

# BIOSORPTION OF COPPER(II) BY *VITEX NEGUNDO* STEM POWDER

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## Abstract

Biological materials for the removal of heavy metal ions from waste water is important due to their extreme toxicity towards aquatic life and humans. Microorganisms and low cost natural biosorbents are being increasingly studied for the removal of heavy metal ions from aqueous solution. In this work, *Vitex negundo* stem powder was taken as a low cost biosorbent for the sorption of Copper(II). The various parameters like Initial metal ion concentration, Initial pH, Temperature and Biosorbent dosage were studied in a batch reactor. Equilibrium was reached after 24 h of contact time. The optimum values of initial Copper concentration, initial pH, temperature and biomass loading are found to be 50mg/l, 4,30°C and 5g/l. Under this optimised condition a maximum percentage removal of 94% and specific uptake of 12mg/g was obtained for Cu(II) sorption. Equilibrium model fits well with Langmiur and Freundlich adsorption isotherms.

**Keywords:** Biosorption, *Vitex negundo*, adsorption isotherms, equilibrium model.

## 1.Introduction

The contamination of wastewaters by toxic metal ions is a worldwide environmental problem. The main sources of pollution are mining and electroplating industries discharging a variety of toxic metals such as Pb, Cu, Ni, Zn, and Cd ions into soils and waters. Reducing heavy metals concentration in the aquatic environment to acceptable limits using economical and eco-friendly technologies becomes more and more urgent. Copper is one of the essential micronutrients for all living cells, but it is harmful to the ecological system at high concentrations (Buck *et al.*, 2007; Buck *et al.*, 2010). Copper is used extensively in various industrial applications and house hold purposes like air conditioning tubing systems, electrical winding, plumbing, electronic chips, metal coating and gear wheel because of its unique physical and chemical characteristics of high electrical and thermal conductivities, corrosion resistivity. Many industries like fertilizer and pesticide industry, wood pulping and paper mills, printed circuit board production, tanning industry, electrical appliances manufacturing units and ore and metal smelting industry are sources of copper effluents (Zhu *et al.*, 2009; Jeon *et al.*, 2010). Therefore, reducing concentration levels of copper in wastewater to acceptable limits is essential before discharging into the environment. Conventional treatment processes, i.e. precipitation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separations, electrochemical reaction and evaporation, have known interests but have also some limitations. Among them, it can be noted that additional wastes as sludge and brines can be generated and sometimes these treatments can be ineffective for dilute effluents and finally present high costs (Grau and Bisang, 1995; Davis *et al.*, 2003). Therefore, biosorption could be an interesting alternative in case of large volumes of slightly polluted solution. The uptake of metals by microbial cells or biological materials do not need the cell viability and biochemical energy and could include the following mechanisms (i) extra cellular accumulation/precipitation, (ii) cell surface sorption, complexation or ionic exchange, (iii) intracellular accumulation after passive diffusion and present generally fast reactions (Brady *et al.*, 1999; Davis *et al.*, 2003). Previous research shows that there is growing interest of searching for a variety of materials as low cost adsorbents including sawdust, cocoa shell, rice husk, modified sawdust of walnut, papaya wood, maize leaf, rice husk ash and neem bark, fly ash and tea-industry waste (Siti *et al.*, 2013). Hence, the conversion of these materials as low cost adsorbents is recognized as a potential and economic application for wastewater treatment.

*Vitex negundo* is also a low cost biosorbent for the sorption of heavy metal ions which is used in this study. It has the following functional groups like hydroxyl compounds, carboxylic acid derivatives, aromatic compounds and amines which is favourable for the sorption of Cu(II). (Sunil Pawar and Vanita Kamble, 2017 ; Kavitha et al., 2013).

### 1.1 Equilibrium modelling

Biosorption isotherms are used to describe equilibrium data and are important for developing equations that can be used to compare different biosorbents under different operational conditions. Sorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature, pH and initial metal concentration. The simplest forms of these isotherms are Freundlich and Langmuir isotherms which in most cases are used to obtain maximum biosorption capacity of the biosorbent.

$$\% \text{Removal} = \frac{(C_o - C) \times 100}{C_o} \quad \dots\dots(1)$$

$$q = \frac{(C_o - C) V}{W} \quad \dots\dots(2)$$

Where  $C_o$  is the initial concentration of metal ions (mg/l),  $V$  is the volume of metal solution (l),  $W$  is the weight of biosorbent (g) and  $C$  is the final concentration of metal ions (mg/l).

#### 1.1.1 The Langmuir Adsorption Isotherm

The equilibrium of the process is often described by fitting the experimental points with models usually used for the representation of adsorption isotherms. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. The basic assumptions on which the model is based are: 1) metal ions are chemically adsorbed at a fixed number of well-defined sites, 2) each site can hold one sorbate ion, 3) all sites are energetically equivalent and 4) there is no interaction between ions adsorbed on neighbouring sites. This model is described by the equation (Zumriye Aksu *et al.*, 1997; Zumriye Aksu 2001):

$$q_{eq} = \frac{Q^o b C_{eq}}{1 + b C_{eq}} \quad \dots (3)$$

where  $q_{eq}$  and  $C_{eq}$  are the amount of adsorbed metal per unit weight of biosorbent and unadsorbed metal concentration in solution at equilibrium, respectively.  $Q^o$  is the maximum amount of metal per unit weight of biomass to form a complete monolayer on the surface bound and  $b$  is a constant related to the affinity of the binding sites.  $Q^o$  and  $b$  can be determined from a plot of  $1/q_{eq}$  and  $1/C_{eq}$ .

#### 1.1.2 The Freundlich Adsorption Isotherm

The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, and with interactions between sorbed molecules, as described by the equation:

$$q_{eq} = K_F C_{eq}^{1/n} \quad \dots (4)$$

where  $K_F$  and  $n$  are the Freundlich constants characteristics of the system.  $K_F$  and  $n$  are indicators of adsorption capacity and adsorption intensity, respectively. Eq. (4) can be linearized in logarithmic form and Freundlich constants can be determined. Both models are developed for a single-layer metal sorption (Zumriye Aksu *et al.*, 1997; Zumriye Aksu, 2001).

## 2. Materials and methods

### 2.1 Preparation of sorbate solution

A 1000 mg/l stock solution of Copper was prepared by dissolving 3.93 g of copper sulphate in double distilled water. The required concentrations of copper ions were prepared from the stock solution by dilution method.

### 2.2 Preparation of the biosorbent

*Vitex negundo* stem powder was used in this study. The *Vitex negundo* stem was obtained from local area; was washed, dried, and crushed in primary crusher and air dried in sun for several days until its weight remains constant. After drying, it was crushed in roll crusher and hammer mills. The material obtained through crushing and grinding was screened through BSS meshes. Finally the products obtained were stored in glass bottles for further use.

### 2.3 Preparation of immobilized biomass beads

Immobilized biomass beads are prepared using 8% (w/v) sodium alginate. A known amount of biomass (*Vitex negundo*) is mixed with sodium alginate and the mixture is constantly stirred under warm condition until the alginate gets dissolved. The suspension is dripped into 2% (w/v) calcium chloride solution through a syringe. The beads are stored in calcium chloride solution for about 30 min before being rinsed in double distilled water.

### 2.4 Batch biosorption studies

Batch experiments were carried out in Erlenmeyer flasks by adding known amount of immobilized biomass beads in 100 ml aqueous Copper sulphate solution. The flasks were gently agitated on a shaker with a constant shaking rate at 150 rpm for 240 min until equilibrium sorption was obtained. Samples were taken from the solution at regular time intervals for the residual metal ion concentration in the solution. The residual concentration of Copper ions in the solutions was determined spectrophotometrically at 457 nm using Neocuproine as the complexing agent (APHA, 1994).

The effect of initial Copper ion concentration on percentage removal of Copper was studied by conducting experiments with different initial copper ion concentrations namely 50 mg/l, 100 mg/l, 150 mg/l, 200 mg/l and 250 mg/l under identical conditions of temperature, pH and biomass loading and the experiment was carried out as described above.

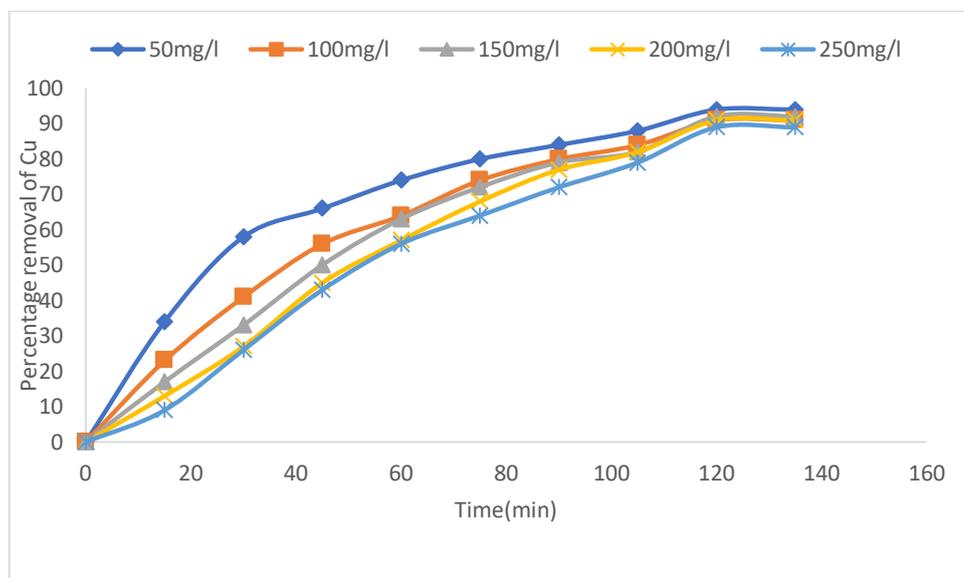
The effect of initial pH on percentage removal of Copper was studied by conducting experiments with different initial pH namely 2,3,4,5 and 6 under identical conditions of initial Cu(II) ion concentration, temperature and biomass loading and the experiment was carried out as described above.

The effect of temperature on percentage removal of Copper was studied by conducting experiments with different temperature namely 25°C,30°C,35°C and 40°C under identical conditions of initial Cu(II) ion concentration, initial pH and biomass loading and the experiment was carried out as described above.

The effect of biomass loading on percentage removal of Copper was studied by conducting experiments with different biomass load namely 1g/l, 2g/l, 3g/l, 4g/l and 5g/l under identical conditions of initial Cu(II) ion concentration, initial pH and temperature and the experiment was carried out as described above.

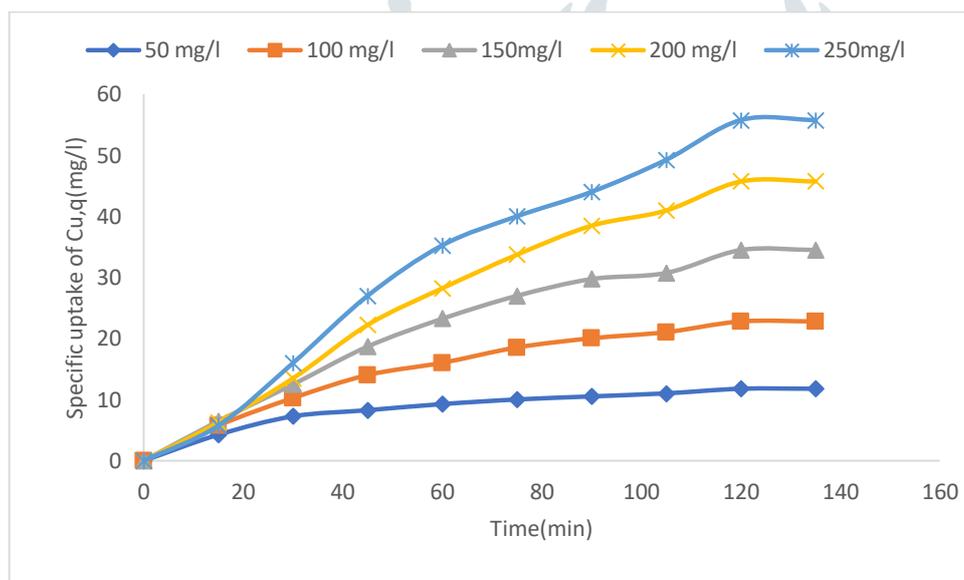
## 3. Results and Discussion

The biosorption of metals using immobilized biosorbent in a batch process depends on both contact time between the adsorbate and adsorbent particles and initial metal ion concentration. The effect of initial metal ion concentration on contact time, percentage removal and specific uptake of Copper was given in Fig 1 and Fig 2 respectively. Fig 1 shows that equilibrium is attained in 24 h, also the sorption of Copper on immobilized biosorbent increases with increasing contact time. The Copper removal efficiency was affected by the initial metal ion concentration, with decreasing removal percentages as concentration increases from 50 mg/l to 250 mg/l.



**Fig. 1. Effect of initial Copper concentration on Percentage Removal of Copper by *Vitex negundo* stem powder**

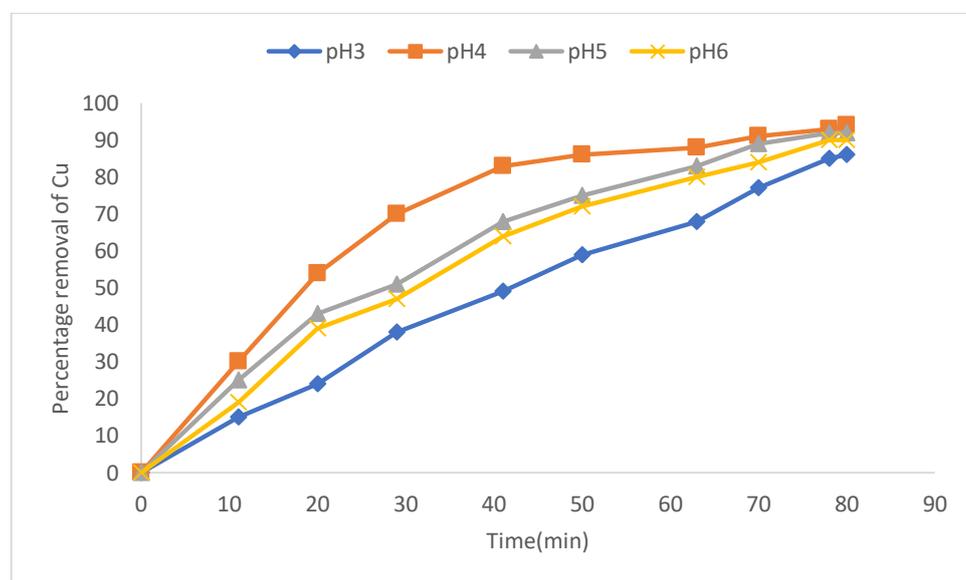
As the initial Copper concentration increases from 50 mg/l to 250 mg/l, the percentage removal of Copper decreases from 94 % to 89 % and the specific uptake of Copper increases from 12 mg/g to 56 mg/g respectively (fig. 2).



**Fig. 2. Effect of initial Copper concentration on Specific uptake of Copper by *Vitex negundo* stem powder**

At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of metal ions. However, at higher concentrations the number of metal ions relatively higher compared to availability of adsorption sites.

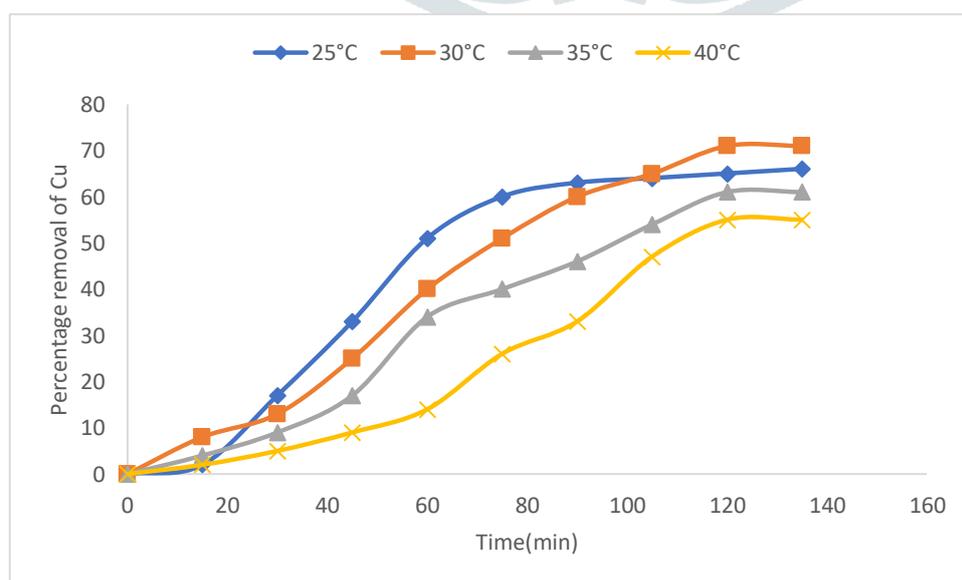
The pH dependency of biosorption efficiency could be explained by the functional groups involved in metal uptake and the metal chemistry. The percentage of metal sorption vary with pH of the medium which is given in Fig.3.



**Fig. 3. Effect of initial pH on Percentage Removal of Copper by *Vitex negundo* stem powder**

The percentage removal of Copper increases from 80% to 94% as the pH increased from 2.0 to 4.0 and thereafter the percentage removal of Copper decreased to 90%. Biosorption of Copper was low at alkaline condition. The maximum percentage removal is found to be 94% at pH 4.0 and selected as the optimum pH. The percentage removal of Copper by immobilized biosorbent was very less at low pH. The result seems to suggest that the biosorption of Copper by immobilized *Vitex negundo* stem powder is mainly due to ionic attraction. This can be explained based on at low pH, highly mobile  $H^+$  ions are adsorbed at the active sites, preventing Copper ions from getting sorbed. At pH values higher than 5.0, percentage removal of Copper decreases because of the increase in concentration of  $OH^-$  ions in the biosorption medium causes the precipitation of Copper. Hence, biosorption studies should not be carried out at higher pH levels which cause precipitation of metal ions. Optimum metal biosorption at pH 4-6 has also been reported for several other biomass types (Wang and Chen, 2009), and is likely due to deprotonation of metal binding anionic sites, such as carboxylic groups at this pH range (Singh *et al.*, 2007).

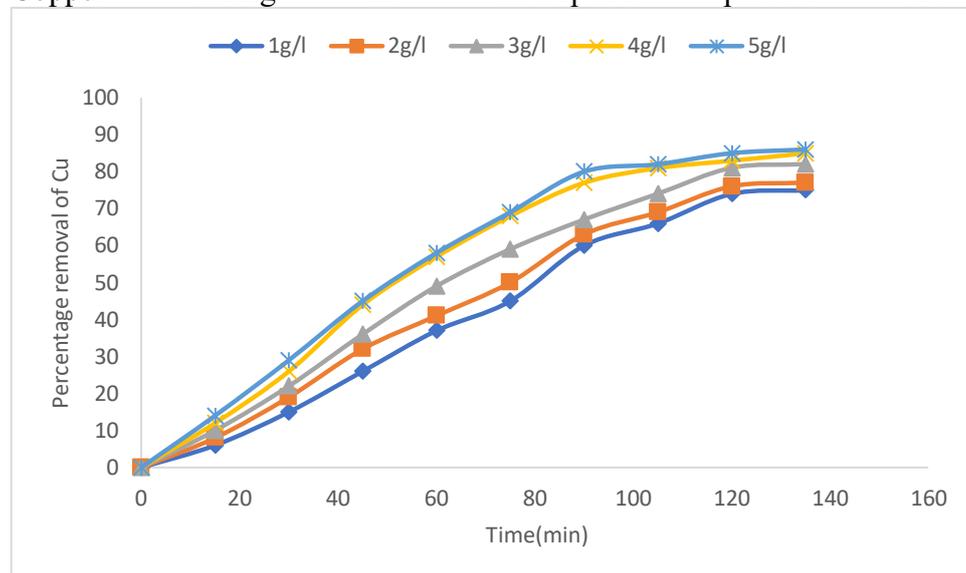
The effect of temperature on percentage removal of Copper was studied in Erlenmeyer flasks with 100 ml of aqueous Copper solution at different controlled temperatures namely 25°C, 30°C, 35°C and 40°C. The effect of temperature on percentage removal of Copper by mmobilized biosorbent was given in the Fig.4.



**Fig. 4. Effect of temperature on Percentage Removal of Copper by *Vitex negundo* stem powder**

A maximum Copper removal of 71% is obtained at 30°C because the number of binding sites is more at this temperature. The percentage removal of Copper by immobilized biosorbent is higher at room temperature and it decreases with further increase in temperature due to the destruction of the cell walls expected, and a reduction in Copper removal is observed.

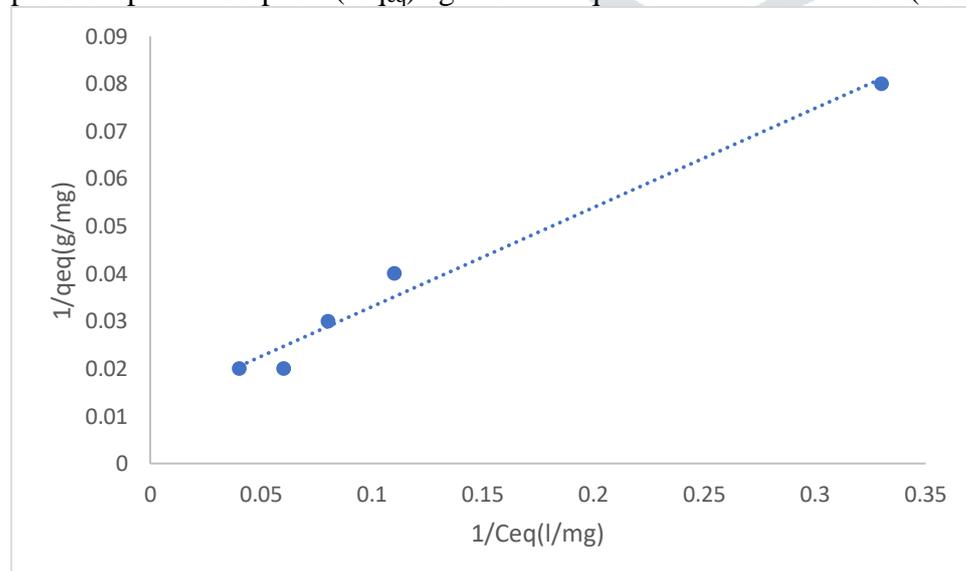
The effect of biomass loading on percentage removal of Copper was studied by conducting the experiments in Erlenmeyer flasks with 100 ml of aqueous Copper solution with different biomass loading namely 1g/l, 2g/l, 3g/l, 4g/l and 5g/l. The results of effect of biomass loading on contact time and percentage removal of Copper during the biosorption process are given in Fig.5.



**Fig. 5. Effect of biomass loading on Percentage Removal of Copper by *Vitex negundo stem powder***

It was observed that the percentage removal of Copper increased from 75 to 86% as the biomass loading increased from 1 g/l to 5 g/l. At low Copper concentration, the ratio of sorptive surface to the total Cu(II) ions available is high and nearly all Copper ions in solution can be bound and removed. The increase in the uptake capacities of immobilized *Vitex negundo stem powder* with increasing metal concentration may be due to higher probability of collision between metal ions and biosorbent particles. A maximum Copper removal of 86% was observed at a biomass loading of 5 g/l.

The biosorption data is analysed according to the linear form of the Langmuir adsorption isotherm. The linear adsorption isotherm constants ( $Q^0$  &  $b$ ) with the correlation coefficients are presented in Table 1. The plots of specific sorption ( $1/q_{eq}$ ) against the equilibrium concentration ( $1/C_{eq}$ ) for Copper is shown in Fig.6.



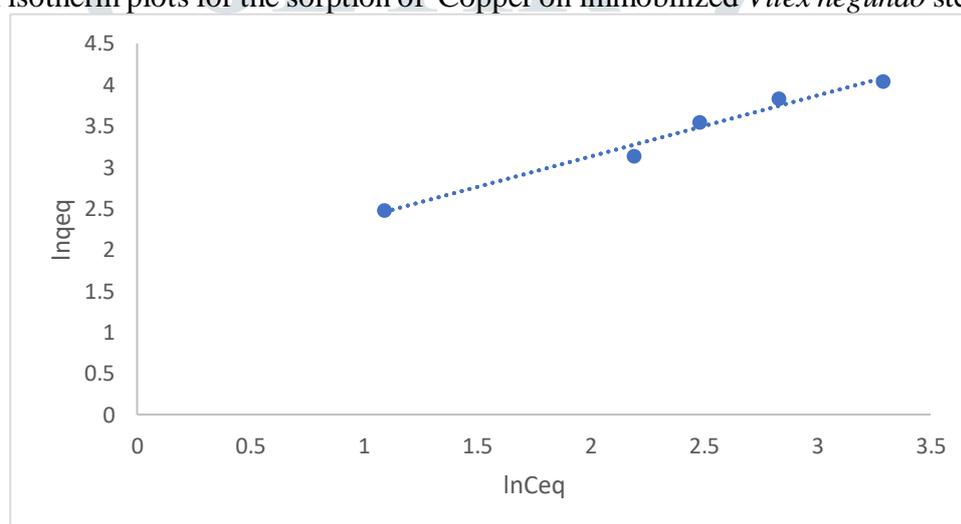
**Fig. 6 Langmuir Adsorption Isotherm for the Biosorption of Copper by immobilized *Vitex negundo stem Powder***

**Table1. Langmuir and Freundlich Constants-Biosorption of Copper by immobilized *Vitex negundo* stem Powder**

<b>Langmuir constants</b>		
<b>Q<sub>o</sub>(mg/g)</b>	<b>b (l/mg)</b>	<b>R<sup>2</sup></b>
82.6	0.058	0.9805
<b>Freundlich constants</b>		
<b>K<sub>F</sub></b>	<b>n</b>	<b>R<sup>2</sup></b>
5.209	1.35	0.9796

Fig. 6. suggests that the linear equilibrium isotherm is a good model for the sorption of Copper. Table1. shows that the sorption constants, b, and sorption capacity, Q<sup>o</sup>. The large value of b implies strong bonding of metals to the immobilized *Vitex negundo* stem powder. Table1 also shows that a very high regression coefficient is found for Copper sorption. The higher correlation coefficients suggest that the Langmuir adsorption isotherm is found to be linear over the whole concentration ranges studied with homogeneous surface by monolayer sorption and provides a suitable model for the sorption of Copper.

The biosorption data from is analysed according to the linear form of the Freundlich adsorption isotherm. The linear Freundlich isotherm plots for the sorption of Copper on immobilized *Vitex negundo* stem powder



is presented in Fig. 7.

**Fig. 7 Freundlich Adsorption Isotherm for the Biosorption of Copper by immobilized *Vitex negundo* stem Powder**

The Freundlich adsorption isotherm constants (K<sub>F</sub> & n) are given in Table 1. From Table 1, the Freundlich constants (K<sub>F</sub> & n) shows monolayer uptakes of heterogeneous distribution of active sites of Cu(II) with lower adsorptive capacity of immobilized *Vitex negundo* stem powder. The adsorption intensity, n, is greater than unity for Cu(II) and indicates that the forces between the surface layers are repulsive. The high R<sup>2</sup> values suggest that the Freundlich adsorption isotherm provides a good model of the sorption system with poor adsorption intensity for Copper over the entire ranges of concentration.

#### **4. Conclusion**

Biosorption experiments were performed as a function of initial metal ion concentration, pH, temperature and biosorbent dosage. Biosorption was influenced by initial Copper ion concentrations and it was found that as the initial Copper concentration increases from 50 mg/l to 250 mg/l, the percentage removal of Copper decreases from 94 % to 89 % and the specific uptake of Copper increases from mg/g to 56 mg/g respectively. The obtained results showed that immobilized *Vitex negundo* stem powder was a good adsorbent for the removal of metal ions and had high adsorption yields for the treatment of aqueous solutions containing copper ions. The equilibrium data fitted very well to Langmuir and Freundlich adsorption isotherm model.

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