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Absorption Capacity of Red Seaweed (*Palmaria Palmata*) In Removing Cadmium from Aqueous Solution

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Abstract

Locally sourced red seaweed *Palmaria palmata* was employed for assessing it efficiency in cadmium removal. A range of concentrations 3.0 – 100 mg/L Cd^{2+} were prepared by dilution of the 1000 mg/L stock solution with deionised water to test for the biosorption process. The result showed that up to 91.2 ± 0.4 % was removed at 10 mg/L. Biosorption isotherms (Langmuir, 1918 and Freundlich, 1906) models have been used in this work to investigate the biosorption of Cd^{2+}. The main objective of this study was to investigate the cadmium removal efficiency by red seaweed *Palmaria palmata*. Preliminary studies suggested that *Palmaria palmata* was a good absorbent for metal removal. Therefore, in this work attempt were made to study the impact of factors such as pH, initial metal concentration, contact time and biomass dosage that may influence the cadmium removal by the seaweed.

Keywords: *Palmaria palmata, cadmium, biosorption, Atomic Absorption Spectroscopy, Fourier-transform infrared analysis.*

1. Introduction

One of the world environmental challenges in the 21st century is pollution. The most common forms include water, air and land pollution. Heavy metals such as cadmium pose a great risk of contributing to pollution worldwide because of their industrial uses and inherent toxicity.[1] Both cadmium and lead can contaminate the water bodies via the food chain, thereby affecting the ecosystem.[2] Bio sorption is an innovative technology that utilises both living and non-living biomass to remove toxic metals from aqueous solutions.[2] Bio sorption has many advantages over conventional techniques such as chemical precipitation, ion exchange, chemical reduction and evaporation. In this study, marine red algae (*Palmaria palmata*) were used to test for cadmium and lead removal in aqueous solution.

Biosorption isotherm models

The biosorption isotherms are mathematical models that explains the behaviour of an adsorbate species between solid and liquid phases. The assumption was that the Langmuir isotherm provides an explanation on monolayer coverage of metal ions over a homogenous sorbent surface.[3] The Langmuir isotherm is mathematically represented as proposed by Langmuir in 1918 as follows.[4]

$$q_e = q_{max}{}^{b}C_e/(1+bC_e) \qquad (1)$$

Where q_e (mg/g) is the observed biosorption capacity at equilibrium. q_{max} (mg/g) is the maximum biosorption capacity corresponding to the saturation capacity otherwise known as total binding sites of biomass, C_e (mg/L) is the equilibrium concentration and *b* (L/mg) is a coefficient related to the affinity between the sorbent and sorbate (*b* is also known as energy of adsorption). The linear relationship can be obtained by plotting ($1/q_e$) vs. ($1/C_e$):

$$1/q_e = 1/(bq_{max}\,C_e) + 1/q_{max} \qquad (2)$$

The parameters *b* and *q* are determined from slope and intercept respectively. This equation can be used to compare the individual bio sorbent by its respective q_{max} value calculated from fitting the Langmuir isotherm model to that of the experimental data.

Metal removal efficiency

Biosorption capacity (q_e),[5] the amount of metal adsorbed per gram of biosorbent, can be calculated at equilibrium in mg/g using the following equation;

$$Q_e\,(C_o - C_e)V/m \qquad (3)$$

Where C_o is the intial concentration of metal ions in a given solution (mg/L)
C_e is the concentration of metal ions remaining in the solution (mg/L), V is the final volume of the solution (Litre) and m is the mass or weight of biosorbent measured in grams.[2]
Moreover, metal uptake can also be calculated in percentage as cited in[2] as shown below;

$$\%\ \text{removal} = (C_o - C_e)/\,C_o\,.100 \qquad (4)$$

Palmaria palmata also known as dulse

A flat red species growing from a discoid holdfast either as a simple blade, with or without marginal proliferations, or with branches, which divide in a forked manner. Plants grow to 50 cm in length , 30 mm to 80 mm wide and between 0.15 to 0.35 mm thick, althoguh thicker where reproductive.[6]

Fig. 1 *Palmaria palmata* (present study)

Some other identifying features of *Palmaria palmata* is that the blade texture varies from leathery to membranous. The colour is purplish or brownish red. The method of reproduction is confusing and the larger thalli that are found on the shore are either male or have sporangia[6]. The identification was further confirmed by Professor David Thomas of school of ocean sciences, Bangor University who specializes in industrial scale microalgal biomass production and utilization, seaweed and halophyte ecology and physiology.

2. Experimental

2.1 *Preparation of cadmium solutions*

The analytical grade salt $Cd\ (NO_3)_2.4H_2O$ from Fisher Scientific U.K was used to prepare a 1000 mg/L Cd^{2+} stock solution. Cadmium nitrate tetrahydrate (0.2716 g) of was dissolved in distilled water to make 1000 mg/L stock solution using 100 mL volumetric flask. A range of concentrations 3.0 – 100 mg/L Cd^{2+} (See methods below and was adapted from[2]) were prepared by dilution of the 1000 mg/L stock solution with deionised water. The initial pH of these sub-stock cadmium solutions was adjusted to pH 5.5 with dilute 2M HCl. Initial metal concentration of 50 mL (volume) of 10 mg/L was measured using flame atomic absorption spectroscopy (Perkin Elmer AAnalyst 100). All samples were diluted and filtered using Whatman No. 40 filter paper before analysis.

2.2 *Preparation of the seaweed*

The *Palmaria palmata* used in this work was collected from Conwy Morfa beach (Lat: 53.2914˚N, Lon: 3.8575˚ W) North Wales, U.K. The collected seaweed was washed several times with tap water,followed by distilled water in order to remove salt and particulate materials from the surface. The seaweed was roughly chopped with scissors and allowed to dry at room temperature for 48 hours before being transferred into an oven for 24 hours to dryat 105℃. The seaweed was then ground to powder using an electrical cyclone mill - and sieved to uniform particles size (0.5 mm).

2.3 *Variation of initial cadmium concentration*

The extent at which cadmium is removed from an aqueous solution is strongly dependent on the initial metal ion concentration. Initial cadmium concentrations were varied (3.0, 5.0, 7.0, 10.0, 25.0, 50.0, 75.0 and 100 mg/L) at constant pH (5.5 ± 0.05). Other parameters that were kept constant include mass, volume, shaking time and temperature: 0.1 ± 0.02 g of algal biosorbent added into 10 mL solution at 30℃ and shaken at 180 rpm for 120 min.

2.4 *Sample digestion and centrifugation*

All samples in triplicate were digested prior to the measurement using the following procedure: The mass of 0.1 g bio sorbent (*P. palmata)* plus 5 mL concentrated nitric acid (70 % extra pure Fisher Scientific U.K) was added in a digestion tube 25 mm in diameter – Fisher Scientific U.K then place in a digestion block at 80°C.

For 1 hr, 100°C. for 1 hr then 120°C. For 2 hr then leave to cool before been filtered using filter paper (20 μm porosity) and finally make up the solution to 50 mL prior to analysis with dH_2O. Furthermore, the solid and filtrate were separated via filtration. The concentration of Cd in the filtrate was then analysed and solid digested with 5 mL concentrated nitric acid, which was diluted to 15 mL with deionised water prior to centrifugation at 3000 rpm and filtered.

2.5 *Effect of varying pH*

The effect of diffferent starting solution pH values on cadmium absorption by the algal samples was measured between pH 2.00 – 8.00 ± 0.05.[2] The pH of each of the starting cadmium solutions was adjusted using 0.02 M HCl to obtain pH 2, 3. 4, 5. 5.5 and 6.0. The other parameters in this experiment - solution volume, shaking time, temperature, initial metal ion concentration and biosorbent amount were fixed at 10 mL, 180 rpm, 120 minutes, 30 ℃, 10 mg/L and 0.1 ± 0.02 g respectively.[2,7]

2.6 *Effect of varying the biomass amount*

In this section of the experiment, the amount of biomass was varied (0.05, 0.1, 0.2 and 0.4 ± 0.02 g) to verify the effect of *P. palmata* on sorption process. The other parameters in this experiment - solution volume, shaking time, temperature, intial metal ion concentration and pH were kept constant .The individual weights were mixed and shaken with 10 mL solution of 10 mg/L at 30 ℃, pH 5.5 ± 0.05, 180 rpm for 120 minutes.[2,7]

2.7 *Cd Atomic Absorption Spectroscopy*

Cadmium standards in the range of 0.2 – 10 mg/L were prepared from a commercial 1000 mg/L stock solution (B) (Fisher Scientific U.K) to get a calibration curve for AAS/ICP analysis. The instrument operating conditions were: wavelength 228.8 nm, lamp current at 4 A, using air- acetylene flame and slit width is 0.1 nm).[8]

2.8 *Fourier-transform infrared analysis (FTIR)*

Raw ground *P. palmata* samples were examined with a Bruker alpha FTIR spectrometer within the wavenumber range 400 – 5000 cm^{-1} under ambient conditions. This method was used to elucidate the chemical characteristics of carboxylate groups and phenolic hydroxyl groups relevant to metallic ion sorption by algal biomass.[9]

3. Result and discussion

3.1 *Effects of initial Cd^{2+} concentration*

Figure 4 highlighted the varying effects of initial Cd^{2+} concentration on solid biomass and that the bio sorption process start at 53.6 ± 10.4 % at 3 mg/L and increases up to 91.2 ± 0.4 % at 10 mg/L before it then starts to depreciate with a steady decrease as the concentration increases. The process of bio sorption is very fast at the beginning with the filtrate (solution) at 3 mg/L for 77. 5 ± 4.2 % while that of solid biomass was just 53.6 ± 10.4 % of same concentration (3 mg/L). The possible reason for the plateau observed in Figure 4 is at higher initial cadmium ion concentrations maybe the binding capacity of the fixed mass of algal powder has been exceeded. This might be due to the exposure of the biomass with metal thereby creating availability of binding sites and contact which may cause the rapid removal of the metal ions by the biomass. However, the removal for solid biomass at 100 mg/L (91.2 ± 0.4 %) was higher when compared to 82. 2 ± 0.4 % of filtrate of same concentration. The reason for this also can be attributed to the binding sites in the filtrate been over saturated and coupled with other competing factors such time of agitation and contact. Statistical analysis using T-test conducted on solid biomass and filtrate solutions suggest that the removal is statistically not significant ($p > 0.05$)

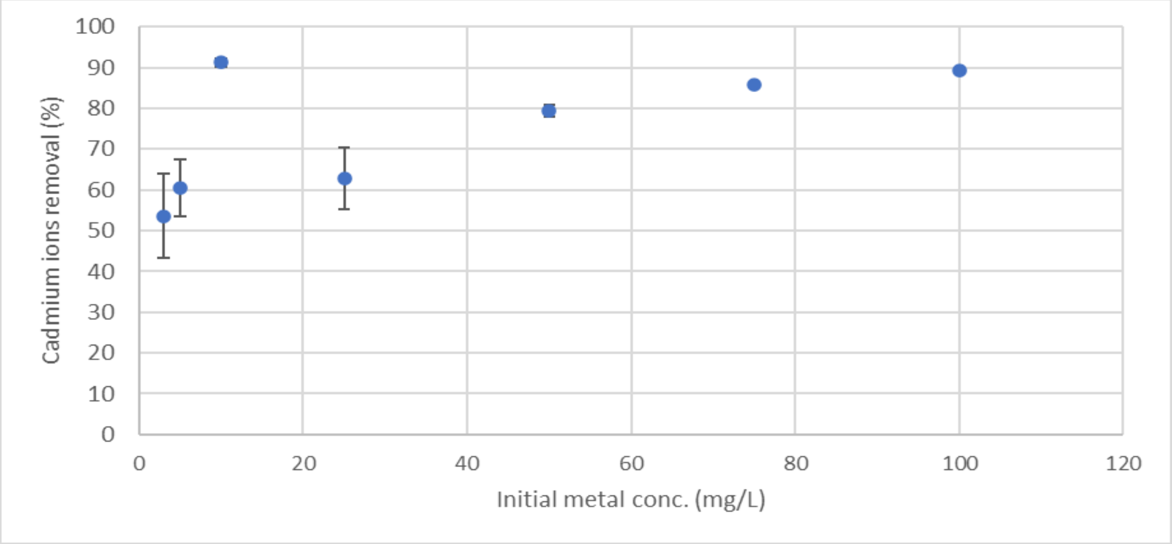

Figure 4. Effect of initial cadmium ions concentration on solid mass removal (T = 30℃, 0.1 g dried algae, at fixed values of pH, contact time etc (see section B for full conditions) n = 5, and standard error bars (SE). SE are the approximate standard deviation of a statistical sample population.

Figure 5 below represents the effects of different initial metal (Cd^{2+}) concentration on filtrate. The data in the figure shows that as the initial metal ions concentration increases the percentage removal of Cd^{2+} ions adsorption also increases. This can be seen in a similar work conducted by Ghoneim *et al.*[2] In current study of filtrate solution the % removal starts at 77.5 ± 4.2 % for 3 mg/L and increases up to 82.2 ± 0.4 % at 75 mg/L Cd^{2+} then decreases gradually as the initial metal concentration increases.

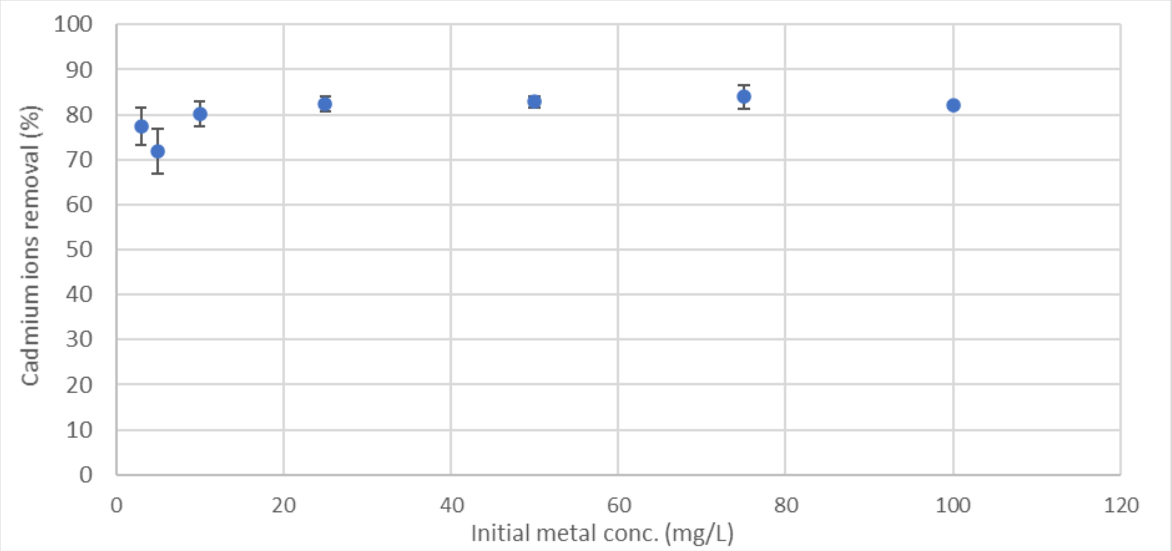

Figure 5. Effect of initial cadmium ions concentration on filtrate (solution) removal (T = 30°C, 0.1 g dried algae, at fixed values of pH, contact time, n = 5, and standard error bars

The possible increase in adsorption can be due to driving forces (concentration gradient).[2] At lower concentrations, all cadmium ions in the solution could interact with the binding sites and therefore, the percentage adsorption increased gradually as Cd^{2+} concentration increases. Alternatively, at higher concentrations greater than 7 mg/L Cd^{2+}, a slight decrease in adsorption may be due to the saturation of all the adsorption sites. This might be due to increase in the number of ions competing for available binding sites in the seaweed.[10]

In figure 6, the result shows an equilibrium linearity between the concentration and the sorption capacity of the marine seaweed (*P. palmata*) and thus, Langmuir model will be more favourable. A review-conducted by Mehta and Gaur [8] reported the sorption capacity of a seaweed cells surface to a particular ion can be greatly depends on many factors. Such as the binding groups for the metal ion, number of functional groups in the algae matrix, the complex formation, the coordination number of the metal ion to be sorbed, affinity constants of the metal with the functional group as well as the chemical state of these sites.

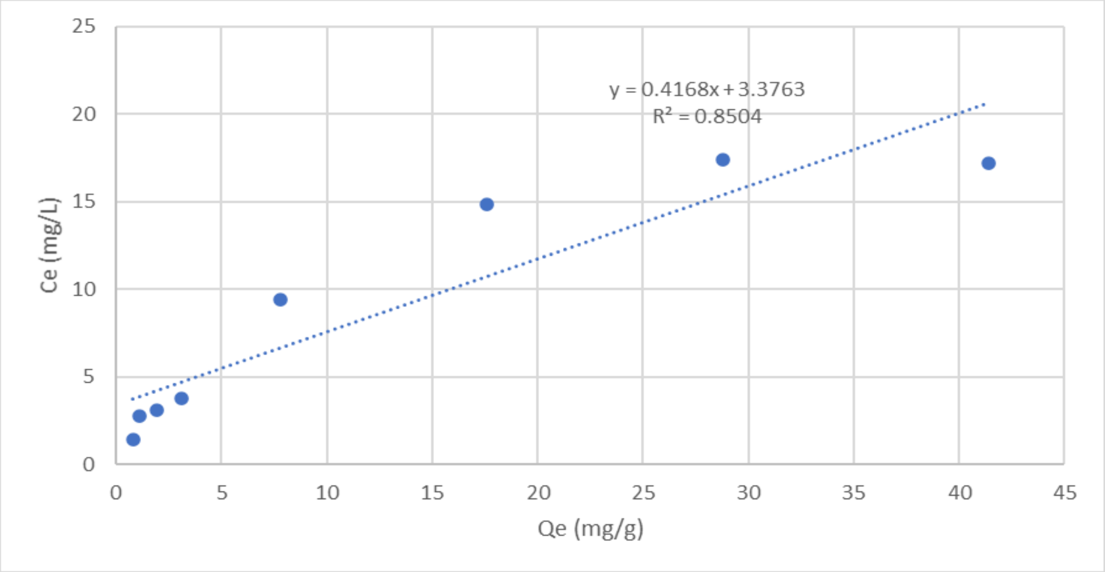

Figure 6. Linearity relationship between sorption capacity and the concentration at equilibrium at fixed conditions (see method section above), $R^2 = 0.85$

The sorption capacity increases at equilibrium with an increase in the initial metal ions concentration. From figure 6 above, the maximum biosorption capacity corresponding to the saturation capacity of biomass can be observe. Table 1 in the appendix presents the result of metal concentration before and after sorption process.

3.2 *Effect of varying pH*

The effect of pH on percentage (%) cadmium removal was tested on the samples with a range of pH values 2.0 – 8.0 in order to identify the maximum pH value for cadmium removal. Similar analysis was carried out on both filtrate (solution) and solid samples. Biosorption of heavy metal ions is believed to be largely depends on the pH of the solution as it affects biomass surface charge; species of biosorbent and degree of ionization.[11] Figure 7 represent the filtrate (solution) of *P. palmata* metal removal in which the metal percentage removal shows an appreciable increase up to 61.50 ± 1. 0 % at pH 5.5 ± 0.05 and then slightly decreased. However, in contrast, when the pH was increased, the partial desorption of protons occurs thereby allowing the sorption of Cd (II) onto the sites left by protons at the surface of biomass,[2] causing the biosorption to reached the maximum (61.50 ± 1.0 %) around pH 5.5 ± 0.05. Moreover, based on these results, it may be suggesting that clear competition for the *P. palmata* sorption sites between Cd (II) and proton.

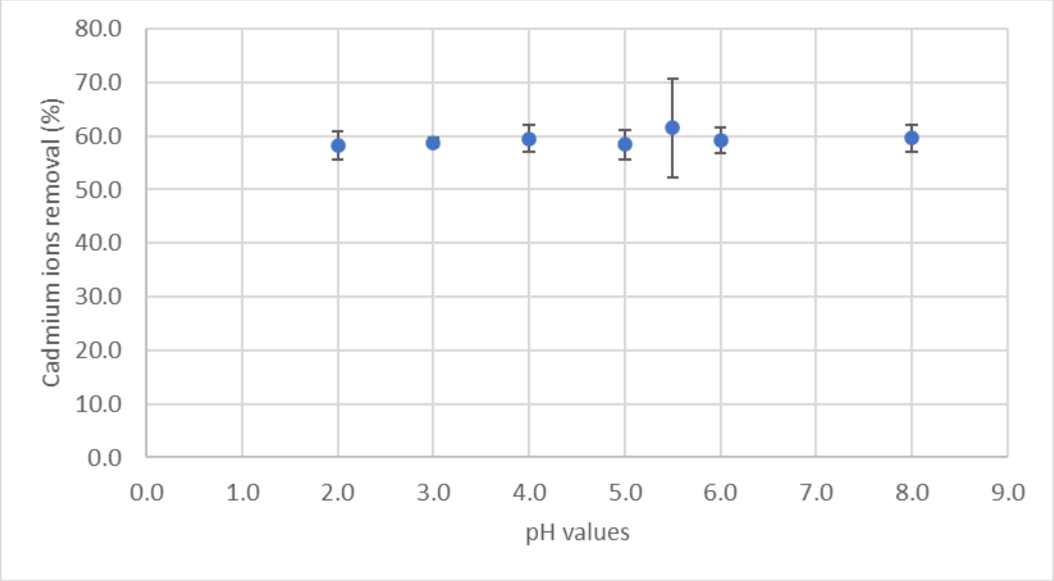

Figure 7. Varying pH effects on cadmium ion metal bio sorption by filtrate solution

The slight decrease in absorption values higher than 5.5 pH, may be because of the amount of OH^- ions been increase in the solution. Thus, causing metal ions to react with OH^- ions and are precipitate as a metal hydroxide at higher pH value.[12] Further studies also reveals that at more alkaline, the percentage removal is low compare with the optimum condition. Memon *et al.*, 2008 cited in their work of [2] believed that, this may not be connected to the binding sites that are likely not activated in the basic conditions. Also, in what can be described as a supportive hypothesis Dursun (2006)[13] justify this by stating that pH of the solution influences both chemistry of the metal in solution and metal binding sites on the cell surface. Another study conducted on the effect of pH for *P.palmata* sample to test for copper and lead reported that the metal ion binding increased with an increasing pH.[1] The removal varied for copper (7.6 % to 16.2 %) and lead (6.45 % to 13 %) respectively.[1] This was in agreement with current and other studies.[1,14,15] In our study as shown in figure 8 revealed that the higher percentage removal of cadmium ion by the biomass compared to filtrate samples. The absorption starts very rapid up to 81.80 ± 5.7 % at pH 2 ± 0.05 and then increases steadily. The highest percentage removal for the pellet was recorded at pH 4 ± 0.05 (90.90 ± 17.08 %) and this values agreed with similar study conducted by Ghoneim *et a l*[2] testing for different pH values in which same marine green algae (Ulva lactuca was tested and found to have removed up to 91.90 % at pH 5.5. In conclusion, it can be suggested that both the solid and filtrate solution of *P. palmata* can be used to remove cadmium ion from an aqueous solution.

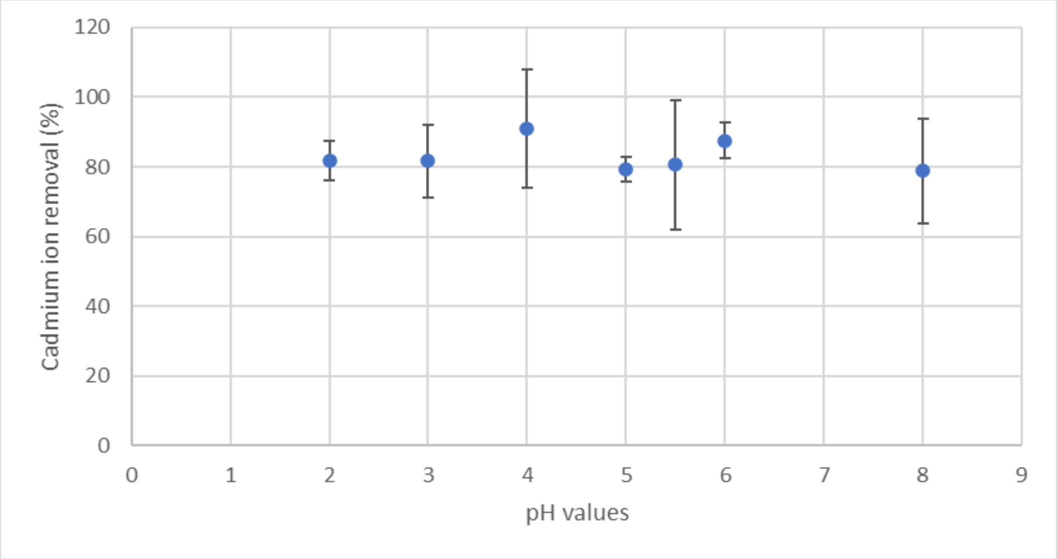

Figure 8. Varying pH effects on cadmium ion metal bio sorption by solid biomass.

3.3 *Effect of biomass amount*

The effect of biomass amount was also considered in which the mass in grams is varied and the result presented in figure 9. In this figure, it was observed that the amount of cadmium ions adsorbed varied with varying alga amount. The figure recorded the percentages removal of 97.0 ± 2.4 %, 96.5 ± 1.1 %, and 96.0 ± 0.1 % and 96.1 ± 1.30 % at weights of 0.050, 0.10, 0.20, 0.40 and 0.50 ± 0.002 g respectively. The highest biosorption cadmium removal was observed at highest amount of biomass of 0.50 g.

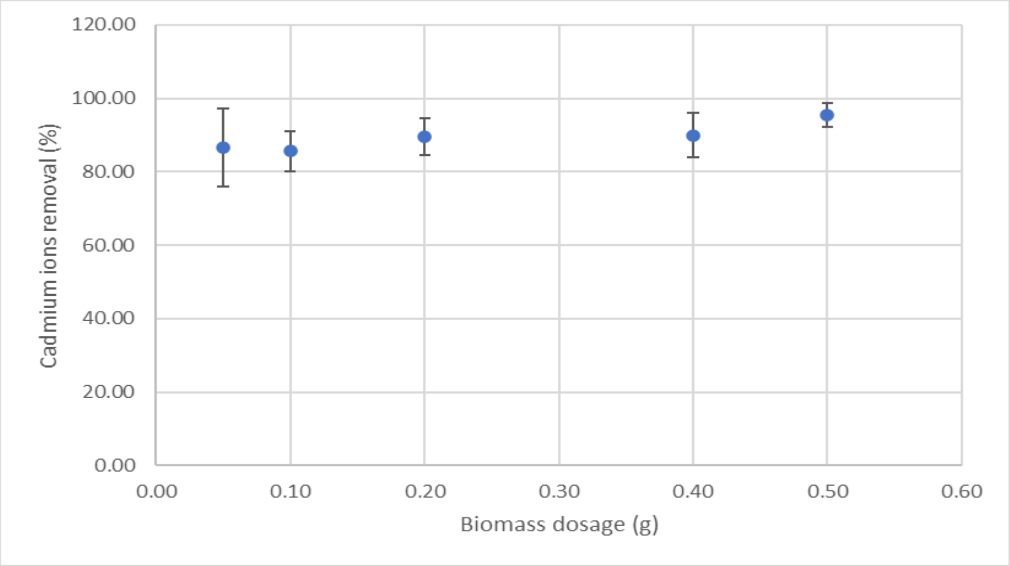

Figure 9. Effects of biomass amount on % cadmium ion removal

Many research studies have shown that high amount of biomass causes cell agglomeration with a consequent reduction in intercellular distance and thereby causing what they called ‘screen effect’ among a dense layer of cells and that will protect the binding sites from the metal ions.’[16] The values obtained in this work are similar to those reported by other researchers[17,18] where they found lower biosorbed metal capacity (q) at high adsorbent concentrations.

3.4 *Fourier-transform infrared analysis (FTIR)*

FTIR analysis conducted on the biomass sample in order to identify the various functional groups in *P. palmata* that are responsible for the metal removal. Figure 10 shows the functional groups present in the algae. The peaks appearing in the FTIR spectrum were assigned to various functional groups base on their respective wave numbers as reported in the literature.[19]

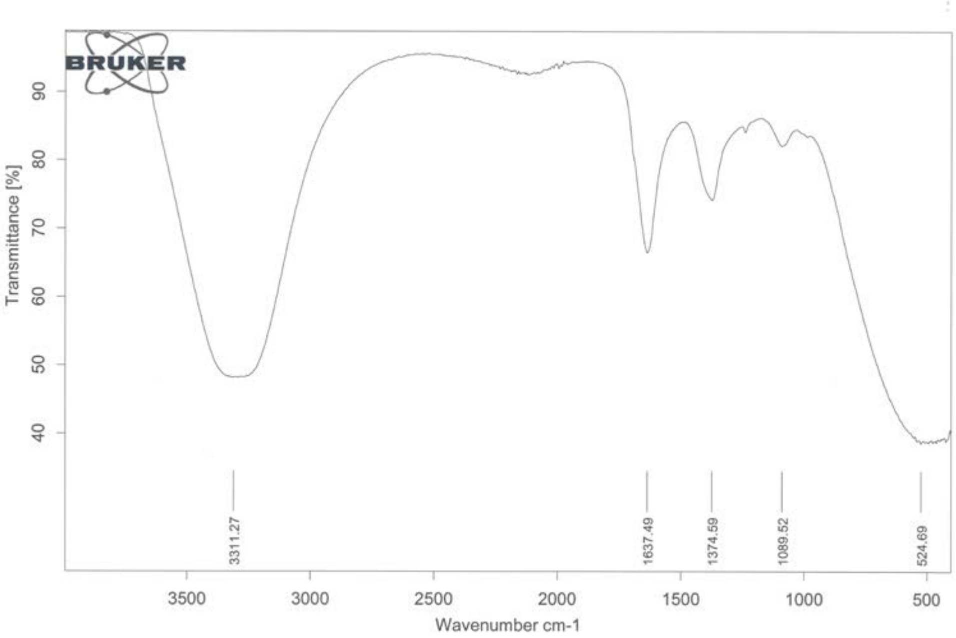

Figure 10. FTIR spectrum of *Palmaria palmata* before biosorption of cadmium

The bands at 3267 and 2925 cm^{-1} indicates the presence of hydroxyl and amino groups respectively. The bands of 3409 and 2985 cm^{-1} was assigned to presence of H-bonded OH stretched and NH_2 in which the presence of hydroxyl and amino groups was predicted respectively.[19] The peak at 2931 cm^{-1} is associated with the stretching vibrations of C-H bond of methyl, methylene and methoxy groups.[19] The band at 2364 cm^{-1} also indicates C-H stretching from CH_2 groups.[19] The peak observed at 1597 cm^{-1} correspond to the C=C stretching which may be attributed to the presence of lignin aromatic bond.[19] Also the presence of peaks at 1313 cm^{-1} indicated the presence of C-O as cited in.[19] Amides was presence at the peak 1248 cm^{-1}.[3] and finally the band at 1028 cm^{-1} shows the presence of alcohol or carboxylic acid.[20]

3.5 *Biosorption isotherm models*

The biosorption isotherms are mathematical models that explains the behaviour of an adsorbate species between solid and liquid phases. The most prominent among these are Langmuir and Freundlich isotherm models (Langmuir, 1918 and Freundlich, 1906). These models have been used in this work to investigate the biosorption of Cd^{2+} and Pb^{2+} ions by *Palmaria palmata* and *Fucus spiralis* respectively. The assumption was that the Langmuir isotherm provides an explanation on monolayer coverage of metal ions over a homogenous sorbent surface.[3] The Langmuir isotherm is mathematically represented as shown in section 1 above.[4]

The Langmuir isotherm tested (figure 11) proved the favourability of cadmium ions adsorption on the biomass ($R^2 = 0.9387$) and this indicates that the bio sorption process fit Langmuir model.

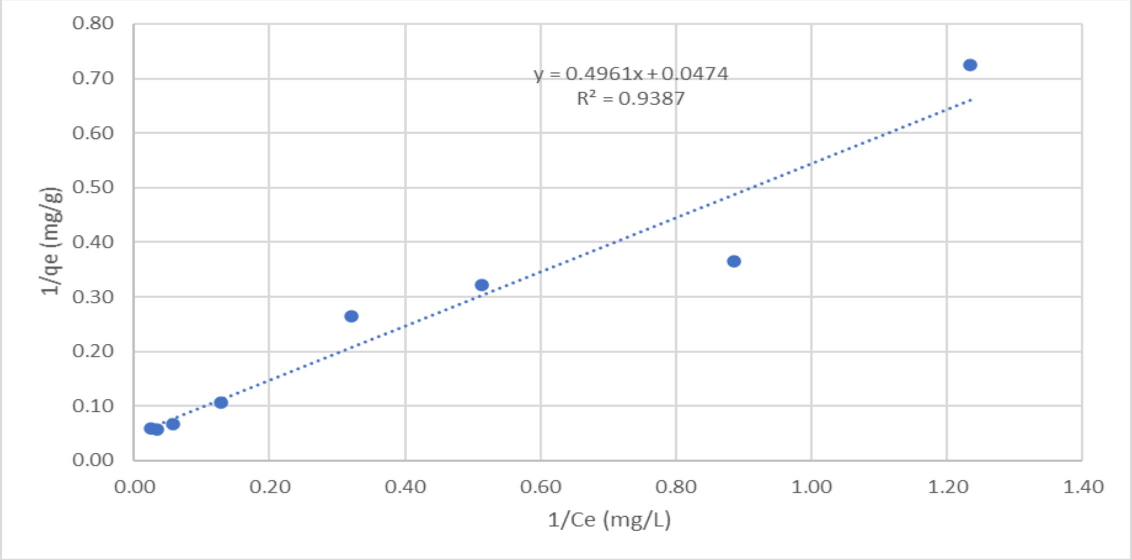

Figure 11 Langmuir isotherm plot for Cadmium ions

Freundlich isotherm model assumes that, the stronger binding sites are occupied first and that the binding strength decreases with an increasing degree of site occupation.[21] As shown in figure 12 below thus, a plot of log q_e versus log C_e gives straight line, from the intercept of which k_f may be calculated and from the slope and 1/n calculated as well. K_f is associated with adsorption capacity and 1/n indicates the adsorption intensity (Freundlich, 1906).

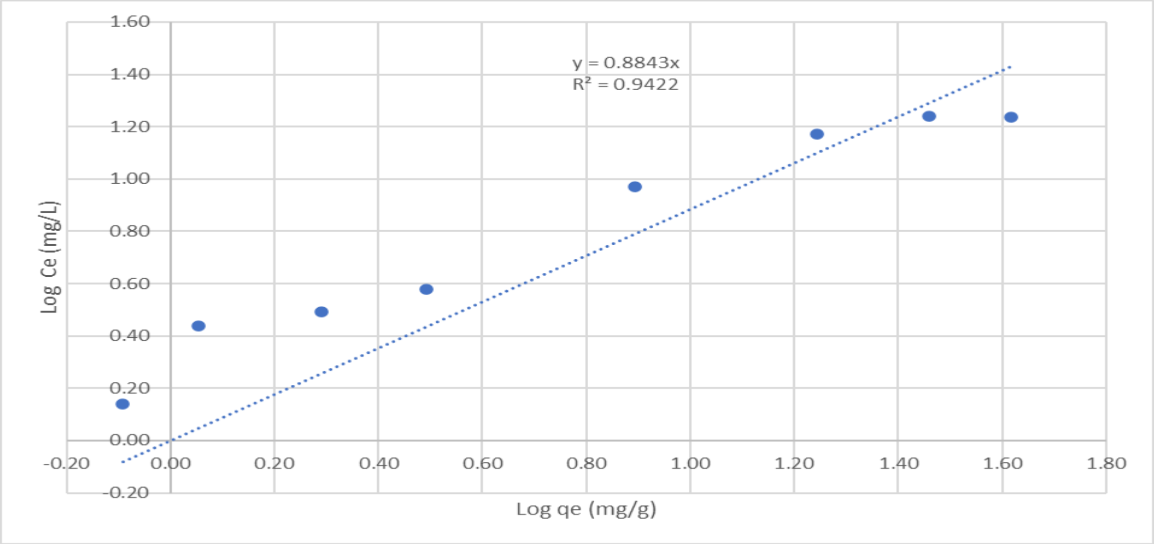

Figure 12 Freundlich isotherm plot of for cadmium ions.

4. Conclusions

In summary, these results elucidated the sorption characteristics of *Palmaria palmata*. The biosorption of Cd by *P. palmata* can be described properly by the Langmuir and Freundlich models. The degree of metal uptake levels depended on contact time, pH and temperature. These physico-chemical parameters are expected to modify the ionic state of the biomass polymers and the form of metals in the aqueous solutions, thus influencing the metal binding properties of *P. palmata.*

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