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Evaluation of Green microalgae potential for the removal of Lead and Chromium metal Ions through Biosorption Process

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Abstract – Environmental heavy metal waste is one of the most serious problems today. Decontamination of the heavy metals has long been a problem in the aquatic environment.Several approaches were created for handling polluted wastewater like chemical precipitation, evaporation, electroplating, mixing of ions, membrane systems, and so on. But these methods are associated with some demerits such as high reagent requirement, generation of toxic sludge, difficulties in both to procure and handling. Overcoming to these limitations is possible through biosorption process which utilizes metal binding capacities of biomaterials and micro-organisms, such as bacteria, yeast, algae and fungi from aqueous system. The elimination of heavy metals (Pb+2 and Cr+6) from the single and multi-metallic metal ion solution was performed under batch mode condition. The Biosorption potential of green micro alga S. obliquus biomass evaluates to purpose of pH, biosorbent dosage, contact time, and initial metal ion concentrations. Metal uptake was observed at the 5-7 pH range for Pb+266.9and Cr+6 23.0µg metal mg –1 dry weight from test solutions single ion within 60 min. However, binary and multi metallic system the uptake capacity was observed reduced due to participation among metal ion species for the binding site. Adsorption isotherms studies follows the Freundlish isotherm model which is regulated by weak van der Waalsforces so it is obvious that desorption / recovery could be possible. Desorption of was done by using EDTA solution and more than 80 % of the adsorbed metal ions was desorbed in the first three consecutive cycles and decrease in both adsorption and desorption values were observed after that. The FTIR study for the algal biomass surface feature community exposed the survival of amino, carboxyl, hydroxyl, and carbonyl groups that are responsible for Pb+2 and Cr+6 biosorption. Therefore this study concluded the biomass of S. Obliquus is a possible layer used to eliminate heavy metals from contaminated marine areas or streams.

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1. INTRODUCTION

The continuously increasing rate of pollution due to global industrialization and urbanization is increasing alarmingly in the past decades. Various types of pollutants contribute to pollute our environment, among all the contaminant, heavy metals is important because when present in higher quantity, can harm aquatic and human life. As these are non-degradable/ destroyable, they are persistent environmental contaminants and enter human or animal body systems through food, air, and water. Therefore they bio-accumulate across a period of time. Commercial and urban wastewaters frequently produce strong ions. Current methods for such wastewaters treatment include precipitation, coagulation/floatation, sedimentation, filtration, membrane processes, electrochemical techniques, ion exchange, and chemical reactions, but each of these methods has its merits and limitations in application. Some of the present methods generate harmful by-products [3]. Environmental friendly processes needed to be develop to restore the environment without generating harmful waste by-products. Biosorption using living organisms have long been reported as an alternative technology for combating the water effluence source by heavy metals. Several microorganisms vise. Bacteria, yeast, fungi[12] and fermentation and food waste mycelia[3, 8], algae[10, 11, 25, 26 & 27],[20] and[23] have already been known for their strong metal binding ability.

Research activities in recent years clearly indicated that many aquatic microorganisms can accumulate high concentrations of metals ions from their surroundings. Kumar et al., evaluate the capability of two microalgae, *Synechocystis* sp. PCC 6803 and *Scenedesmus obliquus* for accumulation of Pb with special reference to the adsorption isotherms and their findings reflect the possibility of using such organisms for removal/ recovery of harmful/ precious metals from the environment [10]. Chlamydomonasreinhardtii's FT-IR biomass study revealed amino, carboxyl, hydroxyl, and carbonyl groups that are essential for metal ion biosorption[12, 14]. This study is an effort to develop a microbial system to clean up the waste water streams without creating harmful waste products.

2. MATERIALS AND METHODS

2.1. Organisms and growth conditions

The test organism *Scenedesmus obliquus* was grown in Chu-10 [25]; (pH 6.8) and BG-11 media [19] (pH 8.0) under 72 µmol photon m^{-2} s^{-1}light intensity and photoperiod of 14:10 h at 25 ± 1^{0}C. In the growth medium, logarithmic phase cultures were diluted correctly at the beginning of each metal uptake trial, and augmented with a specified volume of metal solution. The crops were then incubated in a shaker at 50 rev min-1 under the standard growing conditions, devoid of some gas exclusion. Expansion had been evaluated by dry weight. For all experiments Milli-Q water and acid-soaked glasswares are used. Most the reagents were quality to Merck.

2.2. Time-course study

Exponentially developed Scenedesmus obliquus cells have been taken for analysis. Cells in growth medium alone (no metal ion addition) and in growth medium containing 2 µg mL^{-1} of Pb& Cr ion were incubated under standard growth condition in a shaker at 50 rev min^{-1} (replicates: 4). Upon inserting silicon, 3 ml portion from each culture was gathered and centrifuged at timed intervals. Ion Analyzer (model 757 VA Computrace, Metrohm, Switzerland) obtained and examined supernatant for persistent metal concentration.

2.3. Effects of metal and biomass concentrations

Average growth of 25 milliliters showing different concentrations (0.5 – 4 µgmL-1, at an interval of 0.5 µgmL-1) of Pband Cr was taken in 100 ml Erlenmeyer flasks. Once the research samples have been added, in the shaker flasks were agitated at 50 rev min-1 for 1h under continuous light. At the period stipulated, 3 ml of samples were withdrawn. Samples was centrifuged and supernatant was collected in aqueous phase to determine the residual metal content. Similarly, to study the impact of biomass concentrations, different quantities of biomass were suspended in 25 ml of growth medium with 2 μgmL^{-1}Pb and Cr incubated for the stipulated time. Enduring metal substance was determined as described above.

2.4. Effect of pH

With 1N NaOH or HCl varying from 3.0 to 10.0 at a period of 1.0 before inserting the cells into the sample, the growth medium comprising test metal with various pH values was prepared to assess the effect of pH.

2.5. Isotherm studies

The relation between the quantity of metal adsorbed by an adsorbent and the concentration of the adsorbate at steady temperature is called the adsorption isotherm. Such statistical models include information regarding biosorption pathways and biosorbent surface behaviour. Outcomes of isotherms Freundlich and Langmuir were examined.

3. RESULTS AND DISCUSSION

3.1 Time-course study

The variation of time-dependent accumulation of Pb and Cr by *Scenedesmus obliquus* are shown in Figure 1. The calculation of metal time-course revealed a very quick initial i.e. about 70-80% of accumulation was completed in the initial 30 min of initial contact of metal-bearing solution, and the level of accumulation for Pb attained stability in 60 min with a value of 66.9 ± 6.4 µg Pb mg^{-1} dry wt. for *S. obliquus,* while for Cr ions theequilibrium was recorded after 2h with the maxima of 23.0 ± 4.5.

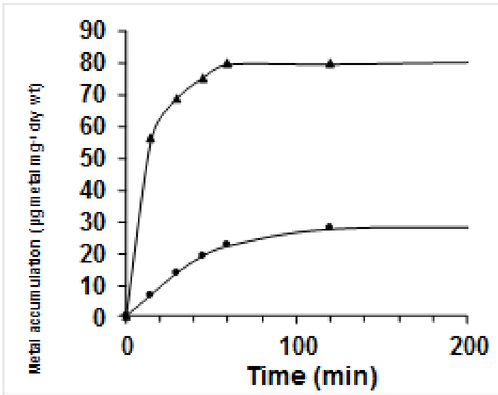

Figure 1.Time-course accumulation of Pb(○) and Cr (■) by *S. obliquus*.

Conversely, for dead biomass of *Microcystis* (field-isolated), *Microcystis*(laboratory-grown), *Spirogyra* and *Lemna*the accumulation value was correspondingly, 24.2, 22.9, 16.9 and 25.8 µg Pb mg^{-1} dry wt. [19]. This implies that *Scenedesmus obliquus* has a potential for Pband Cr accumulation.

3.2 Effect of biomass concentration

The effect of biomass concentration for accumulation of Cr and Pb are shown in Figure 2. The quantity of metal accumulated per unit weight was maximal at lower biomass concentrations and decreased with increasing amount of biomass. This decreased aggregation of metals at higher concentrations of biomass can be due to electrostatic interactions, because more cations are adsorbed on the cell when the cell distances are greater[8], or it could also be likely that higher cell concentration might lead to formation of cell aggregates, thereby reducing the effective biosorption area [26]. The biomass concentration was found to have profound impact on metal accumulation.

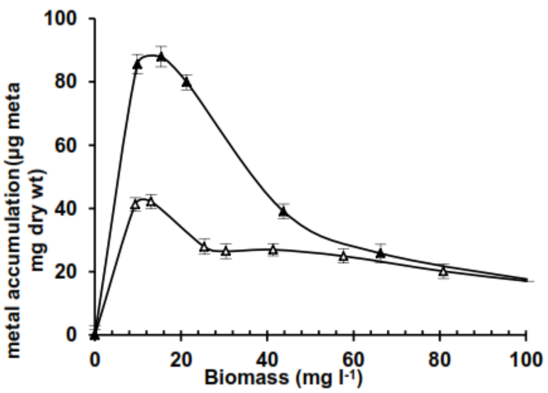

Figure 2.Accumulation of Pb(○) and Cr (■) by *Scenedesmusobliquus*at different biomass concentrations.

3.3 Impact of metal ion concentration

Impact of Pb ion concentrations on accumulation with *S. obliquus* illustrate the primary augment to increasing Pb concentrations equal to 2.5 µgm L^{-1}Pb, subsequent that is constant position was accomplished (Figure 3). In case of Cr ion the steady position nevertheless, experimental at 1.5 µg mL^{-1}Cr, consequently reflecting the availablability of smaller number of Cr binding sites in *S. obliquus.*

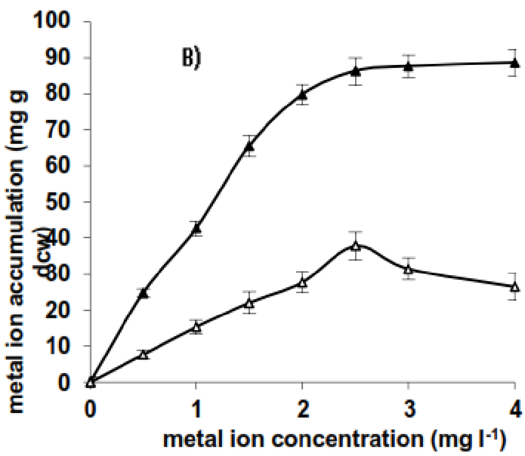

Figure 3.Uptake of Pb(○) and Cr (■) ions per unit biomass of *Scenedesmus obliquus*at different metal concentrations.

3.4. Effect of pH

Metal ion accumulation was established pH dependent process and maximum accumulation was observed between pH ranges of 5-7 for all the four test metals (Table 1).

Table 1: Impact of pH on Pb and Craccumulation by *s. obliquus*

Metal accumulation (µg metal mg $^{-1}$ dry weight)		
pH	Pb	Cr
4	51.40± 2.1[a]	20.12± 1.1[b]
5	65.67±2.2[b]	24.54± 1.3[b]
6	77.91± 2.8[c]	24.60± 1.3[b]
7	79.58± 2.6[c]	27.70± 1.7[c]
8	63.29± 2.5[b]	23.77± 1.3[b]
9	46.03± 1.5[a]	13.83± 1.0[a]

3.5. Adsorption isotherm study

Isotherms to adsorption of Pb are illustrated in Figure 4. The binding data at equilibrium for *S. oblique*, shown in Figure 4, seemed to fit Freundlich isotherm. This physical adsorption is based on *van der Waals* forces and indicates that adsorption equlibrium is established rapidly and is generally reversible. As *van der Walls* adsorption is more a function of the adsorbate, In contrast, isotherm for Cr adsorption followed the Langmuir equation (Figure 4b), appearing a unimolecular layer connecting chemical power.

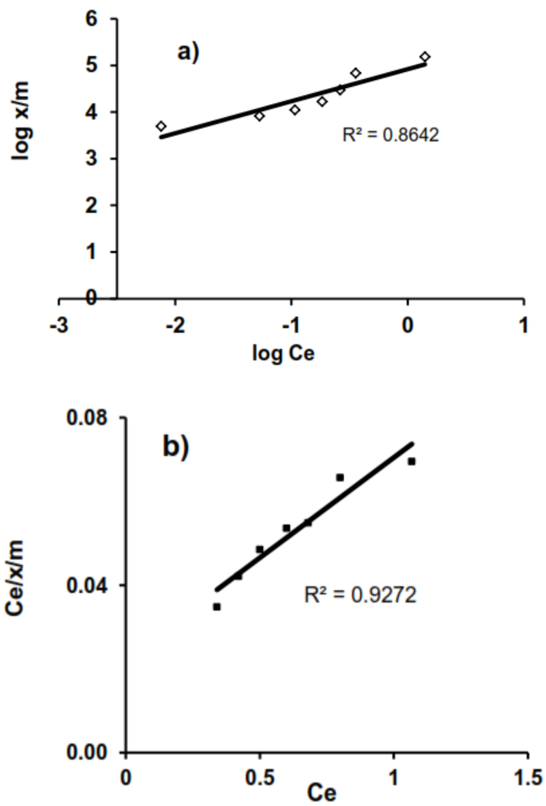

Figure 4.Adsorption isotherms a) Freundlich isotherm for Pb ions b) Langmuir isotherm forCr ions.

3.6 Adsorption/desorption study

Desorption of the adsorbed metal ions from the tested biomass was done by using 10 mM EDTA solution. About 75-80% of the adsorbed metal was desorbed in the first cycle and in the subsequent cycles decrease in both adsorption and desorption values were observed for all the four test metals.

The adsorption of metals from binary heavy metal mixtures was efficient and the adsorption capacity of any particular metal decreased by 10–40% in the existence of those other metallic organisms and the algae's total adsorption efficiency decreased by 30–50%

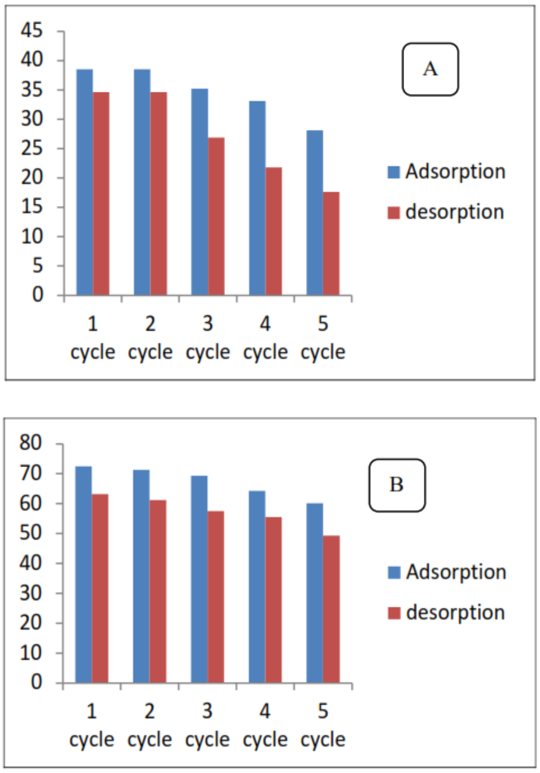

Figure 5. Adsorption/Desorption cycles of (A) Cr and (B)Pb metal ions.

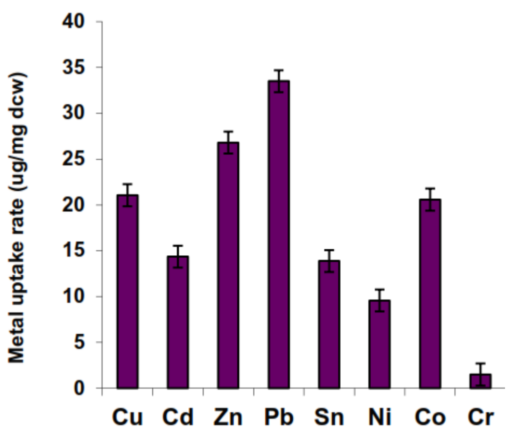

Figure 6.Variation of metal rate uptake of biomass *S. obliquus* in multi-metallic combinations.

3.7 FT-IR Spectroscopy

The basic groups responsible for biosorption of heavy metal at S. The obliquus cells have FT-IR spectra verified. The algal biomass FT-IR spectra shows amino, carboxylic, hydroxyl, and carbonyl groups are present. Figure 7 demonstrates that the absorption of the peaks in the algal biomass treated with Pb and Cr is dramatically lower than in the native one, thereby illustrating the attachment of metal ions to the surface of Scenedesmus.

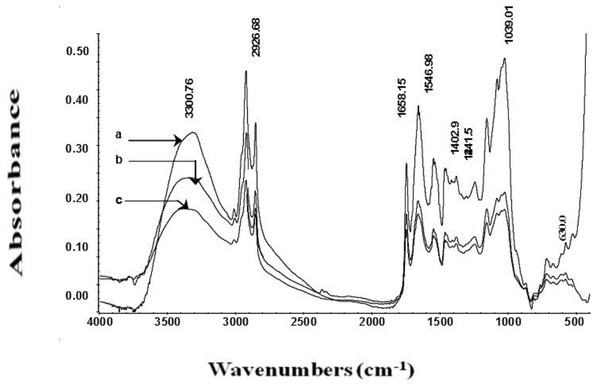

Figure7. Superimpose FT-IR spectra of (a) native biomass, (b) Pb and (c) Cr- treated biomass of *S. obliquus.*

4. CONCLUSIONS

Adsorption isotherm study depicted a multilayer binding for *S. obliquus.* Because Freundlich isotherm suggests a simple reversible binding driven by van der Waals powers, it is apparent that the desorption / recovery of the ionised metals will be much better compared to Langmuir / BET binding, that is controlled by chemical forces. The adsorption of metals from the binary heavy metal mixture was efficient and the adsorption capability of any particular metal declined by 10–40% in the existence to further metal species and regular biomass usage, the total adsorption efficiency of the algae decreases by 30–50%.

Metal sorption hierarchy in multi-metallic combination was Pb>Zn>Cu>Co>Cd>Sn>Ni>Cr. Among tested concentrations Cr was to be the least preferable, whereas Pb was the most preferred metal ion by the test organism. Therefore the findings from the various experimental setups describe in this study shows the *S. obliquus* can be a potent organism for elimination of intense metal from waste water.

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