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Waste Water Treatment for Removal of Copper and Cadmium Ions through Biosorption Process

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Abstract—*Environmental contamination by heavy metal has become one of the most serious problems today. Decontamination of heavy metals in the aquatic environment has been a challenge for a long time. Various methods have been developed to treat contaminated wastewater such as chemical precipitation, evaporation, electroplating, ion exchange, membrane processes, etc. But these methods are associated with some demerits such as high reagent requirement, generation of toxic sludge, difficulty in both to procure and handling. Overcoming 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 removal of heavy metals (Cu^{++} and Cd^{++}) from the single and multi metallic metal ion solution was performed under batch mode condition. Biosorption potential of green micro alga S. obliquus biomass evaluates as a function of pH, biosorbent dosage, contact time, and initial metal ion concentrations. Metal uptake was observed at the 5-7 pH range for Cu^{++}73.3 and Cd^{++}38.7μg metal mg $^{-1}$ dry weight from test solutions single ion within 60 min. However, in the binary and multi metallic system the uptake capacity was observed reduced due to competition between metal ion species for the binding site. Adsorption isotherms studies follows the Freundlish isotherm model which is regulated by weak van der Waals forces so it is obvious that the desorption / recovery could be possible. Desorption of was done by using EDTA solution and more than 80 % of the adsorbed metal ions were desorbed in the first three consecutive cycles and decrease in both adsorption and desorption values were observed after that. The FTIR analysis for surface function group of algal biomass revealed the existence of amino, carboxyl, hydroxyl, and carbonyl groups, which are responsible for the biosorption of Cu^{++} and Cd^{++}. Thus, this study suggested that the biomass of S. obliquus is a potential organism for the removal of heavy metals from waste water.*

1. INTRODUCTION

The continuously increasing rate of pollution due to global industrialization and urbanization is increasing alarmingly in the recent decades. Various types of pollutants contribute to pollute our environment, among all the pollutants, heavy metals are important because when present in higher quantity, can harm aquatic and human life. Because they are non degradable/ destroyable, they are persistent environmental contaminants and they enter human and animal body systems through food, air, and water and bio-accumulate over a period of time. Industrial and municipal wastewaters often contain heavy metal 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 and some of the present methods generate harmful by-products [3]. Environmental friendly processes need to be developed to clean-up the environment without creating harmful waste by-products. Biosorption using living organisms have long been reported as an alternative technology for combating the water pollution caused by heavy metals. Several microorganisms vise. Bacteria, yeast, fungi [12] and waste mycelia from the fermentation and food industry [3, 8], algae [10-11], [20] and [23] have already been identified for their high metal binding capacities.

Research activities in recent years clearly indicated that many aquatic microorganisms can accumulate high concentrations of metals ions from their surroundings. Kumar et al., assess the ability of two microalgae, *Synechocystis* sp. PCC 6803 and *Scenedesmus obliquus* for accumulation of Cu 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]. FT-IR analysis of biomass of *Chlamydomonas reinhardtii* exposed the presence of amino, carboxyl, hydroxyl, and carbonyl groups, which are responsible for biosorption of metal ions [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 [5]; (pH 6.8) and BG-11 media [19] (pH 8.0) under 72 μmol photon m^{-2} s^{-1}PAR light intensity and photoperiod of 14:10 h at 25 ± 1^0C. At the beginning of each metal uptake experiment, logarithmic phase cultures were diluted appropriately in the growth medium and supplemented with a designated amount of metal chloride solution. The cultures were then incubated under the standard growth conditions in a shaker at 50 rev min^{-1} without any gas purging. Growth was measured in terms of dry weight. Milli-Q water and acid-soaked glasswares were used for all experiments. All the reagents were of Merck grade.

2.2. Time-course study

Exponentially grown cells of *Scenedesmus obliquus* were taken for the study. Cells in growth medium alone (no metal ion addition) and in growth medium containing 2 µg mL^{-1} of Cu ion were incubated under standard growth condition in a shaker at 50 rev min^{-1} (replicates: 4). At timed intervals after the addition of metal, 3 ml portion of each culture was collected and subjected to centrifugation. Supernatant were collected and analyzed for residual metal concentration by Ion Analyzer (model 757 VA Computrace, Metrohm, Switzerland).

2.3. Effects of metal and biomass concentrations

Twenty-five milliliter growth medium containing various concentrations (0.5 – 4 µgmL^{-1}, at an interval of 0.5 µgmL^{-1}) of Cu were taken in 100 ml Erlenmeyer flasks. After introducing the test organisms, flasks were agitated in the shaker at 50 rev min^{-1} under continuous light for 1h. 3 ml samples were withdrawn at the stipulated time. Samples were centrifuged and supernatant were collected to determine the residual metal content in aqueous phase. Similarly, to study the impact of biomass concentrations, different quantities of biomass were suspended in 25 ml of growth medium with 2 µgmL^{-1} Cu and incubated for the stipulated time. Residual metal content were determined as described above.

2.4. Effect of pH

To find out the impact of pH, growth medium containing test metal with different pH values were prepared with 1N NaOH or HCl ranging from 3.0 to 10.0 at an interval of 1.0, before introducing the cells into the medium.

2.5. Isotherm studies

The relation between the amount of metal adsorbed by an adsorbent and the concentration of the adsorbet at a constant temperature is called the adsorption isotherm. These mathematical models provide information on biosorption mechanisms and surface behaviour of biosorbent. Results were analysed following Freundlich and Langmuir isotherms.

3. RESULTS AND DISCUSSION

3.1 Time-course study

The variation of time-dependent accumulation of Cu and Cd by *Scenedesmus obliquus* are shown in Fig. 1. The time-course metal accumulation showed an initial very rapid i.e. about 70-80% of accumulation was completed within the first 30 min of initial contact of metal-bearing solution, and the level of accumulation for Cu achieved equilibrium within 60 min with a value of 73.1 ± 6.4 µg Cu mg^{-1} dry wt. for *S. obliquus,* whereas for Cd ions the

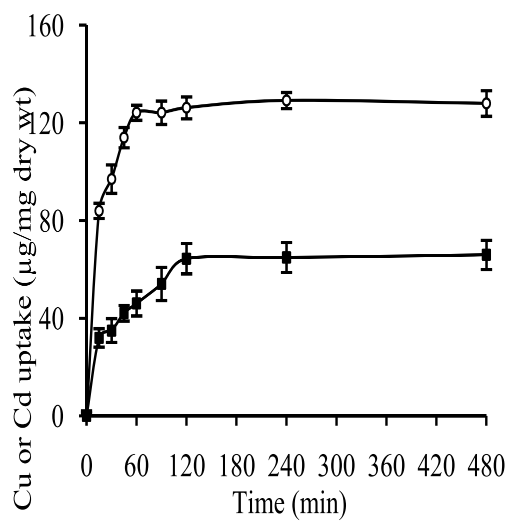

Fig. 1: Time-course accumulation of Cu (○) and Cd (■) by *S. obliquus*.

equilibrium was recorded after 2h with the maxima of 38.5 ± 4.5. However, for dead biomass of *Microcystis* (field-isolated), *Microcystis* (laboratory-grown), *Spirogyra* and *Lemna* the accumulation values were respectively, 24.2, 22.9, 16.9 and 25.8 µg Cu mg^{-1} dry wt. (Singh et al., 2000). This implies that *Scenedesmus obliquus* has a much greater potential for Cu accumulation.

3.2 Effect of biomass concentration

The effect of biomass concentration for accumulation of Cd and Cu are shown in Fig. 2. The amount of Cu accumulated per unit weight was maximal at lower biomass concentrations and decreased with increasing amount of biomass. This reduced metal accumulation at higher biomass concentrations could be attributable to the 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 [2]. The biomass concentration was found to have profound impact on metal accumulation.

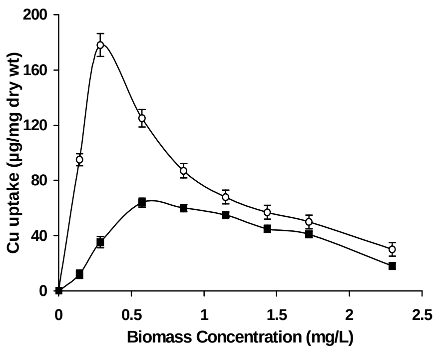

Fig. 2: Accumulation of Cu (○) and Cd (■) by *Scenedesmus obliquus*at different biomass concentrations.

3.3 Impact of metal ion concentration

Impact of Cu ion concentrations on accumulation by *S. obliquus* showed an initial rise with increasing Cu concentratssions up to 2.5 µgm L^{-1} Cu, after which a steady-state was achieved (Fig. 3). In case of Cd ion the steady state was however, observed at 1.5 µgmL^{-1} Cd, thus reflecting the availablability of lesser number of Cd binding sites in *S. obliquus.*

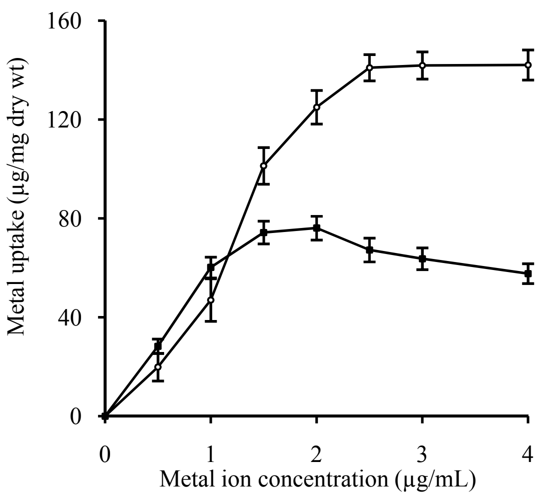

Fig. 3:Uptake of Cu (○) and Cd (■) ions per unit biomass of Scenedesmus obliquusat different metal concentrations.

3.4. Effect of pH

Metal ion accumulation was found to be a 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 Cu and Cd accumulation by *s. obliquus*

Metal accumulation (µg metal mg^{-1} dry weight)		
pH	**Cu**	**Cd**
4	49.92 ± 1.5^{a}	$28.00\pm 1.1b^{c}$
5	53.72 ± 1.8^{b}	$33.17\pm 1.8b^{c}$
6	57.14 ± 1.2^{c}	35.40 ± 1.2^{c}
7	66.00 ± 2.0^{c}	38.69 ± 1.2^{c}
8	55.56 ± 1.6^{ab}	35.77 ± 1.9^{bc}
9	46.07 ± 1.3^{a}	18.74 ± 1.5^{a}

3.5. Adsorption isotherm study

Isotherms for adsorption of Cu are illustrated in Fig. 4. The binding data at equilibrium for *S. oblique*, shown in Fig. 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 Cd adsorption followed the Langmuir equation (Fig. 4b), forming a unimolecular layer involving chemical forces.

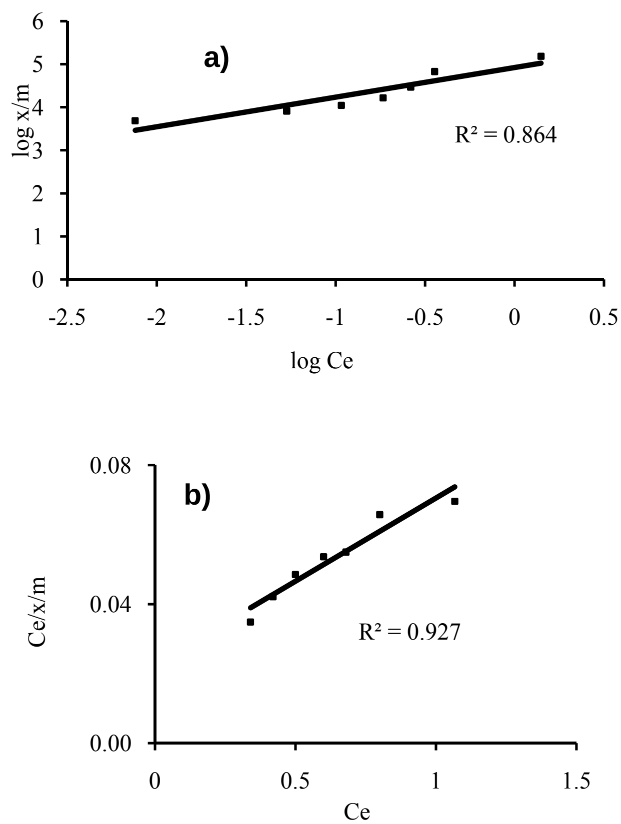

Fig. 4: Adsorption isotherms a) Freundlich isotherm for Cu ions b) Langmuir isotherm for Cd ions.

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 ions were 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.

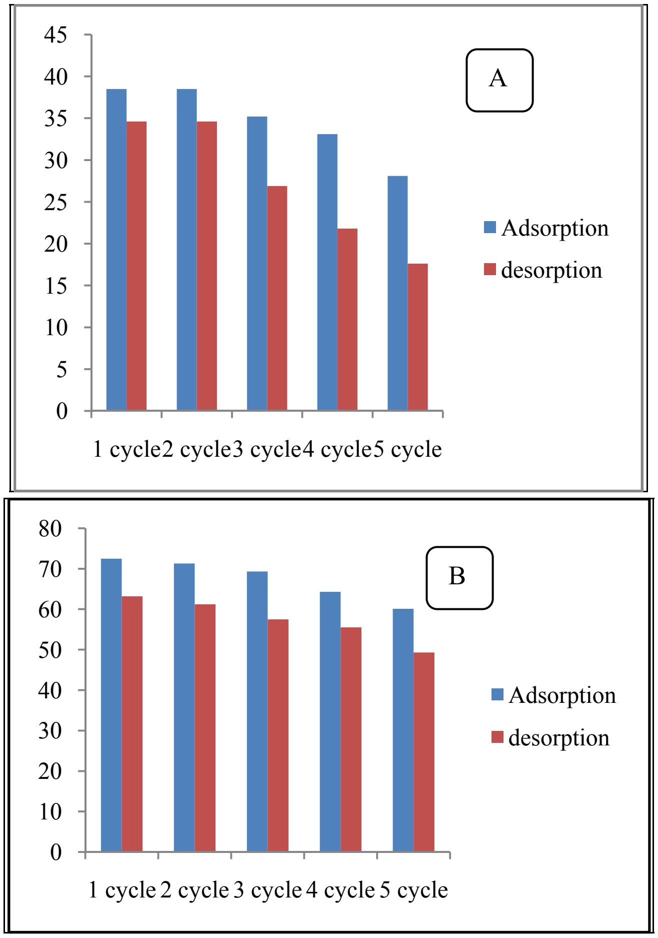

Fig. 5: Adsorption/Desorption cycles of (A) Cd and (B) Cu metal ions.

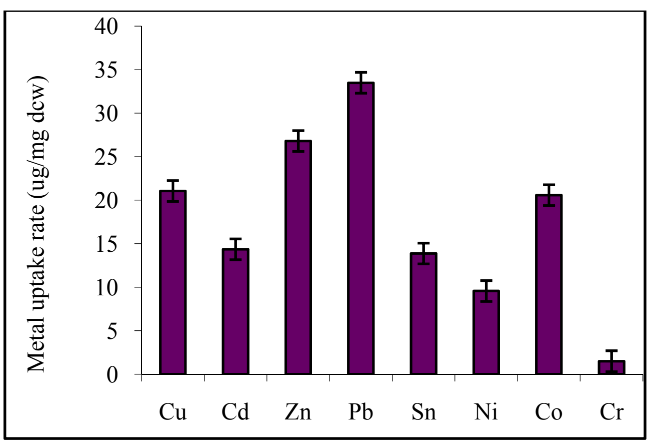

Fig. 6: Variation of metal rate uptake of biomass *S. obliquus* in multi-metallic combinations.

3.7 FT-IR Spectroscopy

The functional groups responsible for heavy metal biosorption on *S. obliquus* cells are confirmed by FT-IR spectra. The FT-IR spectra of the algal biomass indicate the presence of amino, carboxylic, hydroxyl and carbonyl groups.

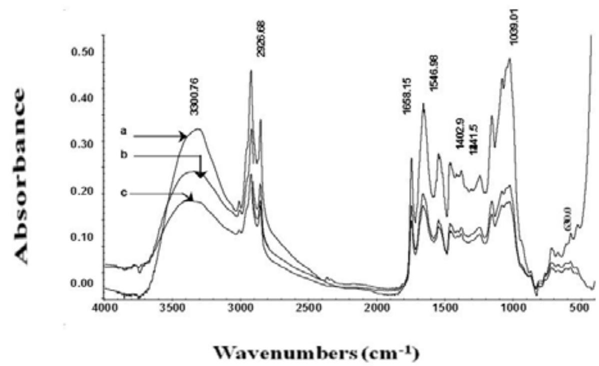

Fig. 7: Superimpose FT-IR spectra of (a) native biomass, (b) Cu and (c) Cd- treated biomass of *S. obliquus.*

Fig. 7 shows the absorbance of the peaks in the Cu and Cd treated algal biomass are significantly lower than that in the native one, thus demonstrating the binding of metal ions on to *Scenedesmus* surface.

4. CONCLUSIONS

Adsorption isotherm study depicted a multilayer binding for *S. obliquus.* As Freundlich isotherm indicates a reversible easy binding, which is regulated by *van der Waals* forces, it is obvious that the desorption/ recovery of the adsorbed metals could be much easier as compared to Langmuir/ BET binding, which is guided by chemical forces. The adsorption of metals from binary mixture of heavy metal was competitive and the adsorption capacity of any single metal decreased by 10– 40% in the presence of the other metallic species and the overall adsorption capacity of the algae decreased by 30–50%. Hence the *S. obliquus* for removal of heavy metal from waste water is a potent organism.

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