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Uptake of heavy metal Cd(II) from aqueous solutions using brown algae *Sargassum myriocystum*

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The uptake of brown marine algae, *Sargassum myriocystum* has been utilized for the exclusion of Cd(II) metal from wastewater. Various parameters such as solution *p*H, optimum temperature, biomass concentration, the contact time and agitation speed have been analyzed for the effective biosorption of Cd(II). Desorption studies of Cd(II) have been performed with various desorbent such as H_3PO_4, HNO_3, HCL, H_2SO_4, NaOH, NaCl, and H_2O among which 0.1M/L HCl is found to be the better desorbing agent. SEM-EDX and FTIR analyses were utilized for metal-algal interaction study. The thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔHº) and entropy change (ΔSº) have been calculated through the Van't Hoff plot. A positive value of 14.72 ΔS Jmol-1K-1, a negative value of free energy (ΔG°) and 42.21 kJ/mol of ΔH kJmol-1 at all the temperatures indicated that the process is feasible and spontaneous. Hence, *S. myriocystum* is an effective and prosperous cost-effective biosorbent approach for Cd(II) from various industrial wastes due to its fast sorption rate, high selectivity and great uptake capacity.

Keywords: Cadmium, Enthalpy, Entropy, Free energy, FTIR, *Sargassum myriocystum*, SEM-EDX,

Environmental contamination is one among the harmful activity the world facing nowadays, which rises with every passing year, causing a series of severe damage to the earth. Heavy metal toxic have acknowledged a lot of interest and are flattering a vital universal problem, owing to industrialized and municipal behaviour, farming overflow, transportation and geographical climatic conditions[1]. Metals comprise of a mixed collection of fundamentals mostly diverse in their chemical and biological functions. These metals are reserved beneath the ecological noxious waste group owing to their deadly property on living organisms. Continuous activity with metals can cause severe health problems[2]. Heavy metal in the surroundings is bio-magnified and is deposited in tissues; as a result, contaminated properties of metals are originated in fauna of upper levels and predominantly in humans. The straight routes of individual contact to that metal into a stream will be any utilization of edible food derived from the river[3]. Nevertheless, conventional methods cover numerous disadvantages namely creation of lethal goods, costly, not all the time useful among little concentrations, more reagent, and power necessities[9]. Adsorption is an inventive skill to facilitate unwanted biomass for the elimination of metals. Various biomasses are used for biosorption of heavy metals namely bacteria, yeast, algae, fungi, and plants[3]. Of the different types of sorbents used the marine algae commonly called seaweeds is used predominantly as biosorbent[4]. This is because of the occurrence of functional groups on the surface of algae[5]. India has 8085 kilometers coastal line, in which an abundance of seaweed species are accessible. About 700 species of marine algae recognized in the various part of India and nearly 60 species are commercially significant. Marine algae contain a big external area which is responsible for adsorption of cations[6]. Industrial activities such as lead-acid battery recycling, battery manufacturing, mining, agricultural activities, painting, metal plating, cleaning, refineries, radiator manufacturing, as well as public waste dumping, are the main sources for heavy metal pollution[7]. Sargassum sp. is well-known seaweed that commonly used in favour of metal removal, because of the elevated amount of fucoidans, laminarin, and alginate in the surface[8]. The use of brown seaweed species was used in industrial effluent discharge sites somewhere biosorbent particles are packed in columns[9]. Sargassum sp. is able to gather a great quantity of metals because of the surface of the brown algae[10]. In the sorption process, the algal surface acts a significant function in metal removal because it contains high concentrations of algal polysaccharides in charge of the biosorption of metals[11]. Various functional groups in seaweeds are responsible for the sorption of heavy metals through various mechanisms. *Sargassum myriocystum*, the major marine macroalgae genus that appears in the class Phaeophyceae is broadly distributed on the southern coasts of Tamilnadu, India. The major purpose is to investigate the possible application of low-cost adsorbents of non-living algae to remediate cadmium contaminations. In this regard, an attempt was made to examine the effectiveness of *S. myriocystum* as a commercial sorbent for Cd(II) adsorption from synthetic metal solutions for Cd(II) uptake, algal characterization using SEM with EDX and FTIR and its application in Cd(II) removal.

Experimental Section

Biomass collection and Pretreatment of biomass

Brown marine seaweed *S. myriocystum* was collected from Mandapam, Ramanathapuram District, Tamilnadu. The brown algal seaweeds were washed thoroughly with distilled water to eliminate salts as well as sand debris sand as well as debris. The seaweeds were dried out overnight at 60°C. The dried samples were pretreated with acid permitted sorbent protonation.

Preparation of adsorbate

The sorption capacity of *S. myriocystum* for the heavy metal cadmium was investigated by using the synthetic metal solution and batch mode. The process parameters such as solution pH, biomass concentration, contact period, temperature, agitation, and initial metal concentration were optimized. The biomasses were characterized before and after metal sorption. Stock solutions of 1000 ppm were prepared by dissolving Cadmium sulfate (analytical grade, MERCK) in 1L of deionized water. Solutions of varying metal concentrations such as 25, 50, 100, 150, and 200 mg\L were prepared by using the stock solution. Cadmium Stock solution: Weighed cadmium sulfate 2.282 g (3CdSO4.8H2O) and dissolved in double distilled water made up to 1 liter with distilled water. 1 mL = 1 mg Cadmium (1000 mg/L).

Optimization of process parameters for batch studies

The batch study was conducted in 250 ml conical flasks containing 100mL of stock solution. The *p*H range of the metal solutions varies from 3.0 to 9.0 *p*H, biomass concentration range varying from 0.5 g to 3.5 g, contact time ranging from 10 min to 180 min, temperature is calculated from 20-500°C, initial metal concentrations at 25, 50, 100, 150, and 200 mg/L, and agitation speed was studied from 50, 100, 150, 200, 250 and 300 rpm. The filtrate containing residual concentration of cadmium was determined by Atomic Absorption Spectrophotometer. All experiments were conducted in triplicates.

Determination of Cd(II) in the solution

Biosorption experiments were carried out in duplicate and average values were used in the analysis. The percent biosorption of metal ion was calculated as follows,

Biosorption (%)=(Ci-Cf) × 100 Ci

Where:

Ci= initial metal ion concentration, mg/L^{-1}
Cf= final metal ion concentration, mg/L^{-1}

An atomic absorption spectrophotometer (Perkin-Elmer A Analyst 300) was used to determine the amount of Cd(II) in aqueous solutions before and after the equilibrium was established. The hollow cathode lamp was operated for Cd(II).

Biosorbent characterization

Scanning Electron Microscope (SEM) /Energy-dispersive X-ray spectroscopy (EDX)

The algal surface morphology of the normal, pretreated, and cadmium-loaded sorbents was investigated by SEM.

Fourier transforms infrared spectroscopy (FT-IR)

FT-IR spectroscopy analysis is used to authenticate the occurrence of the functional groups in brown algae *S. myriocystum* and to examine the chemical modification before and after heavy metal sorption.

Desorption studies

Desorption of Cd(II) from S. myriocystum

Desorption was done by adding 1.0 g of biomass with 100 mL of Cd(II) metal solution of known concentration. Subsequently, 100 mL of seven different chemical agents such as H_2SO_4, H_3PO_4, HCl, HNO_3, NaOH, NaCl, and H_2O were used for desorption experiments. The biomass the mixture was shaken for 30 min in the shaker and the final metal concentration was calculated.

Results and Discussion

Metals removal from solutions can measure a talented practice in the management of polluted water containing heavy metals. Adsorption is based on the capacity of biomass (live or dead) to get together metal ions from wastewater during physicochemical absorption. Several physical and chemical factors decide the whole sorption behaviour[12]. Ion exchange and *p*H are the main mechanisms that influence sorption. The additional an important factor in sorption contains the sorbent character and accessibility of required sites[13]. The effects of algal concentrations, metal ion content, temperature, *p*H, agitation speed and contact time for the sorption of Cd(II) have to be considered. In pilot study the biosorption performance of raw and chemically modified biomass of the brown seaweed *Sargassum myriocystum* for the removal of Cd(II) from aqueous solution was studied. The sorption capacity was significantly increased when compared with raw biomass. The metal removal rates were noticeably rapid wherein 90% of the total sorption occurred within 90 min. Biomass was treated with 0.1 N HCl established the highest potential for the sorption of the metal ions with the maximum uptake capacities.

Optimization of process parameters for batch studies

The heavy metal biosorption is complicated, which is affected by various factors such as the *p*H of the metal ion solution, biomass concentration, initial metal concentration, temperature, contact time and agitation speed. Hence, the batch study was carried out for the effective sorption of the heavy metal cadmium.

Effect of solution *p*H

*p*H of the medium is the most important parameter on metal biosorption from synthetic metal solution. Cd(II) sorption on *S. myriocystum* biomass is carried out by varying the *p*H of the metal solutions. The *p*H of the solution not only affects the presence of metallic ions in solution but also the presence of adsorption sites on the surface of the biosorbent. It is confirmed from Fig. 1 that optimum *p*H was found to be *p*H 5 for Cd(II). From the graph, we conclude that these metal ions stay under the soluble form at *p*H lower than 6, maximizing their biosorption. Our results are in line with the findings reported on *Ulva lactuca* sp. as an inexpensive adsorbent for the elimination of Cd(II) ions from solution at *p*H 5.0 (Ref. 14), on *Caulerpa racemosa* biomass cadmium removal takes place at *p*H 5 (Ref.15), on *Ulva fasciata* biomass for cadmium removal the optimum *p*H 5 and Plackett-Burman design be used to conclude the optimum metal removal[24]. When *p*H increases, electrostatic repulsion decreases and then decrease of positive charge density on the sorption sites finally enhanced metal sorption[16]. Lower *p*H leads to an increase in the negative charge density on the surface of sorbent, which pulls positively charged metal cations and sorption is enhanced[17]. At lower *p*H value, the binding sites would be closely associated with the (H+) ions and restrict the access to binding sites by metal cations as a result of repulsive force. On the other hand, as the *p*H is lowered, the overall surface charges will become positive, which will inhibit the approach of positively charged metal cations[18].

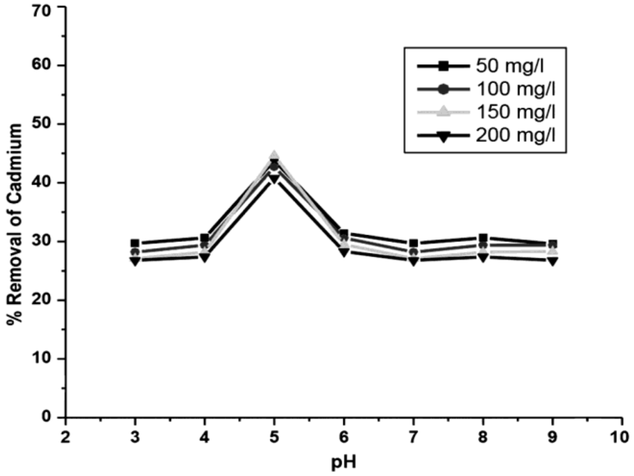

Fig. 1 — Effect of solution *p*H on Cd^{2+} biosorption efficiency (initial concentration 50, 100, 150, 200 mg/L, *p*H 3-9, contact time 30 min, agitation speed 150 rpm, temp 37°C, adsorbent dose 0.5 g/L).

Effect of Biomass concentration

The optimum concentration of biomass for the maximum removal of the metals was 1.0 g for cadmium and the remains constant afterward and this was evident from Fig 2. The sorption ability and removal percentage are uniformly significant in sorption experiments. Our results are in par with several findings, that 1 g each of *Saccharomyces cerevisiae* (native Baker's yeast) and Padina species effectively remove cadmium[19] other work opined that a biomass dose of 2 g is considered for the effective

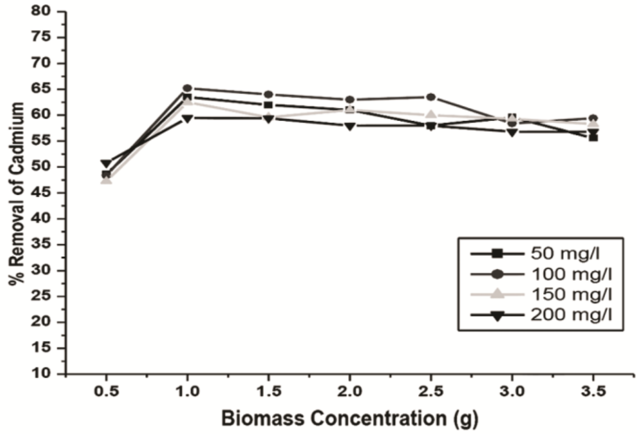

Fig. 2 — Effect of biomass concentration on Cd^{2+} biosorption efficiency (initial concentration 50, 100, 150, 200 mg/L, *p*H 5, contact time 30 min, agitation speed 150 rpm, temp 37°C, adsorbent dose 0.5 – 3.5 g/L). 200 mg/L, *p*H 5, contact time (10 min to 180 min), agitation speed 150 rpm, temp 37°C, 200 mg/L, *p*H 5, contact time 90 min, agitation speed 150 rpm, temp 20-50 °C, adsorbent dose 1.0 g/L).

removal of lead on green algae, *Ulva lactuca* and on brown algae *Sargassum filipendula*. The sorption ability and percentage removal are uniformly significant in sorption experiments for the reason that both factors generally take part in deciding the adsorption performance of a given sorbent[20]. High sorbent concentrations are able to put forth a shell effect, shielding the active sites as of being engaged by metal ions.

Effect of contact time

Biosorption experiments were performed to determine the maximum uptake of metal ions by brown macroalgae *S. myriocystum*. Fig. 3 shows the percentage removal of Cd(II) on to *S. myriocystum* by contact time. The maximum removal of the metals was found to be 90 min for Cd(II) and remained constant afterward. The results obtained in this study are in good correlation with the results reported for the sorption of lead and cadmium by algal seaweed *Lobophora variegate*, the removal rates were noticeably speedy in which 90% of the total sorption occurs in 90 min[21], on *Utricularia aurea* biomass is rapid within 5 min and equilibrium was reached 90 min for Cd(II)[22]. The adsorption of sorbate is fast, and it slowly decreases with time until it reaches equilibrium. The sorption rate is higher in the opening owing to a bigger the surface area of the sorbent, then the free sites decreases there is a competition between the metals and sites[23]. After saturation, the leftover unoccupied sites be complex to take up for the reason that forces among the solute molecules on the surface and liquid[24].

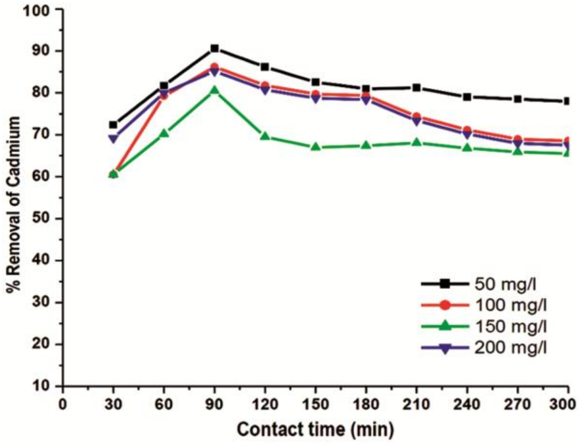

Fig. 3 — Effect of contact time on Cd^{2+} biosorption efficiency (initial concentration 50, 100, 150, adsorbent dose 1.0 g/L).

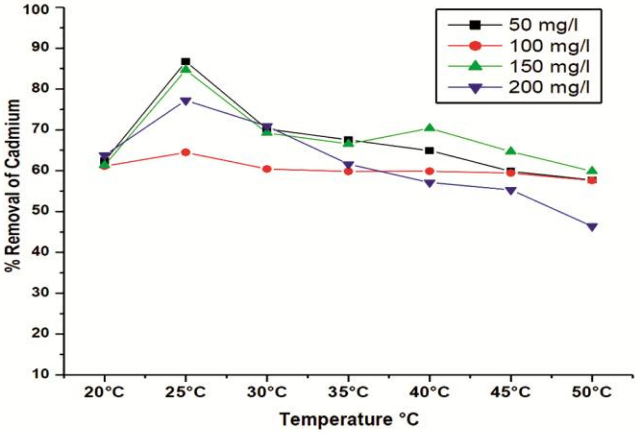

Fig. 4 — Effect of temperature on Cd^{2+} biosorption efficiency (initial concentration 50, 100, 150, adsorbent dose 1.0 g/L).

Effect of temperature

Temperature is a very significant kinetic factor in the biosorption method. It affects the mobility of sorbate ions as well as the biosorption ability of the biosorbent. Fig. 4 it is evident that among the various temperatures selected for the biosorption of Cd(II) the maximum removal was observed at 25°C after that there was a gradual decline in the uptake process showed concluding that 25°C is the optimum temperature. The % removal was found to be 59.75% for Cd(II). Our findings are in good relation with those of, on *Chaetomorpha linum* and *Gracilaria changii* at 25°C for Cadmium[25], on *Nitzschia closterium* for Pb, Cd and Ni at 25°C(Ref. 26). Temperature up to 25°C triggers the opening of pores in the seaweeds increasing the surface area available for the sorption of metals within the pores of algae causing an increase in sorption[27]. Above 25°C, the removal decreases due to many reasons, deactivate the sorbent surface, active sites gets destructed due to bond ruptures[28].

Effect of initial metal ion concentration

The percentage removal of the ions decreased markedly with a rise in initial metal from 50 to 200 mg/L. Fig. 5 indicates the initial metal concentration on the removal of Cd(II). The study revealed the inverse relationship between the percentage metal removal and initial metal concentration that is enhancing in metal concentration the percentage removal was decreased. Similar results have been reported indicating the decrease in the percentage uptake of heavy metals with an increase in the initial heavy metal ion on green algae *Ulva lactuca* the metal uptake decreases from 44.0 mg/L to 702.52 mg/L[49], on *Erythrina variegata* uptake decreases from 23 to 188 mg/L[29].

The initial metal ions concentration plays the main role as a driving force to overcome the mass transfer resistance between the aqueous and solid phases[30]. At lower concentration the ions cooperate with binding sites and therefore facilitating approximately 100% sorption while at higher concentrations, more numbers of ions are left un-sorbed in the metal solution owing to the saturation of the sites[31].

Effect of agitation speed

The study showed maximum percentage removal of the selected metal ions was obtained with an agitation speed of 250 rpm and decreased markedly with a further increase in the agitation speed. Fig. 6 indicates the agitation speed from 50 to 300 rpm on the removal of Cd(II).The percentage removal decreased considerably at agitation rates greater than 250 rpm. After 250 rpm the biosorption capacity decreases were also reported by[32]. Below 250 rpm diminish the homogeneity and the sorbent get deposited, therefore, delaying the stability[33].

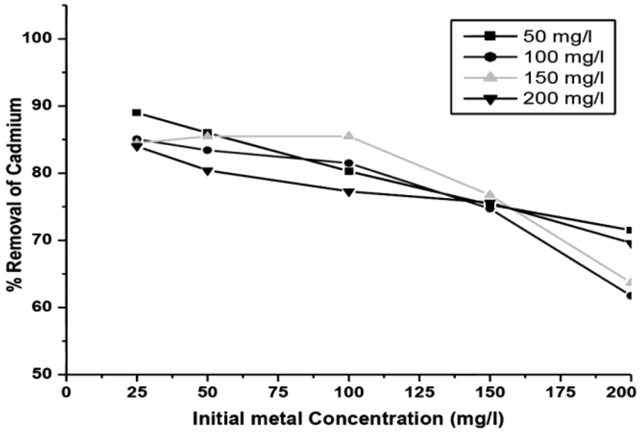

Fig. 5 — Effect of initial metal concentration on Cd^{2+} biosorption efficiency (initial concentration 25, 50, 100, 150 and 200 mg/L, *p*H 5, contact time 90 min, agitation speed 150 rpm, temp 25°C, adsorbent dose g/L).

Characterization of biosorbent before and after heavy metal sorption

The characterization of biosorbents helps in understanding their nature. The characterization techniques are employed to study the physicochemical nature of biosorbents and to identify their binding sites. The physicochemical properties of biosorbents play a major role in the biosorption of metals. The characterization techniques are crucial in highlighting the mechanism of biosorption and to develop a better understanding of the biosorption phenomenon. Hence before performing the biosorption studies, the selected biosorbents were first characterized using various analytical techniques. These include the Fourier Transform Infrared (FTIR) spectroscopy to study the functional groups and Scanning Electron Microscopy (SEM) which offers topographical and fundamental information on solids.

Scanning Electron Microscope (SEM)/Energy-dispersive X-ray spectroscopy (EDX)

Scanning Electron Microscope (SEM)/Energy-dispersive X-ray spectroscopy (EDX) analysis is used to observe the changes in the morphology of the brown algae to establish a mechanism of metal binding; it can provide valuable inputs in determining the distribution of various elemental compositions over the seaweed surface when combined with Energy-dispersive X-ray spectroscopy techniques.

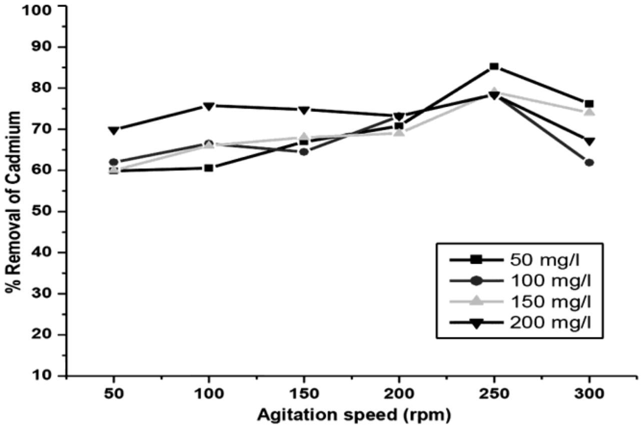

Fig. 6 — Effect of agitation speed on Cd^{2+} biosorption efficiency (initial concentration 25, 50, 100, 150 and 200 mg/L, *p*H 5, contact time 90 min, agitation speed (50, 100, 150, 200, 250 and 300 rpm), temp 25°C, adsorbent dose 1.0 g/L).

Scanning Electron Microscope (SEM)

The divergence in the exterior morphology of normal (Fig. 7a), pretreated (Fig. 7b) and metal loaded biosorbent (Fig. 7c) can be observed by comparing all the figures. HCl treated biomass showed many pores on the surface of the biosorbent, and a rough structure on the surface with a large surface area contributing to improving the metal biosorption capacity. Scanning Electron Microscope analysis confirmed the metal accumulation on the biosorbent. It revealed the surface consistency and the surface of the algal sorbent *S. myriocystum* before and after biosorption. Heavy metal treated biomass showed small particles of unstructured precipitate adhere to the algal surface, which might be due to the presence of Cd(II) on to the *S. myriocystum* surface. This could be further confirmed from the Energy-dispersive X-ray (EDX) analysis. The high concentration of calcium and magnesium are found in raw Sargassum and these bind to alginic monomers (alginic acid is one of the main cell wall components in the brown seaweeds). From the Scanning Electron Microscopic analysis, concluded that the biomass when comes in contact with metal solutions, the heavy metal replace numerous calcium and magnesium in the surface as well as producing strong binding. This might indicate the effective biosorption capacity of the selected biosorbent. Kim *et al.*[5] analysed the unloaded and Cd(II) loaded marine algal biomas using Scanning Electron Microscope. Differences in surface morphology indicated that Cd(II) ions deposited on seaweed waste biomass through surface precipitation. The mound-like the structure indicates that Cd (II) ions precipitated on the seaweed *Kappaphycus alvarezii* and *Eucheuma denticulatum* waste biomass.

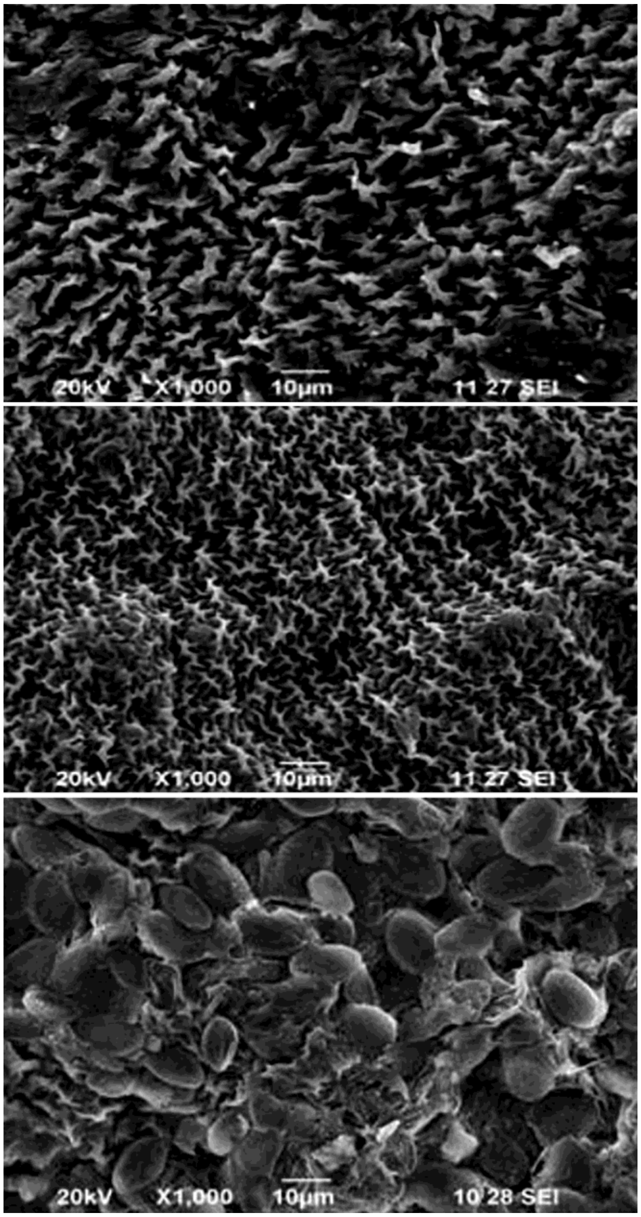

Fig. 7. (a) Scanning electron micrographs of *S. myriocystum* before metalbiosorption. (b) Energy dispersive X-ray (EDAX) spectrum of *S. myriocystum* before metalbiosorption, (b) Scanning electron micrographs of *S. myriocystum* after pretreatment with HCl. (b) Energy dispersive X-ray (EDAX) spectrum of *S. myriocystum* after pretreatment with HCl & (c) Scanning electron micrographs of *S. myriocystum* after Cd^{2+} biosorption. (b) Energy dispersive X-ray (EDAX) spectrum of *S. myriocystum* after Cd^{2+} biosorption.

Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy is used to assess the chemical characteristics of biosorbent. Energy-dispersive X-ray spectroscopy measurements of *S. myriocystum* (control, pretreated and metal loaded) were recorded. This findings showed that the presence of many elements such as calcium, magnesium, sodium, potassium, silicon, sulfurs, carbon, and oxygen in the[34] Energy-dispersive X-ray spectrum of sargassum species. The Energy-dispersive X-ray spectrum of sargassum seaweed after treating with 1000 ppm of chrome tanning solution, showed a disappearance of bands of alkaline earth metals and the appearance of a chromium peak, demonstrating the option of a cation replace mechanism for the gathering of chromium onto the algae.

Fourier Transformation Infrared Spectroscopy

The Fourier Transformation Infrared Spectroscopy **(**FT-IR) spectrum of *S.myriocystum* gives numerous characteristic bands related to functional groups present in the seaweed biomass. As evident from Fig. 8 the normal biomass showed several absorption peaks at 3448.72 and 3425.58 (O-H, H groups), 2924.09, 2854.65, 2862.36, 1450.47 (C-H groups), 2137.13 (C≡C groups) 1743.65 (C═O groups), 1627.92 (N-H groups), 1527.62 and 1535.34 (N-O groups), 1442.75 (H-C-H groups), 1458.18 (C-H groups),1273.02, 1249.87, 1226.73, 1103.28, 1095.57, 1064.71, 1041.56 and 1033.85 (C-N groups), 840.96, 817.82, 810.10, 786.96, 725.23, 717.52 and 709.80 (C-Cl groups), 671.23 and 547.78 (C-Br groups). This indicated the main vibrational frequencies and functional groups responsible for metal sorption. In pretreatment the peaks at 1458.18 correspond to the C-H groups, 879.54 corresponds to the C-H "oop" groups, 840.96 corresponds to the C-Cl groups, 725.23 corresponds to the C-Cl groups in normal biomass were disappeared in biomass after pretreatment. The peaks at 3448.72 correspond to the O-H, H groups shifted to 3425.58, 1041.56 corresponds to the C-N groups shifted to 1033.85 in pretreated biomass. The new peak at 1450.47, 671.23 corresponds to the C-H, C-Br groups appeared newly in the pretreated biomass. The Cd(II) treated *S. myriocystum* showed peaks at 1450.47 corresponds to the C-H groups, 1095.57 corresponds to the C-N groups, in pretreated biomass are disappeared in cadmium ions treated biomass suggesting that CH and CN groups are responsible for sorption of cadmium ions. The peak at 2854.65 responsible to the C-H groups changed to 2862.36 in cadmium treated biomass. The peak at 1442.75, 1249.87, 810.10 responsible for H-C-H and C-N groups are responsible for sorption. Kim *et al*.[5] reported that the untreated seaweed *Kappaphycus alvarezii* and *Eucheuma denticulatum* showed several biomass major peaks: 3430 (-OH and -NH), 2930 (-CH), 1642 (-COO), 1385 (-CH), 1264 (-C-O-C) and 1053 (-C-O). The adsorption peak around -COO stretching shifted from 1642 cm to 1647 cm indicating that the carboxyl groups formed gets complexes with the Cd (II) ions. The Fourier Transformation Infrared Spectroscopy **(**FTIR) band shows various powerful feature curves associated with functional groups in the seaweed *Kappaphycus alvarezii*[35]. The adsorption band at 3420, 2930 and 1385, 2350, 1646 and 1240 and 1050 cm^{-1} are in charge for sorption. The marine microalga *Nannochloropsis oculata* was examined for its cadmium sorption, Fourier Transformation Infrared Spectroscopy **(**FTIR) spectra shows characteristics band with various groups concerned in sorption be OH, COO and CH groups[23].

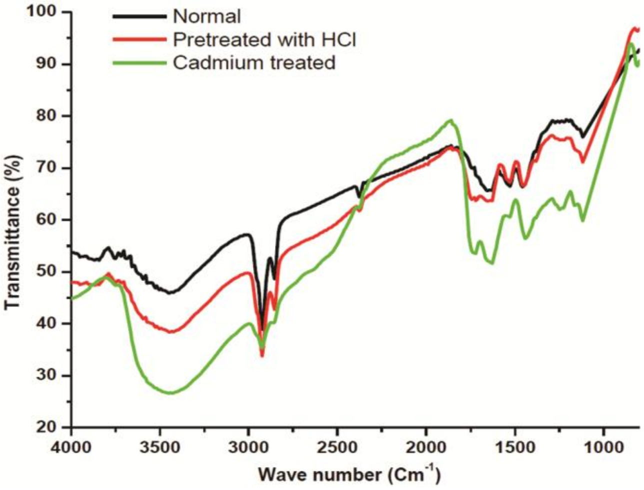

Fig. 8 — FT-IR spectrum of normal, pretreated and cadmium treated biomass.

Desorption studies

Desorption of Cd(II) by *S. myriocystum*

To build the sorption method extra economically reasonable, rejuvenating the overloaded biomass is essential. Normally, renewal process of overloaded sorbent is performed by desorption, using reagents with high effectiveness and does not injure the structure of the biosorbent. When HCl is used as a desorption agent, the biomass exterior is entirely sheltered by H+ ions while the coordination sphere of chelated Cd(II) is disrupted and is shown in Fig 9. Subsequently, the Cd(II) ions will not be able to struggle with H+ ions for adsorption site and subsequent Cd(II) are on the loose from the solid exterior into the solution. By the end of desorption method, the algae protonated to be prepared for the subsequently adsorption cycle. Based on these

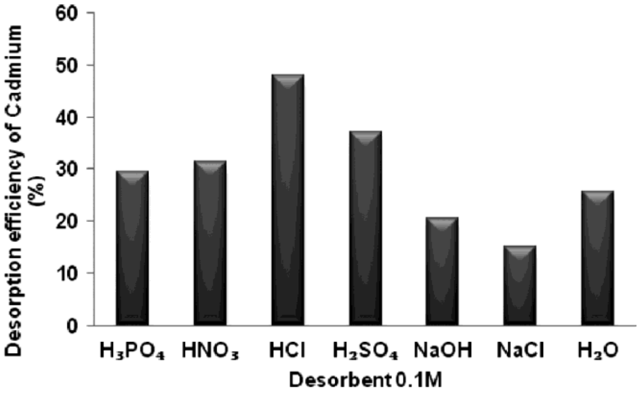

Fig. 9 — Desorption of cadmium from metal loaded biosorbent *S. myriocystum.*

observations and the results stated in the earlier works of literature, HCl was to be establish as an well-organized eluant for the desorption of the metals along with the regeneration of the biomass. It was observed that both biosorption and desorption capacity of *S. myriocystum* almost remain steady for the first four cycles, which shows in attendance no permanent sites on the surface of the biosorbent. On the other hand, at cycles more than four, both the biosorption and desorption efficiencies decrease. This can be recognized by the weakening and loss of biomass that resulted in a decreased number of metal-binding sites. Our results fulfilled that the dry biomass of the brown algae *S. myriocystum* has to be used as a talented, competent and economical sorbent for Cd(II) elimination from polluted water. Ajmal *et al*· reported column and batch HCl study for the desorption of Cd(II) using phosphate-treated rice husk, maximum of 83.9 % in column study[36]. Abdolali *et al* reported that the biomass is a combination of tea waste, maple leaves and mandarin peels for the sorption of cadmium, copper, lead and zinc ions from aqueous solutions[37].

Desorption using 0.1M HCl showed the best desorption efficiency. Desorption of cadmium from activated carbon prepared from *Ceiba pentandra* hulls, for the removal of copper and cadmium using dilute hydrochloric acid solution. Maximum desorption 88% for cadmium occurred with 0.2 M HCl[38]. Cd(II) from metal-loaded biomass of wild cocoyam (*C. bicolor*) adsorbed metals were recovered by 0.01 M HCl[39]. From the green algae *Ulva lactuca* the desorption analysis exposed to HCl gives best result for the elution of metals from loaded algae[40].

Thermodynamics of the sorption process

Thermodynamic parameters are the fundamental concept in which any chemical system tends to attain a state of equilibrium, from the non-equilibrium state and the character of sorbate as well as its degree for the period of sorption was also calculated. The Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the biosorption of Cd(II) ions from aqueous solution onto *S.myriocystum* were determined using the following relations.

$$Kc = qe / Ce$$

By using the above relation, the value of Kc, the equilibrium constant was determined and substituted in the following equation (A),

$$\Delta G^\circ = - RT \ln Kc$$

where, R is the gas constant (8.314 J $mole^{-1}K^{-1}$) and T is the Temperature in Kelvin. ΔG° values for the adsorption of the Cd(II) ions onto *S.myriocystum* biosorbent were calculated by using the above equation $\Delta G^\circ = - RT \ln Kc$. The Gibbs-Helmholtz equation is given below

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

From the equations A & B, the following relation is obtained,

$$\ln Kc = - (\Delta H^\circ / RT) + (\Delta S^\circ / R)$$

Biosorption was carried out by varying the temperature (293K, 298K, 303K, 308K, 313K, 318K and 323K). The Van't Hoff plots were obtained by plotting 1/T vs ln Kc. Enthalpy change ΔH° and entropy change ΔS° are obtained from the slope and intercept of the Van't Hoff plots respectively. Adsorption of Cd(II) metals at optimum pH was carried out by varying the temperature (293K, 298K, 303K, 308K, 313K, 318K and 323K). The Van't Hoff's plots were obtained by plotting 1/T vs ln Kc. The calculated values of thermodynamic parameters ΔG°, ΔH° and ΔS° for the biosorption of Cd(II) onto *S.myriocystum* is reported in Table 1. A positive value of ΔH° for Cd(II) 14.72 kJ/mol whereas a negative value of the free energy (ΔG°) at all the temperatures indicated that the process is feasible and spontaneous. In our study, the value was 42.21 kJ/mol, indicating the sorption by hydrogen bond and ligand exchange. The results are in accordance with the results

Table 1 — Thermodynamic parameters for the removal of cadmium from aqueous solution using *S.myriocystum* biomass.

Metals	Temperature (K)	1/T	q_e mg/g	c_e mg/g	K_C	lnK_c	ΔG $kJmol^{-1}$	ΔH $kJmol^{-1}$	ΔS $Jmol^{-1}K^{-1}$
	293	0.00341	61.1	38.9	1.571	0.452	-1.101		
Cd^{2+}	298	0.00335	65.5	34.5	1.898	0.641	-1.588	42.21	144.02
	303	0.00330	60.4	39.6	1.525	0.423	-1.065		
	308	0.00325	59.8	40.2	1.487	0.397	-1.017		
	313	0.00319	59.85	40.15	1.491	0.399	-1.038		
	318	0.00314	59.44	40.56	1.465	0.382	-1.009		
	323	0.00309	57.6	42.4	1.358	0.306	-8.217		

Table 2 — Comparitive study of various adsorbent for the removal of cadmium from aqueous solution

S.No	Adsorbent	Metal ions	Nature	Reference
1	*Saccharum bengalense*	Cd(II)	Endothermic	Din *et al.*[50]
2	Acacia tortilis seeds	Cd(II)	Endothermic	Ackacha and Meftah[51]
3	Barley straw ash	Cd(II)	Endothermic	Arshadi *et al*.[52]
4	Cork biomass	Cd(II)	Endothermic	Fouad Krika *et al*.[53]
5	Garbage ash	Cd(II)	Endothermic	Mehdi Qasemi *et al*.[54]
6	Fly ash	Cd(II)	Endothermic	Rajesh Kumar et al.[55]
7	Modified biomass ash	Cd(II)	Endothermic	Lei Xu *et al*.[56]
8	Green algae *Chlorella vulgaris*	Cd(II)	Endothermic	Mahendra Kumar *et al*.[57]

reported[41] by for the sorption of Lead (II) Copper (II) and Cadmium (II) ions onto Olive Leaves Powder and also by for the biosorption of cadmium (II) onto *Eriobotrya japonica*[42]. The value of ΔS° as presented in Table 1 was positive and this reflects the affinity of the adsorbent towards the adsorbate species. A positive value of ΔS° suggested increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The negative value of ΔG° indicated that the adsorption process is spontaneous and the degree of spontaneity increases with increasing the temperature[43]. The value of ΔS° can be used to describe the randomness during adsorption process, the positive value of ΔS° reflected the affinity of the adsorbent for particular heavy metal ions and confirmed the increased randomness at the solid–solution interface during adsorption (Al-Dujaili *et al*. 2012). The positive value of ΔH° confirmed the endothermic nature of the adsorption process[43]. The values of thermodynamic parameters similar to our studies were reported[44] for the sorption Cd(II) on *Penicillium simplicissimum*. Our results are in good agreement with the calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the sorption of Cd(II) ions onto *Nannochloropsis oculata* was feasible, spontaneous and exothermic at 298–323 K[45] and some examples are illustrated in Table 2. Isolated green algae *Chlorella vulgaris* has been proven to be a very effective and promising adsorbing biomaterial for Cd (II) removal which show endothermic, feasible and spontaneous behaviour[46]. Some researcher in his findings the cadmium sorption by blue green alga *Anabaena sphaerica* the calculated free energy was to be 11.7 and 14.3 kJ/mol indicating that the biosorption mechanism of Cd(II) and Pb(II) by *A. sphaerica* was chemisorption[47]. Researchers reported that the cadmium sorption into Algerian cork, ΔH° and ΔS° values were estimated at 110.47 kJ mol^{-1} and 0.3795 kJ K^{-1} mol^{-1} for the process, which is endothermic in nature[48]. The thermodynamic parameters showed that the sorption of Cd(II) ions onto *Ceramium virgatum* as feasible, spontaneous and exothermic at 293-323 K[49].

Conclusion

The prospective of *S. myriocystum* for the elimination of cadmium from solutions has been investigated and to optimize the various conditions necessary for effective biosorption. The optimum conditions for the Cd(II) removal was solution *p*H 5, biomass concentration 1 g, contact time 90 min, optimum temperature 25ºC and agitation speed 250 rpm. The percentage removal was about to be decreased by the raise in the initial heavy metal ion. Desorption studies of the metal loaded *S. myriocystum* were performed with seven different chemical agents, of which 0.1M/L HCl was found to be the better desorbing agent. Negative ΔG° values confirmed the feasibility and spontaneous nature of the adsorption process with high preference of the metal ions for *Sargassum myriocystum*. On the other hand, the value of ΔH° is positive, indicating that the sorption is endothermic. The positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of Cd(II) onto *S.myriocystum* biomass. In convenient application, the exploit of dead algae is more efficient and advantageous. Besides, dead algae subjected to different physico-chemical handling methods to improve their performance and the process used is secure and eco-friendly. Based on my findings, biomass of the brown seaweed *S.myriocystum* which is extensively carried out as a cost-effective capable sorbent designed for the uptake of metal Cd(II) as of synthetic metal solution.

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