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REMOVAL OF ZINC FROM AQUEOUS SOLUTION USING COFFEE INDUSTRY WASTE

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ABSTRACT

Biosorption is most economical method for removing toxic metals from waste water. The paper presents the results of studies carried out on sorption of zinc ions from aqueous solutions by a coffee industry waste as a low-cost sorbent. It was found that crushed coffee industry waste possess relatively high sorption capacity as 46.05 mg/g, when comparing with other sorbents. The biosorption studies were determined as a function of initial metal ion concentrations, pH, biosorbent dosage and biosorbent particle size. About 0.1g of coffee industry waste was found to be enough to remove 71.66% of zinc for 20 mg/L of metal ion concentration from 30 mL aqueous solution. The optimum pH value was found to be 7. The experimental equilibrium data were tested with the biosorption isotherms like Langmuir, Freundlich and their equilibrium parameters were determined. The best-adjusted model to the experimental equilibrium data for coffee industry waste was the Freundlich model.

KEYWORDS: Coffee Industry Waste; zinc; Biosorption; Biosorption isotherm; Batch Processing.



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INTRODUCTION

It has been shown that the release of toxic substances and their dispersal in the environment may cause tragic effects on exposed populations. Over the past few decades the huge increase in the use of heavy metals has resulted in an increased flux of metallic substances in aquatic environment. The most important characteristics of these metals are that they are non-degradable and therefore persistent. Furthermore, most of the metal ions are toxic to living organisms. Therefore, in order to have a pollution-free environment, the toxic materials should be removed from wastewater before its disposal¹. The source of environmental pollution with heavy metals is mainly industry, i.e. metallurgical, electroplating, textile, metal finishing industries, tanneries and chemical manufacturing². Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when adsorbed into the body³. Zinc is one of the most important metals often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and not biodegradable and travels through the food chain via bioaccumulation. Therefore there is significant interest regarding zinc removal from wastewaters⁴ and its toxicity for humans at levels of 100-500 mg/day⁵. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L⁶.

Removal of toxic heavy metals from industrial wastewater has been practiced for several decades, the conventional physico-chemical removal methods, such as chemical precipitation, electro plating, membrane separation, evaporation or resin ionic exchange, are usually expensive and sometimes, not effective. Recently, heavy metal ions removal from industrial waste streams became particularly difficult due to implementation of more restrict law regulations that control the concentration of pollutants in effluents discharged into waters and soils on the level lower than 1 mg/kg⁷. Traditional methods of

metal ions removal became inefficient in the removal of metal ions below this concentration. Therefore, there is the need to search for other methods that would be efficient at low concentration of pollutants⁷. Biosorption, based on living or non living microorganisms or plants could be such an alternative method of treatment. Biosorption can be defined as the ability of biological materials to accumulate heavy metals through metabolically mediated or physico-chemical pathways of uptake⁴. It has distinct advantages over conventional methods of treatments, such as this process does not produce chemical sludge, hence no secondary pollution, more efficient and easy to operate.

The effectiveness of biosorption for the removal of heavy metals has been shown in a number of studies. However, only when the cost of the biosorption process can complete with the existing technologies it will be accepted commercially. Kuyucak indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process⁸. Therefore, low cost biomass becomes a crucial factor when considering practical application of biosorption. It leads to a search for biological sorbents among waste materials from food and agricultural industry. These materials can be considered as low-cost sorbents⁷. In the present paper it is proposed to apply coffee industry waste as low-cost biological sorbent for the removal of zinc. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, biosorbent concentration and biosorbent size were evaluated. The equilibrium biosorption data were evaluated by Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

PREPARATION OF BIOSORBENT

The coffee industry waste used in this study was collected at coffee industry which is located in Manchikalapudi, Duggirala (Mandal), Guntur (Dist), Andhra Pradesh. The collected material

was washed with deionised water several times to remove dirt particles. The washing process was continued till the wash water contains no dirt. The washed material was then completely dried in sunlight for 15 days. The dried material was then ground and powdered using domestic mixer. In the present study the powdered material in the range of 60–150 μm average mesh size were then directly used as biosorbent without any pretreatment.

CHEMICAL

Analytical grades of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, HCl and NaOH were purchased from Merck, India. Zinc ions were prepared by dissolving its corresponding sulphate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and NaOH. All the experiments were repeated five times and the average values have been reported. Also, blank experiments were conducted to ensure that no biosorption

was taking place on the walls of the apparatus used.

BIOSORPTION EXPERIMENTS

Biosorption experiments were performed in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different zinc concentrations. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g coffee industry waste biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the biosorbent with whatman filter paper. The amount of metal biosorbed by coffee industry waste was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_o - C_f) \times \frac{V}{M} \quad (1)$$

Where Q is the metal uptake (mg/g); C_o and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (mL); and M is the mass of biosorbent (g). The Langmuir⁹ sorption model was chosen for the estimation of maximum zinc sorption by the biosorbent. The Langmuir isotherm can be expressed as,

$$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \quad (2)$$

Where Q_{\max} indicates the monolayer biosorption capacity of biosorbent (mg/g) and the Langmuir constant b (L/mg) is related to the energy of biosorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{Q} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max} C_f} \quad (3)$$

The Freundlich¹⁰ model is represented by the equation,

$$Q = K C_f^{1/n} \quad (4)$$

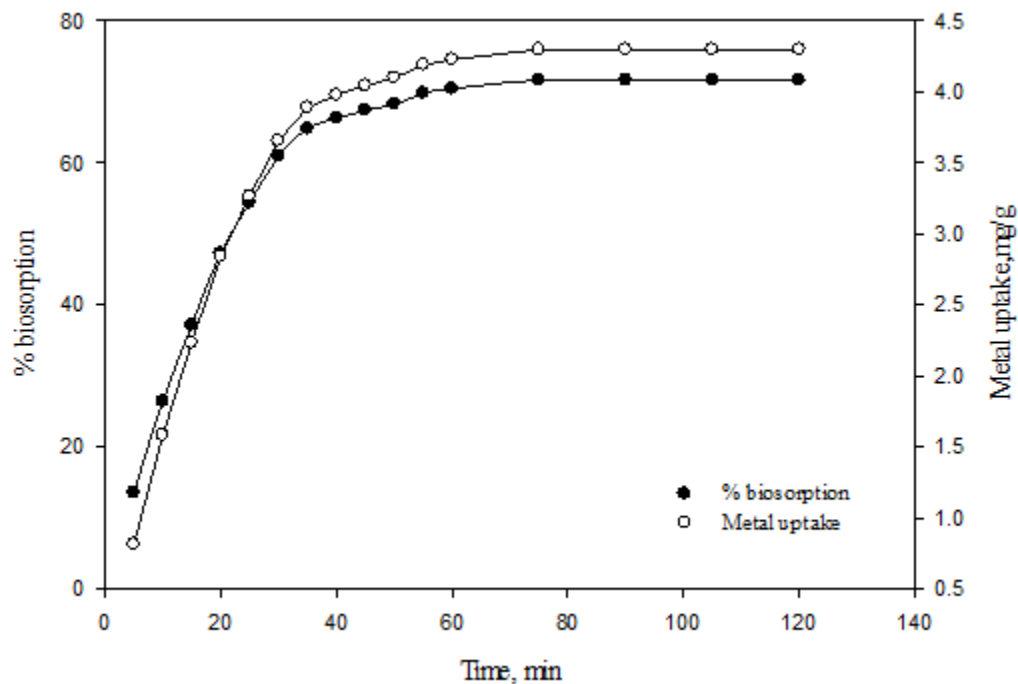
Where K (mg/g) is the Freundlich constant related to biosorption capacity of biosorbent and n is the Freundlich exponent related to biosorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows,

$$\ln Q = \ln K + \frac{1}{n} \ln C_f \quad (5)$$

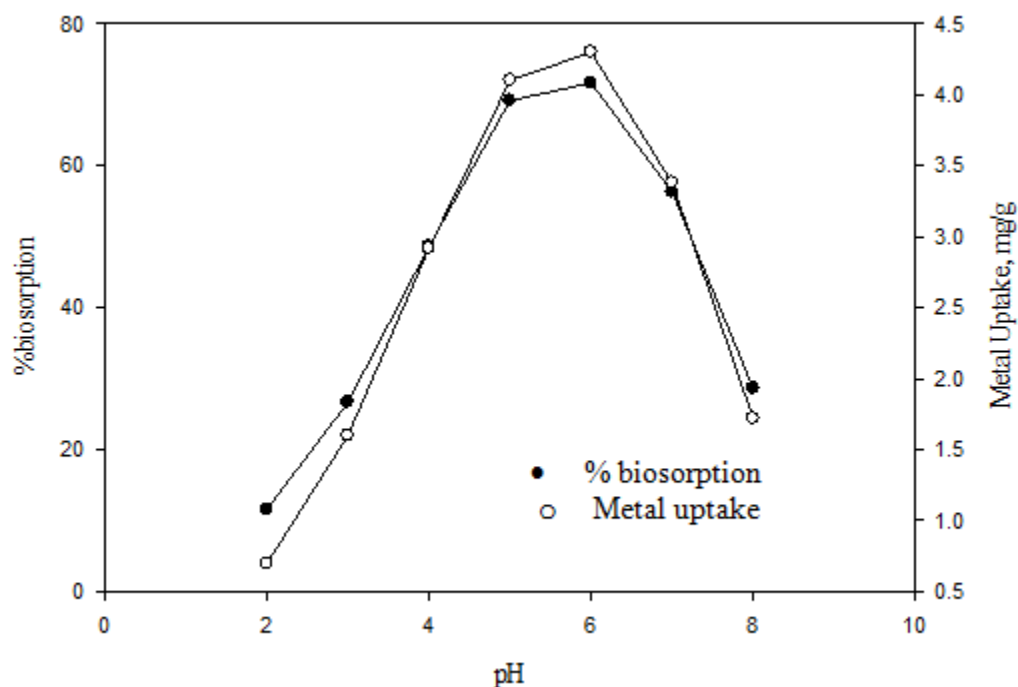
RESULTS AND DISCUSSION

EFFECT OF CONTACT TIME

FIGURE.1
EFFECT OF CONTACT TIME



The data obtained from the biosorption of zinc ions on the coffee industry waste showed that a contact time of 60 min was sufficient to achieve equilibrium and the biosorption did not change significantly with further increase in contact time (Fig.1). Therefore, the uptake and unbiosorbed zinc concentrations at the end of 60 min are given as the equilibrium values (q_e , mg/g; C_{eq} , mg/L), respectively, and the other biosorption experiments were conducted at this contact time of 60 min.

EFFECT OF PH**FIGURE.2
EFFECT OF PH**

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls. Thus pH is an important process parameter on biosorption of metal ions from aqueous solutions since it is responsible for protonation of metal binding sites, calcium carbonate solubility and metal speciation in the solution⁷. It was found that zinc uptake by coffee industry waste was a function of solution pH. As shown in (Fig.2), the uptake of zinc increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in literature for different biomass systems¹¹⁻¹⁵. The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by carbonate groups that have cation-exchange properties. At lower pH values zinc removal was

inhibited, possibly as a result of the competition between hydrogen and zinc ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carbonate groups in coffee industry waste would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface. In this study, these zinc cations at around pH 6 would be expected to interact more strongly with the negatively charged binding sites in the biosorbent. As a result, the optimum pH for zinc biosorption was found as 6 and the other biosorption experiments were performed at this pH value.

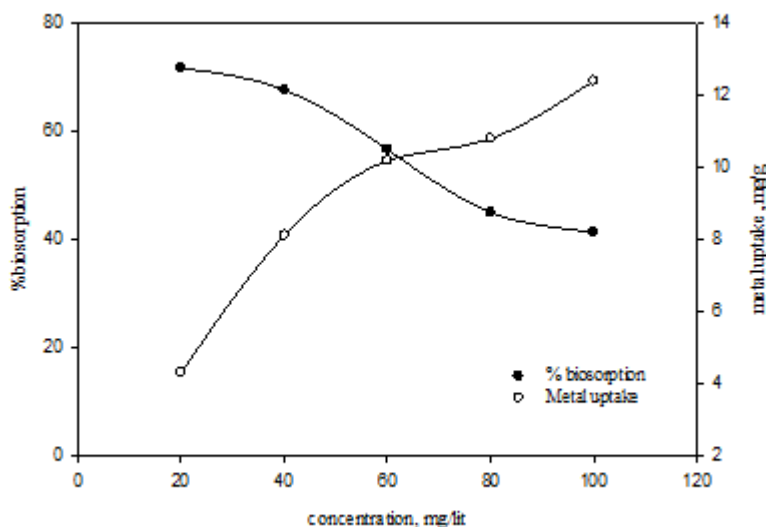
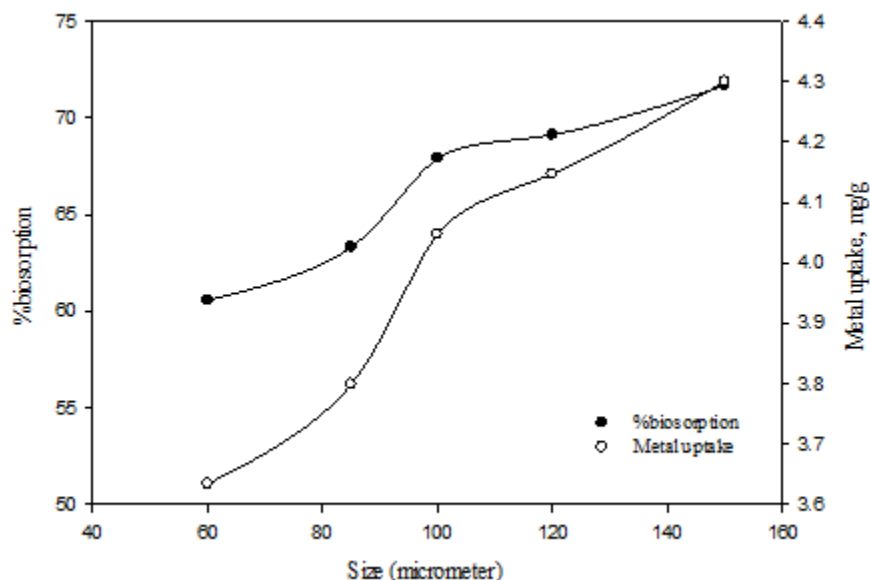
EFFECT OF METAL ION CONCENTRATION**FIGURE.3**
EFFECT OF CONCENTRATION

Fig.3 shows the effect of metal ion concentration on the biosorption of zinc by coffee industry waste powder. The data shows that the metal uptake increases and the percentage biosorption of zinc decreases with increase in metal ion concentration. This increase (5.19 to 23.49 mg/g) is results of the increase in the driving force i.e. concentration gradient. However, the percentage biosorption of zinc ions on coffee industry waste powder was decreased from 86.50 to 78.29%. Though

an increase in metal uptake was observed, the decrease in percentage biosorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage At higher concentrations, lower biosorption yield is due to the saturation of biosorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

EFFECT OF BIOSORBENT SIZE

**FIGURE.4
EFFECT OF SIZE**



The effect of different biosorbent particle sizes on percentage removal of zinc is investigated and showed in (Fig.4). It reveals that the biosorption of zinc on coffee industry waste. Decreases with increase of particle size due to increase of surface area on biosorbent Surface.

EFFECT OF BIOSORBENT DOSAGE

**FIGURE.5
EFFECT OF DOSAGE**

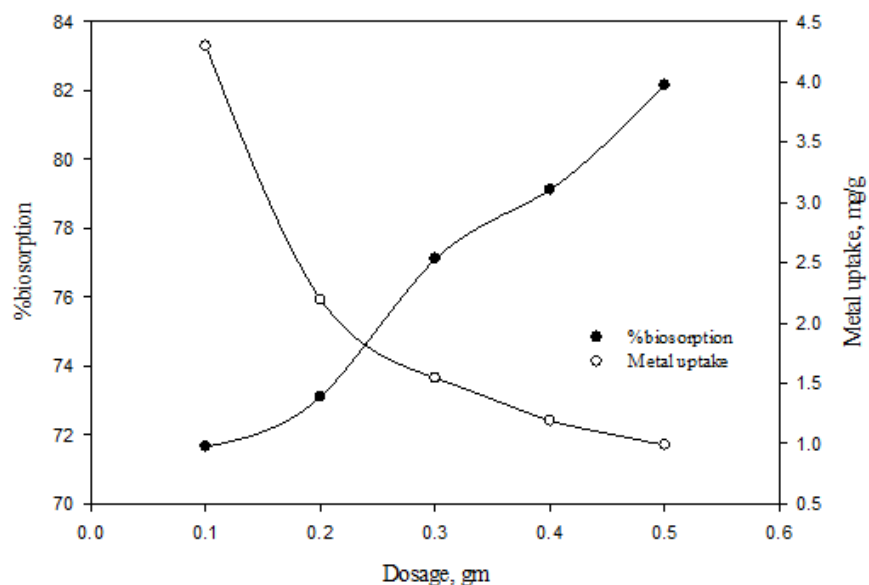
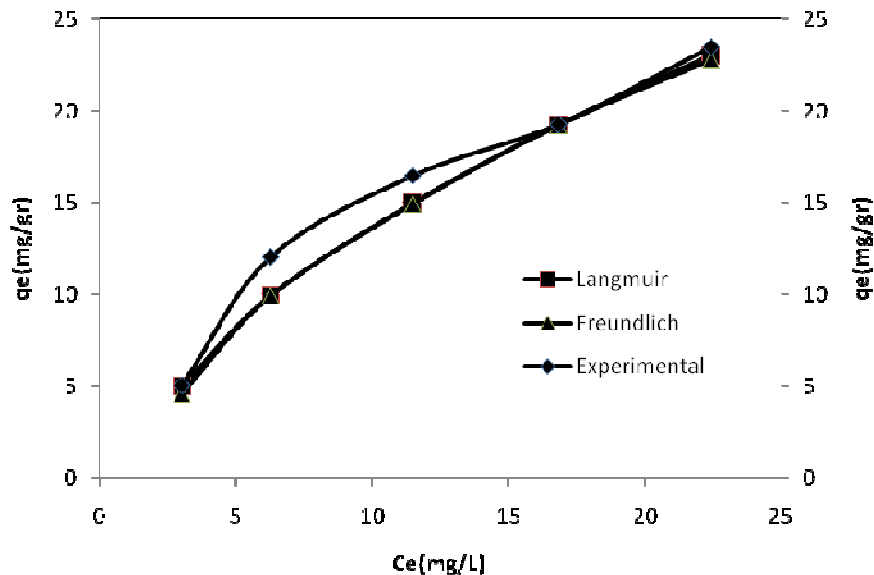


Fig.5 shows the effect of biosorbent dosage on the percentage removal at equilibrium conditions. It was observed that the amount of zinc biosorbed varied with varying biosorbent concentrations. The amount of zinc biosorbed increases with an increase in biosorbent dosage from 0.1 to 0.5 g. The percentage zinc removal was increased from 86.50 to 94.85% for an increase in biomass concentration from 0.1 to 0.5 g at initial concentration of 20 mg/L. The increase in biosorption of amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for zinc removal using pyrolusite as biosorbent [16].

BIOSORPTION EQUILIBRIUM

The equilibrium biosorption of zinc on the coffee industry waste as a function of the initial concentration of zinc is shown in figure 6. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, isotherm constants are given in Table.1. It is found that the biosorption of zinc on the coffee industry waste was correlated well with the Freundlich equation and Langmuir equation under the concentration range studied.

**FIGURE.6
ISOTHERMS**



**TABLE.1
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS.**

Langmuir	$Q(mg/g)$	46.05
	$b(L/mg)$	0.045
	R^2	0.968
Freundlich	$K_f(mg/g)$	2.61
	n	0.71
	R^2	0.998

CONCLUSION

The present study shows that the coffee industry waste was an effective biosorbent for the biosorption of zinc ions from aqueous solution. The biosorption capacity of coffee industry waste was superior due to the higher content of carbonate groups. The effects of process parameters like pH, metal ion concentration, biosorbent dosage and biosorbent size on process equilibrium were

studied. The uptake of zinc ions by coffee industry waste increased by increasing the metal ion concentration and the biosorbent dosage and decreased by increasing the biosorbent size. The uptake was also increased by increasing pH up to 6. The biosorption isotherms could be well fitted by the Freundlich equation followed by Langmuir.

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