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Biosorption Capacity of Dried Spirogyra on Heavy Metals

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Abstract: An increasing number of hazardous heavy metals are discharged into the environment through natural and anthropogenic activity, creating serious environmental problems. The toxicity of chromium and copper affects soil and water, which further harms microbes, animals and plants. Biosorption has proved to be an effective method in expulsion of heavy metals from environment. Accumulation of heavy metals by algae has been observed by earlier works. In this study, *Spirogyra*has been examined for biosorption capacity of copper and chromium in different conditions. Various parameters, such as, initial metal concentrations; biomass and pH were considered for the experiment. The biosorption capacity was checked by flame atomic absorption spectrophotometer. The optimum metal concentrations were 10 mg/L for chromium and 20 mg/L for copper. 2.5 g/L biomass was observed to show the maximum biosorption at pH 6. The contact time throughout the experiment was maintained for 1 h.

Keywords: chromium, copper, biosorption, Spirogyra.

Introduction

Metals having a specific gravity of 5 g/cm³ or more are considered as heavy metals. Almost sixty heavy metals are known in Earth¹. Although heavy metals are essential for human body as trace elements, they become hazardous in high concentration. Major heavy metals, such as, copper, lead, chromium, nickel, zinc, arsenic harms humans and animals as well as plants when exposed in excessive concentrations². The release of heavy metals in the environment mainly occurs through various anthropogenic activities including fossil fuel burning, smelting processes, mining, industrial effluents and transport sectors. The presence of heavy metals in environment has negative impact on both micro and macro organisms and in turn affecting human health³.

Despite having various physical and chemical methods of removal of metal, the metal concentrations in environment, specifically water and soil is showing an increasing pattern. This brings to the need for efficient biological techniques to improve heavy metal removal from environment⁴. The utilization of living organisms, such as, plants and microbes in biologically removal of toxic organic wastes have gained importance gradually. The process of degrading wastes at controlled conditions using living organisms are termed as bioremediation⁵. Phytoremediation along with bioaugmentation plays an effective role in removal of heavy metals like arsenic, chromium, copper and magnesium. *Jatropha multifida* along with microorganisms such as *Pseudomonas*, *Azotobacter* and *Rhizobium* remove heavy metals. Biosorption requires identification of proper adsorbents that are able to remove the heavy metals with high efficiency.

The first biosorption study of heavy metals was done by Adams and Holmes in the year 1935 where they used tannin resin and *Acacia mollissima*. Several fungi and brown algae are able adsorb heavy metals.

Biosorption is observed to be carried out with a fast surface reaction followed by slow uptake of the metal. Surface adsorption occurs in the first step there after starts the diffusion of metal ions in the cellular structures⁷. *Acanthopora spicefora*, a red algal species, showed immense biosorption activity against a series of heavy metals, such as, Cr (VI), Cr (III), Hg (II), Cd (II) and Pb (II)⁸. Seaweeds, fungi and bacteria can also act as biosorbent for certain heavy metals. Seaweeds, due to their macroscopic nature are considered as a convenient heavy metal adsorbent. *Saccharomyces cerevisiae* executes good biosorptive activity against metals like cadmium and copper⁹.

Previous studies confirm the removal of metals like chromium, copper, iron, manganese and zinc ions using live *Spirogyra* biomass¹⁰. The aim of the present study is to determine the biosorption capacity of dried *Spirogyra* biomass against chromium and copper. In this experiment the filamented, green, unbranched *Spirogyra* are collected and dried for determination of removal of chromium and copper.

Materials and Methods

Chemicals used

Analytical grade chemicals purchased from Sigma Aldrich and S.D Fine-Chem were used throughout the experiment. Copper sulphate was purchased from S.D Fine-Chem.

Collection of Sample

The algal biomass wascollected from pond water in Thanjavur district, Tamil Nadu.

Isolation and Maintenance of Spirogyra

The algal biomass collected from the water body was washed with distilled water and inoculated in Bold's basal medium maintaining the temperature at 20°C. The culture was kept in 12/12 light and dark cycle¹¹.

Preparation of Biosorbent

The algal biomass was thoroughly washed with distilled water for removal of dirt and other impurities. Excess water was squeezed out and further kept on filter paper to reduce the water content. The biomass was sun dried for 4 d followed by drying them in oven at 70°C for 24 h. The dried biomass was ground and sieved to select the particles between 150 and 250 mess sizes.

Preparation of stock Solutions

Copper Solution

0.393 g hydrated copper sulphate (CuSO₄.7H₂O) was dissolved in 1 L distilled water to prepare the stock solution for copper. pH range of 1-10 was maintained by mixing 1 N HCl and 1 N NaOH¹².

Chromium Solution

3.74 g of analytical grade potassium chromate was dissolved in 1 L distilled water resulting in preparation of stock solution for chromium. The working concentrations were obtained by diluting the stock solution with distilled water. The pH was adjusted with addition of HCl and NaOH solutions.

Batch Biosorption Studies of Copper and Chromium Using Spirogyra

The adsorption features of biosorbent*Spirogyra*were investigated as a function of pH, initial heavy metal concentration, biosorbent dosage and contact time ¹³. 2.5 g of algal biomass was inoculated to 100 ml of individual heavy metals solutions and the flasks were kept at room temperature at 120 rpm rotary shaker. The pH of the samples was adjusted to the required value with 0.1M of HCl or NaOH throughout the experiment. At the end of the adsorption, 10 ml sample was collected and centrifuged. The supernatant was observed for presence of metal residues by analyzing the absorbance on Flame atomic absorption spectrophotometer. The experiments were carried out in triplicates.



Figure 1.Optimization of Metal Concentration of Chromium and Copper



Figure 2.Optimization of Biomass Concentration of Spirogyra in biosorption of Chromium and Copper



Figure 3.Effect of pH on biosorption of Chromium and Copper by Spirogyra

Results and Discussions

Optimization of Metal Concentration

The concentration of chromium and copper in the synthetic effluents was initially determined for the maximum biosorption. Controls were prepared for each sample to nullify the effect of metals saturation during the experiment.

Sl. No.	Initial Chromium Concentration (mg/L)	Control Readings	Final Chromium Concentration (mg/L)	Actual Biosorption	Percentage Biosorption
	(ing/L)	(IIIg/L)			(70)
Ι.	5	4.971	1.501	3.499	69.98
2.	10	9.652	2.296	7.704	77.04
3.	20	19.830	8.606	11.394	56.97
4.	50	48.774	33.376	16.624	33.24
5.	80	77.058	67.600	12.400	15.5
6.	100	99.919	86.764	13.236	13.236

Table 1.Optimization of Chromium concentration

Optimization of Chromium

The adsorption capacities determined at different chromium concentrations at an adsorbent (*Spirogyra* biomass) dosage of 2.5 g/L at pH 6 for 1 h contact time were recorded. The percentage biosorption increased with increasing metal concentration upto 10 mg/L followed which the biosorption started decreasing.

Sl. No.	Initial Copper Concentration (mg/L)	Control Readings (mg/L)	Final Copper Concentration (mg/L)	Actual Biosorption (mg/L)	Percentage Biosorption (%)
1.	5	4.235	1.765	3.235	64.70
2.	10	8.997	2.506	7.494	74.94
3.	20	18.904	4.397	15.603	78.01
4.	50	48.643	14.979	35.021	70.04
5.	80	77.413	29.796	50.204	62.75
6.	100	98.002	40.177	59.823	59.82

Optimization of Copper

Optimization of adsorption capacities for copper concentrations was performed with adsorbent dose of 2.5 g/L at pH 6 for 1 h contact time. The biosorption efficiency increases upto 20 mg/L after which it starts decreasing.

Spirogyra, in previous study, showed better biosorption capacity of copper when compared to certain other heavy metals. Due to high specificity of the active binding sites of *Spirogyra* biomass for copper, the algae adsorbed copper more easily resulting in its removal¹⁰.

Optimization of Biomass

Table 3.Optimization of Biomass of Spirogyra on exposure to Chromium

Sl. No.	Initial Chromium Concentration (mg/L)	Adsorbent dose (g/L)	Final Chromium Concentration (mg/L)	Actual Biosorption (mg/L)	Percentage Biosorption (%)
1.	10	1	7.954	2.046	20.46
2.	10	2	5.134	4.866	48.66
3.	10	2.5	2.395	7.605	76.05
4.	10	3.5	3.407	6.593	65.93
5.	10	5	6.654	3.346	33.46

The effect of adsorbent dose was studied with varying amount of adsorbents at pH 6. The concentration of the both the metals were taken according to metal concentration optimized, that is, 10 mg/L for chromium and 20 mg/L for copper. The contact time of the adsorbent and the metal was maintained for 1 h.

The biosorption increased along with biomass concentration upto 2.5 g/L in both the cases. After 2.5 g/L of adsorbent, the biosorption rate showed declination. The higher biomass concentration caused screening effect of dense outer layer of cells, blocking the binding sites from metal ions resulting in lower metal removal per unit biomass.

SI.	Initial Copper	Adsorbent	Final Copper	Actual	Percentage
No.	Concentration	dose	Concentration	Biosorption	Biosorption
	(mg/L)	(g/L)	(mg/L)	(mg/L)	(%)
1.	20	1	17.886	2.114	21.14
2.	20	2	14.331	5.669	56.69
3.	20	2.5	15.568	8.432	84.32
4.	20	3.5	12.998	7.002	70.02
5.	20	5	14.159	5.841	58.41

Table	5.Change	in Bioso	rption ef	ficiencv	of <i>Spi</i>	<i>rogvra</i> on	exposure	to chro	omium	along	with r	bН
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Sl. No.	pH of Synthetic	Final chromium	Actual	Percentage
	Effluent	Concentration	Biosorption	Biosorption
		(mg/L)	(mg/L)	(%)
1	3	6.045	3.955	39.55
2	4	7.008	2.992	29.92
3	5	6.732	3.268	32.68
4	6	3.054	6.946	69.46
5	7	2.865	7.135	71.35
6	8	4.888	5.112	51.12
7	9	6.781	3.219	32.19

The overlange in Dieser prior enterency of Spire Q, were enpositive to copper along with p	Table 6	Change in	n Biosorption	efficiency	of Spirogyraon	exposure to	copper	along wi	th p]	H
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Sl. No.	pH of Synthetic	Final Copper	Actual Biosorption	Percentage
	Effluent	Concentration		Biosorption
		(mg/L)		(%)
1	3	17.965	2.035	20.35
2	4	17.036	2.964	29.64
3	5	16.017	3.983	39.83
4	6	14.007	5.993	59.93
5	7	13.061	6.939	69.39
6	8	15.984	4.016	40.16
7	9	15.083	4.917	49.17

Effect of pH

In order to determine the effect of change in pH in the efficiency of biosorption, the experiment was carried out with a range of pH from highly acidic to alkaline conditions. The time of exposure was maintained for 1 h with 2.5 g/L biomass concentration and sample concentration of 10 mg/L of chromium and 20 mg/L of copper individually.

The results denoted the dominance of pH 6.0-7.0 in which the most remediation was observed. There was a considerable change in efficiency of the process at extreme acidic and alkaline conditions of synthetic effluents of both chromium and copper. At lower pH, the protonated cell wall ligands repulse the metal cations

and do not allow the cell surface to adsorb the metal. With increase in pH, amino, phosphate and carboxyl group ligands are activated which supports in the sorption of heavy metals ¹⁴.

Conclusion

The study was conducted to understand the effect of Spirogyra as biosorbent for bioremediation of chromium and copper. The role of various factors affecting the process was also studied. *Spirogyra*proved to be a potential biosorbent for removal of chromium and copper. The experiment resulted that the algal biomass offered to be a better option than conventional physical and chemical processes used in heavy metal removal. The abundance of the *Spirogyra* biomass makes the substrate readily available and the process results to be of low cost with high efficiency.

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