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# Bioadsorption of Selenium by Pretreated Algal Biomass

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## ABSTRACT

*The presence of heavy metals in aquatic environment is known to cause severe damage to aquatic life. Most of the heavy metals are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical and chemical means of separation. Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. The biomass is capable of absorbing and adsorbing metal ions from aqueous solution. In this study the effect of pretreatment of Algal biomasses like Spirogyra on the Se biosorption capacity were investigated under laboratory conditions. For this purpose, the biomasses were subjected to physical treatments such as heat and autoclaving and chemical treatments such as sodium hydroxide and acetic acid. Under laboratory condition, all the pretreated biomass increased biosorption of Se in comparison with live biomass. The maximum metal removal efficiency for Se was observed under the biomass dried at 60$^{o}$ C for 12 h in an Oven (spirogyra – 50%; Nostoc – 52.4%) resp.*

**Key words**: Bioadsorption, pretreatment, *Spirogyra sp*; *Nostoc sp*; Spectrophotometer.

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## INTRODUCTION

The traditional approaches for removing or recovering metals, such as precipitation, oxidation/reduction, ion exchange, filtration, electrochemical processes, membrane separations, and evaporation, all exhibit several disadvantages, such as high cost, incomplete removal, low selectivity, high energy consumption, and generation of toxic slurries that are difficult to be eliminated [2].

Algae, in common with other microbial groups, can accumulate metals from their external environment by means of physico-chemical and biological mechanisms. Nonviable microbial biomass frequently displays a higher affinity for metal ions compared with viable biomass, probably due to the absence of competing protons produced during metabolism. To avoid the

problems of metal toxicity for microbial growth, or inhibition of metal accumulation by nutrient or excreted metabolites, the decoupling of the growth of the biomass from its function as a metal-sorbing material is seen as one of the major advantages of biosorption [1].

The use of dried, nonliving or chemically pretreated microorganisms seems to be a preferred alternative to the use of living cells in industrial applications for the removal of heavy metal ions from wastewater. The use of dead cells offers the following advantages over live cells: the metal removal system is not subject to toxicity limitations, there is no requirement for growth media and nutrients, the biosorbed metal ions can be easily desorbed and biomass can be reused and dead biomass-based treatment systems can be subjected to traditional adsorption models in use. As a result, the use of dead fungal biomass has been preferred in numerous studies on biosorption of toxic metal ions from aqueous solutions [6, 7].

Living cells can be pretreated using physical or chemical means in order to increase metal biosorption capacity. Physical pretreatment methods have included heat treatment, autoclaving, freeze drying, and boiling. Chemical pretreatment methods, such as introducing fungal cells to acids, alkali and organic chemicals, showed enhancement of metal biosorption by different fungal biomasses [1].

The uptake of heavy metals by biomass is usually classified into three categories: (1) cell surface binding, (2) intracellular accumulation and (3) extracellular accumulation. Being metabolism independent, the cell surface binding can occur in either living or inactivated microorganisms, whereas the intracellular and extracellular accumulation of metals are usually energy-driven processes, and thus can take place only in living cells. Non-viable microbial biomass frequently exhibits a higher affinity for metal ions compared with viable biomass probably due to the absence of competing protons produced during metabolism. To avoid the problems of toxicity of metals for microbial growth, or inhibition of metal accumulation by nutrient or excreted metabolites, the decoupling of the growth of the biomass from its function as a metal-sorbing material is seen as one of the major advantages of biosorption [8].

## MATERIALS AND METHODS

### Algae culture conditions:

The algae isolates Viz., *Spirogyra sp* and *Nostoc commune* were used for this experiment. The Spirogyra sp isolates were inoculated in modified Bold's basal medium and *Nostoc commune* in Chu's 10 (modified) medium, for mass multiplication and incubated under fluorescent light (3000 lux) at a temperature of 25 ± 1°C for 18 days. Biomass was then harvested by filtration, washed with generous amounts of deionized water, resuspended and washed again.

### Pretreatment of biomass:

Thirty grams of wet biomass (algae) was then pretreated in 4 different ways. The treatment details are, T1- Live biomass (Type A); T2 - Dried at $60^0$C for 12 h in an Oven (Type B); T3 - Autoclaved for 15 min at 121 0C at 15 lbs (Type C); T4 - Boiled for 15 min in 500 ml of 0.5 N sodium hydroxide solution (Type D); T5- Boiled for 15 min in 200 ml of 10% (v/v) acetic acid solution (Type E). After each pretreatment with chemicals, the biomass were washed with generous amounts of deionized water and then dried at $60^0$C for 12 hrs. The sodium hydroxide

pretreated biomass was washed with deionized water until the pH of the solution was in a near neutral range (pH 6.8-7.2).

**Adsorption experiment:**

All adsorption properties for pretreated biomass were measured with standard equilibrium experiment. A series of vials contained 0.1g of biomass and 100ml of heavy metal solutions of know concentration and the contents were shaken at 20ºC for 4hr in a rotating shaker (100rpm). After experiment, mycelial pellets were filtered through gauze, and the supernatant liquid was used for metal analysis, by atomic absorption spectrometer.

**Measurement of metals**

Total metal concentration in the solution was measured with a UV Double Beam Spectrophotometer. Biosorption experiments were conducted in triplicate and average values were used in the analysis. The amount of metal ion (mg) biosorbed per gram (dry weight) of biomass was calculated using the following equation:

$$Qe = \left(\frac{C0 - C}{m}\right)V$$

Where, Q = amount of metal ion biosorbed per gram of biomass, mg/g; $C_0$ = initial metal ion concentration, mg/l; C = final metal ion concentration, mg/l; m = dry weight of biomass in the reaction mixture, g; V = volume of the reaction mixture, lit. [10].

## RESULTS AND DISCUSSION

The findings related to selenium bioadsorption by live and pretreated algal biomasses are presented in the table 1. for each algae.

**Table.1: Adsorption capacity of native and pretreated *Spirogyra sp* & *Nostoc commune.***

| Pretreatment methods | Biosorption capacity, Qe (mg/g) | |
|---|---|---|
| | *Spirogyra sp.* | *Nostoc commune* |
| No pretreatment | 7.62 | 8.69 |
| **Physical methods** | | |
| Dried at $60^0$C for 12 h in an Oven | 12.5 | 13.1 |
| Autoclaved for 15 min at $121^0$ C at 15 lbs. | 10 | 10.22 |
| **Chemical methods** | | |
| Boiled for 15 min in 500 ml of 0.5 N sodium hydroxide solution | 8.36 | 10 |
| Boiled for 15 min in 200 ml of 10% (v/v) acetic acid solution | 10 | 11.01 |

Pre-treatment of living biomass T1- Live biomass (Type A) using; T2 - Dried at $60^0$C for 12 h in an Oven (Type B); T3 - Autoclaved for 15 min at 121 0C at 15 lbs (Type C); T4 - Boiled for 15 min in 500 ml of 0.5 N sodium hydroxide solution (Type D); T5- Boiled for 15 min in 200 ml of 10% (v/v) acetic acid solution (Type E) resulted in an improvement in selenium biosorption in comparison with living biomass.

It showed that all kinds of physical and chemical pretreatment to algae were beneficial to increase the adsorption ability on selenium. Nonviable microbial biomass frequently displays a higher affinity for metal ions compared with viable biomass that might probably due to the absence of competing protons produced during metabolism. It avoids the problem of metal toxicity for microbial growth and inhibition of metal accumulation by nutrient or excreted metabolites [3].

**Figure 1. Effect of on biosorption of selenium (II) by *Spirogyra sp.***
*T1- untreated biomass; T2- oven dried biomass; T3- Autoclaved biomass; T4- NaOH treated biomass and T4- Acetic acid treated biomass.*

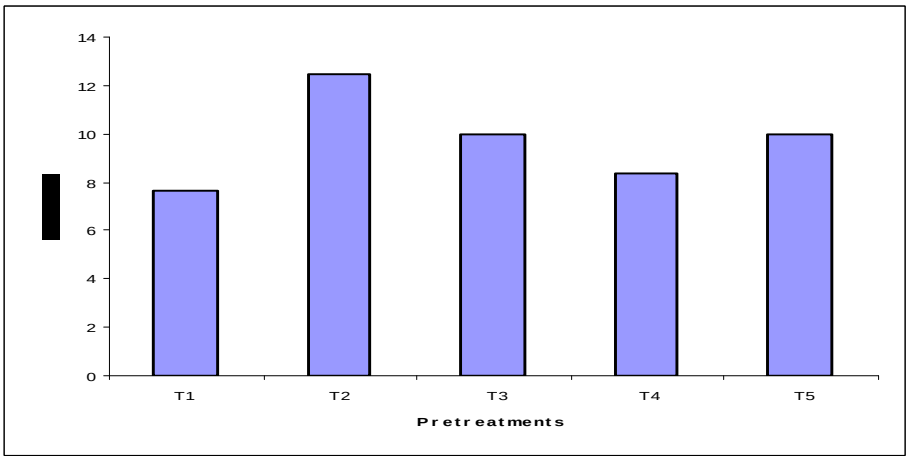
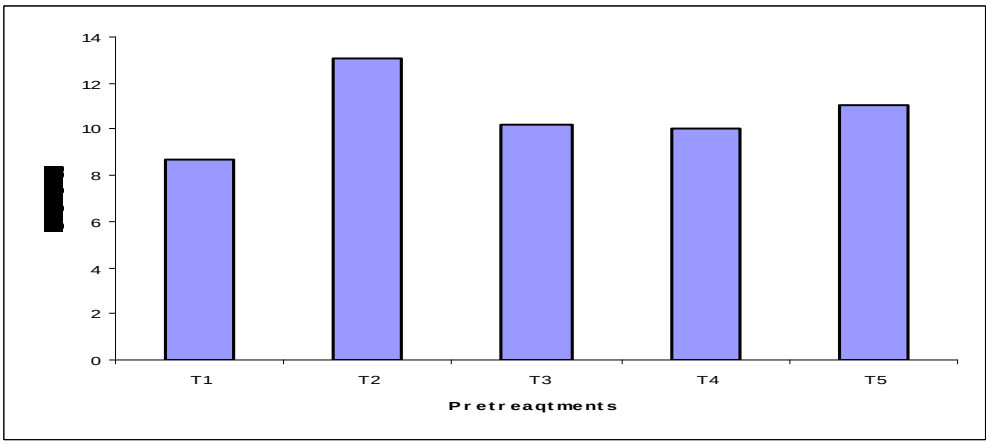



**Figure 2. Effect of on biosorption of selenium (II) by *Nostoc commune***
*T1- untreated biomass; T2- oven dried biomass; T3- Autoclaved biomass; T4- NaOH treated biomass and T4- Acetic acid treated biomass.*




It was observed that Qe values obtained for all the physically pretreated biomasses were high in comparison with living biomass (from 7.62 to 12.5 mg/g and from 8.69 to 13.1 mg/g) by *Spirogyra sp.* and *Nostoc commune* resp. Oven dried at $60^0$C for 12 h biomass showed the maximum improvement on selenium sorption. The bioadsorption capacity of autoclaved biomass

increased in comparison with live biomass may be attributed to the exposure of latent binding sites.

The sequestration of metallic species by algal biomasses which constitutes the basis of its biosorbent behavior has mainly been traced to the cell wall. The cell wall is not necessarily the only site where the sequestered metals are located. They may also be found within the cell, associated with various organelles, or may crystallize in the cytoplasm [9]. The drying and then grinding of blue green algal biomass reveals the sites where metal ions could be sequestered and so increase the probability of encountering metal ions.

Figure 1 & 2 shows the effect of pretreatment with alkali. Pretreatment of biomass with NaOH showed increase on biosorption of selenium by approximately in comparison with living biomass (from 7.62 to 8.36 mg/g and from 8.69 to 10 mg/g) by *Spirogyra sp.* and *Nostoc commune* resp. In some study, NaOH treated biomass of *Penicillium digitatum* also showed enhancement of Cd (II) bioadsorption [4].

Removal of surface impurities, rupture of cell membrane and exposure of available binding sites for metal bioadsorption after pretreatment may be the reason for the increase in metal biosorption.

**Figure 3. Effect of pretreatment on spirogyra sp. on percent removal of selenium.**

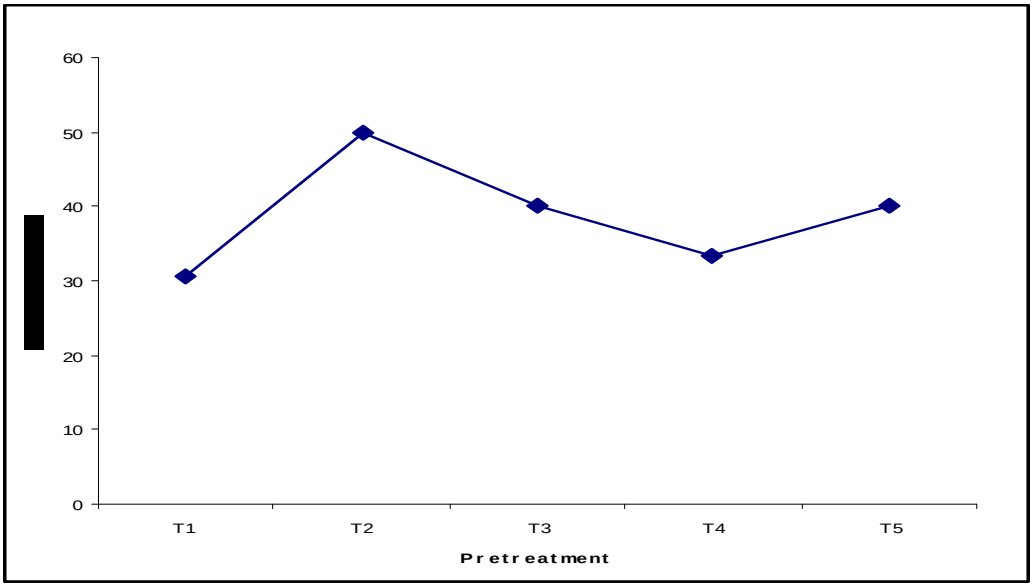
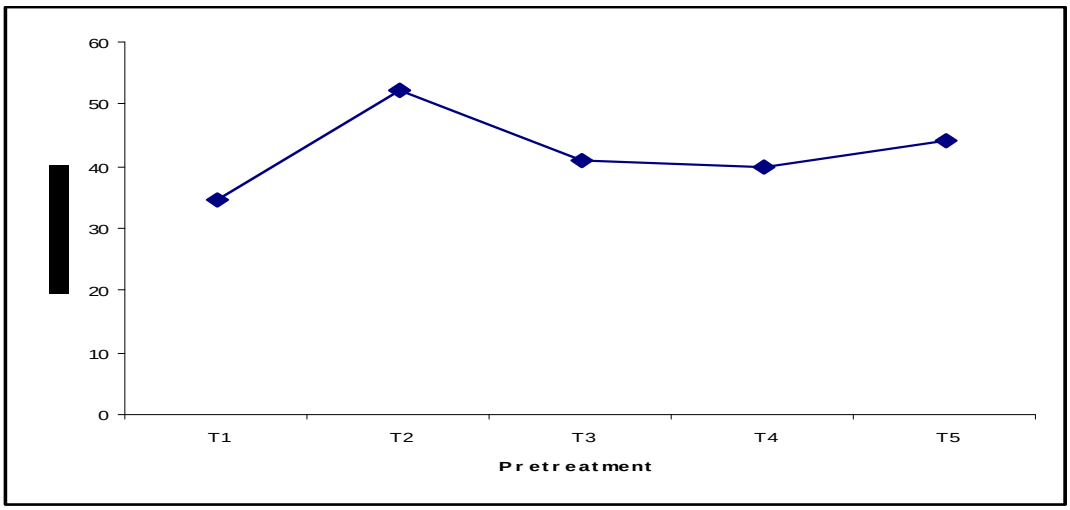



Figure 1 & 2 shows the effect of pretreatment with acid. Acetic acid treatment significantly increased the biosorption of selenium, some researchers observed that the acid pretreatment can strongly enhance the adsorption capacity of *Aspergillus oryzae*[5] .

**Figure 4. Effect of pretreatment on *Nostoc commune* on percent removal of selenium.**




## CONCLUSION

According to the results of the present experiment, it is obvious that the biomass of *Spirogyra sp.* and *Nostoc commune* pre-treated physically or chemically is able to remove selenium ions from aqueous solution. It may be advantageous to use this novel algal biomass after physical and chemical pretreatment. Thus the algal biomass of *Spirogyra sp.* and *Nostoc commune* may be applied as potent biosorbent for removing selenium ions from effluents.

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