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REMOVAL OF CADMIUM (II) FROM AQUEOUS SOLUTIONS USING MARINE MACRO ALGAE AS THE SORBING BIOMASS: ISOTHERMS AND SPECTROSCOPIC CHARACTERIZATION

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ABSTRACT

The present study attempts to analyze the biosorption trend of biosorbent *Sargassum sp* (macroalgae) biomass for removal of toxic heavy metal ion Cd (II) from solution as a function of initial metal ion concentration, pH, temperature, sorbent dosage. The sorption data fitted with various isotherm models and Freundlich model was the best one with correlation coefficient of 0.999. Kinetic study results revealed that the sorption data on Cd (II) with correlation coefficient of 0.999 can best be represented by pseudo second-order. The biosorption capacity (q_e) of Cd (II) is 9.75 mg/g on *Sargassum sp* biomass. Thermodynamic studies showed that the process is exothermic (ΔH° negative).Free energy change (ΔG°) with negative sign reflected the feasibility and spontaneous nature of the process. The SEM studies showed Cd (II) biosorption on selective grains of the biosorbent. The FTIR spectra indicated bands corresponding to –OH, COO−, –CH, C=C, C=S, and –C–C– groups were involved in the biosorption process.

Keywords: Biosorption, Free energy change, Cadmium (II),*Sargassum sp*, FTIR, SEM.

INTRODUCTION

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution, which is a serious cause of water degradation. Numerous metals such as cadmium, mercury, lead, chromium, copper, manganese, etc., are known to be significantly toxic. The presence of toxic heavy metals in water has caused several health problems with animals, plants, and human beings[1]. Among toxic heavy metals, cadmium is one of the most dangerous for human health[2]. Cadmium is highly used as corrosion resistant and in protective coating for iron, steel, and copper. The industrial uses of cadmium are increasing in plastics, paint pigments, electroplating, batteries, mining, and alloy industries[3]. Cadmium is a highly toxic element and considered as a carcinogen. It can enter the human body by eating food, drinking water, breathing or smoking. Most of the cadmium that enters the body goes to kidney and liver and can remain there for many years and can cause serious damage to kidney and bones[4]. The use of natural biomaterials is a promising alternative due to their relative abundance and their low commercial value. Recently, many industrial, agricultural and forestry sources are used as sorbents such as, red mud[5], sunflower stalks[6], spent grain[7], wheat bran[8], Aspergillus niger[9], olive pomace[10], tree fern[11], maize bran[12], saw dust and neem bark[13], citrus peels[14], Rosa gruss an teplitz[15], Echornia Speciosa[16], Cupressus sempervirens, Eucalyptus longifolia and Pinus halepensis[17], Carpobrotus edulis, Euphorbia echinus, Senecio anthophorbium and Launea arborescens[18]. The World Health Organization (WHO), has set a maximum guideline concentration of 0.003 mg/L for Cd(II) in drinking water[19].The primary objective of the present study is to explore the potential of non-living brown marine macroalgae,Sargassum, in their natural and modified form for the removal of Cadmium from aqueous medium. The secondary objective is to study the effect of pH and agitation time on adsorption capacity of the algae. Further, the experimental data are fitted to Freundlich and Langmuir adsorption isotherm models and Lagergren first order kinetic equation. In addition, attempts are made to interpret the experimental results on the basis of interaction between the biomass and the metal ion.

EXPERIMENTAL

Preparation of biosorbent

Sargassum sp, a macro alga were collected from Andaman Nicobar Islands, Port Blair, India. The alga was washed with demineralized water thrice, dried in hot air oven at 70^0C for 24 h and ground by domestic mixer. The biosorbent was kept in humidity control oven to maintain the humidity for entire equilibrium studies.

Preparation of stock solution

Cadmium chloride solution was prepared by dissolving 3.582 g cadmium chloride salt in 1000 mL standard volumetric flask with de-mineralized water. The primary stock solution thus prepared gave approximately 2000 ppm of Cd^{2+} in solution. From the stock solutions, experimental test solutions were prepared by diluting the primary stock solution with de-mineralized water. The pH range was adjusted by rational addition of specified mineral acid.

Equilibrium studies

The experiments were carried out in 250 mL Erlenmeyer conical flasks, at a constant agitation speed (160 rpm) with 50 mL solution and required amount of adsorbent using orbital shaker (Kemi make). Initially the effect of contact time (0–120 min) on the sorption capacity of *Sargassum sp* was evaluated. The equilibrium time was obtained and the experiments were conducted for the same time for all conditions. Batch experiments were carried out to investigate the adsorption behavior of Cd^{2+} on *Sargassum sp.*

Analysis of heavy metal ions

The concentrations of unadsorbed Cd^{2+}, in the sample solutions were determined using an Atomic Absorption Spectrophotometer (PerkinElmer model AA 400). The metal uptake (q_e) was calculated using the general definition:

$$q_e = \frac{V \times (C_T - C_e)}{M} \tag{1}$$

Where, q_e is the metal uptake of mg $Cd^{2+}.g^{-1}$ biomass, V is the volume of metal containing solution in contact with the biosorbent in L, C_T and C_e are the total and equilibrium (residual) concentration of metal in the solution mg L^{-1}, respectively, and M is the amount of added biosorbent in g.

Metal % of removal by *Sargassum sp* was determined by Eq. (2) as follows:

$$R(\%) = (C_T - C_e)/C_T * 100 \tag{2}$$

Where R is the percentage of Cd (II) adsorbed by biomass, C_T is the total concentration of metal ions in mg L^{-1} and C_e is the concentration of metal ions at time t in mg L^{-1}.

Characterization of biomass

FTIR studies

The powdered biomass, prior and after adsorption was air dried, and demoisturized at 60^0C in humidity control oven. The powder was analyzed by Fourier transform infra red spectrophotometer. FTIR studies were conducted by Potassium Bromide (KBr) pellet method (Jasco 5300) in the wave number range of 400.00–4000.00 cm^{-1}.

Scanning electron microscopy

The dried bio mass powders and the corresponding metal ion loaded powders were coated with ultra-thin film of gold by an ion sputter (JFC-1100), exposed under electron microscope (JEOL, JX-8100) at working height of 15 mm with voltage ranging between 10 and 25 kV.

RESULTS AND DISCUSSION

Effect of contact time

Biosorption studies Experiments were conducted to estimate the time required to reach the equilibrium by taking an initial charge of 50 mL of aqueous solution containing Cd^{2+} and required quantities of biomasses *Sargassum sp* in powdered form. The data on concentration of metal ion C_T in solution with time were shown plotted in Fig.1 for Cd^{2+} using macro algae *Sargassum sp*. The metal uptake shown faster at initial stages of contact, and subsequent slowing down as the equilibrium is approached (Fig. 1). In the initial stages of contact, large number of vacant sites is available and hence the uptake is faster. The slowing down of metal uptake later stages may be due to difficulty in occupying the remaining vacant sites. Repulsive forces between the solute molecules on the adsorbent and aqueous solution (bulk phase) may also most probably contribute to the slowing down of uptake of metal at equilibrium. The effect of contact time on% adsorption of Cd^{2+} was studied over a duration time period of 0–180 min, using 0.1 g of *Sargassum sp* biomass powder, (dp = 0.074 mm); 50 mg L^{-1} of aqueous cadmium solution at pH 5.0 and at 180 rpm. Cadmium removal more than 50% was observed within first 15 min; the rate of percent removal declined gradually till the end of 120 min contact time (optimum contact time) and remained constant thereafter as shown in Fig. 1. Approximately 93% removal of cadmium from the solution was observed within 120 min of contact time and after that there was no appreciable change. Hence for rest of the study the optimum contact time for all experiments was taken as 2h. Similar procedure was adopted for 2, 5, 10, 20 g L^{-1} of biomass concentrations in aqueous solutions and the results indicated the same contact time of 120 min as optimum time for all the other studies.

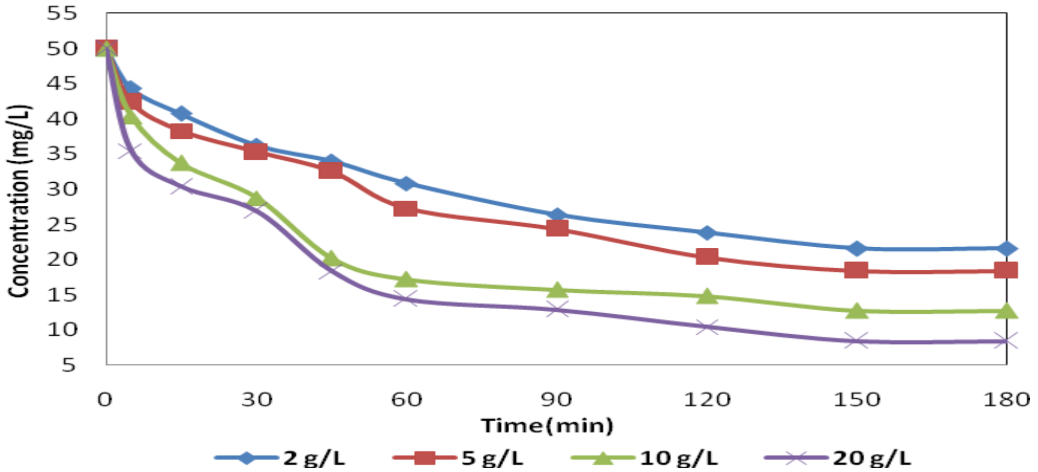

Fig.-1: Variation of aqueous metal ion (Cd^{2+}) concentration with time using macro algae *Sargassum cinereum* as biosorbent at 25°C, Cd^{2+} 50 mg/L and pH 5.

Effect of pH

pH of the biosorption medium is one of the essential parameter affecting the uptake of heavy metal ions from aqueous solutions by biosorbents[20-21]. One of the factors significantly affecting biosorption of metal ions is its acidic nature. This parameter directly related to the ability of hydrogen ions with that of the metal ions to bind themselves to active sites on the biosorbent surface[22-23]. The percent removal of biosorption was increased from 62.41% to 80.11% for Cd^{2+} at a total metal ion concentration of 24 mg/L when pH was increased from 3.0 to 5.0 (Fig. 2). The maximum biosorption was found to be 80.11% at pH 5.0 and at pH beyond 5.0, the biosorption of Cd^{2+} ions declined.

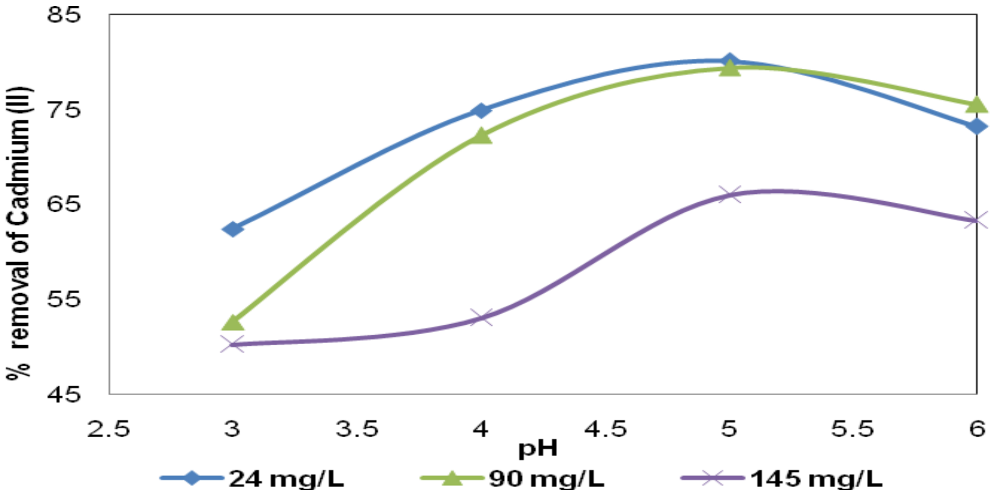

Fig.-2: Effect of pH on percent biosorption at various total metal ion (Cd^{2+}) concentrations at a temperature of 25°C, 20g/L biomass of *Sargassum cinereum*.

Effect of metal ion concentration

The increase in total Cd^{2+} concentration from 24 g/L to 186.3 mg/L decreased the percent of removal from 84.11 to 59.24 at a sorbent dosage of 20g/L, temperature 25°C and pH 5(Fig.3). This can be attributed to the reasons cited above that, further available sorption sites on the *Sargassum sp* were found to be limited. The adsorption capacity (q_e) of the biomass increased with increasing Cd^{2+} initial concentration. An increase in the initial ion concentration provides a larger driving force to overcome all mass transfer resistances between the solid and the aqueous phase, which results in higher metal ion adsorption.

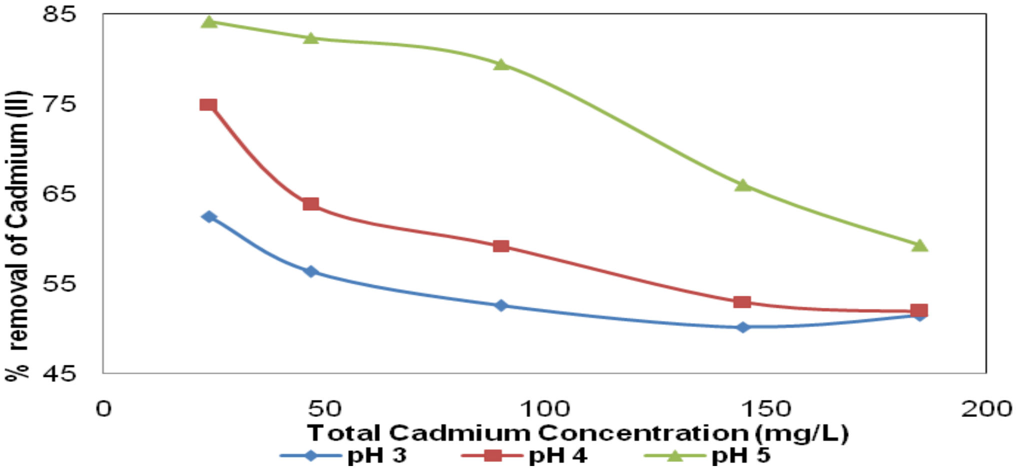

Fig.-3: Variation of %Removal of Cadmium metal ion with total concentration of Cd^{2+} at temperature of 25°C, 20 g/L macro algae *Sargassum cinereum*.

Effect of adsorbent dosage

Biosorbent dosage determines the potential of biosorbent through the number of binding sites available to remove metal ions at a specified initial metal ion concentration. The % removal of Cd^{2+} increased from 52.92 to 82.35% at a pH value of 5, while the uptake capacity showed a decrease from 12.675 to 1.972 mg/g as the biomass weight increases from 2 g/L to 20 g/L at an total Cd^{2+} Concentration of 47.9 mg/L (Fig.4). The similar trend followed in both different particle sizes also. The increase in percent biosorption of metals by increasing the biomass dosage is due to an increase in the number of active sites and surface area available for biosorption. Similar trends have been reported in the literature[24-25].

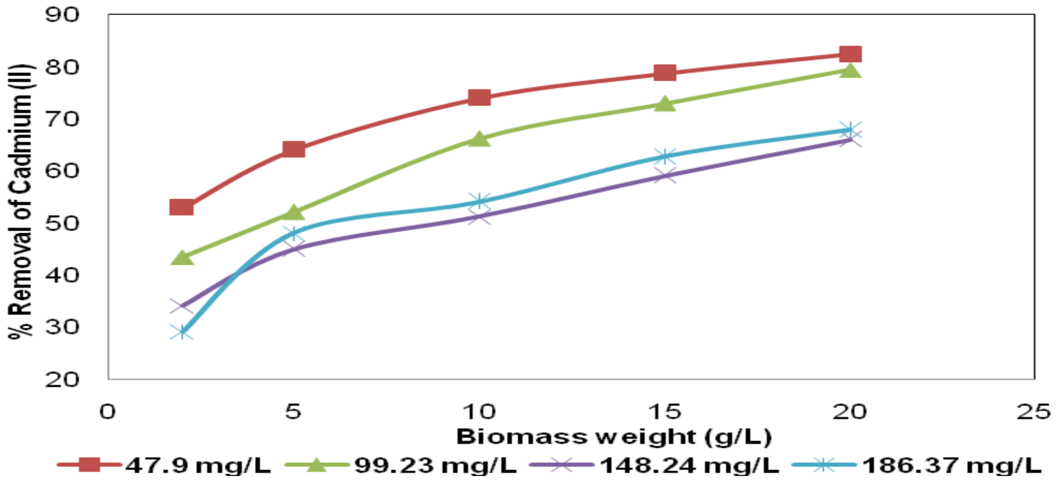

Fig.-4: Variation of % Cd^{2+} biosorption with various biomass weights at various total metal ion concentrations, at temp of 25^0C and pH 5.

Effect of temperature

All the experiments with Cd^{2+} were conducted in the temperature range of 15–45^0C. The effect of temperature on % removal of Cd^{2+} showed in Fig.5. The capacity of cadmium sorption by *S. Cinereum* biomass decreased from 82.35 to 67.92 % with an increase in temperature in the range 15-45^0C at total concentration of 48 mg/L. It may be due to the rise in temperature has a tendency to desorb the adsorbed metal ions from the interface to the solution. The same trend was supported by the earlier authors[26-27].

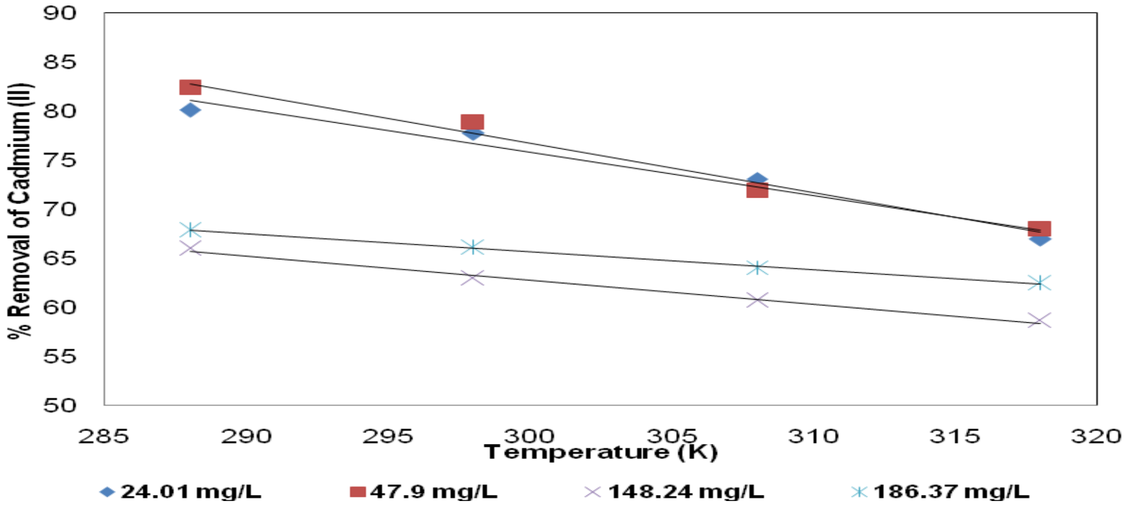

Fig.-5: Variation of percent biosorption of Cd^{2+} metal ion with temperature using macro algae *S. cinereum* at different total metal ion concentrations and at pH of 5.

Biosorption isotherm models

The sorption equilibrium data are conveniently represented by sorption isotherms, which correspond to the relationship between the mass of the solute sorbed per unit mass of sorbent q_e and the solute concentration for the solution at equilibrium Ce. The biosorption isotherms were investigated using two equilibrium models, which are namely the Langmuir and Freundlich.

Langmuir isotherm

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in non-linear form and is represented by the equation:

$$\frac{C_e}{q_e}=\frac{1}{q_m b}+\frac{C_e}{q_m} \qquad (3)$$

Where, q_m is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface bound at high Ce (mg.g^{-1}), and b is a constant which accounts for the affinity of the binding sites (L mg^{-}1). q_m represents the limiting adsorption capacity when the surface is fully covered with metal ions and helps in the evaluation of adsorption performance, particularly in cases where the sorbent did not reach its full saturation during contact. From the plots between (C_e/q_e) and Ce the slope (1/q_m) and the intercept (1/b q_m) can be calculated. The linear Langmuir adsorption isotherms of Cd^{2+} for the biosorbent obtained at different temperatures are given in Fig. 6. The Langmuir adsorption constants evaluated from the isotherms at different temperatures with correlation coefficients are presented in Table 1. From the Langmuir isotherm for cadmium, the biosorption affinity constant 'b' and maximum capacity (q_m) were estimated on the *Sargassum sp* biomass at 25^{0}C. The biosorption affinity constants '*b*' and maximum capacity (q_m) to form a complete monolayer onto the surface of the *S. cinereum* biomass at 25°C were estimated as 0.0196 (L mg^{-1}) and 9.75 mg/g. C_e *vs* C_e / q_e plot yielded a straight line with R^2 (0.9651) indicating the present sorption data could be best represented by the Langmuir model.. The higher adsorption capacity,q_m (mg/g) indicated the strong electrostatic force of attraction. From the value of b, a dimensionless parameter R_L at different initial metal ion concentrations was calculated and the values were shown in Table-1.

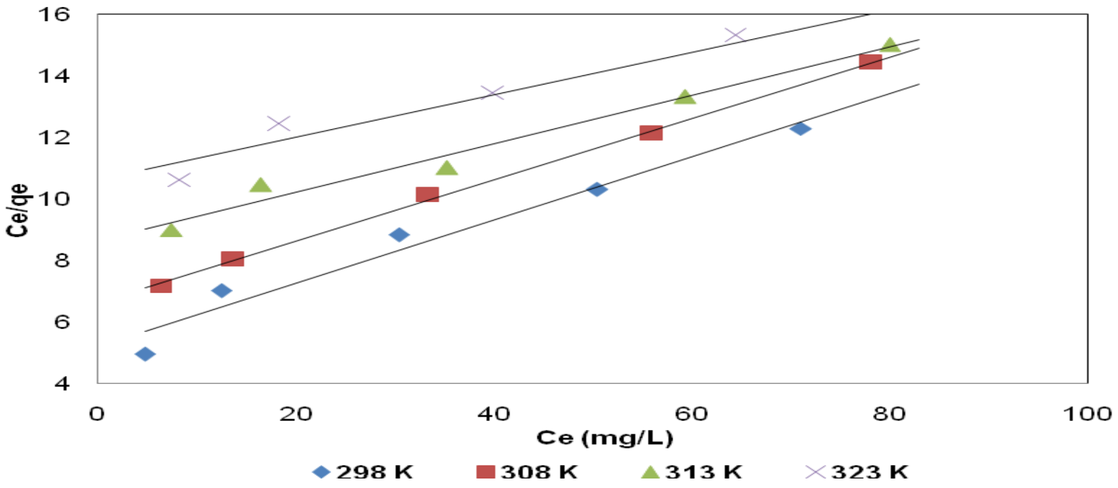

Fig.-6: Langmuir plot for biosorption of Cd^{2+} over macro algae *S. Cinereum* as biosorbent at various temperatures for biomass weight 20g/L and at pH 5.

Freundlich isotherm

Freundlich adsorption isotherm was proposed by Boedecker which was later modified by Freundlich[28]. The Freundlich adsorption equation can be written as:

$$q_e = K_f C_e^{\frac{1}{n_f}} \qquad (4)$$

Taking logarithm on both sides: $\log q_e = \log K_f + \frac{1}{n_f} \log C_e$ (5)

Where, 'qe' is equilibrium adsorption capacity (mg/g), 'Ce' is the equilibrium concentration of the adsorbate in solution, 'K_f' and nf are constants related to the adsorption process such as adsorption capacity and intensity respectively. The plots in Fig. 6 shows linear that the isotherm drawn for biosorption of Cd^{2+} onto *Sargassum sp* and fitted well at various temperatures. The values of n_f and K_f are found to be 0.329, 1.471 respectively at 25^{0}C, 0.243, 1.375 respectively at 35^{0}C and 0.170, 1.252 respectively at 40^{0}C and 0.135, 1.210 (Table-1). The values of high correlation coefficients indicated that the sorption data were very well represented by Freundlich model. Freundlich constant n_f between 1 and 10 indicates a trend more favorable for biosorption by macro algae *Sargassum sp*. This is also suggestive that the metal ion under study could well be separated from its aqueous solution with high adsorption capacity.

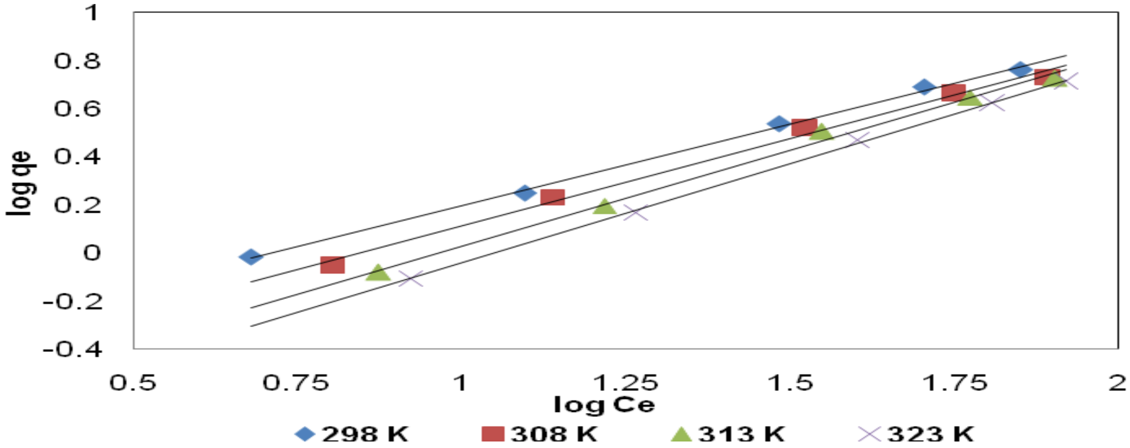

Fig.-7: Freundlich plot for biosorption of Cd^{2+} over macro algae *Sargassum cinereum* at different temperatures for biomass weight 20g/L and at pH 5.

Table-1: Langmuir & Freundlich isotherm model parameters and R_L values at different initial metal ion concentrations for Cd^{2+} biosorption by *Sargassum sp*

Temp. (K)	Langmuir constants			Freundlich constants			Separation factor	
	q_m(mg/g)	b(L/mg)	R^2	k_f	n_f	R^2	C_T(mg/L)	R_L
298	9.75	0.0196	0.9651	0.329	1.471	0.9982	24	0.679
308	10.02	0.0150	0.9988	0.243	1.375	0.9943	47.9	0.51
313	12.67	0.0091	0.9783	0.170	1.252	0.9951	99.23	0.34
323	14.51	0.0064	0.9588	0.135	1.210	0.9992	148.24	0.26

Adsorption kinetic models

The kinetic data helps in tracing the rate determining step of transport mechanism and is required for selecting optimum operating conditions for full-scale batch or continuous process. In the present study pseudo first order and pseudo second order kinetic models have been attempted to fit the present biosorption data.

Pseudo-first-order/Lagergren kinetic model

The pseudo-first-order or Lagergren kinetic rate equation for the adsorption of liquid–solid system was derived based on solid adsorption capacity. It is one of the most widely used adsorption rate equations for adsorption of a solute from a liquid solution. The pseudo first order kinetic equation can be expressed as:

$$\frac{dq}{dt} = \mathrm{k}_1(\mathrm{qe} - \mathrm{qt}) \tag{6}$$

Where, 'q_e' is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg/g), 'q_t' is the amount of solute adsorbed at any given time't' and 'k_1' is the rate constant. By using the boundary conditions and simplifying, the Eq. (6) yields.

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{7}$$

'k_1' can be computed from the slope of the linear plot between ln (q_e-q_t) vs't' for different adsorption parameters such as pH, temperature, adsorbate concentration, adsorbent dose. The first order kinetic plot is drawn for Cd^{2+} metal using *Sargassum sp* at a given temperature and pH. The pseudo first order rate constant k_1 could be obtained from the slope of the plot between log (q_e-q_t) and time, t. in Fig. 8 showed that the Lagergren pseudo-first order kinetic plot does not fit well for the adsorption of Cd^{2+} onto *Sargassum sp* as they do not follow a straight line.

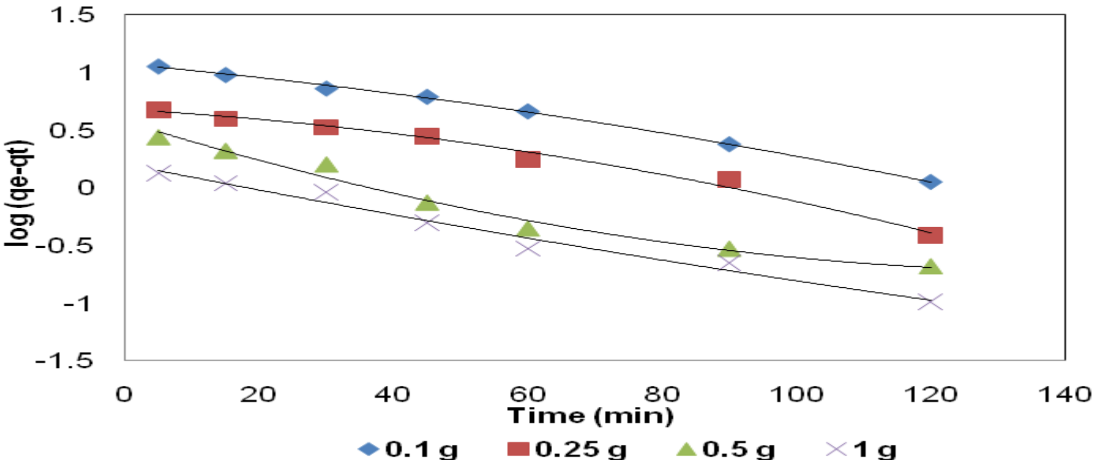

Fig.-8: First order kinetic plot for biosorption of metal ion (Cd^{2+}) at 25°C, C_0 50 mg/L and pH 5.

Pseudo-second-order kinetic model

In view of the above the fitness of the sorption data was tested using pseudo-second-order reaction model. The pseudo-second-order reaction model could be expressed by the rate expression as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

On integration for boundary conditions when t = 0 to t > 0 and qt = 0 to qt > 0 and further simplifications, Eq. (8) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

The plot (Fig. 8) of t/q_t vs. t of Eq. (9) gave a linear relationship from which the q_e and k_2 values were determined. The rate constants and the correlation coefficients for pseudo-second-order kinetic model were calculated and summarized in Table-2. These values showed that the pseudo-second order kinetic plots fit well the adsorption data of cadmium metal for both the biosorbents.

This kinetic model can be proposed to predict the kinetics of adsorption of Cd^{2+} on the macro algae and plant biomass. Thermodynamic parameters Gibbs free energy ΔG° is the basic criterion for deciding whether the chemical process does occur/proceed or not. The spontaneity of the reaction can also be judged by the sign and magnitude of ΔG°. The negative sign for ΔG° is an indicative of the spontaneity of any chemical process. To design any chemical process system one should have the knowledge of changes that are expected to occur during chemical reaction. The rate and extent of changes are more informative in the design of process equipment. In view of the above, analysis has been carried out on the effect of thermodynamic parameters on the biosorption of Cd^{2+} on *Sargassum sp*. The thermodynamic parameters such as changes in standard free energy change ΔG°, enthalpy ΔH°, entropy ΔS° for any given adsorption process could be determined from the Equation:

$$\Delta G^\circ = -RT\ln K_C \qquad (10)$$

Where ΔG°, is the free energy change, expressed as J mol^{-1}. b is the Langmuir equilibrium constant for the process. The values of b (Table 1) at different temperatures were processed according to the following Van't Hoff equation.

$$\log\frac{Cad}{C_e} = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \qquad (11)$$

Where, b is in L mg^{-1}, R is universal gas constant (8.314 J/mol.K) The enthalpy changes (ΔH°) and entropy changes (ΔS°) for the adsorption process of Cd^{2+} using *Sargassum sp* were obtained from the plot of ln b drawn against 1/T and were compiled in Table 3. The negative value for ΔG° indicates the spontaneity of biosorption process. The free energy values increased positively with increase in temperature for the adsorption of Cd^{2+} shown that the spontaneity of the biosorption process reduces with increase in temperature. The negative ΔH° values indicated exothermic nature of the adsorption. The negative value of ΔS° suggested a decrease in the randomness at solid/solution interface during the adsorption of Cd^{2+} ions on to *Sargassum sp.*

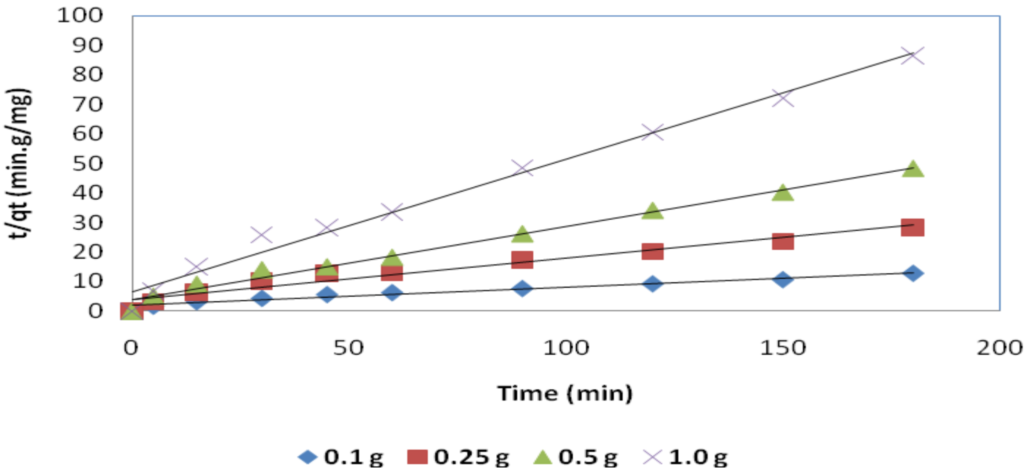

Fig.-9: Second order kinetic plot for biosorption of metal ion (Cd^{2+}) at 25°C, C_0 50 mg/L &pH 5.

Table 2. Kinetic parameters for Cd^{2+} biosorption on *Sargassum sp*.

W(g L^{-1})	K$_2$(gmg^{-1} min^{-1})	q_e (mg g^{-1})	q_e (exp) mg g^{-1}	r^2
2	0.0013	17.54	12.67	0.9832
5	0.0034	7.64	6.31	0.9752
10	0.0113	4.19	3.54	0.9957
20	0.0217	2.31	1.972	0.9933

Table-3: Thermodynamic parameters for Cd^{2+} biosorption *Sargassum sp*.

C_0 (mg L^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol $^{-1}$K)	ΔG^0 (kJ mol^{-1})	Temp. (K)
24	-22.589	-63.771	41.593	298
47.9	-26.652	-76.454	50.200	308
99.23	-14.614	-37.746	26.429	313
148.24	-10.293	-29.076	19.685	323

Biomass characterization

FTIR Analysis

The FTIR differences of spectra in pure algal biomass adsorbent were compared to the spectra obtained in metal ion loaded algal biomass to determine whether the observed differences are due to interaction of the metals ions with functional groups (Fig. 10a). The absorption peaks were tabulated in Table 5 for pure biomass and Cd^{2+} loaded algal biomass. The band peak at 3304.78 cm^{-1} is assigned to the binding -OH and binding -NH groups and the peak is shifted to the 3451.23 cm^{-1} indicating the involvement of these groups in the biosorption process. The band at 1654.99 cm^{-1} is due to the -CQO of carboxylic acid and is shifted to 1637.91 cm^{-1} for Cd^{2+} loaded biomass. The significant change in the wave number reveals, that the involvement of the carboxylic acid in the ion exchange process. The band at 1420.14, 1248.04 and 1033.82 cm^{-1} were due to the C-N, $-SO_3$ and C-O in benzene ring groups and the peaks were slightly shifted to 1403.67, 1252.83 and 1054.76 cm^{-1} respectively for Cd^{2+} loaded biomass (Fig. 10b). These results indicated the involvement of these functional groups in biosorption process. The characteristic absorption peaks detected in the pure biomass at 2936.13, 2175.00 and 1549.01 cm^{-1} was representing CH_2 stretching vibrations, CRN in the polyacrylonitrile and amide (N-H) were not detected in metal loaded biomass. Because of changes in metal-laden biomass, it could be concluded that N-H was involved in binding the metal and the same correlation was reported on Pleurotus ostreatus.

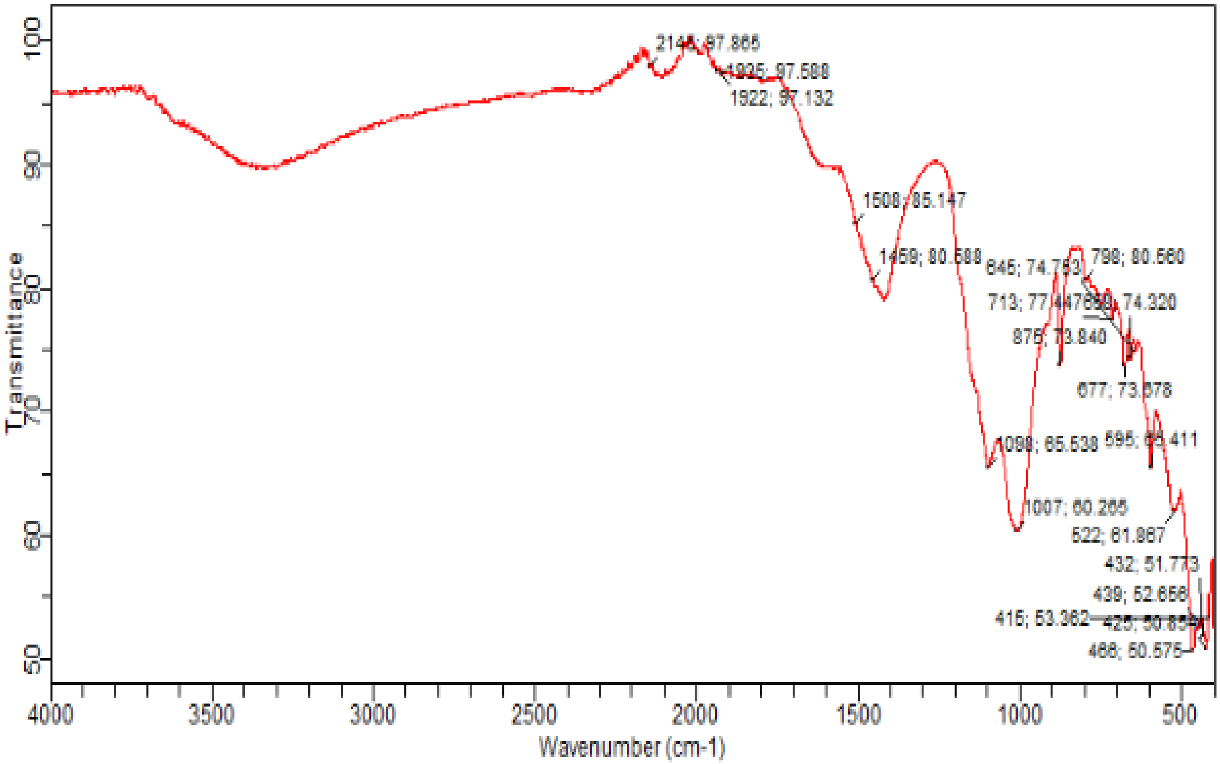

Fig.-10. (a).FT-IR Spectrum of unloaded *Sargassum cinereum* biomass

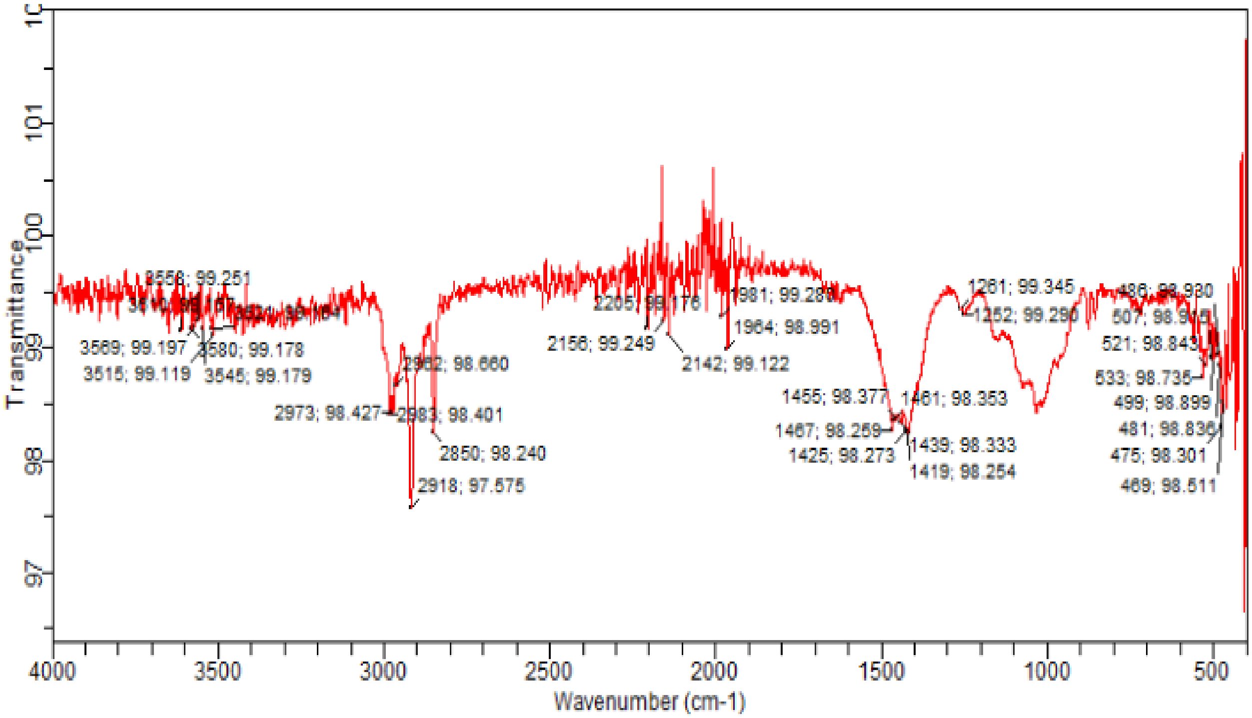

Fig.-10: (b).FT-IR Spectrum of Cd^{2+} loaded *Sargassum cinereum* biomass

Table-4: Band positions of *Sargassum cinereum* biomass and loaded with Cd^{2+}

S.No	Band shift position, cm^{-1}		Description
	Un loaded Biomass	Loaded with Cd^{2+}	
1	2947.68	2918	C–H stretching vibrations due to lignins
2	2145.97	2156	Thiocyanate (–SCN)
3	1925.97	1964	Combination of aromatic bonds
4	1508.85	---------	–NH stretching vibration at peptidic bond of protein[30]
5	1459.80	1439	Symmetric bending vibrations of alkane bonds ($-CH_3$)[29]
6	1098.65	1078	C–N, $PO^3{}_4$ (ortho phosphate) and organic siloxanes[31]
7	1007.60	1013	C–O characterized by polysaccharides in the biomass[32]
8	876.73	865	(–CH)- 1,3 substitution at aromatic aryl rings
9	798.80	---------	presence of siliceous (Si–C)[33]

Scanning Electron Microscopy (SEM)

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope which provides images of the sample surface by scanning it with a high energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface. In this investigation, possible mechanisms involved in the sorption of the toxic elements in the biomasses and differences due to the application of the amendments were investigated using scanning electron microscopy. The SEM images were taken by applying 10 kV voltage with different magnification times for the clarification of surface. The SEM micrographs of *Sargassum sp* biomass before and after biosorption were studied and are depicted in Fig.11. It is evident from analysis that the surface areas of algal and plant biomasses are uneven, heterogeneous with pores on the surfaces. SEM images of native biomasses show that number of pores with different diameters and different pore areas. The change in morphology indicates the accumulation of liquid phase concentration of charge moieties onto algal and plant biomass surface areas. Further, pores facilitate the good possibility for metal ions to be adsorbed. After adsorption the particles have granular, complex, uneven and porous surface textures that were not found in the native biomass of *Sargassum sp*. The similar results were observed in case of Cd^{2+}, Cu^{2+} on the surface of the Acacia leucocephala bark powder.

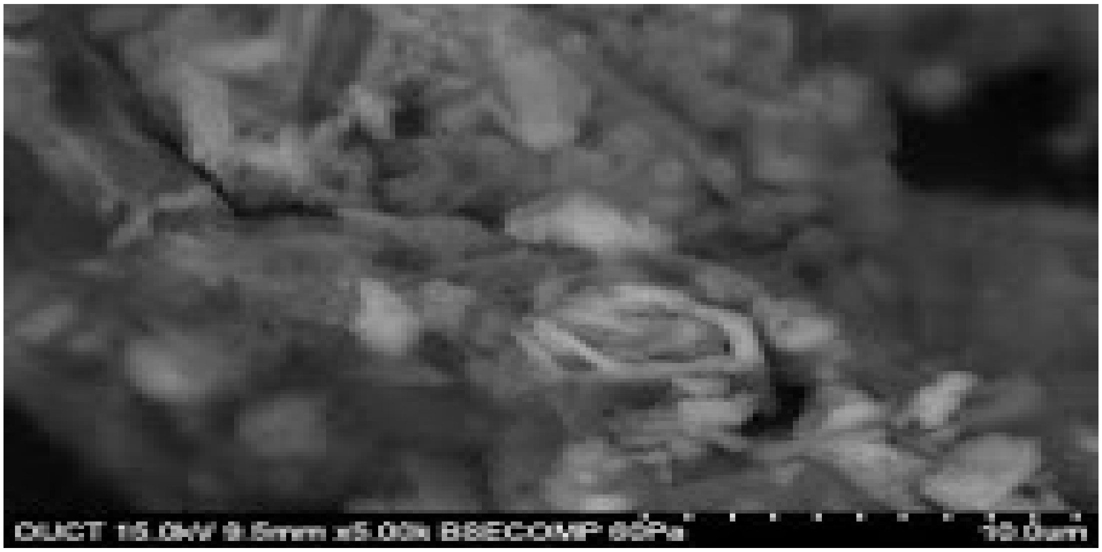

Fig.-11(a): SEM of Algae powder *Sargassum cinereum* without metal ions

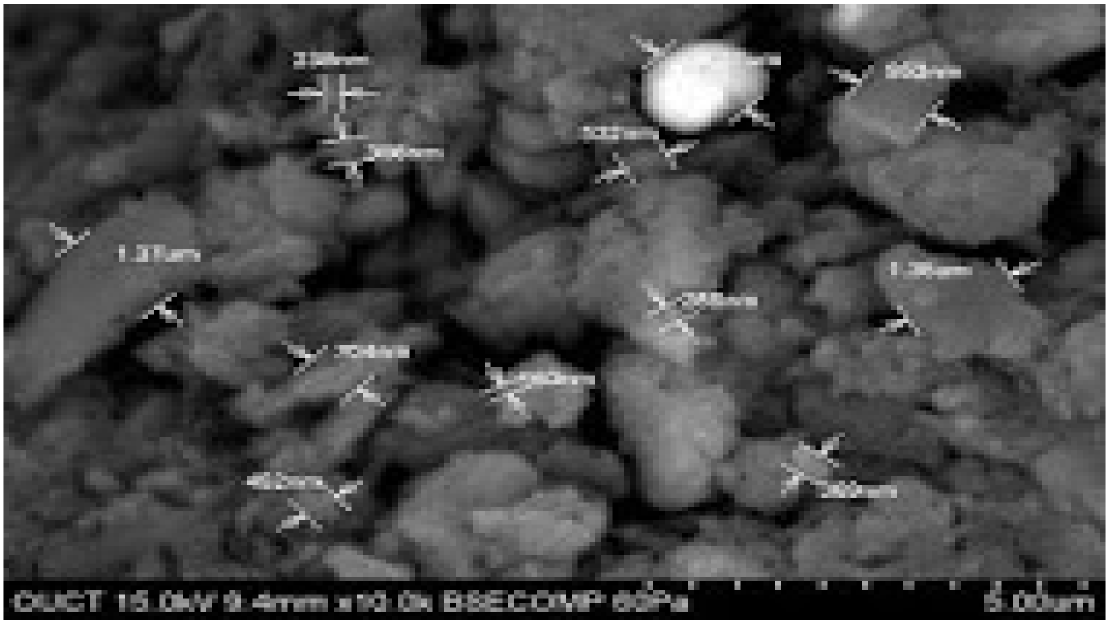

Fig.-11(b): SEM of Algae powder *Sargassum cinereum* loaded with Cd^{2+} ions.

CONCLUSION

The potential of *Sargassum sp* for removal of Cd (II) ions from aqueous solutions was dependent on the solution pH, initial metal ions concentrations, biosorbent dose, contact time, and temperature. The equilibrium data have been analyzed using Langmuir, Freundlich isotherms.

The characteristic parameters for each isotherm and related correlation coefficients, R^2, were determined. The Langmuir biosorption isotherms were demonstrated to provide the best correlation for the biosorption of Cd (II) ions onto *Sargassum sp*.The kinetic results provided the best correlation of the experimental data of biosorption of Cd (II) onto *Sargassum sp* by pseudo second order equation. The performance of *Sargassum sp* as cadmium adsorbents compares favourably with other adsorbents like modified lignin, chelating resin, natural clays, and activated carbons. The SEM studies showed Cd^{2+} biosorption on selective grains. The FTIR spectra indicated bands corresponding to -OH, COO-, -CH, CQC, CQS and –C-C-.

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