BIOSORPTIVE REMOVAL OF HEAVY METAL ZINC FROM SYNTHETIC WASTEWATER USING DUCKWEED

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ABSTRACT

This study focused on the removal of Zinc from wastewater consisting of its solution using the aquatic plant Duckweed. Batch experiments were setup for studying the biosorption by Duckweed at different initial metal ion concentrations, pH and surrounding temperatures using Atomic Absorption Spectrophotometer. The results from different initial metal ion concentrations experiment concluded that up to 20 mg/g, best sorption of Zinc was seen. The initial pH plays a vital role in removal of Zinc from solution. As a pH of upto 6 in solution showed maximum sorption, higher pH deteriorated the growth of the plant. For different surrounding temperatures, 20-24°C promoted maximum growth. However, plant was also able to grow and adsorb at higher temperatures. At the end of experiment, when all the parameters were standardized, snails were introduced in a setup containing these parameters to check their effect on plant's efficiency. The removal of Zinc was enhanced. The results indicated that Duckweed plant is highly adaptive and continues to clean wastewater even in stress conditions.

KEY WORDS: Biosorption; Duckweed plant; Zinc

1. INTRODUCTION

The increase in industrial activity during recent years is greatly contributing to the increase of heavy metals in the environment, mainly in the aquatic systems[1]. Water pollution due to heavy metals is an issue of great environmental concern[2]. Heavy metals, such as cadmium, copper, lead; chromium, zinc, and nickel are important environmental pollutants, particularly in areas with high anthropogenic pressure[3]. These toxic materials may be derived from mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives[4]. Among them, major Zinc pollution occurs through road travel and road runoff, through erosion from igneous rocks, leaching from pipings and fittings, zinc fumes from industries and zinc refineries, fertilizers and leather tanning processes[5].

Interestingly, small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity. They also have a harmful effect on human physiology and other biological systems when they exceed the tolerance levels[6]. Excessive absorption of zinc suppresses copper and iron sorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish[7]. Therefore, heavy metals must be removed as much as possible from effluents before discharging them into the water bodies.

The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. But, the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents[8]. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials such as duckweed plants. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake[9]. The roots of Duckweed are home to large number of microorganisms which feed off the minerals and organic chemicals that pollute the wastewater. While digesting the pollutants, the microorganisms produce by-products such as sugars and amino acids, which are absorbed by the plant roots as food. The plants in turn supply oxygen and low levels of nutrients to the microorganisms for their rapid growth[10]. Present work aims to study the removal of heavy metal Zinc from its solution using Duckweed plants with varying parameters such as salt concentration, pH and surrounding temperature.

2. MATERIALS AND METHODS

The Ducweed plants were grown hydroponically (in the absence of soil). The wastewater used here was a solution of Zinc salt so as to check the biosorption at lab-scale. Physico- chemical analysis was carried out according to the standard methods for examination of water and wastewater for determination of optimum parameters such as pH, temperature, light and dark cycles. Quantification of Zinc being absorbed in the plant and the level reduced in the solution was checked[11, 2, 12].

In the end, after optimizing the parameters, snails were introduced in a fresh set up with obtained parameters to analyze their effect along with Duckweed in the treatment of zinc solution.

2.1. Materials

2.1.1. Preparation of Biosorbate: A solution of zinc sulfate was prepared in five opaque vessels having a capacity more than 500 ml. To prepare the solution different concentrations of zinc salt such as 4, 12, 20, 28 and 36 mg were added in 50 ml of deionized water. The solution was diluted up to 500 ml. The zinc content of solutions in all the vessels was then quantified using Atomic Absorption Spectrophotometer (Buck Scientific model 210 VGP).

2.1.2. Preparation of Biosorbent: Pre-preparation: Few Duckweed plants (Lemna spirodela), used as the biosorbent were obtained from a pond in old Bhopal, Madhya Pradesh, India and were cleaned using tap water and distilled water. They were then grown and cultured to get large number of cloned plants. The clones were introduced to the biosorbate set up in the ratio of 100 plants per vessel. 1% sucrose was added in each vessel to increase the growth rate.

2.1.3. Preparation of Diacid: A solution of $HClO_3$:HNO_3 was prepared in the ratio of 5:1.

***2.1.4. Collection of Snails*:** They are present in abundance in the area where duckweeds grow. In this study, Ramshorn snails were used as they were found inhabiting the duckweed pond. They occur in red or black colour and their shell resembles a flat coil. They were collected using a sieve or a net and maintained in vessel containing pond water and some duckweed.

2.2. Biosorption Experiments: The protocol was created by the corresponding author and is also similar to those earlier reported[11, 2, 12]. Batch experiments were conducted with varying parameters such as initial metal ion concentrations, pH and surrounding temperatures on the adsorption of zinc ions. The residual metal ions were analyzed using Atomic Absorption Spectrophotometer, at wavelengths of 213.9 nm for Zinc. The detection limit of 3ug/L was used while air was used as the oxidant and acetylene was used as fuel. The sensitivity of Zinc in reagent water was 0.02 mg/L.

2.3. Calculation of removal percentage of metal ions by Duckweed: The percent removal of Zinc from synthetic wastewater was calculated from the formula[13]:

$$\% \text{ Removal} = [(C_o - C_f)/ C_o]*100$$

Where C_o is the initial concentration and C_f is the final concentration of Zinc.

2.4. Effect of Initial Metal Ion Concentration: Five opaque vessels were taken with 50 ml distilled water. A concentration range of 4- 36mg/500ml was used in the experiment. 5 ml of 1% sucrose solution was added and the volume was made up to 500 ml. With about 100 duckweed plants in each vessel, outdoor conditions were maintained. The duckweed plants were removed from the mixture after 10 days by filtration and the concentration of the residual ions in the solution was determined using Atomic Absorption Spectrophotometer. The amount of metal ions adsorbed from solution was determined by difference between the initial and final concentrations.

2.5. Effect of pH: Experiments were conducted at room temperature to study the effect of initial solution pH on the adsorption of the metal ions by contacting initial metal ion concentration which showed the maximum adsorption in previous experiment. The pH of each of the metal solutions was adjusted to the desired value with 0.1 M sodium hydroxide and /or 0.1 M nitric acid. The studies were conducted at pH values of 4, 5, 6, 7 and 8. The vessels containing the mixture were left for 10 days. The sorbent was removed from the solution by filtration and the residual Zinc ion concentration in the solution was analyzed by Atomic Absorption Spectrophotometer. The percentage of Zinc adsorbed in each setup was calculated.

2.6. Effect of Temperature: The adsorption of the metal ions by duckweed was studied at various temperatures (16-30°C). Around 100 duckweeds were introduced into each of the five vessels and 500 ml of each metal ion solution (20 mg/ml) was added into each tube. The duckweeds in five vessels were then kept at varying temperatures of 16°C, 24°C and 30°C. The filtrates were analyzed using Atomic Absorption Spectrophotometer. The amount of metal ions adsorbed was calculated for each sample. The mean of all three results for a particular time was then calculated in tabular form.

2.7. Effect of Snails: After getting all the parameters required for maximum biosorption, as shown in Table 1, a final experiment was conducted which was created by the author. While maintaining all the suitable parameters 8-10 snails were introduced in each vessel and observed for 10 days. Later, the sorbent was removed from the solution by filtration and the residual Zinc ion concentration in the solution was analyzed by Atomic Absorption Spectrophotometer.

3. RESULTS AND DISCUSSION

The effects of different parameters are shown in Table 1. Almost complete adsorption occurred up to an initial metal ion concentration of 20 mg/g after which the efficiency decreased. The amount of Zn (II) ions adsorbed increased with increase in initial metal ion concentration up to a level after which the plant reached a saturation level. Table 2 shows a comparison of zinc uptake capacities (mg/g) of various macrophytes. It can be seen that after *P. lucens*, duckweed is the most promising plant for removing zinc ion from wastewater.

Duckweed is a plant which generally grows in slightly acidic water. The result of the pH study showed that maximum sorption occurred up to pH 6. The percentage Zn (II) adsorbed is quite lower at higher pH. This implies that the initial pH would play a vital role in the removal of the Zn (II) ions from solution. This data was similar to experiment conducted with Water hyacinth (*E. crassipes*)[14], where a pH range of 9.4 - 10.02 were tested for zinc sorption. It was shown that zinc uptake by the plants was slower in strongly basic solutions and the plants still survived.

The results can also be compared to another experiment conducted by Afif and Manap, (2008), the removal efficiency of zinc was determined by water lettuce. Each parameter with varying quantity of pH was setup in four containers including control. The result was ph 7 achieved highest removal efficiency (80.41 %), followed by pH 5 (72.22 %), pH 9 (76.47 %) and the control (70.41 %).

As Duckweed is a plant which usually grows at colder temperatures (around 24°C), it was able to grow and adsorb at higher temperatures as well when given appropriate pH and nutrition. The values of the parameters show that duckweed plant is a good adsorbent for the removal of zinc from wastewaters. In the end, when snails were added in the setup to assess their effect on duckweed's ability to absorb, it was seen that despite the fact that snails thrive upon nutrients from wastewater as well as on duckweed, the rate of Zinc sorption was enhanced to about 95%. This could have occurred due to very high reproducibility rate of duckweed. So, both the plants and the snails were contributing towards the Zinc removal process.

CONCLUSION

The duckweed plant, which grows as a weed in ponds and lakes, could be used as a potential biosorbent for the removal of Zinc from wastewater. The batch sorption studies have shown that the sorption of Zinc is pH dependent and adapts easily with change in environmental temperatures. The amount of Zinc ions adsorbed decreased with very high initial metal ion concentration. Maximum adsorption was obtained within the first 2 days. The Duckweed is clearly the wave of the future. The exciting part of this technology is that we now have a promising and economical means of recycling domestic and industrial waste through a natural biological process that does not pollute the environment or consume vast amounts of valuable energy resources. In addition, it promises to provide an inexhaustible supply of raw materials for future generations while maintaining a clean, ecologically stable environment.

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Table 1. Effect of various parameters such as initial metal ion concentration, pH of solution and temperature on biosorption by Duckweed

Initial metal ion (mg/g) concentration	% Zinc ion removed	pH	% Zinc ion removed	Temperature (°C)	% Zinc ion removed
4	100	**4**	96	**16**	85
12	100	**5**	100	**24**	90
20	100	**6**	100	**30**	65
28	96.79	**7**	82.5	**-**	-
36	69.44	**8**	65	**-**	-

Table 2. Comparison of zinc uptake capacities (mg/g) of various macrophytes

Adsorbent	Zinc adsorbed
M. spicatum[16]	15.59
M. spicatum[17]	13.5
P. lucens[18]	32.4
S. herzegoi[18]	18.1
E. crassipes[18]	19.2