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INFLUENCE OF OPERATING CONDITIONS ON THE REMOVAL OF Zn(II) AND Cu(II) IONS FROM AQUEOUS SOLUTIONS USING *CARISSA CARANDUS* - A BIOSORBENT

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ABSTRACT

In this investigation an attempt has been made to remove Zn(II) and Cu(II) from aqueous solution by using *Carissa carandus* Leaves as an inexpensive biosorbent. Various parameters such as initial metal concentration (5-25mg/L), biosorbent dosages (1-3g/L), pH (2-8) and contact time (30-240min.) having an impact on adsorption efficiency were studied. Equilibrium contact time was found to be 150 minutes for both Zn(II) and Cu(II). The removal efficiency for Zn and Cu at these contact times was 86.60% and 84.74% respectively. The pH (6) was found optimum for adsorption of Zn(II) and Cu(II). These metals show maximum removal capacity at 2.0g/L (adsorbent dosage) and 10-15mg/L (initial metal concentration). The adsorption data were modeled by using both Langmuir and Freundlich classical adsorption isotherm. The data are better fitted by the Freundlich isotherm as compared to Langmuir and the adsorption capacity (Q_m) was found to be 19.05 mg/g and 166.66 mg/g for Zn(II) and Cu(II) respectively.

Keywords: Biosorption, *Carissa carandus* leaves, Zinc and Copper removal, Adsorption isotherm.

INTRODUCTION

Environmental contamination by heavy metals is a serious growing problem throughout the world. Human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in metallic substance in aquatic environment[1]. Heavy metal ions such as Zn, Cd, Hg, Cu, Pb etc. are highly toxic and can cause damaging effects even at very low concentration. They tend to bioaccumulate in the food chain and can be highly dangerous to human health[2]. Even though Zn(II) is a very essential requirement for a healthy body, excess zinc can be harmful and cause zinc toxicity[3] . Excessive adsorption of zinc can also suppress copper and iron absorption. Zinc enters into the aqueous environment through waste water from zinc plating industries, batteries, pulp and paper manufacturing process, viscose rayon yarn and fibre production.

Prolonged inhalation of Cu(II) spray is claimed to cause an increase in the risk of lung cancer[4]. Copper is discharged into the environment due to electro deposition of metals, rayon industries, metallurgical processes, mining and battery manufacturing[5] and agricultural activities[6].

Various physio-chemical methods have been developed for removal of heavy metals from contaminated water, which include chemical precipitation, membrane processes (reverse osmosis, nanofiltration, etc.), solvent extraction, ion exchange, electrofloatation[7-8]. However, these processes may be ineffective or expensive, especially when the heavy metal ions are in solution containing in the order of 1-100 mg/L[9]. Adsorption is the most widely used process and present in many natural, physical, biological and chemical systems. Commercial Activated Carbon (CAC) has been widely used adsorbent for treatment of wastewater[10-11] . However, it is an expensive adsorbent and need to complexing agents to improve its removal efficiency. This problem has lead to investigate various low-cost adsorbents including chitosan[12], zeolites[13], fly ash[14], clay[15], bone char[16], peat moss[17] etc.

Bioadsorption[18] has become familiar for many researchers as an alternative pathway for heavy metal removal. The various biosorbents were evaluated includes bacteria[19], fungi[20], algae[21], plant products papaya wood[22] , sunflower stem[23] , rice husk[24] , black tea leaves[25] etc.). These have shown adequate capacity for heavy metal removal from contaminated water at low cost.

In the present investigation, leaves of *Carissa carandus* has been used as biosorbent for removal of Zn(II) and Cu(II) from aqueous solution. Various experimental conditions such as initial metal concentration, biosorbent dosages, pH and contact time were studied and the isotherms were tested for Langmuir and Freundlich equations.

EXPERIMENTAL

Preparation of Adsorbent

The leaves of *Carissa carandus* were obtained from *Foysagar Telephone Exchange, Ajmer, Rajasthan, India.* It was washed by doublelly-distilled water to remove dust and particulate materials from its surface. The substance was dried at room temperature in shade for 10 days and then in an air oven at 120^{o} C for 72 hours. It was grinded into fine powder in a mechanical grinder and sieved to a particle size of 0.3-0.5 mm. The adsorbent was stored in polypropylene jars for further experiments.

Preparation of Stock solution

The stock solutions of Zn(II) (1000ppm) and Cu(II)(1000ppm) were prepared by dissolving $ZnSO_4$ and $CuSO_4$ respectively in double distilled water. The analytical grade salts were used for analysis. The desired solutions were obtained by diluting the stock solution in double distilled water. The pH of the solution was adjusted using M/10 HCl and M/10 NaOH.

Biosorption experiments

The biosorption studies were conducted by using desired quantities of the bio adsorbent (leaves powder of *Carissa carandus*) added to 100 mL of heavy metal solution in a 250 mL conical flask at room temperature. The samples were placed on a rotary shaker at 300 rpm and taken at regular intervals. The adsorption experiments were carried out by varying contact time (30-240 minutes), metal –ion concentration (5-25 mg/L), pH (2-8) and also the biosorbent dosages (1-3 g/L).
The samples were filtered through Whatman No.42 and the concentration of the residue heavy metal solution was determined by using ECIL Atomic Absorption Spectrophotometer.
All the experiments were performed triplicate to assess reproducibility. Adsorption equilibrium[26] was calculated by using the equation-

$$q_e = (C_0-C_e)\ V\ /\ W \tag{1}$$

Where:
q_e = metal concentration retained in the adsorbent phase (mg/g)
C_0 = initial concentration of metal ion in solution (mg/L)
C_e = equilibrium concentration of metal ion in solution (mg/L)
V = volume of liquid (L)
W= weight of the adsorbent (g)

RESULTS AND DISCUSSION

Effect of Contact Time

The effect of contact time on the uptake of the studied cations onto the biosorbent is shown in the Fig. 1. This was achieved by varying the contact time from 30 – 240 minutes at room temperature (298K).
Equilibrium contact time was found to be 150 minutes for Zn(II) and Cu(II). The removal efficiency for Zn and Cu at these contact times was 86.60% and 84.74% respectively. Fig. 1 shows that biosorption of Zn and Cu was rapid within the first 30 minutes of contact time due to vacant sites on biosorbent. The rate of adsorption of metals gradually decreased with increase in contact time due to decrease of sorption sites.

Effect of pH

The pH of the metal solution was a key parameter for biosorption of Cu(II) and Zn(II). Optimization of pH was done at pH range (2-8). According to Fig. 2 at a low pH<=2 adsorption of metals is negligible

with increasing pH in the range of 4.0 to 6.0 metal uptake on biosorbent also increases but different proportion depending on the metals until reaching a plateau.
At lower pH the H^+ ions are much more than metal ions so they compete powerfully with metal ions for active sites of biosorbent, thus resulting their adsorption decrease. At higher pH the effect of competition from H^+ ions decreases and the metal ions get adsorbed on surface of adsorbent, resulting an increase in the metal uptake. For the rest of experiments the optimum pH of 6.0 was chosen for adsorption of Cu(II) and Zn(II).

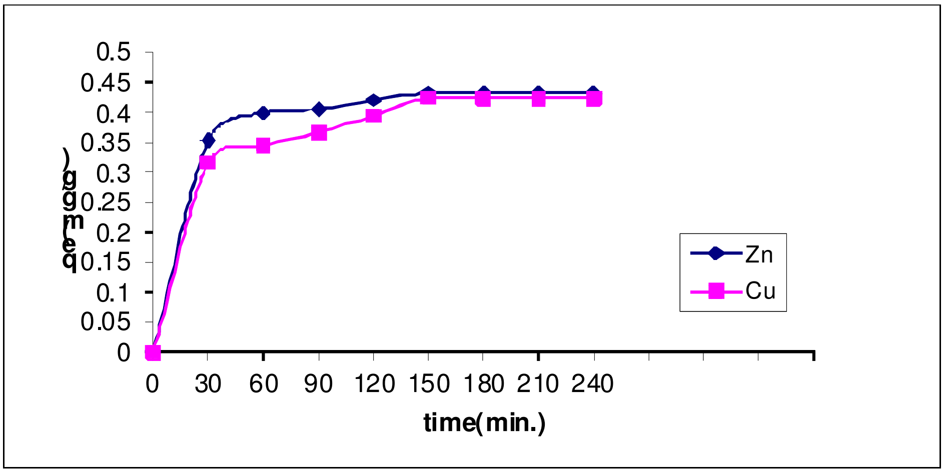

Fig.-1: Effect of contact time

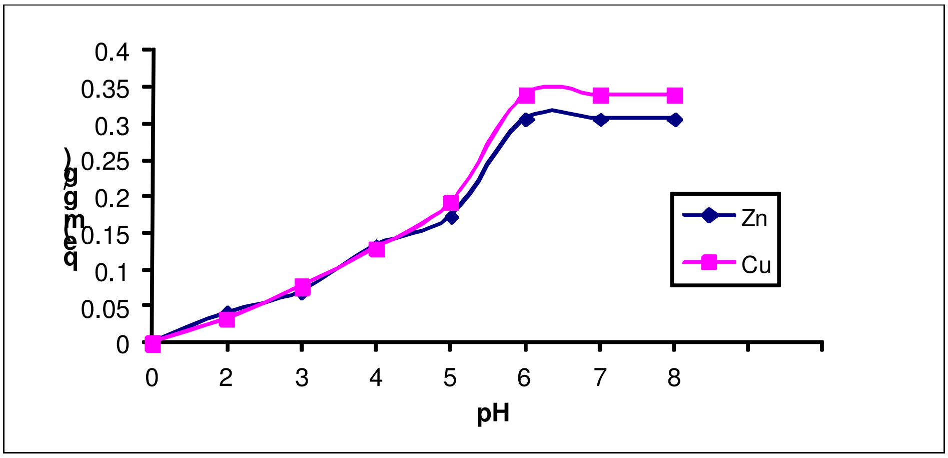

Fig.-2: Effect of pH

Effect of Adsorbent Dosages

The effect of adsorbent dosages on removal of Zn(II) and Cu(II) has been presented in Fig. 3. The experiments were carried out by varying the biosorbent dosages from (1.0-3.0g/L). The sorption capacity of biosorbent increases with increasing the adsorbent dosages. This is due the availability of more functional groups and surface area at higher dosages. It was observed that Zn(II) shows 18.59% adsorption at an adsorbent dosage of 1.0g/L but at a higher dosage of 2.0g/L a removal efficiency of 85.58% is achieved.

On further increasing the adsorbent dosage to 3.0g/L an increasing trend in removal efficiency is observed but it is slightly higher than that obtained at an adsorbent dose of 2.0g/L. In case of Zn(II) and Cu(II) maximum removal was attained at 2.0g/L of adsorbent weight.

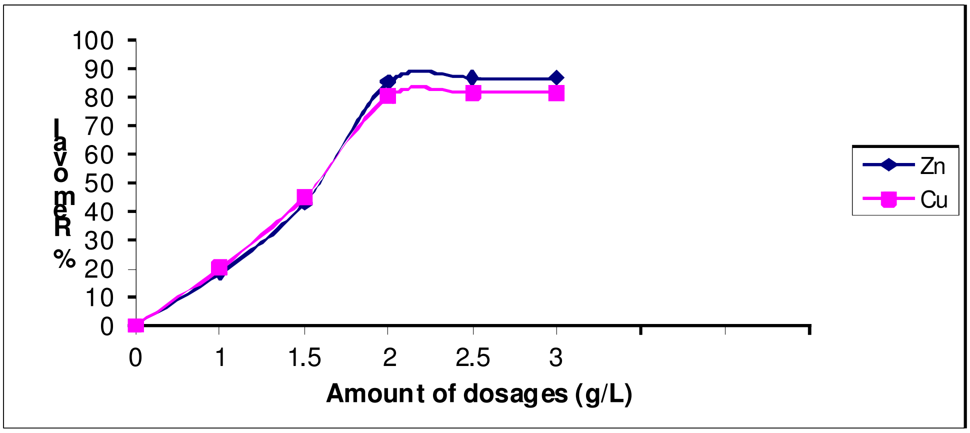

Fig.-3: Effect of adsorbent dosages

Effect of Adsorbate Initial Concentration

Studies were performed with Zn(II) and Cu(II) with initial concentrations ranging from 5 to 25 mg/L at a pH of 5.0, with a biosorbent dosage of 2.0 g/L. It was observed that there is a decrease of the removal percentage with increase in initial metal concentrations from 5 to 25 mg/l. (Fig. 4). It may be explained on the basis that at lower concentrations of metal ions more adsorption sites are available on adsorbent but at higher concentration competing metal ions are increased for the available adsorption sites[27]. The percentage removal of Zn(II) and Cu(II) remained constant at initial metal concentrations of 15-30 mg/L.

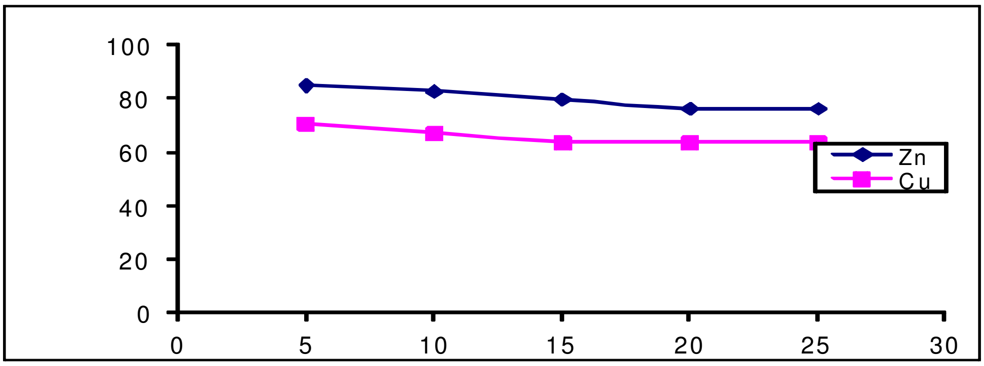

Fig.-4: Effect of adsorbate initial concentration

Adsorption Isotherm Models

Langmuir Isotherm

The Langmuir isotherm[28] is represented by the following equation-

$$C_e / q_e = C_e / Q_m + 1 / Q_m b \qquad (2)$$

Where-

C_e = equilibrium concentration of solute (mg/L)

q_e = the amount of solute adsorbed at equilibrium time (mg/g)

Q_m = adsorption capacity (mg/g)

b = free energy of adsorption

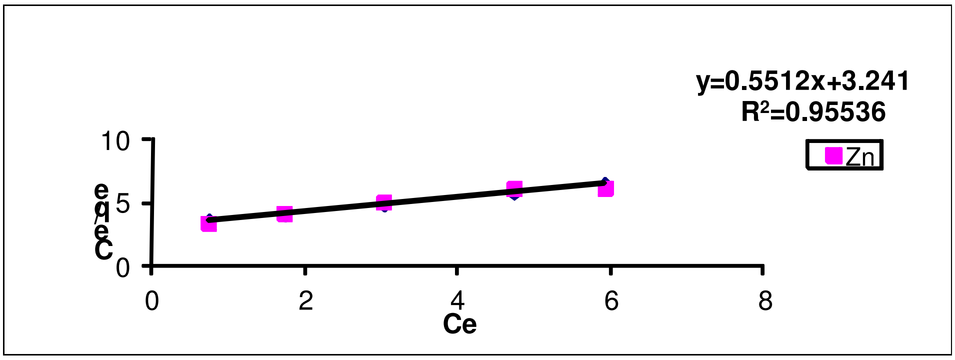

Fig.-5: Langmuir Adsorption Isotherm of Zn

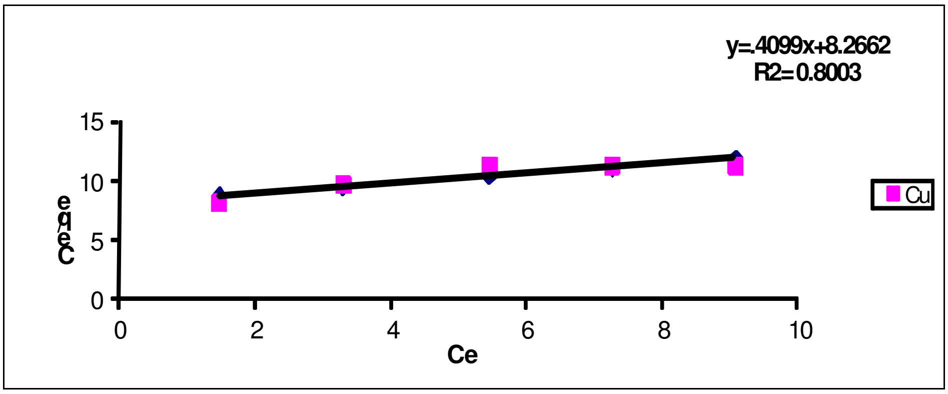

Fig.-6: Langmuir Adsorption Isotherm of Cu

Freundlich Isotherm

The Freundlich isotherm[28] may be written as-

$$\log q_e = \log K_f \;+\; 1/n \;\log C_e \qquad (3)$$

Where

C_e = equilibrium concentration of solute (mg/L)

q_e = the amount of solute adsorbed at equilibrium time (mg/g)

K_f = indicator of sorption capacity (mg/g)

$1/n$ = intensity of the sorption

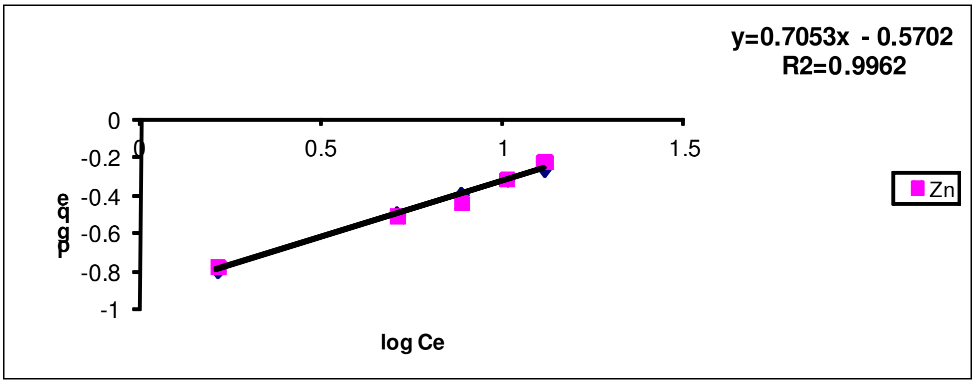

Fig.-7: Freundlich Adsorption Isotherm of Zn

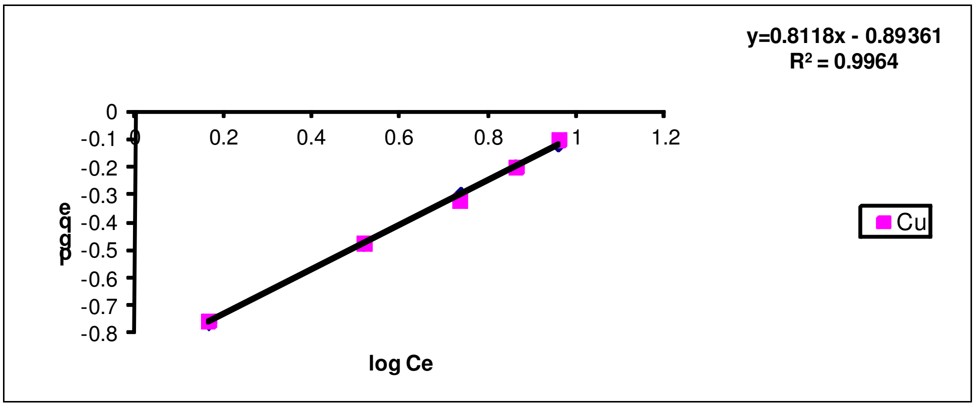

Fig.-8: Freundlich Adsorption Isotherm of Cu

The isotherm adsorption data shown in Fig. 5,6 and in Fig. 7,8 are fitted to obtain the Langmuir and Freundlich isotherm model parameters. The parameters are represented in Table-1.
Results show that the adsorption of Zn(II) and Cu(II) are best explained by Freundlich model as the value of correlation regression (R^2)for both metals are 0.9938 and 0.9813 respectively.

Table-1: Langmuir and Freundlich constants

Elements	Langmuir			Freundlich		
	Q_m	b	R^2	K	n	R^2
Zn	19.05	0.17	0. 955	0.565	1.4178	0.9962
Cu	166.66	0.049	0.8003	0.4091	1.2316	0.9964

CONCLUSIONS

The current investigation shows that *Carissa carandus* leaves is very effective biosorbent in removal of Zn(II) and Cu(II) ions. The adsorption of Zn(II) and Cu(II) ions are dependent on initial concentration of the metal ion, adsorbent dosages, pH and the contact time. In adsorption isotherm analysis, the Freundlich isotherm model well described the adsorption of both the metals. Hence, this biosorbent can be used as a low cost adsorbent in the treatment of wastewater containing Zn(II) and Cu(II) ions.

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