and 16% respectively. There seemed to be a drop in the adsorption capacity, most probably

due to the aggregation of the NLP particles as previously mentioned in the text.

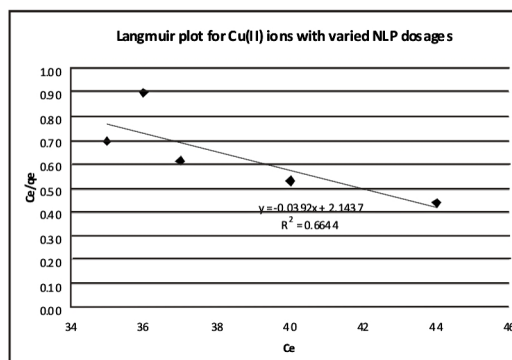
**Table 2 : Equilibrium amount of copper ions adsorbed per gram of NLP**

NLP dosage (g/L)	Equilibrium adsorption amount, $q_e$ (mg/g)
0.4	100
0.6	75
0.8	60
1.0	50
1.2	40
Percent Cu(II) adsorption (%) [b]	Possible precipitation (%) [a-b]
40	16
30	30
24	39
20	45
16	48

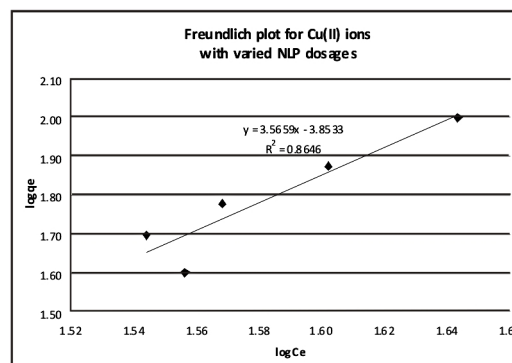
When comparing results obtained in **Table 1** and **Table 2**, it is found that the percentage of copper ions adsorbed is lower than the percent removal from the original solution. This means the remaining copper must have precipitated or taken part in other chemical reactions to cause its removal from the solution. The percentage of possible precipitation is given in the last column of **Table 2**. A relationship between the percent removal, percent adsorbed and percent precipitated for copper ions is represented graphically in **Fig. 4**. As a summary, the total metal removal increases with NLP dosage, but the removal due to adsorption decreases with the increase of NLP dosage. For all experiments carried out, the pH was found to be in the range of 4.5 to 5.



**Fig. 4 :** Total amount of Cu(II) removed from the solution



**Fig. 5 :** Langmuir plot for Cu(II) ions with varied NLP dosages



**Fig. 6 :** Freundlich plot for Cu(II) ions with varied NLP dosages

With the results obtained from **Fig. 2** and **Fig. 3**, adsorption isotherms were plotted. Equations (3) and (6) were used to generate the Langmuir and Freundlich data respectively. Results obtained are depicted

graphically in Fig. 5 and Fig. 6. The isotherm parameters are given in Table 3.

**Table 3 : Langmuir and Freundlich isotherm constants and correlation coefficients.**

Langmuir	
$q_m$ (mg/g)	-25.51
$b$ (L/mg)	-0.0018
$R^2$	0.6644
$R_L$	-1.91 (not favourable)
Freundlich	
$k_f$ (mg/g)	0.0021
$n$	0.28 (favourable)
$R^2$	0.8646

From the results obtained, it is obvious that the Cu(II) adsorption process fits a Freundlich (multilayer) adsorption mechanism, as the results produced a straight line with a reasonable regression value of 86.46%. Moreover, the Freundlich adsorption was found to be favourable with the value of  $n$  between 0 and 1 (Table 3). Further investigations need to be done to study the mechanism of the adsorption process on NLP.

## CONCLUSION

As a conclusion, NLP was found to be a reliable biosorbent for the removal of Cu(II) ions from solutions. Adsorption using lower NLP dosage was found to give larger adsorption capacity values. In this study, the optimal dosage of NLP was found to be 0.4 g/L, which was able to adsorb 40% of the Cu(II) ions from the solution at temperature 298 K and pH 5.11. The adsorption capacity at these conditions was found to be 100mg/g. This is relatively high compared to many other biosorbents. The adsorption capacity may be improved by altering the experimental conditions such as the concentration, pH and temperature. The adsorption favourably fit a Freundlich

isotherm, indicating a multilayer adsorption process of Cu(II) ions on NLP.

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