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Biosorption of copper (II) from aqueous solution by *Ocimum bacilicum* seeds biomass

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Abstract

The feasibility of using *Ocimum bacilicum* seeds for the removal of copper (II) ions from aqueous solution has been investigated. Batch biosorption studies were conducted to study the effect of different experimental parameters such as initial metal ion concentration, contact time, agitation speed, biosorbent dose and pH. The results indicated that sorption equilibrium was established within 30 minutes of contact time. The copper (II) sorption was strictly pH dependent and maximum removal was observed at pH 5. Effective biosorption of copper (II) was taken place at 150 rpm. Maximum biosorption capacity was found to be 73.1 mg/g. The equilibrium data fitted well to the Langmuir isotherm model with R^2 = 0.997. The study revealed that *Ocimum bacilicum* could be used as biosorbent for the removal of heavy metals ions on large scale.

Key words: Heavy Metals, Biosorption, Copper, Biomass, Pollution

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1. Introduction

The heavy metals in industrial wastewaters are hazardous to the aquatic ecosystem and pose possible human health risk. Because of their toxicity, heavy metals in soil or water, bring a serious threat to the universal ecosystem. Excessive levels of heavy metals in the human body, like copper (II) can cause a range of morphological and physiological disorders [1]. From the eco-toxicological point of view, copper (II) and zinc are contaminants. Their high concentration ranges thus pose a serious threat to biota and environment. In addition, toxic pollutants such as heavy metals, have a number of applications such as electroplating, steel and alloys, pigments, plastics, batteries, leather tanning, paints and paper [2]. The heavy metals are toxic metal present in higher concentration than permissible limits [3-12] so there need of heavy metal analysis of water, used by humens and food items.

It is essential to remove heavy metals from industrial wastewater before transport and cycling into the natural environment. A number of technologies have been developed over the years to remove heavy metals from industrial wastewater. The most important technology includes coagulation/flocculation. Other conventional chemical methods include precipitation, ion-exchange, electrochemical processes and membrane technology. All the chemical methods have proved to be more costly and less efficient than the biosorption process. In addition, chemical methods increase the pollution load on the environment [2].

In present study we used *Ocimum basilicum* seeds as a biosorbent and explore the potential of *Ocimum basilicum* seeds to treat waste water contaminated with copper (II) ions. Check the equilibrium parameters such as initial pH, initial metal ion concentration, biosorbent dose and agitation speed on the biosorption efficiency of copper from aqueous solution and by application of isotherm models the data evaluation.

2. Material and Methods

2.1. Sample Collection

Seed of *Ocimum bacilicum* (Niazboo) were used as biomaterial in this study which was collected from plant and dried it. Analytical grade $CuSO_4.5H_2O$ was used for the preparation of stock metal solution of 1000 mg/L. A series of solutions were prepared by diluting the stock solution [13].

2.2. Analytical procedures

Perkin-Elmer Aanalyst 300 atomic absorption spectrometer equipped with an air-acetylene burner and controlled by Intel personal computer was used to determine concentrations of copper (II) in aqueous solutions before and after the equilibrium established. The hollow cathode lamp was operated at analytical wavelength of 324.8 nm for copper (II) and slit as 0.2 nm.

2.3. Batch experimental studies

In all experiments 100 mL solution of copper (II) was thoroughly mixed with 0.1 g seeds of *Ocimum bacilicum* as a biosorbent at 100 rpm and 30°C for 2 hours. To check the influence of pH, initial metal concentration and contact time. Different conditions of pH (2–7), initial metal concentration (50,100,150, 200, 250, 300 mg/L) and contact time (15, 30, 60, 120, 240, 480 min) were evaluated during study. The pH of the medium was adjusted with 0.1N solutions of HCl and NaOH. The flasks were placed on a rotating shaker (PA 250/25. H) and removed from the shaker after specified time. After this solutions were filtered through filter paper Whatman No. 40 (ashless). Preliminary tests were performed at 30 °C using an initial concentration of 100 mg/L having pH 5. The quantity of biomass was varied from 0.1 to 3 g for determine the *Ocimum bacilicum* dose required for optimum level of biosorption.

2.4. Metal uptake

The copper (II) uptake was calculated by the simple concentration difference method. Uptake of copper (II) in the sorption syetem was calculated from following mass balance equation (1) [14]:

$$q = \frac{V\,(Ci - Ce)}{M} \quad \text{------------1}$$

Where q is the biosorption of matel ions, V is the volume of the solution, Ci is the initial concentration of matel ions, Ce is the final (or equilibrium) concentration of matel ions in solution and M the dose of the biosorbent.

2.5. Equilibrium isotherms

Equilibrium isotherm equations are used to describe the experimental data. Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. So to examine the relationship between sorption (q_e) and aqueous concentration (C_e) of metals at equilibrium, sorption isotherm models are widely employed for fitting the data, for which the most widely used models are the Freundlich and the Langmuir isotherm model [14-15]. The Langmuir isotherm applies to adsorption on completely homogenous surface with negligible interaction between adsorbed molecules. The linear form of the equation can be written as;

$$\frac{Ce}{q_e} = \frac{1}{bq_{max}} + \frac{Ce}{q_{max}} \quad \text{-----------2}$$

Where Ce is the supernatant concentration after the equilibrium of the system (mg/L), *b* the Langmuir affinity constant (l/mg), and q_{max} the maximum adsorption capacity of the material (mg/g) assuming a monolayer of adsorbate uptaken by the adsorbent. The Freundlich isotherm is the earliest known relation describing the sorption equation. It does not indicate finite or infinite uptake capacity of the adsorbent. The Freundlich isotherm (empirical model adsorption in aqueous systems) was also tested with our experimental data. The linear form of the equation can be written as

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K \quad \text{----------3}$$

Which have a straight line with a slope of 1/n and an intercept of log (K) when log (q_e) is plotted against log (C_e), where K and 1/n are empirical constants and depends on several environmental factors. Where K is the measure of sorption capacity, 1/n is sorption intensity.

3. Results and Discussion

3.1. Effect of initial metal ion concentration on biosorption of copper (II)

The effect of initial metal ion concentration on metal uptake capacity is an important parameter. The initial metal ion concentration was varied from 50 to 300 ppm and metal uptake capacity increases with the increase in concentration (Fig. 1). This biosorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal ions more quickly. However, at higher concentrations, metals need to diffuse to the biomass surface by intraparticle diffusion and more hydrolyzed ions will diffuse at a slower rate [16].

3.2. Effect of pH on biosorption of copper (II)

The biosorption of copped was strongly affected by the pH of the solution. Result showed that maximum copper (II) sorption was obtained by the use of *Ocimum bacilicum* seeds at pH 5 which was 60.5 mg/g (Fig. 2). The metal uptake increased with the increase in pH from 1 to 5 after that it decrease down at pH 7. It was evident that removal of copper (II) decreased by increased pH of the solution. The metal sorption mechanism depends on the surfaces of biosolids and nature of the physicochemical interaction of ions [17-18]. The pH influences the protonation or deprotonation of the adsorbent.

3.3. Effect of agitation speed on biosorption of copper (II)

The influence of agitation speed on metal uptake range was taken from 0 to300 rpm. The maximum copper (II) removal efficiency was obtained at 150 rpm which is 63.1 mg/g (Fig. 3). The increase in stirring speed from 50 to 150 rpm resulted in an increase in copper (II) ion removal efficiency. It is known that the mass transfer rate increased with the increase in stirring speed. The boundary layer thickness decreased with increase of stirring speed which results in a reduction in surface film resistance. Therefore, the metal ions adsorbed to the biosorbent surface more easily. Further increase in stirring speed did not show an increase in the biosorption efficiency [19].

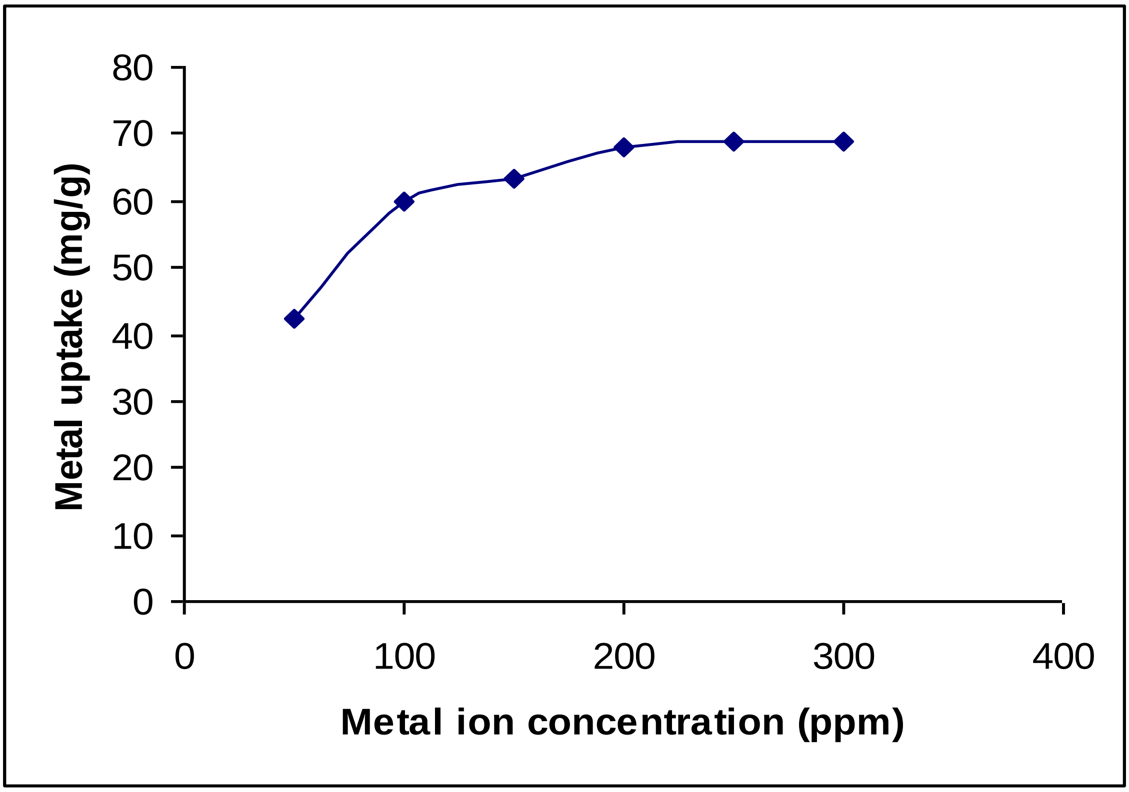

Fig. 1. Effect of initial metal ion concentration on biosorption of copper (II) by *Ocimum bacilicum* seeds

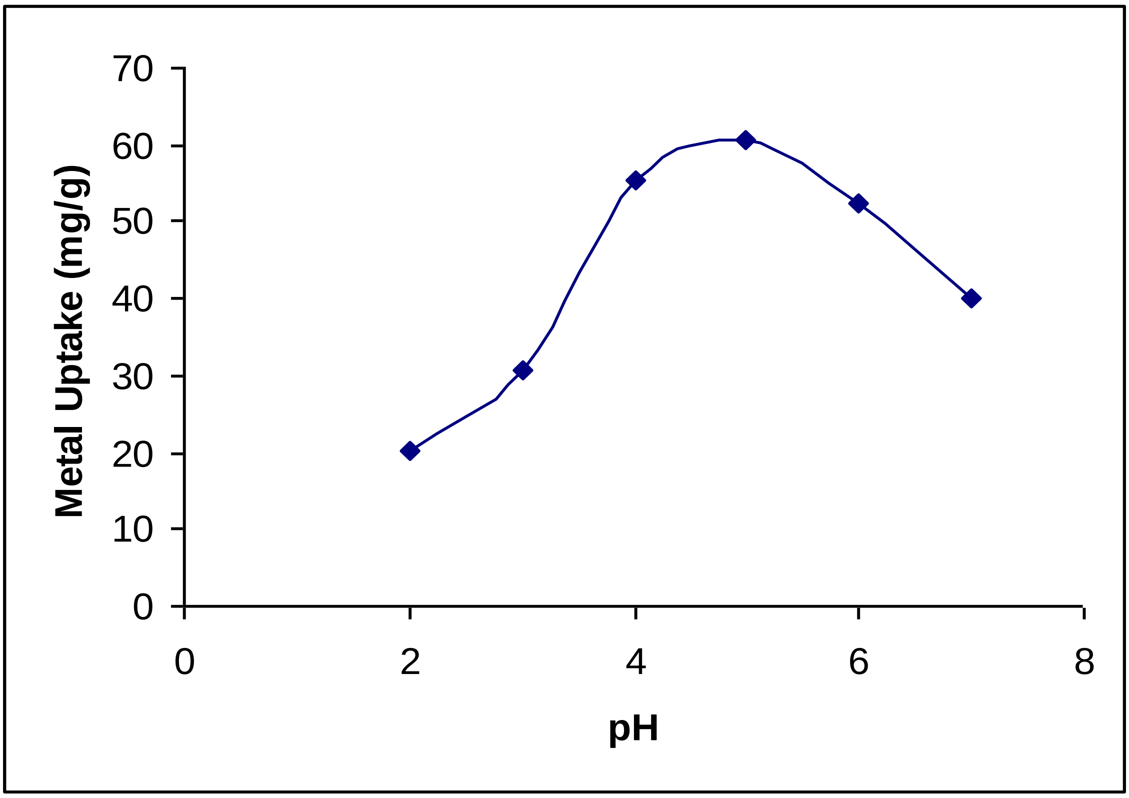

Fig. 2. Effect of pH on biosorption of copper (II) by *Ocimum bacilicum* seeds

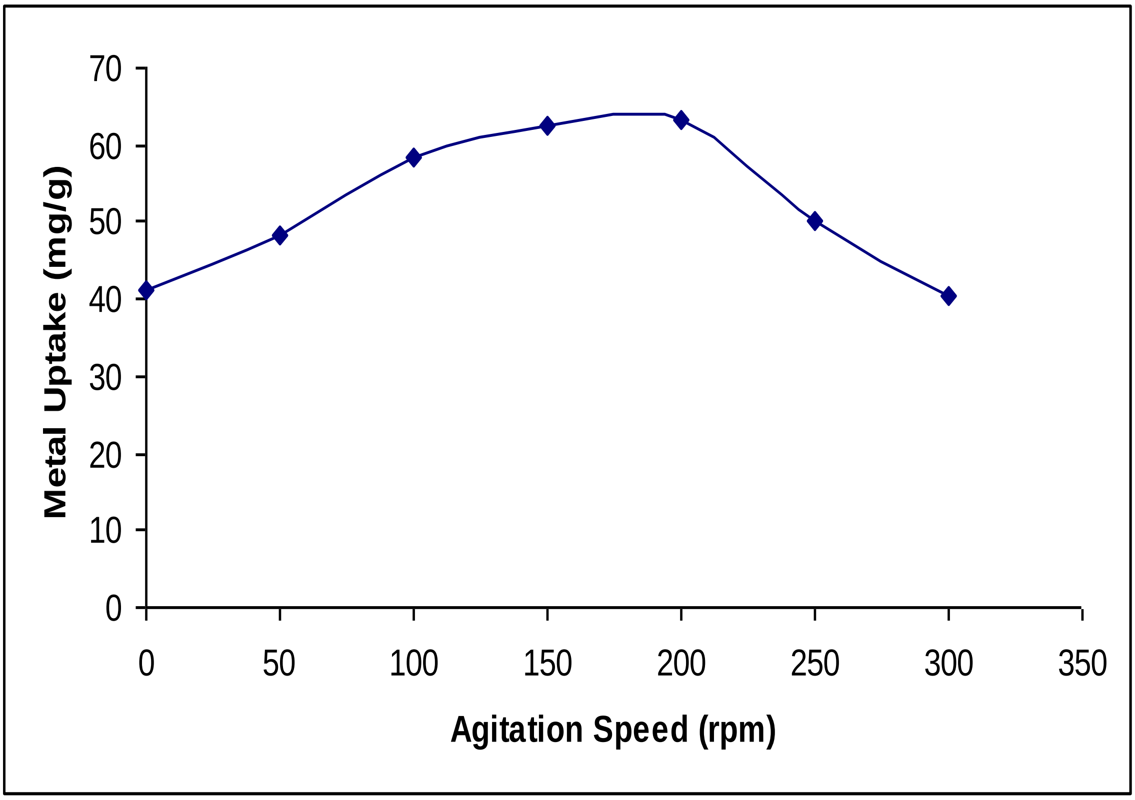

Fig. 3. Effect of agitation speed of copper (II) by *Ocimum bacilicum* seeds

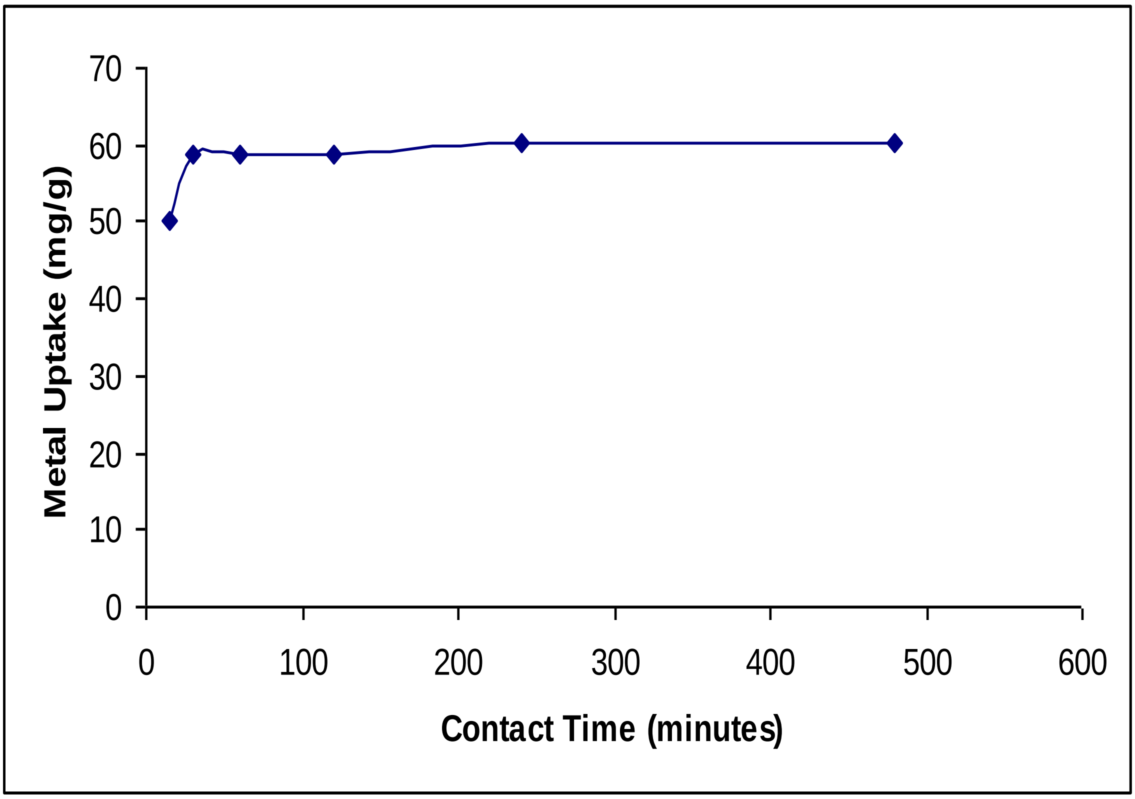

Fig. 4. Effect of time of copper (II) by *Ocimum bacilicum* seeds

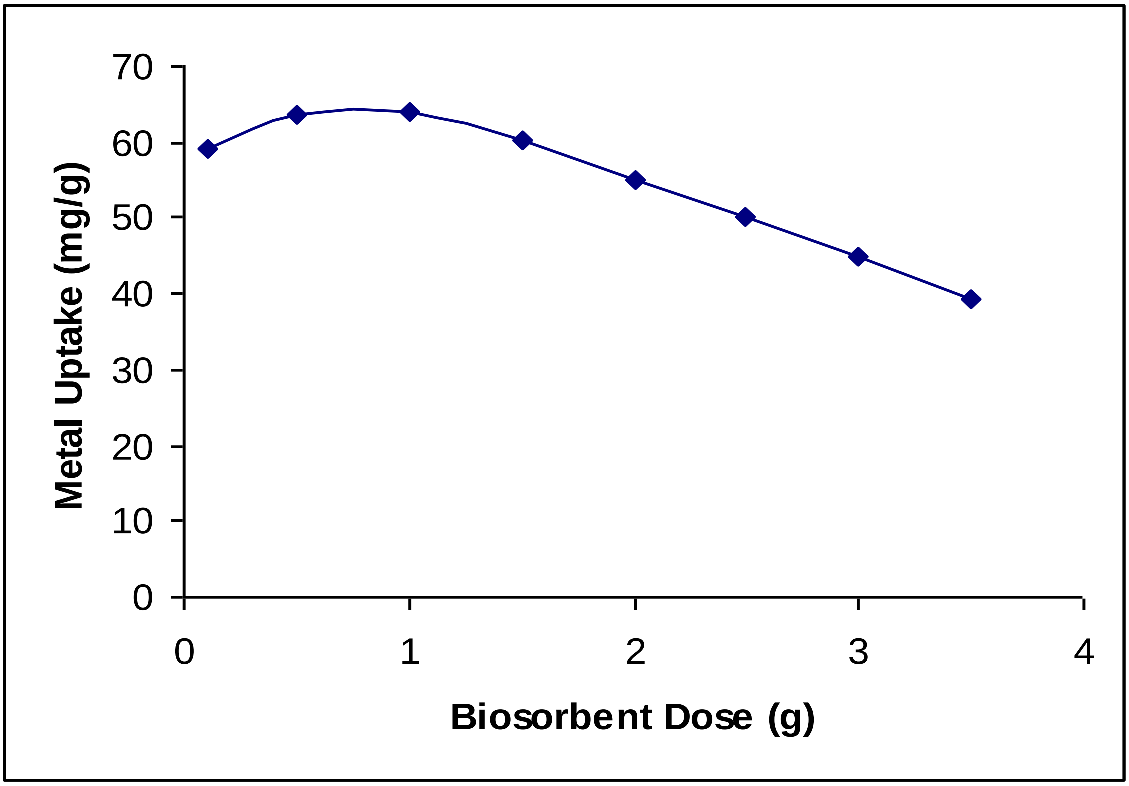

Fig. 5. Effect of biosorbent dose of copper (II) by *Ocimum bacilicum* seeds

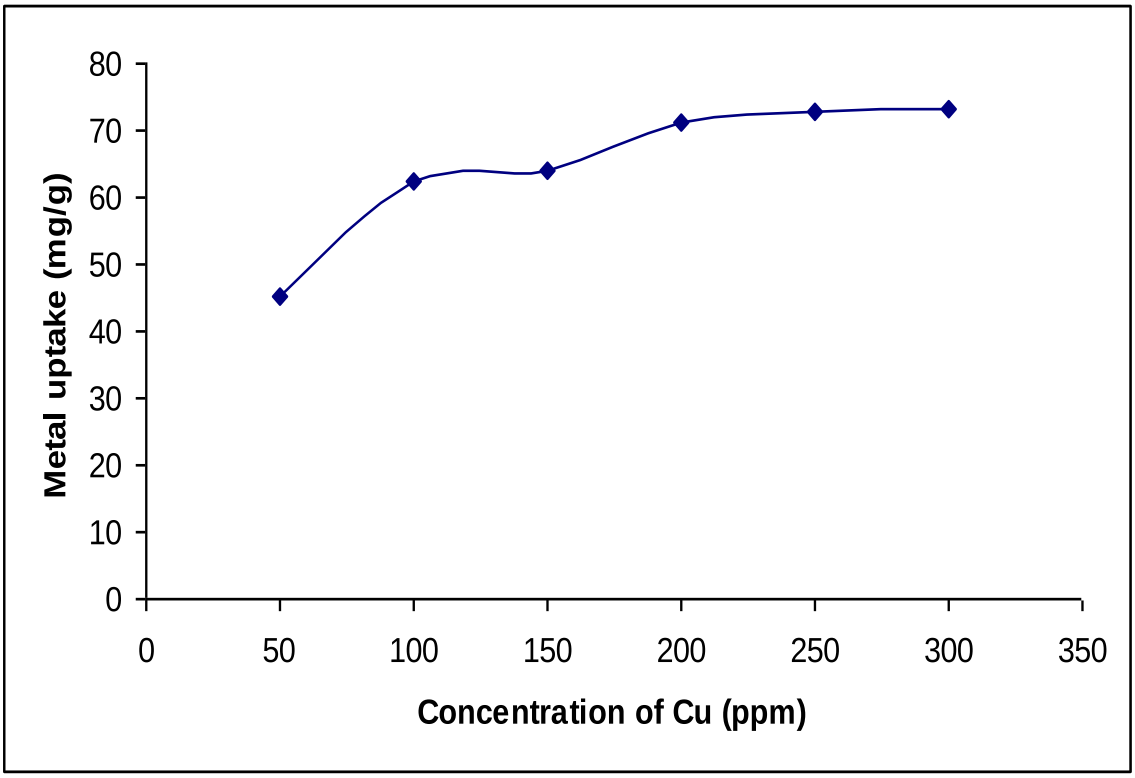

Fig. 6. Sorption equilibrium study of copper (II) by *Ocimum bacilicum* seeds

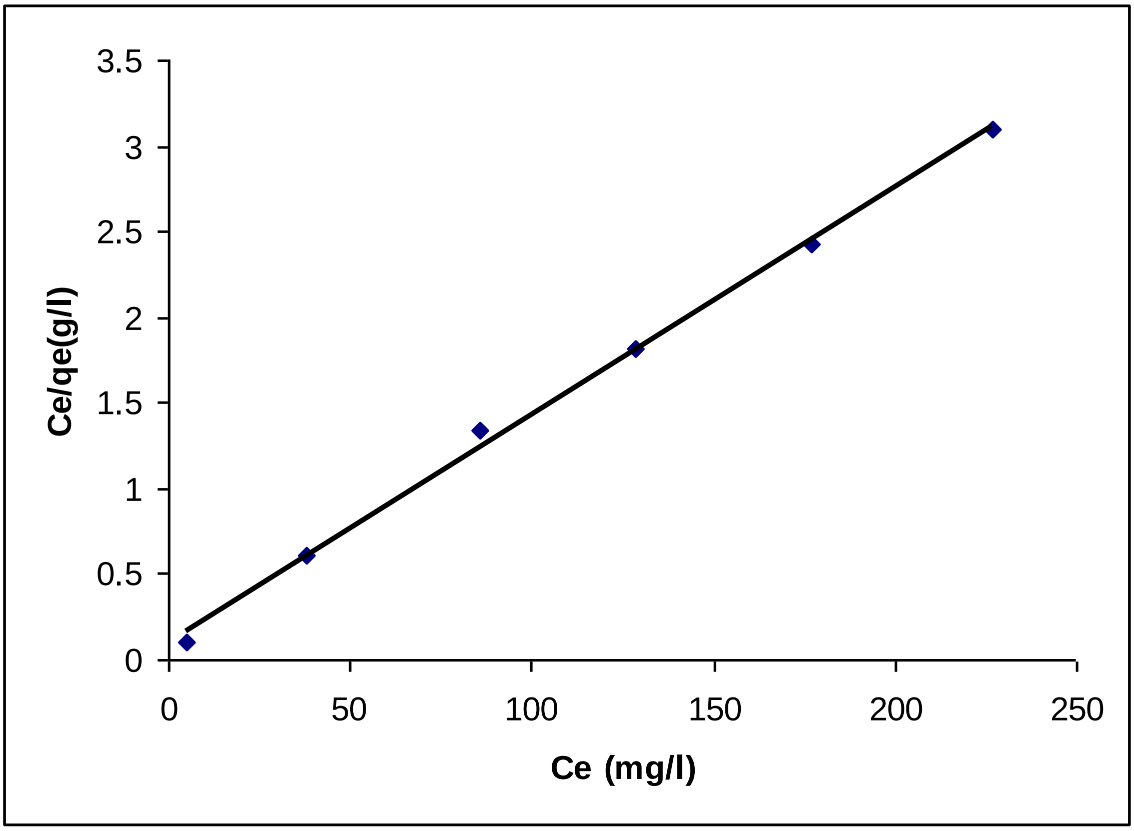

Fig. 7. Langmuir adsorption isotherm of copper (II) by *Ocimum bacilicum* seeds

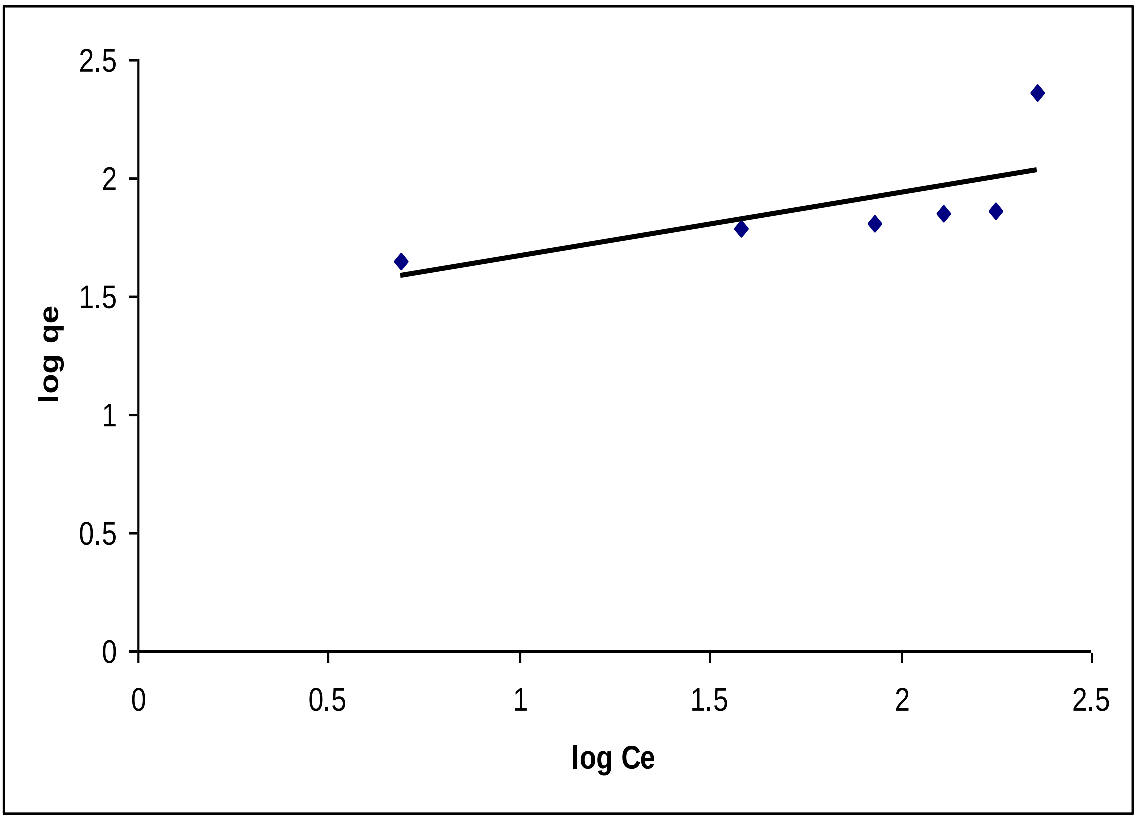

Fig. 8. Freundlich adsorption isotherm of copper (II) by *Ocimum bacilicum* seeds

Table 1: Langmuir and Freundlich isotherms for the biosorption of copper (II) by *Ocimum bacilicum* seeds

Metal	Experimental	Langmuir			Freundlich		
		q_{max} (mg/g)	B	R^2	1/n	K	R^2
Cu	73.10	75.19	0.79	0.997	0.270	24.80	0.869

3.4. Effect of time on biosorption of copper (II)

Effect of contact time on biosorption of copper (II) by using *O. bacilicum* seeds was varied from 15-480 minutes. The maximum copper (II) removal efficiency was obtained after 480 minutes which is 60.2 mg/g (Fig. 4). The plots indicate that the metal ions adsorbed increase rapidly in the beginning and become very slow in the end. The majority of metal ion in adsorption equilibrium was achieved in between 15 and 50 min for copper (II) ion and the sorption tends toward saturation. The initial faster rate of metal sorption may be explained by the large number of sorption sites available for adsorption. For the initial bare surface, the sticking probability is large and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium [20].

3.5. Effect of biosorbent dose on biosorption of copper (II)

Influence of biosorbent dose on copper (II) biosorption was examined by varying dosages from 0.1 to 3.5 g. The maximum metal biosorption capacity was attained when 1.5 g biosorbent was used which is 68.5 mg/g. The uptake capacity of metal ion per unit mass of biosorbent (mg/g) decreases with increase in dose of adsorbent, which may be due to lower utilization of adsorption capacity of the sorbent at higher dosage [21].

3.6. Sorption equilibrium study

The metal uptake capacity was estimated by applying optimized conditions. 50-300 ppm of Copper (II) solutions was analyzed. At 300 ppm the maximum metal uptake capacity of *Ocimum bacilicum* seeds was noted which is 73.1 mg/g. Modeling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures [22].

3.7. Langmuir and Freundlich adsorption isotherms

The equilibrium data was used in the form of equation 3 and 4 to plot Langmuir and Freundlich isotherms. The linearized Langmuir and Freundlich isotherms obtained for Copper (II) represents in fig 7. The data on conversion to the Langmuir model yielded straight line for metal, with correlation coefficient R^2 more than 0.99 (Table 1).

The values of R^2 regarded as a measure of the goodness of fit of experimental data on isotherms models. The value of R^2 for the Freundlich model was less than 0.99.Therefore our data is not applicable to Freundlich isotherms.
Langmuir suggested that, in such a case, when a strong chemical bond seems between molecules of the adsorbate and the surface of the adsorbent, the phenomenon is called chemi sorption or chemical adsorption.

4. Conclusions

The results demonstrate that *Ocimum bacilicum* seeds are an effective biosorbent to remove copper (II) from aqueous solution. 73.10 mg/g copper (II) was removed in batch experiments. Biosorption process was affected by pH 5, biosorbent dose 1.5 g, agitation speed 150 rpm, contact time 30 minutes and high metal ion concentration. The equilibrium data fitted well to Langmuir isotherm with correlation coefficient of 0.997. The study revealed that *Ocimum bacilicum* biosorbent could be used as an adsorbent for the removal of other heavy metals on large scale.

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