Biosorption of Cadmium and Lead from Semi-Synthetic Industrial Wastewater by *Sargassum* sp

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Abstract: ***In this research the batch removal of cadmium and lead ions from semi-synthetic wastewater solution using Sargassum sp. was determined. FTIR analysis showed that hydroxyl and carboxyl groups could be very effective for capturing these ions. pH, biomass dosage, contact time and initial concentration that were effective on the bioadsorption process were investigated. And then Langmuir and Freundlich isotherm models were used for the mathematical description equilibrium data. The experimental adsorption data of Cd^{2+} ions was fitted to the Langmuir isotherm.***

Keywords: Bioadsorption, isotherm models, *Sargassum* sp., semi-synthetic wastewater

1. Introduction

Heavy metal pollution is presently a main environmental problem because metal ions persist in the environment due to their non-degradable nature. Biological and chemical processes cannot break down heavy metals unlike organic contaminants. Consequently, they can only be transformed into a smaller amount of toxic species [1]. However, most of the conventional treatment processes such as chemical precipitation or coagulation become less useful and more cheaply when the adsorbates are in a low concentration range [2]. Living microorganisms can remove adsorptive pollutants like metals and dyes but dead biological material can also remove [3].The heavy metal ions can be trapped by the cellular structure of a microorganism and consequently sorbed onto the binding sites of cell wall [4].Biosorption process consists of two phases: one phases is a solid phase (biomass, sorbent, biosorbent, biological material) and another is a liquid phase (solvent, usually water) containing a dissolved species to be sorbed (sorbate, metal ion) principally, process, which is metabolism- independent accumulation of metals, is often rapid [5].

Biosorption of heavy metals by algal biomass is an advantageous unusual, a proper and economically reasonable method used for wastewater and waste clean-up because it uses algal biomass occasionally considered waste from some biotechnological processes [6,7,8] or simply its high availability in coastal areas make it suitable for developing new by-products for wastewater treatment plants [9].

Brown algae include in the division of Phaeophyta. Brown algae include high concentrations of alginic acid and sulfated polysaccharides. The polysaccharides are not present in terrestrial plants. The function of these polysaccharides is to allow marine algae to selectively absorb metallic ions in a saline medium through ion exchange [10].

Biomass of brown marine macroalgae is a renewable biological resource, which is available in large quantities and can form a good base for the development of biosorbent material [11]. The objective of the present work is to study the effective of brown algae on the biosorption of heavy metal from the semi synthetic wastewater.

2. Materials and Methods

The brown algae were collected from the Chaung Tha Beach located in Shwe Thaung Yan Township, Ayeyawady division in Myanmar. These were rinsed to remove the salts and other impurities with fresh water. The wet brown biomasses were dried under the sunlight. The dried biomass were crushed and sieved and the 2mm particle size fraction was kept for the experiments.

The industrial wastewater was collected from the Mandalay industrial zone (2). The semi-synthetic wastewater was prepared by mixing the Cd (II) and Pb (II) [1000 mg/ L] in the industrial wastewater. In order to obtain the optimum pH, the batch equilibrium sorption experiments were maintained at pH range of 3-6 by adjusting it with 0.5 M H_2SO_4 and NaOH. Experiments were carried out in the conical flask, using 1L of metal solution and 5 gram of biomass (dry matter).

These conical flasks were placed in the water bath shaker and ambient temperature. After the sorption equilibrium was reach (3 hrs), the solution was separated from the adsorbents by filter paper.

The metal concentration in solution was analyzed by using atomic adsorption spectrophotometer (AAS). Batch biosorption experiments were determined with the various parameters such as pH, contact time and initial metal concentration. The adsorbents were examined with the FTIR spectrophotometer before and after cadmium and lead biosorption. This technique was used to identify the chemical relevant to metallic ion sorption by the algal adsorbents. The equilibrium was used to calculate the uptake amount of metal by the biosorbents.

$$Q = \frac{V(C_i - C_f)}{M}$$

Where, Q is the metal uptake capacities (mg metal per g biosorbent). C_i and C_f are the initial and final metal concentration in solution (mg/l), V is the volume of the solution (ml) and M is the weight of adsorbents.

Langmuir and Freundlich model were used to fit the experimental data. The Langmuir isotherm can be expressed as

$$q = \frac{q_{\max} bC_f}{(1 + bC_f)}$$

where: b is constant which is related to the affinity of binding sites and q_{max} is the maximum biosorption upon complete saturation of the surface.

The Freundlich model is represented by the following equation.

$$q = kC_f^{(1/n)}$$

where: k and n are the Freundlich constant, k refers to the adsorption capacity and n is adsorption intensity.

3. Results and Discussion

3.1 Characterization of Biomass

The results of FTIR spectrum showed in the figure 1 that there were different functional groups detected on the surface of the algal biomass before and after bioadsorption. The band at 1029 and 3190 cm^{-1} were attributed to alcohol groups. The band at 1228 cm^{-1} was attributed to sulphate (SO_3) groups present in the fucoidan biopolymer. 1409 cm^{-1} band was identified to carboxylic (COOH) groups present in the alginate biopolymer. The bands at 1598 cm^{-1} was identified the amino groups present in proteins. According to the FTIR results, the peaks at hydroxyl, sulphate, carboxyl and amino groups were generally shifted after the biosorption. These groups are negative charges so they are capable of capturing the heavy metals ions.

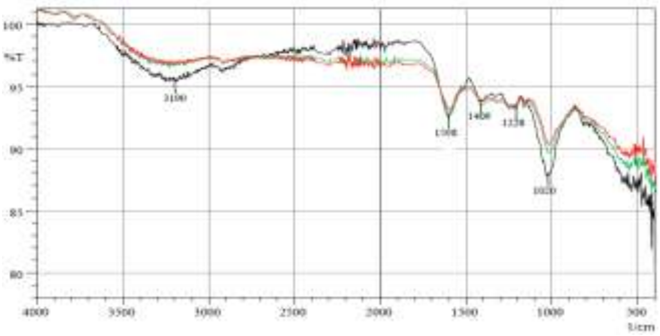


Figure 1: FTIR spectra obtained for algae before biosorption (black) and saturated with Cd^{2+} (red), Pb^{2+} (green)

3.2 Effect of pH

The pH value affects on the metal ion solubility and biosorbent total charge in the biosorption process while protons can be adsorbed or released. The effect of pH on the biosorption capacities of *Sargassum* sp. showed in the figure 2 that the pH is an important parameter for the bioadsorption process. As the results pH 4 is the highest uptake capacities in the lead ions among other pH range. In the higher pH, the lead ions are precipitated as hydroxides during the biosorption process. In contrast, the cadmium biosorption capacities were the highest at the pH5.

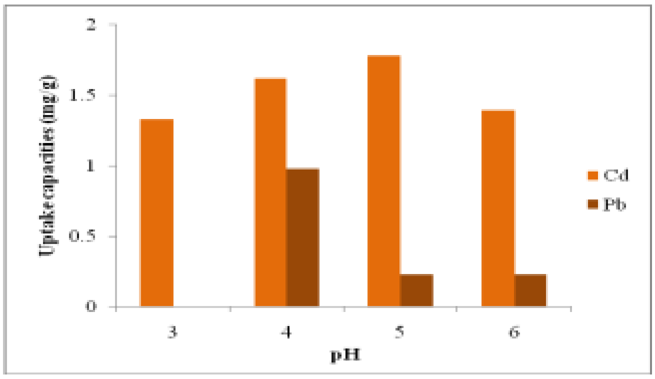


Figure 2: The effect of initial pH on the biosorption of metal from the metal solution by *Sargassum* sp. Orange bars: Cd^{2+}, Brown bars: Pb^{2+}

3.3 Effect of Biosorbent Dose

The effect of biosorbents dosage on sorption capacity by *Sargassum* sp. showed in figure 3. For the determination of the optimum biomass dosage, the range 0.1-1.5 g/100ml of *Sargassum* sp. were suspended in the synthetic waste solution, at pH 4 and 30°C for 3 hour. In the removal of cadmium ions, the uptake capacity is 6.67 mg/ g at 0.1 g/100ml of adsorbents. When the biosorbents dosage was increased to 1.5 g/100ml, the uptake capacity decreased to 1.048 mg/g. On the other hand, the uptake capacity of adsorbent in the lead ions is 10.08 mg/g at 0.1g/100ml.Also the uptake capacities decreased to 0.71 mg/g at 1.5g/100 ml of lead ions. The metal uptake capacities decreased while the adsorbent dosage increased. This is because the sorbent dosage influences the density of reactive groups available for metal binding and on the external surface area of the sorbent.

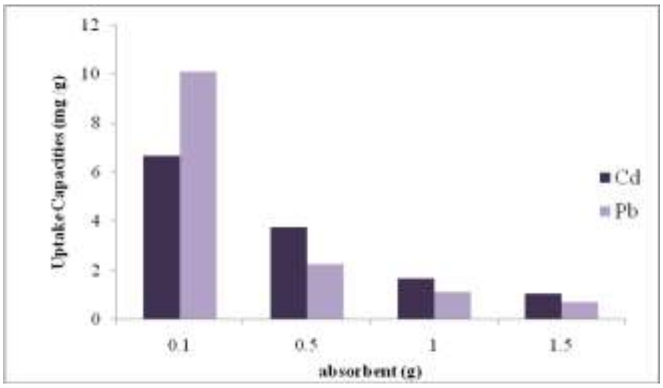


Figure 3: Effect of Biosorbent dosage on Metal Biosorption (Cd^{2+} and Pb^{2+}) by *Sargassum* sp.

3.4 Effect of Initial Metal Concentration

The uptake capacity of biosorbent at different metal concentrations showed in figure 4. The results indicated that the uptake capacity gradually increased between the concentrations of two metallic ions (Cd^{2+}, Pb^{2+}) 100 mg/Land 600 mg/L. This can be assumed that the 5gram of adsorbents contained enough biosorption surfaces and sites for these concentration ranges.

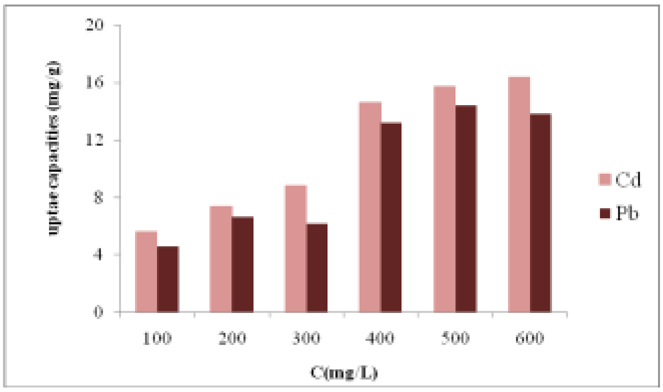


Figure 4: Effect of Initial Metal Concentration on Metal Biosorption by *Sargassum* sp.

3.5 Effect of Contact Time

The cadmium and lead biosorption capacity were determined by *Sargassum* sp. upon the contact time that showed in figure 5. According to the experimental data, the cadmium uptake capacity was reached a peak at the contact time1 hr. However, the lead uptake capacity was slowly increased between 1 and 2 hour. And then, there was a slight rise in the lead ions at 3 hour. This can be assumed that the biomass surface composed of different kinds of functional groups with different affinities to the metal ions.

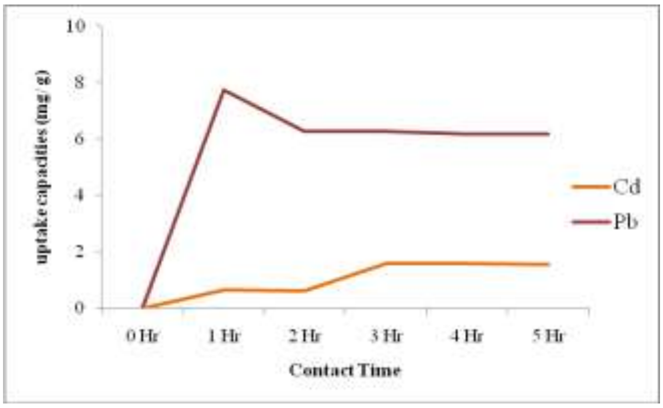
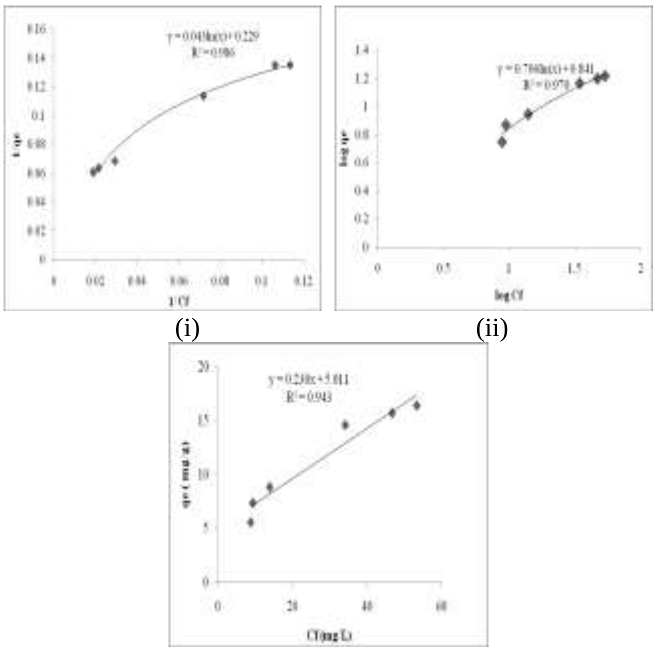


Figure 5: Effect of contact time on Cadmium and lead biosorption by *Sargassum* sp.

3.6 Biosorption isotherm models

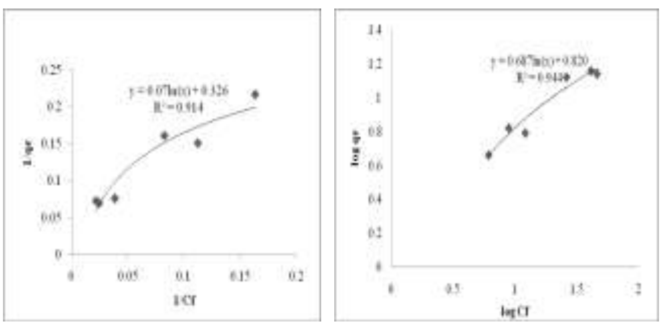
The relationship between the mass of the adsorbed component and the concentration of this component in the solution can be described with the biosorption isotherm. The biosorption isotherms for the Cd^{2+} and Pb^{2+} in *Sargassum* sp. were adjusted by Langmuir isotherm, Freundlich isotherm and linear model that showed in figure 6 and figure 7. In the assumption of Langmuir theory, adsorption takes places at specific homogeneous sites within the adsorbent. The basic assumption of Freundlich isotherm is that adsorption can be interacted between adsorbed molecules on heterogeneous surfaces. The Langmuir isotherm is widely used in adsorption isotherm.

The correlation regression coefficient of Langmuir for cadmium (R^2) is 0.986. The regression coefficient of Cd^{2+} is better defined by Langmuir than by Freundlich equation. However, the linear regression of Cd^{2+} ions is 0.94 so this is not as good as the two other biosorption model. According to the results, the experiment for the Cd^{2+} was fitted in the Langmuir. And then, the Freundlich exponential factor (n) for Cd^{2+} ions is 1.85. On the other hand, the regression coefficient (R^2) of Pb^{2+} in the Langmuir isotherm is 0.914 and in the Freundlich is 0.944. In the linear model, the regression value is 0.881 for the adsorption of lead ions. The value of coefficient in Freundlich is larger than the other two models. So the adsorption of Pb ions is well fitted to the Freundlich. The exponential factor (n) is 1.74. The results of biosorption model for Pb^{2+} ions are not as good as Cd^{2+} ions. The Freundlich exponential factor indicates the degree of nonlinearity between solution concentration and adsorption. If the constant value is greater than one, the adsorption can be a physical process [12].

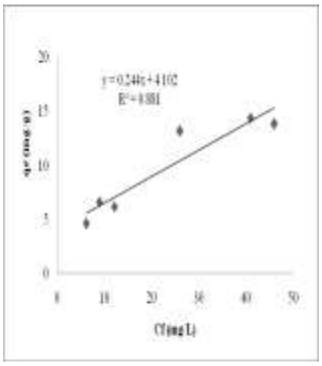


(i) (ii) (iii)

Figure 6: Bioadsorption isotherm for Cd^{2+} by *Sargassum* sp. (i) Langmuir, (ii) Freundlich and (iii) Linear



(i) (ii)



(iii)

Figure 6: Bioadsorption isotherm for Pb^{2+} by *Sargassum* sp. (i) Langmuir, (ii) Freundlich and (iii) Linear

4. Conclusion

In this research, the batch removal of Cd^{2+} and Pb^{2+} ions from synthetic wastewater solution using algal adsorbents was studied. By analyzing the FT-IR, the functional groups which can bind to metallic ions were observed in *Sargassum* sp. These functional groups are alcohol, sulphate, carboxylic and amino groups. pH is strongly influenced on the metal adsorption capacity. The contact time to reach equilibrium for each metal ion was not same. The experimental data well describes by the Langmuir on adsorption of Cd^{2+} ions. However, the Freundlich model can represent the isotherm better for the Pb^{2+} ions than the other isotherms.

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