

Biosorption Of Cu(II) Ions From Aqueous Solution Using Azadirachta indica (Neem) Leaf Powder

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Abstract

Biosorption is considered as a potential method for the removal of heavy toxic metals from waste solution and as alternative to other conventional process such as precipitation, ion exchange, electrochemical treatment and evaporative recovery, especially, when the concentration of the heavy metal ion is low. In order to qualify for industrial applications, biosorbents have to be produced at low cost. In the present study, (Azadirachta indica) neem leaves Powder (NLP), was investigated for the removal of Cu(II) ions from aqueous solution. Characterisations of the NLP was conducted, and the effects of contact time, particle size, Cu(II) ion concentration as well as effect of chemical treatment were studied in batch process. Batch biosorption experiments were carried out at a fixed adsorbent dosage of 1.0 g/L, initial ion concentration of 100 mg/L, a temperature of 333K and a pH range of between 5-6. The surface area of NLP was found to be about 2.3102 m^2/g. The analysis with FTIR indicated that possible hydroxyl and carboxyl functional groups are involved in metal Cu(II) ions biosorption. Adsorption isotherms were modelled by the Langmuir and Freundlich isotherm equations, with the former providing a better fit for the data. 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 aqueous solution.

Keywords: Biosorption, Neem leaf powder, Copper(II) ions, Heavy metals, Wastewater

1. Introduction

The pollution caused by heavy metals is a major environmental problem of global concern with wastewater effluent coming from different industrial processes such as fertiliser industry, metal cleaning, mining, refineries, pulp and paper industries and bath plating industries. All these are recognised to be the major source of toxic heavy metals in the industrial waste stream (Amarasinghe and Williams, 2007).

Copper is a major element needed for human health that plays a vital function in the metabolism of lipids, carbohydrates and also in proper functioning of the heart and blood vessels, but when in excess it becomes toxic. An average of 100-150 mg of Cu (II) ions is needed in the human body. The specification of metals in aqueous environment depends on both pH and concentration. Even though Cu (II) ion is an essential nutrient for the increase of algae, it is still toxic to plants and animals (Jha, et al., 2011).

Excess amount of Cu(II) ions in the environment may pose a substantial health hazard like liver and kidney failure, anaemia, gastrointestinal bleeding, nausea, dizziness, respiratory problems and even death. 1.5 mg/L is the maximum recommended quantity of Cu(II) ions that should be present in drinking water according to WHO (world health organisation). There have been strict environmental regulations concerning the effects caused by toxic heavy metals as a result of their discharge by industrial activities in many countries (Jha, et al., 2011).

Various technologies currently are applied for heavy metals removal from industrial waste stream, such as ion exchange, precipitation, adsorption, absorption, reverse osmosis, flocculation and precipitation (Amarasinghe and Williams, 2007). However, problems sometimes occur to these technologies as a result of many factors: large investment, low efficiency, higher energy requirement and the production of large volume of sludge. Adsorption using activated carbon is a well-established and widely acceptable technology due to the numerous advantages such as easy operation and higher efficiency. However, adsorption onto activated carbon is expensive and may require additional chemicals to improve efficiency. This leads to the searching of a cost effective and efficient method for the removal of heavy metals from waste stream (Qi and Aldrich, 2008).

Biosorption has recently attracted considerable amount of attention as alternative method used for the removal and recovery of toxic metals occurring in waste effluents compared to other conventional technologies due to numerous advantages such as low sludge production, low investment and operational cost and above all higher efficiency (Krishnani,et al., 2008).

There is currently great number of investigations found in literature for the adsorption of heavy metals by the use of various types of biomass.

This study will focus on the use of a plant based biosorbent developed from neem leaves to study the adsorption characteristics of Cu(II) ions found in waste water effluent and also to find out if modified neem leaves is capable or have an acceptable adsorption capacity for removing copper ions in wastewater. Parameters like contact time, concentration of biosorbate and particle size will be analysed in the study.

2. Materials and Methods

2.1 Materials

Aqueous copper concentration ($CuCl_2 \cdot 2H_2O$) was used as heavy toxic metal model for this experiment. The Azadirachta indica (Neem) leaf used in the present study was collected freshly from a local tree. The collected leaves were washed with distilled water to remove all impurities that might be present. The neem leaves (Azadirachta indica) were also treated using NaOH (Sodium hydroxide) solution in order to enhance the capacity of the Cu(II) ions uptake. The oridinary Neem leaf powder and the modified Neem leaf powder were labelled NLP and MNLP.

2.2 Characterisation of Neem Leaf

To understanding the binding mechanism of copper ions on the adsorbent surface, spectroscopic analysis was carried out using a Fourier transform infrared (FTIR) spectrometer to determine the functional groups available in the neem leaf (Febriana, 2010). For studying the surface morphology of the biosorbent, particulate size was taken for analysis. The surface morphology of Azadirachta indica (neem) leaf ware visualized by a scanning electron microscope (SEM) coupled with EDX. Surface area and pore diameter was determined using a gas adsorption surface analyser (Micromeritics ASAP 2010).

2.3 Batch Biosorption Experiment

Batch biosorption experiments were conducted. In general, the effects of particle size, contact time and metal concentration on adsorption of copper were performed. The experiment was carried out in a 250ml conical flask filled with 100ml of Cu(II) solution at 100mg/L concentration. 1.0 g/L of NLP was added into the conical flask and placed on a water bath shaker at a temperature of 60^{o}C (Febriana, 2010) and agitation rate of 125 rpm.

The batch adsorption experiment was carried out using both the Ordinary neem leaf powder (NLP) and also the modified neem leaf powder (MNLP).

After all the adsorption experiments, the adsorbent were filtered, dried and the samples are brought for elemental analysis and electron microscopy with FEI, Quanta 400, SEM-EDX, surface area analysis with Micrometrics, ASAP 2020. The amount of Cu(II) ions in the solution was analysed for residual metal ion concentration by Elmer, AAnalyst 400Atomic Absorption Spectrometer (AAS) instrument. Metal uptake is then evaluated from equation

$$q_e = \frac{C_o - C_e}{M} V \quad (1)$$

(Ngah and Hanafiah, 2008a)

Where Co and Ce are initial and final copper concentration, V is the volume of the biosorbate and M is the weight of the biosorbent.

3. Results and Discussion

3.1 Surface Area of Biosorbent (ASAP)

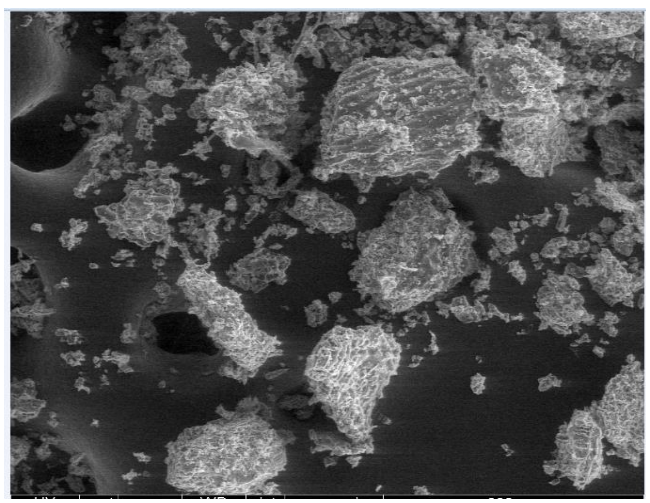
The NLP (Neem leaf powder) surface area was found to be $2.3102m^2/g$ from the ASAP analysis. The surface area of the NLP was found to be higher and in some cases lower than other biosorbents. Generally the greater the surface area of a biosorbent, the greater the metal biosorption (Ngah and Hanafiah, 2008b). Surface area of NLP was found to be higher than rubber leaves, $0.46m^2/g$ (Ngah and Hanafiah, 2008a), spirogyra spp., $1.31m^2/g$ (Gupta et al., 2006), rice bran, 0.46 m^2/g (Montanher et al., 2005) and soya meal shell, $0.76m^2/g$ (Arami et al., 2006). Also the NLP was found to be lower than activated carbon, $1100m^2/g$ (Ozacar and Sengil, 2002), Sargasssum sp, 8.13 m^2/g (Sheng et al., 2008), and Moringa oliefera, 4.01 m^2/g (Kumari et al., 2006).

Based on the conclusion of many researchers, surface area and pore sizes might be involved in the biosorption mechanism and since NLP does not have a highly porous structure, biosorption might occur through chemical sorption with the presence of functional groups and ion exchange.

3.2 Surface Topography (SEM/EDX)

SEM (Scanning electron microscope) and EDX (Energy-dispersive X-ray spectroscopy) are useful analytical equipment for evaluating the characteristics of adsorbent elements. Fig. 1 and Fig. 2 show the SEM-EDX results for NLP and MNLP before Cu(II) ion adsorption. Although the SEM results for the NLP before and after bisosorption looks almost the same, EDX results is different, in Fig. 1 it clearly indicates that NLP consist of mainly C and O, and small amounts of, Ca, Mg, K, P and S. In Fig. 2 due to modification using NaOH, it can clearly be seen how Na has been attached to NLP.

While Fig. 3 and Fig. 4 shows SEM and EDX for NLP and MNLP after the biosorption on which Cu(II) ions presence is been confirmed. From the SEM results, non-uniformed bright spots indicate Cu(II) ions presence, which signifies that not all the functional groups are responsible for Cu(II) ions adsorption from the solution. After the adsorption for the NLP, Mg and K are been replaced by Cu(II) peaks, likewise for the MNLP, Na, Mg and K are also been replaced by Cu(II) peaks, making the Cu(II) peaks to be visible in the spectra. This clearly indicates that ion-exchange might be one of the mechanisms for Cu(II) removal.



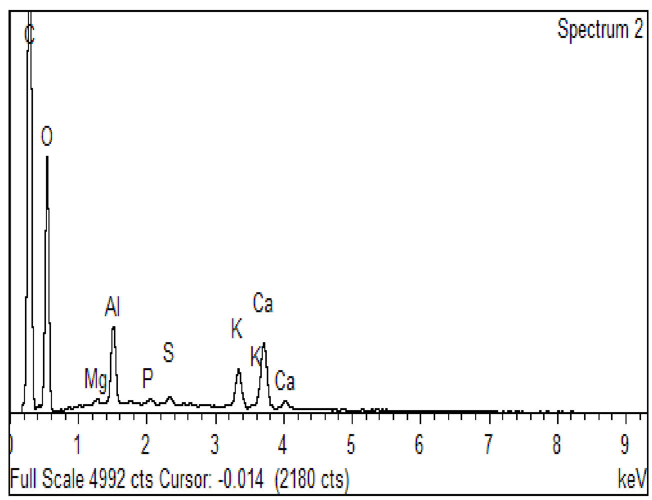


Fig. 1: SEM and EDX images of NLP before Cu(II) ions Adsorption

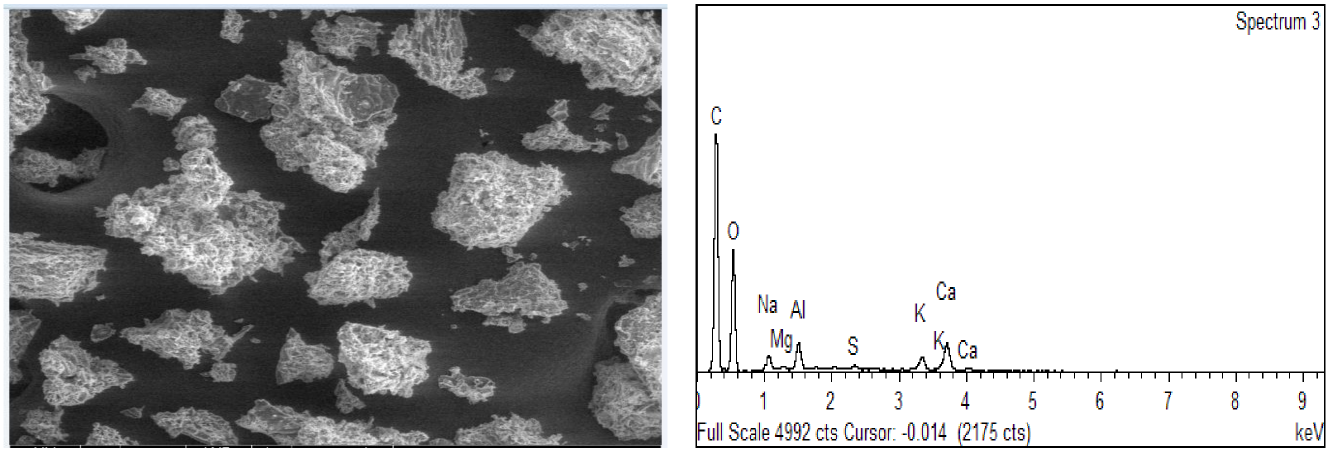


Fig. 2: SEM and EDX images of modified NLP before Cu(II) ions Adsorption

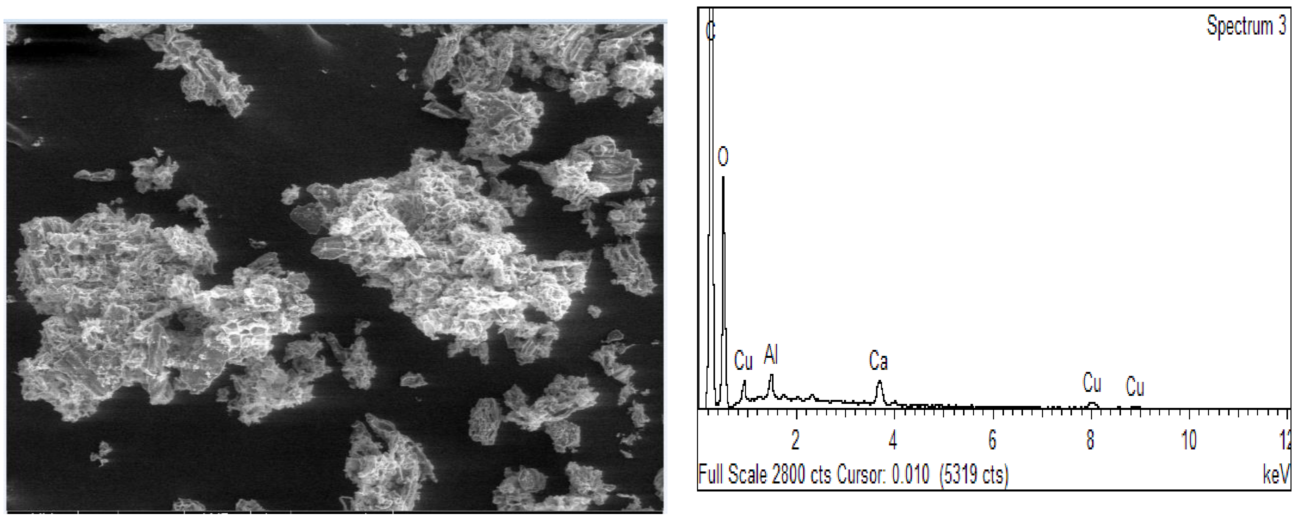


Fig.3: SEM and EDX images of NLP after Cu(II) ions Adsorption

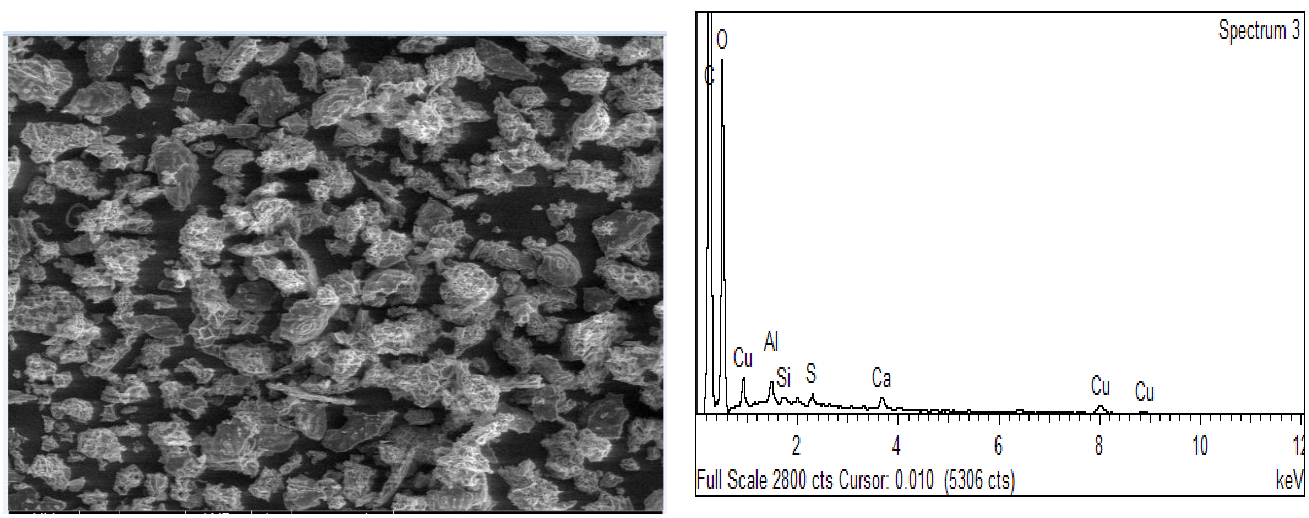


Fig. 4: SEM and EDX images of Modified NLP after Cu(II) ions Adsorption

3.3 Surface Functional Groups

Different adsorption peaks displayed by the FTIR indicates the presence of various functional groups on the surface of both the NLP and MNLP before and after adsorption. Based on the attribution of peaks in the table, it can be shown that NLP contains different types of functional groups and different biosorption processes such as ion exchange, electrostatic attraction and complexation might be involved in the adsorption mechanism. By comparing the fresh NLP, MNLP and Cu(II) loaded NLP and MNLP, it can be observed that there are shift in some certain cases in wave number indicating metal binding process on the NLP and MNLP surfaces. The relevance of a shift in the spectra is that there is an effect of chemical treatment or metal adsorption on the functional groups (Yazici et al., 2007). For the fresh NLP as shown in Fig: 3.5 the spectra show a band of range 3862.04 - 595.09 cm^{-1}. After Cu(II) ions biosorption the spectra changes to 3905.83 - 582.36 cm^{-1} as in Fig. 3.5 b. Also Fig. 3.6 a and b shows the MNLP spectrum in the range of 3943.09 - 581.56 cm^{-1} before Cu(II) ions adsorption, but after loaded with the Cu(II) metal the band changes in the range of 3988.17 - 582.26 cm^{-1}. The lower spectrum values in all cases did not change significantly only a minor shrinkage. This is an indication of complex formation between Cu(II) ions and anionic species (Sarioglu et al., 2007). Based on the changes on the FTIR spectra, it can be assumed that Hydroxyl and carboxyl groups might be functional groups involved in the adsorption of Cu(II) ions.

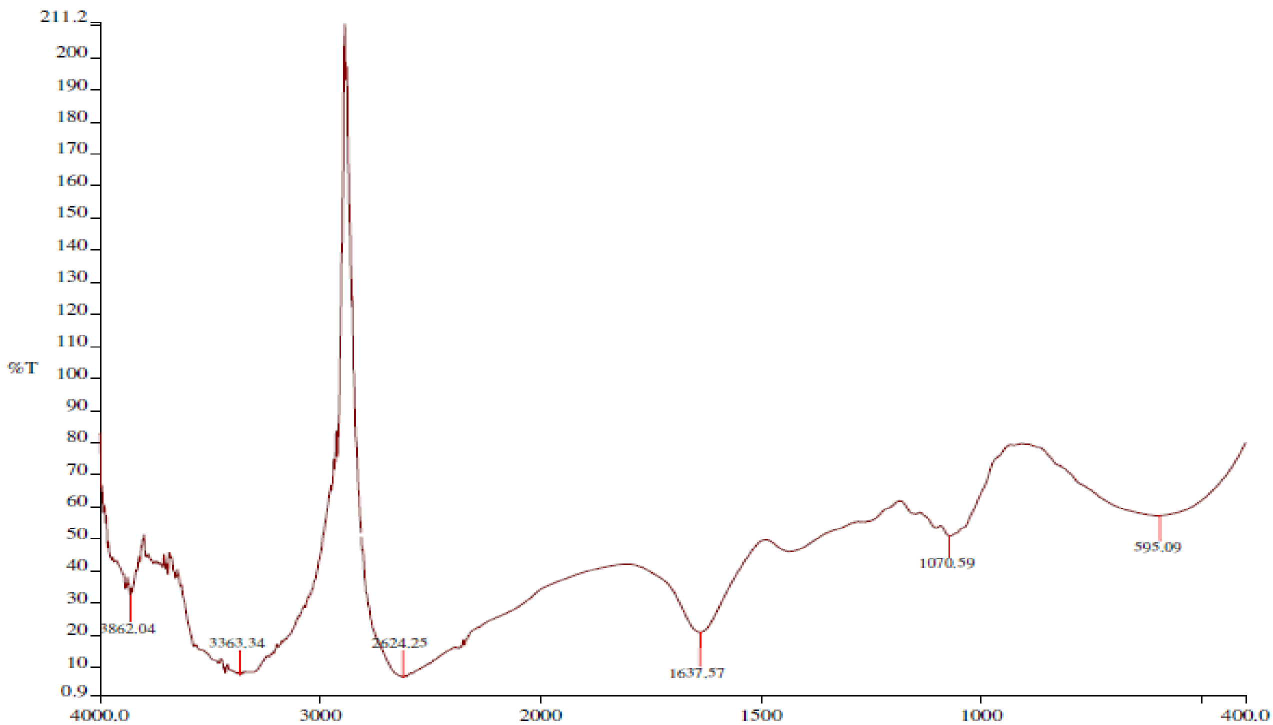


Fig. 5 FTIR spectra for ordinary NLP before adsorption

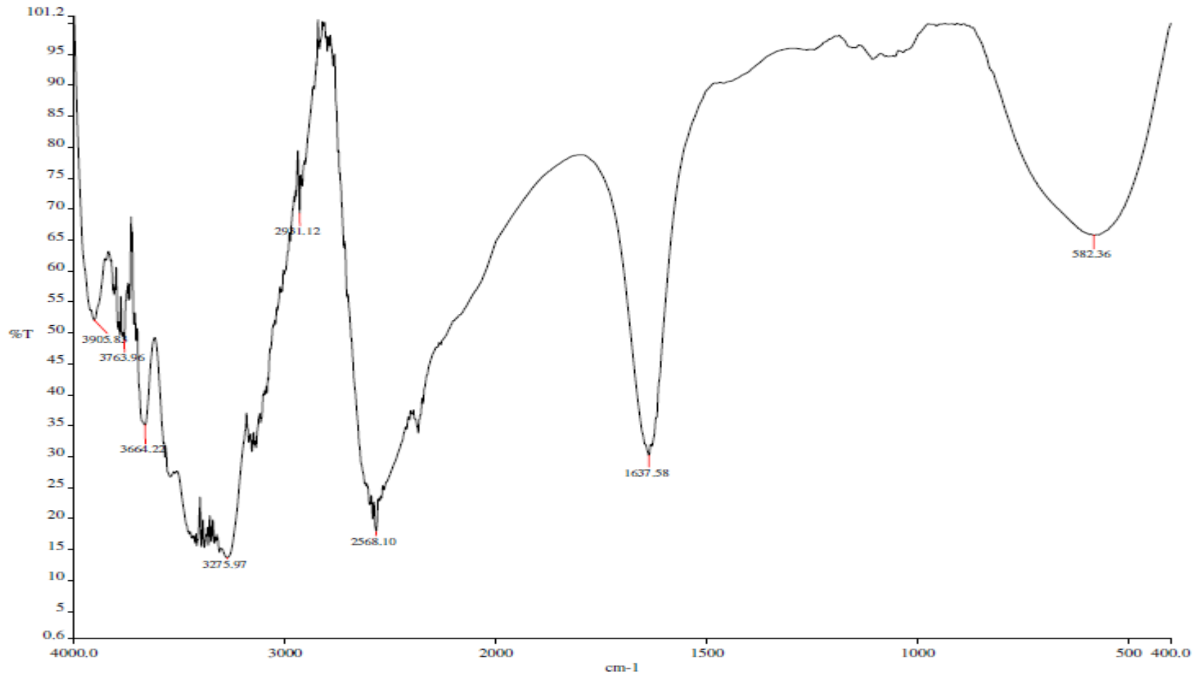


Fig. 6 FTIR spectra for NLP after Cu((II) ions adsorption

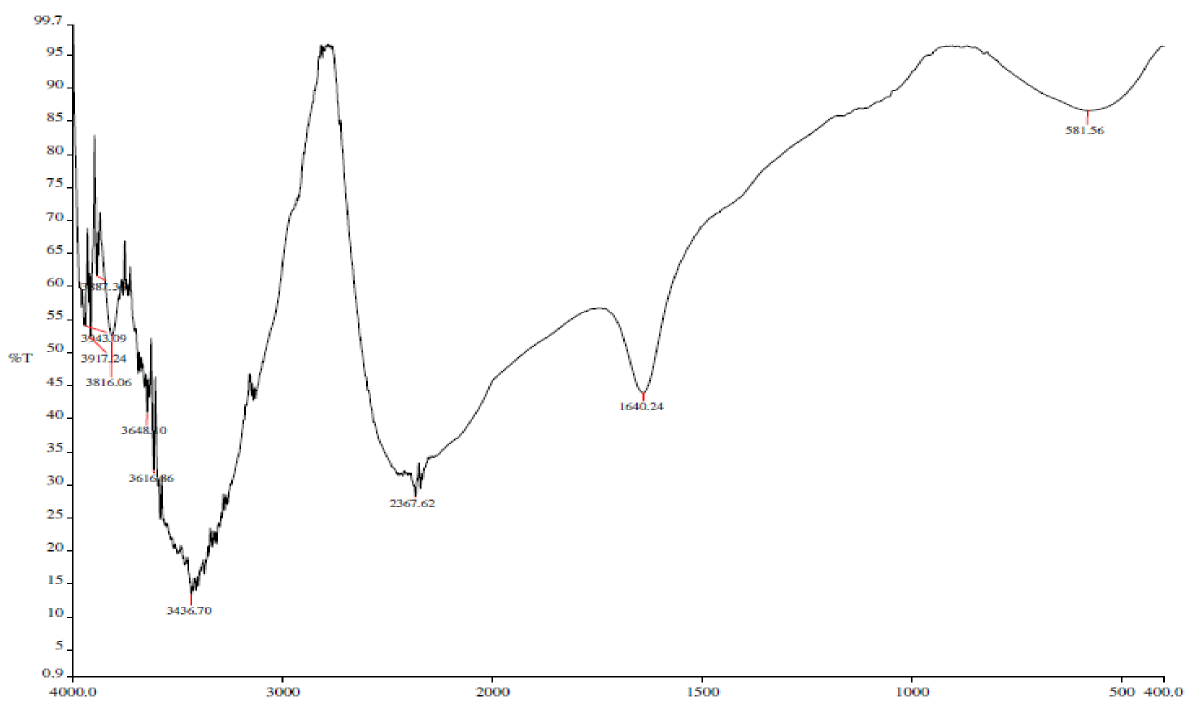


Fig. 7 FTIR spectra for ordinary MNLP before adsorption

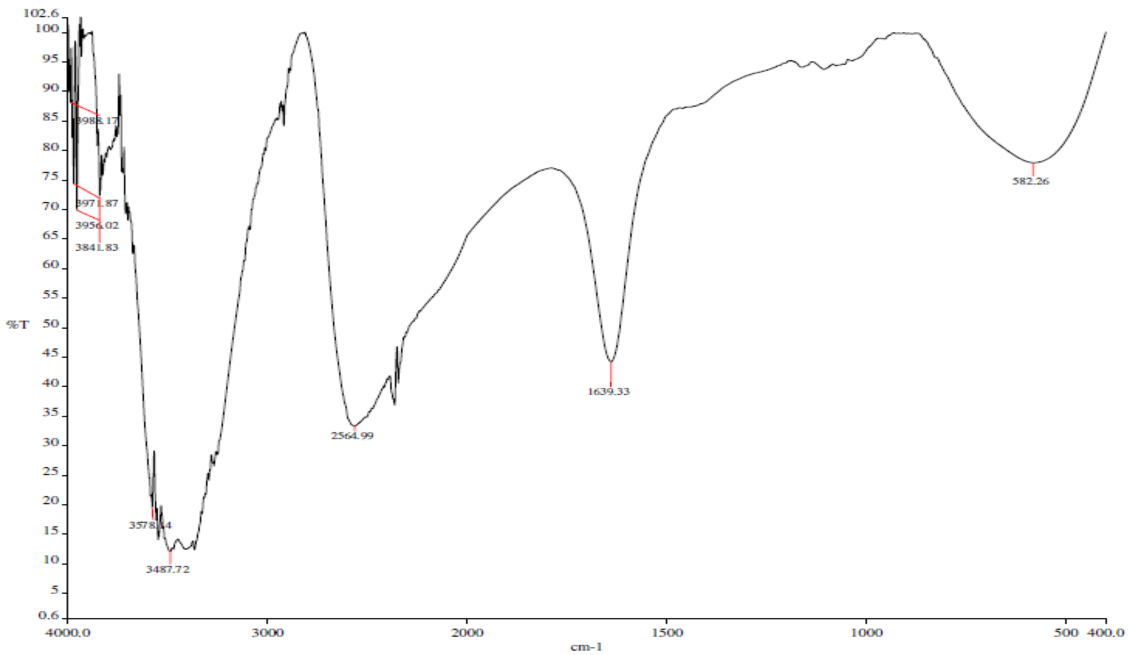


Fig. 8 FTIR spectra for MNLP after Cu((II) ions adsorption

3.4 Effect of Contact Time

Time course profile for the biosorption of Cu (II) ions using NPL and MNLP for a solution of 100 mg/L is shown in Fig. 9 The plot indicates that biosorption of Cu(II) was rapid in the first 60 minutes. This is due to the free binding sites, and slowed down until equilibrium was attained within 120 minutes in which the binding sites on the biosorbent where been saturated and attaining plateau values at 150 minutes. For the ordinary NLP and MNLP more than 50% of biosorption was achieved within the first 30-40 minutes. In both NLP and MNLP, it can be observed that the equilibrium time was found to be 60 and 40 minutes respectively.

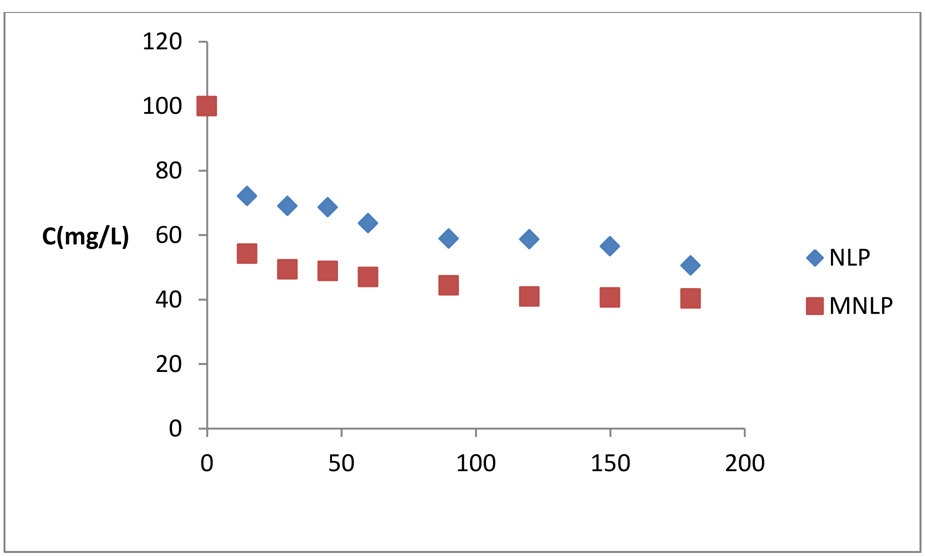


Fig. 9: Effect of residence time for the adsorption of Cu (II) ions on NLP at 333K and MNLP dosage of 1.0 g/L.

3.5 Effect of Cu (II) Ion Concentration

The biosorption of Cu (II) by NLP and MNLP was studied at different initial metal concentration of 100 mg/L, 500 mg/L and 750 mg/L. As shown in Fig. 10 for the ordinary NLP, the 100 mg/L has an adsorption efficiency of 36.3%, as calculated from the graph, while the 500 mg/L and 750 mg/L has an adsorption efficiency of 34% and 58.7%. Also for the MNLP as shown in Fig. 11, the biosorption efficiency at 100, 500 and 750 mg/L was found to be 77.4, 59.3 and 68.52%. This shows that the biosorption efficiencies decrease with increase in concentration. From the results obtained, it can be concluded that, the MNLP has a better adsorption capacity than the ordinary NLP.

According to Ngah and Hanafiah, (2008) a higher adsorption capacity recorded by higher Cu(II) concentration indicates better driving force between aqueous and solid phase, hence the mass transfer resistance will be overcome.

"At low concentrations, biosorption sites took up the available metal more quickly. However, at higher concentrations, metal ions need to diffuse to the biomass surface by intra-particle diffusion and greatly hydrolysed ions will diffuse at a slower rate" (Arshad et al., 2008).

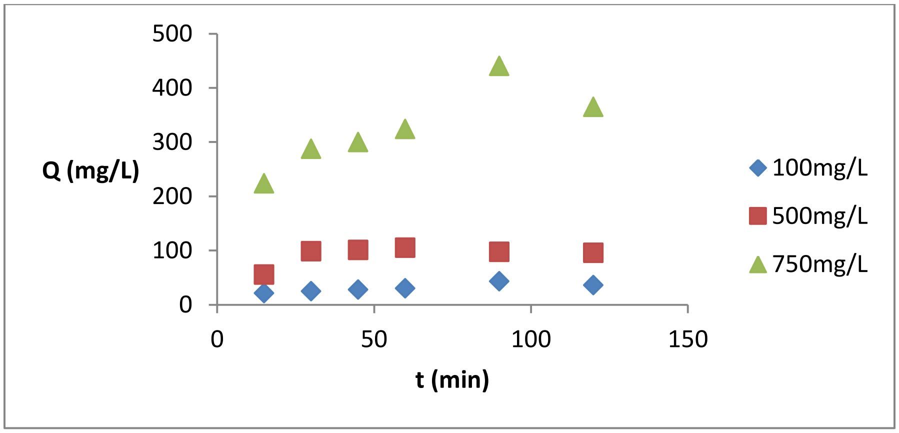


Fig.10: Effect of initial metal concentration for the adsorption of Cu (II) ions on NLP at 333K and NLP dosage of 1.0 g/L.

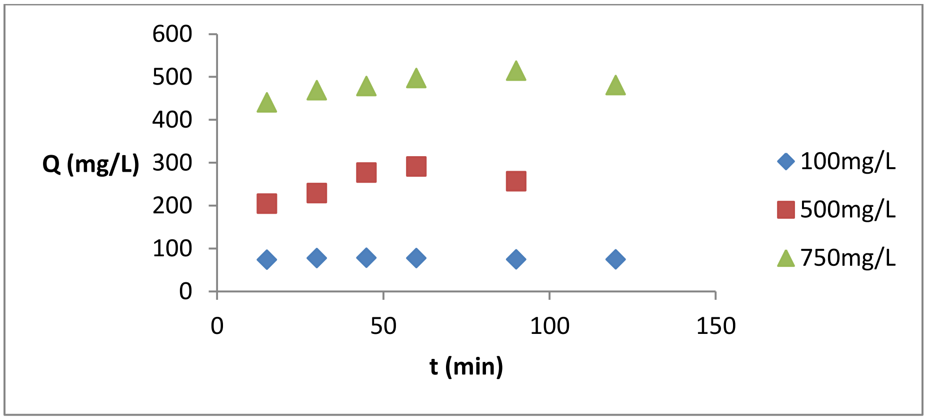


Fig: 11 Effect of initial metal concentration for the adsorption of Cu (II) ions on MNLP at 333K and MNLP dosage of 1.0 g/L.

3.6 Effect of Particle Size

Particle size of the adsorbent is another vital factor that needs consideration in the biososrption research. The effect of varying the biosorbent particle size on the adsorbance capacity Q (mg/g) is shown in Table 1. This indicates that more Cu (II) ions are removed by the smaller particles. This may be due to the surface area increase, which provides more binding sites for the Cu(II) ions. The maximum biosorption occurred with a particle size of 32-45 um. At the smaller particle size, the removal efficiency of the MNLP was found to be more than the ordinary NLP. The biosorption capacity of NPL at 100 mg/L initial metal concentration was found to be 36.3 mg/g and 27 mg/g for 32-45 and 45-62um sizes respectively. While that of the MNLP was found to be 78 mg/g and 59.7 mg/g for 32-45 and 45-62um sizes respectively. This corresponds to similar studies by Arshad et al., (2008) in which neem leaves and neem bark were utilised. The results show that smaller particles of 0.25mm for neem leave and 0.2mm for neem bark has higher adsorption capacity. Also another study by Kumar et al. (2006) uses 72um-212um size of Neem leaves. The result clearly shows that decreasing the particle size increases the surface area, which in turn increases the adsorption capacity.

Table 1: Adsorbance capacity Values for NLP and MNLP at various particle sizes.

Time (min)	**Q(mg/g)**			
	NLP		**MNLP**	
	32-45 um	45-62 um	32-45 um	45-62 um
15	31	21.2	73.3	45.8
30	41.1	25	77.2	50.6
45	41.3	27.5	78	59.4
60	41.3	29.9	77.4	55.6
90	44	31.4	74	51.1
120	49.4	36.3	73.8	59.1
150	46	31.3		59.7

3.7 Adsorption Isotherms

Adsorption isotherms are very important tools used in describing the stability of adsorbate at a fixed temperature and pH. Adsorption units can be design and operated using the isotherm model, which describes the various behaviour of adsorption (Yang et al., 2011). The application of biosorption technique in the commercial scale requires proper quantification of the biosorption equilibrium. Equilibrium of an adsorption is reached whenever there is equal amount of ion adsorbed and desorbed. In this current study, the most frequently used adsorption isotherms, Langmuir and freudlich are been used. The Langmuir and freudlich coefficient values and parameters are summarized in Table: 2. The Langmuir coefficient shows a wide range of values (Table 3). The Langmuir monolayer capacity q_{max} have a value of 7.97 mg/g for the NLP and 56.8 mg/g for MNLP. The Langmuir equilibrium coefficient b had value of 0.0195 L/mg for NLP and 0.162 for MNLP. It is likely that the sites in the MNLP holding the Cu(II) ions are energetically non- uniform and nonspecific, therefore the adsorption coefficients have wide range of variation (Sharma and Bhattacharyya, 2005).

The value of freudlich coefficient n was found to be 0.37 for NLP, while it is 2.94 for MNLP. K_f is 0.024 for NLP and 0.924 for MNLP. The values match to the favourable adsorption process.

Biosorption of Cu(II) ions based on the values of the correlation coefficient (R^2) was found to fit better with the Langmuir isotherm.

Table 2. Isotherm constants of Freundlich and Langmuir models for the adsorption process.

	NLP	MNLP
Langmuir		
q_{max} (mg/g)	0.156	8.445
b(L/mg)	48.234	6.582
R^2	0.968	0.986
Freudlich		
k_f (mg/g)	0.024	0.924
N	0.37	2.94
R^2	0.939	0.804

4.0 Conclusion

Pollution of the environment by toxic heavy metals discharge from industrial wastewater is a widespread phenomenon. Biosorption readily provides an efficient option to other physiochemical process of removing toxic metals. This study shows clearly that Neem leaf which is cheap and abundant material can be used as an effective biosorbent for the removal of Cu(II) ions from industrial wastewater. The study also shows that the efficiency of the removal can be increase by the process of chemical modification of the NLP (Neem leaf powder). The biosorption process also depends on some factors such as the contact time, particle size and biosorbent concentration. The isotherm study indicates that the sorption data can be modelled by Langmuir isotherms. Hydroxyl and carboxyl group, based on the FTIR spectra data obtained might be involved in the Cu(II) ions binding. Meanwhile, the EDX spectra revealed ion exchange as another possible copper binding mechanism. Since neem leaves are very cheap, abundant and can be easily modified at relatively low cost, the adsorbent could be applied for the removal of copper ions from wastewater.

5.0 References

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