

REMOVAL of HEAVY METALS IONS from AQUEOUS SOLUTIONS USING BIOSORPTION onto BAMBOO

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ABSTRACT

Feasibility of biosorbent of England bamboo plant origin was tested for removal of priority metal ions such as Cu and Zn from aqueous solutions in single metal state. Batch single metal state experiments were performed to determine the effect of dosage (0.5, 1 and 1.5 g), pH (3, 4, 4.5, 5 and 6), mixing speed (90, 111, 131, 156 and 170 rpm), temperature (20, 25, 30 and 35 °C) and metal ion concentration (10, 50, 70, 90 and 100 mg/L) on the ability of dried biomass to remove metal from solutions which were investigated. Dried powder of bamboo removed (for single metal state) about 74 % Cu and 69% Zn and maximum uptake of Cu and Zn was 7.39 mg/g and 6.96 mg/g respectively, from 100 mg/L of synthetic metal solution in 120 min. of contact time at pH 4.5 and 25°C with continuous stirring at 170 rpm. Experimental results have been analyzed using Langmuir and Freundlich isotherms. Both equilibrium sorption isotherms were found to represent well the measured sorption data, but Freundlich isotherm was better than Langmuir isotherm. The effect of time was studied and the rate of removal of Cu (II) and Zn (II) ions from aqueous solution by bamboo plant was found. The rates of sorption of copper and zinc were rapid initially within 5-15 minutes and reached a maximum in about 60 minutes.

INTRODUCTION

Today, the world is facing the problem of water pollution. Due to rapid development and industrialization in many countries, the levels of industrial pollution have been steadily rising.

The pollution problem of industrial waste water is becoming more and more serious in the world. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land. Moreover, contamination of ground water is today a

major concern in the management of water resources [1].

Heavy metals are one of the major pollutants in the environment as a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. The major sources of heavy metal contamination are considered to be from industry such as zinc from paint, rubber, dye, wood, preservatives and electroplating industries and nickel from paint and powder batteries processing industries. [2]

Metals are of special concern because they are non-degradable and therefore persistent. The effect of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Zinc causes nausea and vomiting [3] and long term exposure to nickel causes decrease in body weight, heart and liver damage [4]. Some metals may be either beneficial or toxic, depending on concentration [5].

Therefore, the elimination of heavy metals from water and wastewater is important to protect public health and wild life [6].

The conventional methods used to remove heavy metals include chemical precipitation, ion exchange and electrochemical treatment. [7, 8, 9]. The search for new, effective and economical technologies involving the removal of toxic metals from wastewater has directed attention to biosorption based on metal binding capacities of various biological materials at little or no cost [10].

Dead biological materials are capable of removing heavy metal ions from solutions through a process involving a number of diverse mechanisms collectively known as biosorption [11].

Biosorption is a process employing a suitable dead biomass to sorb heavy metals from dilute aqueous solutions (1 to 100 ppm) and reduce their concentration to below (1 ppm) [12].

Biosorption process removes heavy metal from wastewater without creating hazardous sludge at costs much lower than conventional

methods. Regeneration of the biosorbent and concentration of the metal solution for eventual recovery further increase the cost effectiveness of the process [13].

A search for a low-cost and easily available biosorbent has led to the investigation of materials of agricultural and biological origin, along with industrial by-products, as potential metal sorbents [14].

Although several studies were available explaining the utilization of several low cost adsorbents, most of these work stand at the laboratory level and only a very few cases have been directly implemented in practical applications at industrial level [15].

Agricultural by-products could be heavy metal adsorbents which could be selective for some metal ions. Agricultural materials such as banana and orange peels [16] maize cob, coconut husk fibers [17], nut shells [18], soybeans and cotton seed hulls have been evaluated for their adsorptive properties. These materials have been reported to adsorb different pollutants such as heavy metals ions.

The research into the utilization of agricultural by-products as adsorbents for the removal of heavy metals from aqueous solutions has been on the increase. This is because these agricultural by-products are naturally occurring; hence they are available at little or no cost. They also have advantage over the conventional adsorbents such as activated carbon particularly because of their low cost and high availability. There is also no need for complicated regeneration processes when using agricultural by – products and they are capable of binding to heavy metals by biosorption[19].

. The aim of this work is to characterize a new biosorbent to be used for removal of toxic heavy metals, i.e, Cu (II) and Zn(II) from aqueous solutions.

Evaluate the single biosorption data in terms of equilibrium isotherms using the Langmuir and Freundlich adsorption isotherm model.

Study the effect of different experimental conditions such as pH, biosorbent dose, initial

metal concentration, temperature and mixing speed on sorption process.

Sorption Isotherm Theory

Different isotherm models have been utilized for describing sorption equilibrium for wastewater treatment. Langmuir and Freundlich equations are being used for present work. The Langmuir sorption isotherm describes the surface as homogeneous assuming that all the sorption sites have equal sorbate affinity and that adsorption at one site does not affect sorption at an adjacent site [20]. The linear form of the Langmuir isotherms may be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (1)$$

The values of q_{\max} and b can be calculated from the slope and intercept of the plot C_e/q_e versus C_e .

The Freundlich sorption isotherm (an empirical equation) however, describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. The linear form of Freundlich sorption isotherm can be represented as [21]:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (2)$$

Where n and K_f are the Freundlich isotherm constants. The values of n and K_f can be calculated from the slope and intercept of the plot $\log q_e$ versus $\log C_e$.

Materials and Methods

Preparation of Adsorbent (Bamboo)

The Bamboo from united Kingdom was collected from Guildford in UK, the biomass washed with tap and deionized water, dried and then ground using a food processor and passed through a different size of sieve in order to obtain uniform particle size and washed 2-3 times in deionized water at room

temperature then soaking with deionized water several times to remove any contamination in it and after that dried at a temperature 80°C for two days. Dried biomass was used for further sorption experiments.

Preparation of Solutions

In this experimental works, the biosorption experiments were conducted by using aqueous stock solution (1000 mg L⁻¹) of Cu(II) and Zn(II) which was prepared using salts of Cu(SO₄)₂·5H₂O and ZnSO₄·7H₂O. The concentration ranges varied between 10 to 100 mg L⁻¹ with distilled water for single metal and aqueous solution depending on dilution equation.

Batch sorption experiment

Using the different amount of biosorbent in a 250mL conical flask containing 100mL of test solution, batch sorption studies were carried out at desired pH value, contact time, temperature, mixing speed, sorbent weight and sorbate concentration. Different initial concentration of Cu (II) and Zn (II) solutions were prepared by proper dilution from stock 1000 mg/L Cu(II) and Zn(II) standard, pH of the solution was monitored by adding 0.1M HCl and 0.1M NaOH solution as required. Necessary amount of biosorbent was then added and content in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 170 rpm. The time required for reaching equilibrium condition estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of flask separated from biosorbent by filter and was analyzed for remaining Cu (II) and Zn (II) concentration in the sample. The amount of Cu (II) and Zn(II) sorbed per unit mass of the biosorbent was evaluated by using Eq. 4:

$$q = \frac{V(C_i - C_f)}{s} \quad (3)$$

RESULTS AND DISCUSSION

Effect of pH

The most important single parameter influencing the sorption capacity is the pH of the adsorption medium. Biosorption capability of waste biomass (Bamboo) for Cu(II) and Zn(II) (100 mg/L) in the single metal sorption system at different pH values (3 to 6) is presented in Fig. 1

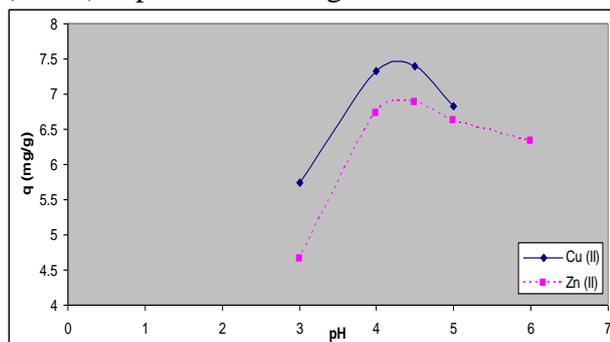


Fig. 1: Effect of pH on ions uptake [Co=100 mg/L, t=1hr, w=1.0 g/100 mL, mixing speed=170 rpm and Temp. =25°C]

It can be noticed from Fig. 1 that the uptake of copper increased from 5.75 mg/g at pH=3 to 7.39 mg/g at pH=4.5 and then decreased to 6.83 mg/g at pH=5 but the uptake of zinc increased from 4.65mg/g at pH=3 to 6.88 mg/g at pH=4.5 and then decreased to 6.32 mg/g at pH=6.

The adsorption of metal ions depends on solution pH, which influences electrostatic binding of ions to corresponding metal groups. The maximum biosorption of Cu (II) and Zn (II) was observed at pH 4.5. When pH was further increased up to 5 and 6.0 for copper and zinc respectively, the percentage adsorption is decreased. Because OH⁻ ions increased the hindrance of diffusion as well as some of the divalent cations may react with OH⁻ ion and precipitated and thereby decreased the free metal ions available in the solution. At lower pH, there may be competition between H⁺ and metal ions and thus decreased the adsorption capacity of biomass for the metal ion. These results are in close agreement with Shafqat et al. [22].

The pH of the metal solution plays a crucial role in biosorption process. As the pH is shifted, the equilibrium will also shift. The best initial pH of Cu(II) and Zn(II) onto waste biomass (bamboo) was observed at pH=4.5. Thus, all further experiments were performed at pH=4.5.

Effect of Dosage

Effect of biosorbents dosage on percentage removal of Cu(II) and Zn(II) was investigated by varying adsorbents dosage in the range of 0.5 g/100 mL to 1.5 g/100 mL and shown in Fig. 2.

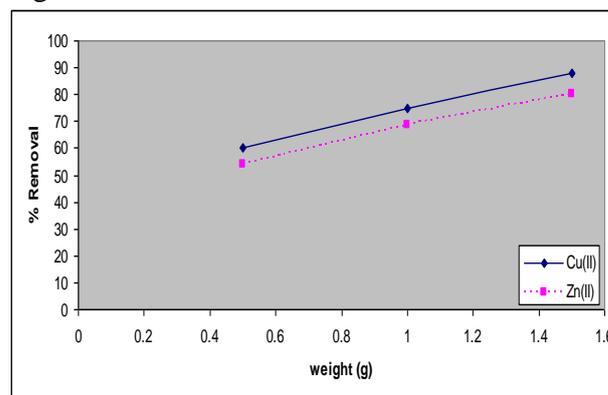


Fig. 2: Effect of biomass (bamboo) dosage on ions percentage removal. [Co=100 mg/L, t=1hr, mixing speed=170 rpm, pH=4.5 and Temp. =25°C]

From Fig. 2, the phenomenon of increase in percentage removal of Cu (II) and Zn (II) with increase in adsorbent dose due to the increased surface area of the biosorbent, which in turn increases the number of binding sites.

Effect of mixing speed

Adsorption studies were carried out at varying mixing speeds (90-170) rpm. It was observed that the uptake of adsorption increased with the increase of stirring speed up to 170 rpm as shown in Fig. 3.

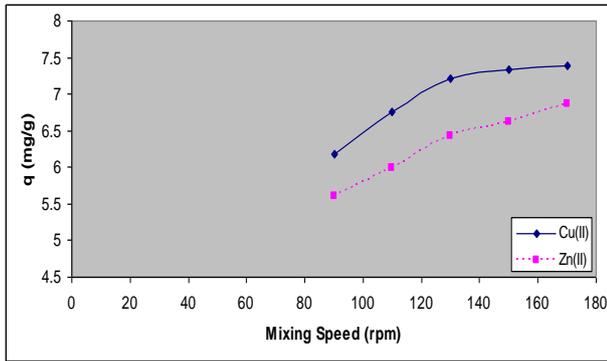


Fig. 3: Effect of mixing speed on ions uptake [Co=100 mg/L, t=1hr, w=1.0 g/100 mL, pH=4.5 and Temp. =25°C].

The increase of adsorption efficiency with the increase of mixing speed could be mainly due to resistance to mass transport in the bulk solution at lower mixing speeds. A thin liquid film surrounding the adsorbent particles offered resistance to mass transport by diffusion. As the mixing speed increased, there would be decrease in the thickness of the boundary film thereby decreasing the effect of film diffusion.

Effect of Metal Concentration

Equilibrium batch adsorption experiments were conducted keeping the dosage of biosorbent constant 1 g of biosorbent biomass per 100 mL of solution and pH=4.5 at different concentrations of metal ions for Cu(II) and Zn(II). Fig. 4 shows the effect of metal initial concentration on the equilibrium uptake for biomass.

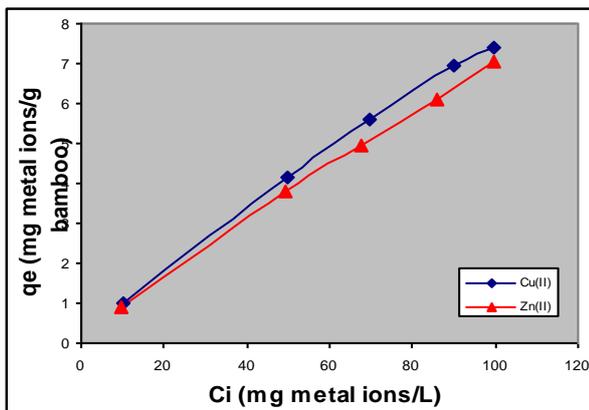


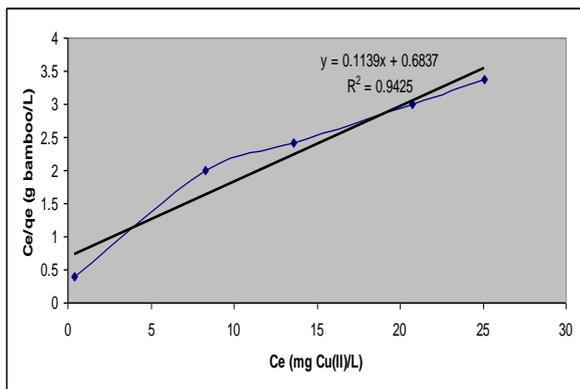
Fig. 4: Effect of Cu (II) and Zn (II) initial concentration on the equilibrium uptake for

bamboo biomass [mixing speed=170 rpm, t=1hr, w=1.0 g/100 mL, pH=4.5 and Temp.=25°C]

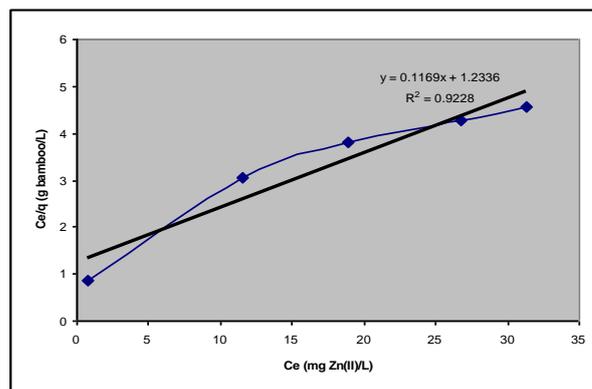
It was observed that the uptake capacity increased with the increased in initial metal concentration this is because at higher initial solute concentrations, the ratio of the initial amount of solute to the available surface area is high.

Adsorption isotherms were used to characterize the interaction of each copper species with the biosorbent. This provides a relationship between the concentration of metal ions (Cu (II) and Zn (II)) in the adsorption medium and the amount of metal ions adsorbed on the solid phase when the two phases are at equilibrium. In order to analyze adsorption isotherms, Langmuir and Freundlich adsorption isotherms [21] were used to adjust (fit) the experimental data obtained for biosorption of Cu (II) and Zn (II) from copper and zinc solution by bamboo biomass.

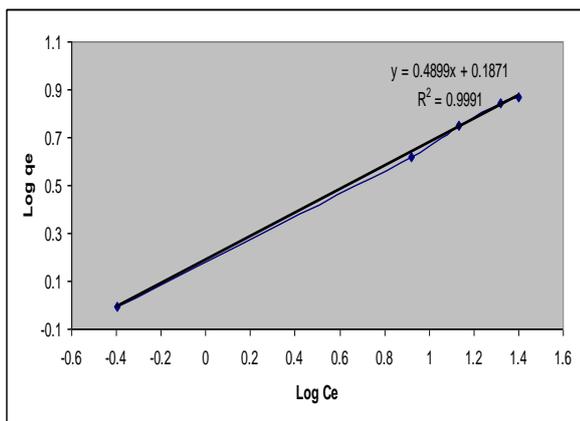
The adsorption constants (the ultimate sorption capacity (kF) and the sorption intensities (n) in the Freundlich model and the maximum uptake capacity (qmax) and the equilibrium constants (b) in the Langmuir model) and correlation coefficients obtained from the linearized Langmuir and Freundlich isotherms are provided in Fig. 5 and Fig. 6.



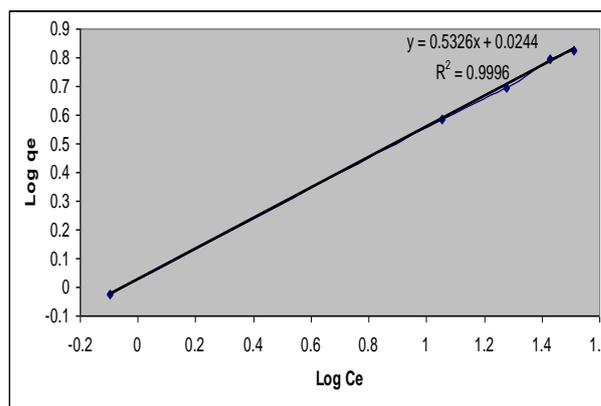
(a) Linearized Langmuir equation.



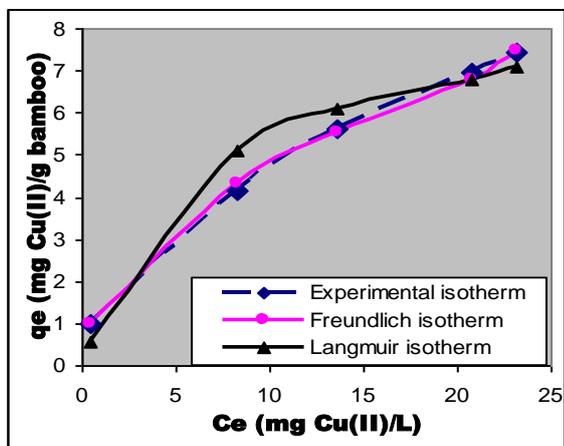
(a) Linearized Langmuir equation



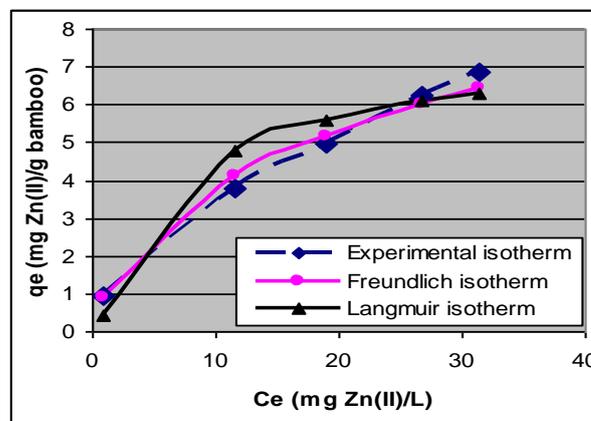
(b) Linearized Freundlich equation.



(b) Linearized Freundlich equation.



(c) Experimental and adjusted isotherms.



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Fig. 5: Equilibrium biosorption isotherms [for $C_0=10-100$ mg/L] for Cu (II) ions [mixing speed=170 rpm, $t=1$ hr, $w=1.0$ g/100 mL, pH=4.5 and Temp.=25°C].

Fig. 6: Equilibrium biosorption isotherms [for $C_i=10-100$ mg/L] for Zn (II) ions [mixing speed=170 rpm, $t=1$ hr, $w=1.0$ g/100 mL, pH=4.5 and Temp.=25°C]

Table 1: Summary of Freundlich and Langmuir equilibrium biosorption isotherms results.

metal	Linear Freundlich isotherm constants			Linear Langmuir isotherm constants		
	kF	1/n	R2	qm ax	b	R2
Cu(II)	1.5	0.48 9	0.99 9	8.7	0.16 6	0.9 7
Zn(II)	1.1	0.53 2	0.99 9	8.5	0.09 4	0.9 6

The parameters of the two models and the correlation coefficient (R2) for each model was calculated and shown in Table 1.

Results in Table 1 show that, the 1/n values are less than 1. This indicates that the isotherms can be characterized well by a convex Freundlich isotherm (favorable type) because low values of the sorbate liquid – phase concentration yield large values of the solid-phase concentration. When 1/n values greater than one (concave curve), the isotherm is considered to be unfavorable for sorption because high values of the liquid-phase sorbate concentration are required to get sorption to occur on the sorbent. Then the Freundlich isotherm parameters 1/n measures the intensity of metal ions on the biomass surface [25].

It is observed from Table 1, Fig. 5 and Fig. 6 that the equilibrium data are well represented by Freundlich isotherm equation when compared to Langmuir equation.

The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multilayer adsorption.

Although both heavy metals (Cu(II) and Zn(II)) were adsorbed to various extent by the waste biomass (Bamboo), the order of adsorption at all concentration was: Cu(II)>Zn(II) (i.e. the sorption rate of Cu(II) is greater than that of Zn(II)).

Effect of Temperature

The effect of temperature on the Cu (II) and Zn(II) sorption from aqueous solutions by bamboo was studied by varying the temperature between 20 and 35 °C as shown in Fig.7

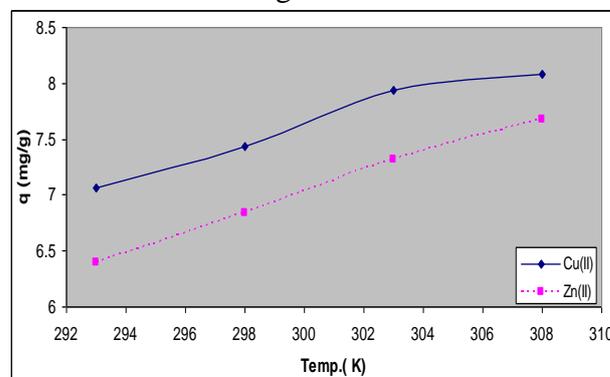


Fig.7: Effect of temperature on Cu (II) and Zn (II) uptake [$C_0=100$ mg/L, $t=1$ hr, $w=1.0$ g/100 mL, $pH=4.5$ and mixing speed= 170 rpm]

The initial concentration was fixed at 100 mg/L and initial pH was adjusted at 4.5, it can be seen that the uptake increases as the temperature increases. This behavior confirms that the adsorption process is endothermic process. Our results are in a good agreement with those obtained for removal of copper ions using dehydrated wheat bran [26]. This is because the attractive forces between biosorbent surface and metal ions are stronger and the sorption increases. This behavior is typical for the adsorption of most metal ions from their solutions onto natural materials.

Also, it can be noticed that the sorption of metal ions (Cu(II) and Zn(II)) increased slightly with the increase in temperature up to 308 K. This trend of temperature was also observed by Qaiser, et al. [27] for Cr(VI) biosorption by tree leaves.

At high temperature, the diffusion increases, due to the increased tendency of the metal to interact with the biosorbent surface, which results in an increase in sorption as temperature increases. The increase in the adsorption with increasing of temperature

suggests strong adsorption interactions between functional groups of biomass surface and the metal ion, which support the chemisorption.

CONCLUSIONS

The biosorption of metal ions named Cu (II) and Zn (II) onto bamboo plant led to the following conclusions:

Best biosorption of metal ions occurred at pH 4.5.

The adsorption of metal ions (Cu (II) and Zn (II)) per unit weight of Bamboo decreased as the percent adsorption increased with increasing the adsorbent dosage.

The uptake capacity of bamboo increased with the initial metal concentration, temperature and mixing speed increased

Bamboo has proved to be an efficient for the removal of Cu (II) and Zn (II) ions from aqueous solutions with low concentrations (10-100 mg of metal ion/L) at a laboratory scale. So its utilizing in industrial waste water treatment plants would be convenient to provide economic metal decontamination of large amounts of waste waters of low concentrations waste streams.

The single component isotherms for Cu (II) and Zn(II) ions indicated that the biosorption of these metal ions onto bamboo (each one alone) for low range concentration (10-100 mg/L) satisfied the Langmuir and Freundlich isotherms. But Freundlich model represented the data a little better than Langmuir one. According to the Freundlich isotherm constants, the adsorption of metals was in the order of: Cu(II)>Zn(II).

The adsorption uptake capacity for copper larger than the adsorption uptake capacity for zinc for all conditions because the ionic radius for copper smaller than the ionic radius for zinc.

Acknowledgment

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Nomenclatures

Symbol	Definition	Units
b	Longmuir equilibrium adsorption constant	L /mg
C1	Concentration of metal ion in stock solution	mg/L
C2	Concentration of metal ion in diluted solution	mg/L
Ce	Metal ion concentration in solution at equilibrium	mg/L
Ci	Initial metal ion concentration in solution,	mg/L
kF	Freundlich constant related to adsorption capacity	(g/L)-1/n
n	Freundlich constant related to intensity	
q	Metal uptake	mg/g
qe	Metal uptake at equilibrium	mg/g
qmax	Maximum metal uptake	mg/g
R2	Square correlation coefficient	
T	Absolute temperature	K
t	Contact time	min.
V	Volume of initial metal ion solution used	L
V1	Volume of stock solution	L
V2	Volume of diluted solution	L

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