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Algae as a biosorbent for the heavy metal removal from Tannery waste water

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Abstract* - *The findings of a research on algae as a biosorbent for heavy metal removal from Tannery waste water. The study's objectives included starting the metal bio-sorption process using pure and mixed cultures, administering metal ions to the model solution, and exposing the population to metal-containing wastewater. Various exposure periods were used to compare exposed samples' rates of metal biosorption to those of control samples to keep tabs on the process. The findings of this investigation indicate the efficiency of chlorophyta in the heavy metal biosorption process.

Keywords - Algae, Biosorbent, Heavy metal, Tannery waste water, Biosorption

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INTRODUCTION

Industrial discharge contains a wide range of organic and inorganic pollutants. Toxic and/or carcinogenic heavy metals are among the pollutants that pose a threat to humans and other living things. Pb, Zn, Cu, Ar, Cd, Cr, Ni, and Mercury are the most dangerous heavy metals found in a wide variety of products (Hg). A few causes include dyes containing metals, pesticides, fertilizers, fixing agents (which are added to dyes to improve dye adsorption into fibers), mordants, pigments, and bleaching agents. The limits on heavy metals in wastewater are tightening in developed countries. Indian authorities have set the current maximum contamination levels for certain metals at 0.05 parts per million (ppm) or more (milligrams per milliliter). Chromium is obtained in a variety of ways, including leather tanning, electroplating, nuclear power plants, and the textile sector (1).

Due to its carcinogenic properties, cadmium has been linked to a variety of health issues, including bone demineralization and renal failure. Cadmium is a carcinogen categorized as Category-I by the International Agency for Research on Cancer (IARC) and as Category B-I by the US Environmental Protection Agency (USEPA). It is found in metal refineries, smelting, mining, and the photography industry. To produce enzymes, tissue grows and bones are formed, copper is required in large amounts. It is dangerous and carcinogenic if consumed in excess levels of copper(II), which may lead to a variety of unpleasant side effects such as headaches, vomit, nausea, and even liver and kidney failure. The USEPA has set a limit of 1.3 parts per million (ppm) for copper in industrial effluents. There are industrial uses for copper, including smelting and mining as well as electroplating and surface polishing in electrical appliances and electrolysis in electronics. For example, nickel is a human carcinogen that may cause kidney and lung illness as well as digestive problems as well as skin irritations and rashes as well as pulmonary fibrosis when it is exposed to it in the environment. Zinc is essential for human health, but too much may lead to skin irritation, nausea, vomiting, and anemia, among other side effects. Lead, too, is harmful to human health since it damages kidneys, liver, the reproductive system, and the brain. Lead is also found in paint and gasoline. As a neurotoxic, mercury poses a threat because it may disturb the central nervous system. If the concentration is exceeded, it might cause pulmonary, chest, and dyspnea. When exposed to arsenic, people are more likely to develop cancers of the skin, lung, bladder, and kidneys, as well as experience muscular weakness, lack of appetite, and nausea (2-5).

Removal of heavy metals using traditional techniques

Heavy metals such as nickel, copper, zinc, cadmium, chromium, lead, and mercury are important contaminants that pollute fresh water reservoirs as a result of industry discharges of massive volumes of metal-contaminated wastewater. They accumulate in the environment, such as in the food chain, due to their persistent, non-biodegradable, and poisonous nature, and create major health problems. Many traditional treatment technologies have been utilized to remove heavy metals from polluted wastewaters throughout the previous few decades. Chemical precipitation, ultrafiltration, ion exchange, reverse

osmosis, electrowinning, and phytoremediation are some of the most often utilized procedures (6).

Biosorption

The biosorption process is aided by the presence of distinct functional groups in the cell walls of different biosorbents. Hydroxyl (found in alcohols and carbohydrates) and carboxyl are two functional groups capable of biosorbing heavy metals. Other functional groups include amino (found in proteins and nucleic acids), ester (found in lipids), and sulfhydryl (in fatty acids, proteins, and organic acids) (found in DNA, RNA and tissue plasminogen activator). In order to study and analyze the functional groups of a biosorbent that contribute to the removal of an individual metal, a variety of analytical methods can be used. These methods include titrations, infrared and energy-dispersive X-ray spectroscopies as well as X-ray absorption fine structure spectroscopies (7).

Algae as Biosorbent

Algae may be divided into microalgae and macroalgae. In fresh or salt water, macro-algae (sometimes called seaweeds) are multicellular plants. Brown, red, and green algae may be found in three distinct color varieties based on their level of pigmentation. Since algae's cell wall contains chitin, polysaccharides, proteins and lipids, all of which include key functional groups that aid in biosorption, they are able to absorb a lot of nutrients from the water they live in. Functional groups such as oxygen, nitrogen, sulphur, and phosphorus were shown to be the key contributors to algal heavy metal biosorption (8-11).

METHODOLOGY

Heavy metal

We selected Nickel and zinc as a heavy metal

Algae origin

We employed algae from two different cultures in the studies. *R. subcapitata* algae were used in Culture 1 from a lyophilized pure culture grown in the lab. Culture 2 consisted of a diverse population of algae.

The culturemedium

- SolutionI:NH_4Cl,1.5g;$MgCl_2 \times 6H_2O$,1.2g;$CaCl_2 \times 2H_2O$, 1.8g; $MgSO_4 \times 7H_2O$, 1.5g; and KH_2PO_4,0.16g.
- Solution II: $FeCl_3 \times 6H_2O$, 0.08g and disodiumedetate

(Na_2EDTA) × $2H_2O$, 0.1g.

- Solution III: H_3BO_3, 0.185g; $MnCl_2 \times 4H_2O$, 0.415g; $ZnCl_2$, 0.003g; $CoCl_2 \times 6H_2O$, 0.0015g; $CuCl_2 \times 2H_2O$, 0.00001g; and $Na_2MoO_4 \times 2H_2O$,0.007g.
- Solution IV: $NaHCO_3$,50g.

A total of ten cubic centimeters of basic solution I was placed in a 1 dm^3 volumetric flask, followed by 1 cm^3 samples of the other basic solutions (II, III, and IV); lastly, it was supplemented with deionized water up to a 1 dm^3 volume.

Tannery waste water

The wastewater utilized in the experiment was waste water from a Tannery.

Metal Determination in algae andwastewater

Algalculture

R. subcapitata culture 1 was first multiplied in 1 dm^3 round-bottomed flasks with cotton wool stoppers. A graft of clean *R. subcapitata* culture was injected after the newly prepared medium had been aerated for 30 minutes and the pH had been adjusted to 8.3 0.2. The flasks were placed on magnetic stirrers running in low gear to avoid the precipitation of salts in the medium. The culture was placed to a water tank for additional multiplication after reaching 6 dm^3.

Culture 2 was taken from a natural standing water reservoir and consisted of a mixed population of algae.

Both cultures were maintained at 24°C (2°C) and were constantly lighted with L36W/840 cool white fluorescent bulbs.

The procedure was monitored by taking regular measurements of the number of algae in the growth media. A microscope and a Sedgwick-Rafter Counting Cell were used to count the number of algae (specimens). The experiment started after generating a culture with a density of 2,400,000 specimens in 1 cm^3 of media.

Tannery *wastewaterExperiment*

A total of 50 cm^3 of *R. subcapitata*-containing growth media was placed in 200 cm^3 glass bioreactors (Culture 1). A total of six times the process was carried out: once every 1, 5, 10, 30, 40, 60, and 120 minutes. Zinc and nickel ions concentrations in wastewater and algal biomass were determined using this approach after an incubation time. The control sample consisted of wastewater that had not been exposed to algae.More or less the same number of algae was found in both cultures:

around 2,400,000 organisms per cubic centimeter.

All of the experiments were repeated twice (including the control sample).

METHOD USED

After a set incubation period, the concentration of metal ions in the algal biomass and in the culture medium or wastewater was measured to manage the biosorption process. The efficiency of the method was evaluated using the control samples as a benchmark. The concentrations of nickel and zinc in both cultures were determined before to the experiment. This was done at Chemistry and Biotechnology laboratory, K.M.C.Language University, Lucknow(U.P), India.

Mathematical description

The biomass's bio-sorption capability was calculated as follows:

$$q = \frac{(C_0 - C) \times V}{m}$$ ……..eq(1)

Where,C0 is the initial metal concentration in the solution (mg/dm3), C is the equilibrium metal concentration in the solution (mg/dm3), and m is the mass of dry bio-sorbent (g). Two kinetic models based on the sorption capacity of the bio-sorbent were used to determine the speed of the process and the factors that determine it: Lagergren's equation is used to represent first-order effects:

$$\ln(q_{eq} - q) = \ln q_{eq} - k_1 t$$ ……(2)

where q_{eq} and q are the mass of metal ions adsorbed on the bio-sorbent at equilibrium and in time t, respectively (g); and kI is the pseudo-first-order model's speed constant (min–1). Second-order, as shown by the equation:

$$\frac{t}{q} = \frac{1}{k_{II} q_{eq}^2} + \frac{1}{q_{eq}} t$$ ……(3)

Where, kII is constant of the speed of pseudo-second order model (g/mg·min).

RESULTS AND DISCUSSION

Experiment usingwastewater

The efficiency of nickel ions removal from wastewater was similar for both cultures in the early stages of the process, and was 0.31–0.32 mg/gd.m. in the first minute (Figure 1). The sorption of nickel by R. subcapitata algae was about 20% more effective than when employing a mixed population after the 20th minute. After 60 minutes, both cultures (Culture 1, 0.74 mg/gd.m. and Culture 2, 0.59 mg/gd.m.) had reached their maximal sorption capacity, removing 46.1 percent nickel from the wastewater in pure culture and 35.9 percent in mixed culture. Desorption of nickel ions from biomass to wastewater was found in both cultures after that period.

When Culture 2 was used instead of Culture 1, the effectiveness of removing zinc ions in the first minute was four times greater (Figure 1). In the 60th minute, both populations reached high zinc ion saturation (Culture 1, 3.05 mg/gd.m. and Culture 2, 3.70 mg/gd.m.) and had equal percentages of Zn ions removed (87.2 percent for pure population and 86.5 percent for mixed population).

To summarize, as compared to nickel, the effectiveness of zinc ions sorption was more than four times greater when employing R. subcapitata and more than six times higher when utilizing a mixed chlorophyta population after a one-hour incubation period.

It was determined that 1 hour is the ideal contact period for both populations for the most effective elimination of zinc and nickel ions from the model solution and effluent. The use of R. subcapitata to remove nickel ions from the model solution is the lone exception, in which case the effective contact time may be reduced to 5 minutes. Even so, 1 hour is required to reach the maximal sorption capacity in this situation.

The research found that independent of the kind of culture or the presence of other chemicals, zinc ions removal efficiency is high (about 86.5 percent–93.1%) (Figure 2). Because of the variety of functional groups at the binding sites, the mixed population should theoretically have a better efficiency of zinc ions bio-sorption. However, the results of the experiment demonstrate that R. subcapitata chlorophyta has a strong affinity for removing those ions.

Nickel is removed from wastewater at a greater rate than in the model solution, according to the experiment. Furthermore, in the case of wastewater, the efficiency of the process is higher when pure culture is used rather than mixed population, demonstrating that R. subcapitata has a better affinity for the removal of nickel (46.1 percent) in the presence of substances such as sulfates or surfactants used to wash equipment in the wastewater. The mixed population demonstrated to be a superior biosorbent (34.3%) than the pure culture (25.8%) in the case of the model solution having only minor quantities of salts as part of the culture medium and five entering metals, as predicted. In general, nickel ions biosorption effectiveness is low at this concentration and under these circumstances. Zinc ions have

been shown to hinder nickel sorption in two-component systems in experiments. This might explain why just a small fraction of those ions are removed.

To summarize, zinc ions removal efficiency was substantially greater than nickel removal efficiency, regardless of culture type (model solution, 88.1 percent –93.1 percent and wastewater, 86.5 percent –87.2 percent) (model solution, 25.8% –34.3 percent and waste-water, 35.9% –46.1 percent). These findings back up previous studies that showed that bio-sorption-capable bacteria can effectively totally or partly treat wastewater containing dozens of milligrams of nickel and zinc ions per liter, with nickel removal rates of over 50% and zinc removal rates of over 90%.

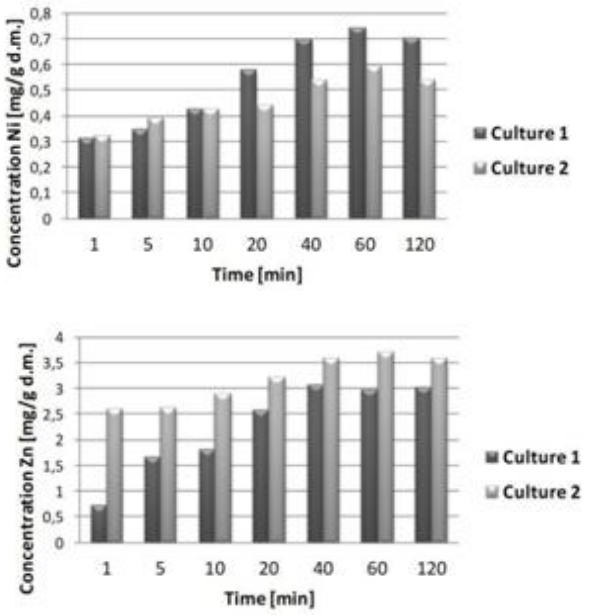

Figure 1: Nickel and zinc contents in the algal biomass vary depending on exposure period (wastewater)

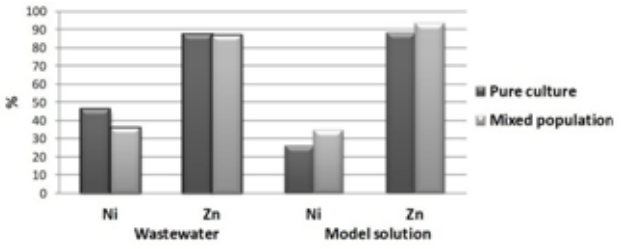

Figure 2: Nickel and Zinc Percentage removal after 60 min

Bio-sorptionkinetics

For both cultures, pseudo-first order (Eq. 2) and pseudo-second order (Eq. 3) kinetic models were examined to see whether they fit the experimental kinetics data (Table 1).

By graphing t/qt vs. t, the pseudo second-order adsorption parameters qeq and kII were calculated (Figure 3 and 4).

By comparing the data, it can be inferred that the second-order kinetic model better represents the bio-sorption process in both cultures, independent of medium type (model solution or sewage). Higher R2 correlation coefficients and q values, which are significantly closer to the experimental values (qexp) in the pseudo-second order model than in the pseudo-first order model, show this. Other researchers investigating the usage of other kinds of bio-sorbents reported similar findings. The pseudo-second-order kinetic model proposes that the bio-sorption process is constrained by the rate of chemical interactions between heavy metal ions and functional groups found in bio-sorbent cell walls.

Table 1: Kinetics parameters for the bio-sorption of Nikel and Zinc

	Pseudo –First order				Pseudo –second order		
	-1 q_{exp}(mg/g)	q_{eq}(mg/g) k_I (min)		R^2	2 q_{eq}(mg/g)	k_{II}(g/mg·min)	R
Nickel							
Model study—Culture 1	0.348	0.185	0.0659	0.6579	0.343	2.1060	0.9979
Model study—Culture 2	0.805	0.541	0.0498	0.7392	0.809	0.1213	0.9992
Wastewater—Culture 1	0.743	0.371	0.0541	0.4914	0.732	0.1878	0.9954
Wastewater—Culture 2	0.592	0.483	0.2125	0.8950	0.581	0.3622	0.9957
Zinc							
Model study—Culture 1	1.639	1.211	0.0059	0.7342	1.628	0.0611	0.9934
Model study—Culture 2	1.811	1.155	0.0850	0.6114	1.821	0.2405	0.9952
Wastewater—Culture 1	3.052	1.632	0.0062	0.5734	3.024	0.0272	0.9896
Wastewater—Culture 2	3.702	2.422	0.0325	0.7431	3.721	0.1028	0.9915

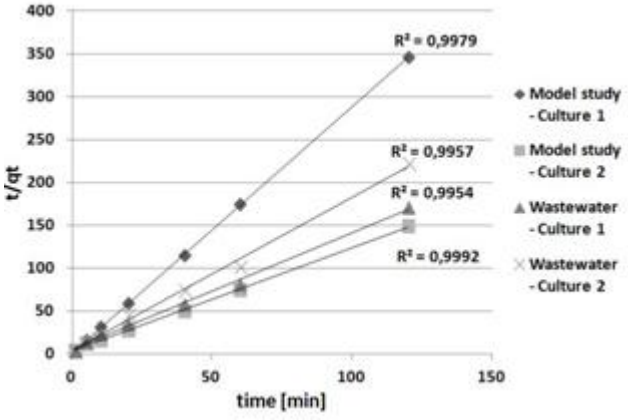

Figure3: Pseudo-second-orderforNi(II)bio-sorptionmodel

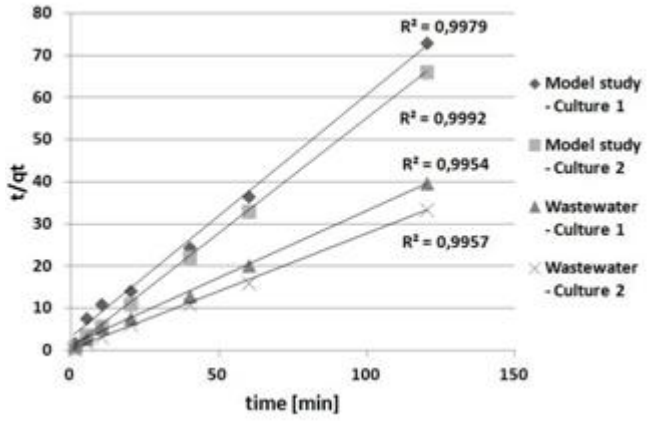

Figure 4: Pseudo-second-orderforZn(II)bio-sorptionmodel

CONCLUSION

The purpose of this study was to determine the efficacy of two bacterial cultures in eliminating heavy metals. For centuries, a diversified, mixed chlorophyta population gathered from a natural water reservoir has been exposed to heavy metal compounds and other constituents present in eutrophicated habitats. As a consequence, many dangerous environmental substances, such as heavy metals, have acquired resistance mechanisms and tolerance in the population.

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