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Biosorption of Copper (II) from Aqueous Solution using *Oscillatoria.Splendida*

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Abstract: Water is an essential for sustaining life and environment that we have always thought to be available in abundance and free gift of nature. Excessive Copper concentration has been reported in ground waters of more than 20 developed countries including India where 19 states are facing acute diarrhea, Stomach Cramping, Vomiting problems.

This thesis presents results pertaining to the adsorptive studies carried out on Copper removal onto algae bio sorbent (*OscillatoriaSplendida*). Batch sorption studies were performed and the results revealed that bio sorbent demonstrated able to absorb the Copper. Influence of varying the conditions for removal of Copper, such as the Copper concentration, the dosage of varying the conditions for removal of Copper, such as the Copper concentration, the dosage of adsorbent, the size of adsorbent ,the concentration of metal solution studies were investigated. Experimental data showed good fit with the Langmuir's adsorption isotherm model. Maximum Copper sorption was observed at Operating.

It was observed that the metal uptake increase and percentage adsorption of the metals decrease with increase in the initial metal ion concentration. It reveals that the effect of different adsorption particle on the adsorption of copper is significant. The adsorption of the metal is decreased with increase in particle size for *OscillatoriaSplendida*. The amount of copper adsorbed increases marginally in adsorbent dosage of *OscillatoriaSplendida*.

Key Words: Adsorbent, Adsorption Isotherms, Biosorption, Copper, *Oscillatoria Splendid a*.

Introduction:

Copper is an essential trace nutrient to all high plant and animal life. In animals, including humans, it is found primarily in the blood stream, as a co-factor in various enzymes and in copper-based pigments. However, sufficient amounts of copper can be poisonous and even fatal to organisms (Merck, 2008).For instance, the extreme consumption of copper leads to gastrointestinal problems, kidney damage and anemia and lung cancer. In addition, it is toxic in its ionic form at concentrations above 5 mg/L. For these reasons, the US-EPA and WHO organizations have recommended copper concentration in drinking waters not to exceed 1.3 PPM (Zanaty et al., 2013)

Biosorption is a process that utilizes inexpensive dead biomass to sequester toxic heavy metals. Biosorption has retained a great attention for the last decades as an alternative to conventional processes (such as precipitation, ion exchange and complexing resins, membrane processes, solvent extraction etc.) for the removal of metal ions from dilute solutions. An efficient biosorbent requires a series of properties to be

combined: (a) low cost, (b) large availability, (c) high efficiency and affinity (in terms of both equilibrium and kinetics), (d) sufficient stability (mechanical and chemical), (e) possible recycling showed the high efficiency of biomass, its cost-effectiveness and reusability after several sorption/desorption cycles. Brazil profits from a great diversity and abundance of biomass that can be applied to metal recovery: agriculture wastes, biopolymers, bacterial biomass, fungal biomass and algal biomass, for example. Brazilian coasts are offering a number of different algal biomass that could be used for metal biosorption, especially brown algae. (S.J. Kleinübing *et al.*, 2011) Biosorption can be defined as the ability of the biological material to accumulate heavy metals through metabolically mediated or physiochemical pathways of uptake (Nadeem *et al.*, 2008). Many chemical reactions are involved in the process of biosorption like ion exchange, complexation, chelation and adsorption by physical forces. Furthermore, numerous chemically active groups are responsible for biosorption viz carboxyl, hydroxyl, carbonyl, amine, imine, amide, sulfhydryl, thioether and sulfonate (Zafar *et al.*, 2007).

2. Materials and Methods:

2.1. Materials and Methods:

The *Oscillatoria Splendida* used in this study was collected from fresh water (rivers, wells etc.). The collected material was washed for several times then it was kept drying in sunlight for nearly 15 days. The dried material was powdered using domestic mixer. In the present study the powdered material is separated into 4 different fractions using sieves were then directly used as adsorbent without pretreatment.

By taking 3.92 gm of copper sulphate in 1000 ml Volumetric flask and make up with the distilled water gives 1000 ppm metal stock solution. Then prepared 20, 40, 60, 80 and 100 ml from 1000 ppm metal stock solution in 5 different 1000 ml volumetric flasks and make up these flasks with distilled water.

2.2. Adsorbent Characterization:

They occur in island saline lakes, and a few species tolerate temperatures up to 56-60°C. Some species are mat-formers in streams and a number are planktonic in fresh water lake and warmer marine waters. A few species occur in terrestrial habitats subjected severe drying or in a shallow ephemeral freshwater in Polar Regions where freeze-drying accompanies winter. *Oscillatoria Splendida* species have been associated with toxic blooms. *Oscillatoria Splendida* species have a worldwide distribution in fresh-water, marine, and brackish waters.

These genera are considered members of the order *Oscillatoriales* which all filamentous cyanobacteria that only produce vegetative cells. They do not produce Heterocysts (non-photosynthetic cells that fix nitrogen) or akinetes (resting cells that later reproduce). It is Gram-negative and its size is Trichome is 1.0 - 100+ micrometers in diameter. Production of hepatotoxins and neurotoxins has been observed in some species of these genera.

Mechanism of Adsorption: Quantitative analysis by Atomic Absorption Spectrometer:

In the atomic absorption process light at the resonance wavelength of initial intensity I_0 is focused on the flame cell containing ground state atoms. The initial light intensity is decreased by an amount determined by the atom concentration in the flame cell. The light is then directed on to the detector where the reduced intensity I is measured. The amount of light absorbed is determined by comparing I to I_0 .

The atomic absorption spectrometer used for present study consists of back ground connection accessory. It is designed for the use with flame absorption, flame emission techniques. A efficiency burner system offers both spoiler and impact head for optimal performance with all sample types with built in gas controls.

Standards required for analysis of the metal required were prepared according to the data given under how spoiler conditions.

Before switching on the instrument the pressure reading of air and acetylene were checked. Then lamp of the required metal was placed in proper place and parameters viz., lamp current, integration time, number of replicates, liner or non liner mode, number of standards with concentration were entered.

3. Results and Discussion:

3.1. The Effect of Contact Time:Effect of contact time on percentage adsorption of copper onto *OscillatoriaSplendida* was studied over an agitation time of 1-60 min, using 0.1 g of *OscillatoriaSplendida* 50 ml of 10 ppm solution of individual metal concentration at pH 6, temperature 303⁰K and 180 rpm shaking speed.The data obtained from adsorption of copper ions on to the *OscillatoriaSplendida* showed that the contact time of 45 mins was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time it is shown in Fig1. Therefore, the uptake on adsorbed copper concentrations at the end 45 mins is given as the equilibrium value.

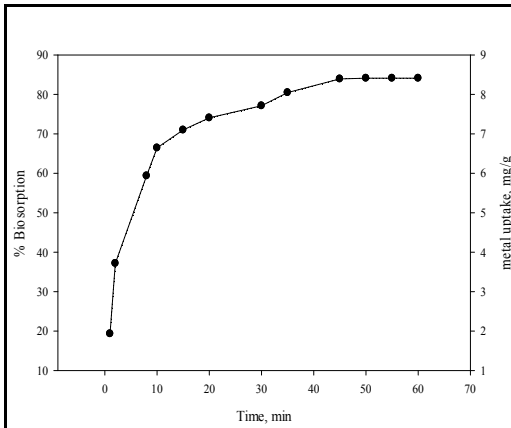


Figure 1: Effect of contact time on the percentage removal of Copper.

3.2. Effect of Metal Ion Concentration:

Experiments were under taken to study the effect of initial copper concentration on the copper removal from the solution. From the data the copper metal uptake increases and percentage adsorption of the metals decreases with increase in the driving force i.e. concentration gradient. However, the percentage adsorptions of copper ions on *Oscillatoria* were decreased from 84 to 70%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of copper displays an opposite trend which is shown in Fig2 .At lower concentration, almost all the copper present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher initial copper ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites.

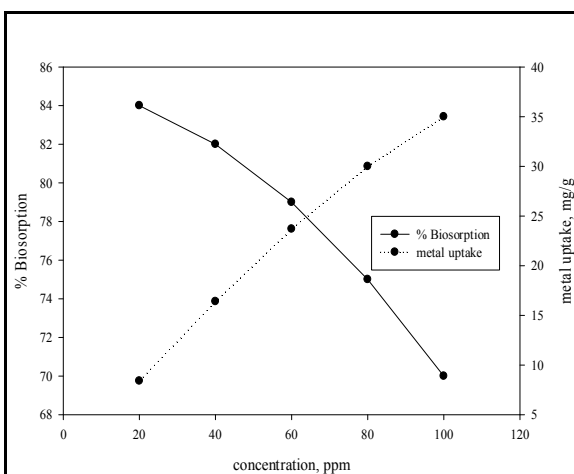


Figure 2: Effect of concentration on the percentage Biosorption of Copper.

3.3. Effect of Adsorbent Size:

The effect of different adsorbent particle sizes (85 to 200 μm) on percentage removal of copper on *Oscillatoria Splendida* was investigated and showed in Fig3. It reveals that the adsorption of copper on *Oscillatoria Splendida* decreases from 84 to 75% with the increases in particle size from 85 to 200 μm with 20 mg/L copper of concentration in solution. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases adsorption capacity. A marginal decline was also observed in uptake of copper with increases in size of the particle.

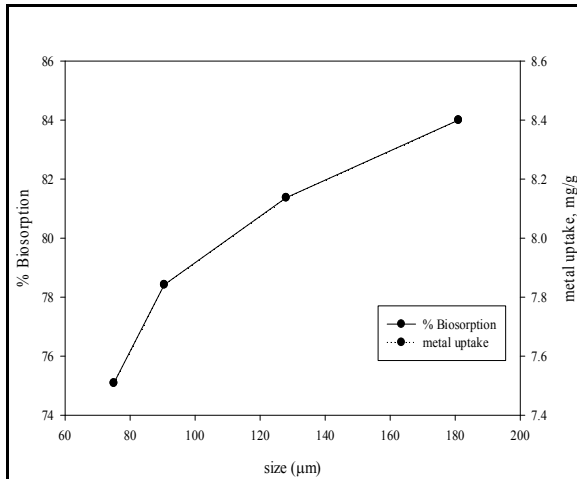


Fig: 3 Effect of adsorbent size on percentage Biosorption.

3.4. Effect of Adsorbent Dosage:

The amount of copper adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 at an initial concentration of 20 mg/L. The percentage copper removal was marginally increased from 84 to 94.66 for an increase in adsorbent concentration from 0.1 to 0.5 g. This show that very small dosage of adsorbent i.e 0.1g is sufficient to treat about 50ml of 20 mg/L copper concentration solution effectively which is shown in Fig4. Although binding sites available for adsorption depend upon the biomass added to the solution (Bhatti et al.,2007)

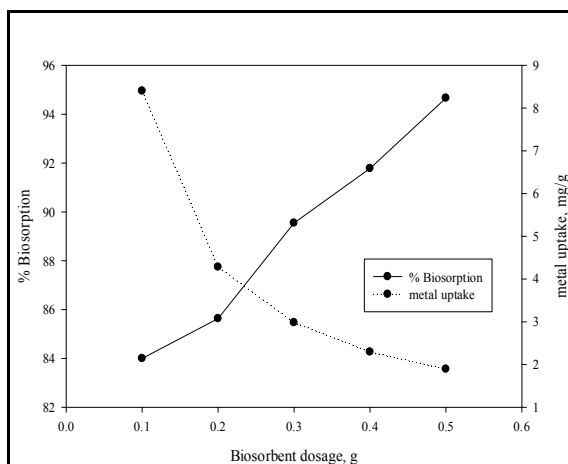


Fig:4 Effect of adsorbent dosage on percentage Biosorption.

2.6. Metal uptake:

The Cu^{2+} uptake were calculated by the simple concentration difference method using the mass balance equation:

$$q_e = V(C_i - C_e) / M$$

where V is the volume of the solution (L), C_i and C_e are the initial and final concentrations (mg/L) in solution and M is the mass of the sorbent (g). All data represent the means of three independent experiments.

2.7. Equilibrium isotherm modeling

Equilibrium sorption data is interpreted mostly by equilibrium isotherms. Isotherm parameters and essential thermodynamic assumptions of these isotherms provide insight into both sorption mechanisms and surface properties and affinities of a sorbent.

Three most common isotherms were employed to explain solid–liquid equilibrium in this study.

2.7.1. Langmuir isotherm

The Langmuir isotherm theory considers monolayer coverage of adsorbate over a homogeneous adsorbent surface (Langmuir, 1918). Specific homogeneous sites within the sorbent are assumed to be occupied by sorbate with no further adsorption at the site. The Langmuir parameters can be determined from a linearized form of equation represented by

$$q_e = q_{\max} * b * C_e / (1 + b C_e)$$

2.7.2. Freundlich isotherm

Freundlich isotherm assumes that as the adsorbate concentration increases, concentration of sorbate on the sorbent surface also increases (Freundlich, 1906). Mathematically, it can be expressed as

$$q_e = K C_e^{1/n}$$

$$\log q_e = \log K + (1/n) \log C_e$$

where q_e is metal ion sorbed (mg/g), C_e (mg/L) is the equilibrium concentration of metal ion solution, k and n are Freundlich

4. Conclusions:

The biomass of the *Oscillatoria Splendida* demonstrated a good capacity of adsorption, highlighting its potential for efficient treatment processes. The data obtained from the aqueous solution of copper ions on the *Oscillatoria Splendida* showed that a constant time of 45 min was sufficient to achieve equilibrium and adsorption did not change with further increase in contact time. From the data the copper metal uptake increases and percentage adsorption of the metals decreases with increase in the driving force i.e. concentration gradient. However, the percentage adsorptions of copper ions on *Oscillatoria* were decreased from 84 to 70%. It was observed that the metal uptake increase and percentage adsorption of the metals decrease with increase in the initial metal ion concentration. The adsorption of copper on *Oscillatoria Splendida* decreases from 84 to 75% with the increases in particle size from 85 to 200 with 20 mg/L copper of concentration in solution. It reveals that the effect of different adsorption particle on the adsorption of copper is significant. The adsorption of the metal is decreased with increase in particle size for *Oscillatoria Splendida*. The percentage copper removal was marginally increased from 84 to 94.66 for an increase in adsorbent concentration from 0.1 to 0.5 g. The amount of copper adsorbed increases marginally in adsorbent dosage of *Oscillatoria Splendida*. The experimental data gave good fit with Langmuir isotherm and the adsorption coefficient agreed well with the conditions of favourable adsorption which is shown in Fig 5&6 and also shown in Table 2.

Table 1: Range of variables covered in the present study.

Variables	Minimum	Maximum	Max/Min
Time of contact (min)	1	60	60
Initial metal ion concentration (Mg/L)	20	100	5
Average size of the adsorbent (μm)	85	200	2.35
Adsorbent dosage (g)	0.1	0.5	5

Table 2: Equilibrium constants for copper onto *Oscillatoria Splendida*

Isotherm	Constants	Copper
Langmuir	Q_{max} (mg/g)	32.36
	b (L/mg)	0.0618
	R^2	0.9964
Freundlich	K_f (mg/g)	3.162
	n	0.5663
	R^2	0.9654

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