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Adsorption of Mercuric Ion by Marine Algae Enteromorpha

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Abstract

Toxic mercury has been found in many industrial and wastewater, and its removal becomes a challenging environmental protection aim. For this purpose, the biosorption of mercury on the marine green algae Enteromorpha has been studied.

The amount of mercury uptake increased steeply by increasing the weight of algae biomass and reached equilibrium for an uptake of 26 mg/g at pH 7.0 in agitation experiment. In column experiment, the mercury uptake capacity by Enteromorpha algae was found equal to 43.0 mg/g at optimum pH 7.0. The uptake process is relatively fast and equilibrium reached after 16 minutes of stirring. The biosorption mechanism is described by the kinetic-thermodynamic model and Temkin adsorption isotherm. Comparison of FTIR and thermal analysis of pure algae and algae material after mercury uptake indicates binding of mercury to algae biomass.

Introduction

Heavy metals are commonly associated with pollution and toxicity problems. Significant sources of heavy metals to environment are metals industries, waste disposal, agricultural materials, and fossil fuel combustion **[1]**. The toxic effects of heavy metals include competition for sites with essential metabolites, replacement of essential ions, inhibition of enzyme, and damage of cells **[1-2]**. Natural waters are contaminated with several heavy metals arising mostly from mining wastes and industrial discharges. The contamination of waste water and soil with heavy metal ions is a complex problem, since these metals are toxic in both their elemental and chemically combined forms **[3-7]**. From an environmental protection point of view, heavy metal ions should be removed at the source in order to avoid pollution of

natural waters and subsequent metal accumulation in the food chain **[3]**. In fact removal of this contamination has received much attention in recent years. Column application was studied in order to compare the capacity of algae with that of Sweden wood powder.

Conventional methods for removal are chemical precipitation, chemical oxidation, chemical reduction, ion exchange, filtration, electrochemical treatment and evaporation. [**8-10**]. All these procedures have significant disadvantages, which are for instance incomplete removal, high-energy requirements, and production of toxic sludge or waste products that also require disposal. These methods often are very expensive.

Alternative methods for heavy metal removal have been developed in the last decade, such as biosorption of heavy metal ions on biomass. Marine algae, a renewable natural biomass, have attracted the attention of many investigators and used as dead nonliving materials. Algae has an ability to adsorb and remove heavy metals because they have a uniform cell size and a number of different metal binding sites on their cell walls. These sites include carboxyl groups, polysaccharides and sulfydral groups **[11-16]**. Algae were found accumulating heavy metal in their habitat and thus they are used as heavy metal pollution monitors in fresh and salty water such as river, sea and ocean in different regions of the world. Algae have been also used in on-site bioremediation of polluted natural water **[17-21]**.

Mercury being one of the 'big three' toxic heavy metals and occurs as pollutant in two forms: organic mercury and inorganic mercury. Inorganic mercury occurs when elemental mercury is combined with chlorine, sulfur or oxygen. Inorganic and organic mercury are both toxins that can produce a wide range of adverse health affects. The organic form occurs when mercury is combined with carbon. The most common form of organic mercury is methyl mercury which is produced primarily by small organisms in water and soil when they are exposed to inorganic mercury. Humans also have the ability to convert inorganic mercury to an organic form once it has become absorbed into the bloodstream. Organic mercury bioaccumulates and passes up the food chain due to organism inability to process and eliminate it [**3**]. Inorganic mercury compounds are less toxic than organic mercury compounds (primarily due to difficulties in absorption). Absorbed inorganic mercury is readily converted to an organic form by physiological processes in the liver**.** In general, mercury causes several health effects such as: fatigue, mental depression, headache, hallucinations, depressed immune system, memory problems, loss of sense of pain, gastrointestinal disorders, loosing of the teeth, weight loss, vomiting, and fever **[1, 2]**.

The present work focused on the ability of green algae Enteromorpha, collected from Riviera Region near Manara in Lebanon, to adsorb Hg^{2+} from aqueous medium at 25°C. The equilibrium isotherm, the uptake kinetics, the effect of pH, time, and concentration were studied. In addition, column application was studied in order to compare the capacity of algae with that of Sweden Wood powder.

In order for the biosorbent material to be cost effective and competes with established ion exchange resins, it needs to be efficient metal binders and perform well under process contact conditions as well. This requires optimization of the size, durability, hardness and porosity of biosorbent particles. The stability and efficiency

of the algae was improved by mixing the algae with inorganic material such as silica gel or the biomass of the sawdust of the Sweden wood.

Experimental

Chemicals

All reagents are from Fluka: disodium ethylenediamine tetra acetic acid (EDTA), mercuric chloride $HgCl_2$, xylenol orange indicator, hexamine, nitric acid, sodium acetate and acetic acid for acetate buffer pH (2-8), and sodium dihydrogen phosphate and phosphoric acid for phosphate buffer pH (8-10).

Equipments and Instruments

The potentiometric measurements were carried out using Denver instrument Model 225 pH – Ion selective electrode meter fitted with a combined glass electrode (reading to ± 0.01 pH unit). The reaction flask was kept constant at 25^{o}C (± 0.1^{o}C) by using a thermostat Model Heto HMT 200. The shaker (Wiggen Hauser OS- 150, Germany) and centrifuge (Sigma 203) were used for agitation experiment. Infrared data were collected on a Schimadzu 8300 FTIR spectrophotometer using the KBr pellet method. Thermal analysis was performed on Setaram-Labsys instrument using TG-DSC module. The heating rate was 3^{0}C/min for the range 25 – 800^{o}C. Dry nitrogen was passed over 10 mg of the sample placed in a platinum crucible.

Algae collection

The raw algae Enteromorpha was harvested from the Lebanese coast at Manara, washed with tap and deionized water in order to remove extra salts, sun dried, and grounded to particle size (0.5 mesh). Finally, the fine powder is oven dried at 60 °C for 24 hours and ready to be used in metal uptake study [**22**].

Metal analysis

Titration with EDTA ($2.0x10^{-4}$ M) was used in order to determine the concentration of Hg^{2+} (10-500 ppm) using xylenol orange as indicator for color change from purple to yellow. Hexamine buffer was used to adjust the pH to 5.0-6.

Effect of mass of algae on metal uptake

The effect of mass of algae on metal uptake was studied in batch system. 25 mL solution of 200 ppm mercury (at pH 4.25) in 100 mL Erlenmeyer flask was shaken with different masses of algae for 2 min at 200 r.p.m and left to stand for 24 hrs in water bath at 25^{o}C and then analyzed for the remaining mercury [**23**].

pH effect on metal uptake

The mass of algae used in this experiment is the optimum mass 0.3 g done in batch system using 100-mL Erlenmeyer flasks with a reaction volume of 25 mL mercury solution (200.59 mg/L) at 25^{o}C. The mixture was shaken for 2 min (at 200 r.p.m) and left to stand for 24 hrs, at different pH using sodium acetate buffer to cover the pH range 3.0 - 7.0, phosphate buffer for pH 8.0 – 10.0 and HCl/NaOH solutions for pH 2.0 – 8.0 [**24**].

Effect of mercury concentration on metal uptake
This experiment was done as above at only pH 7.0 using sodium acetate buffer but with different mercury concentrations (10, 25, 50, 100, 150, 250, 300, 400 and 500 ppm).

Effect of residence time on metal uptake
This experiment was done at 25^{o}C with 25 mL mercury 300 (ppm) and 0.3 g algae in 100-mL Erlenmeyer flasks at pH 7.0 (using sodium acetate buffer) and shaking at 200 r.p.m with variable time (2, 4, 8, 16, 30, 45, 60, 90 minutes) [**24**]

Mixing of algae with silica
An alga (0.30 g) was mixed physically with different masses of silica (0.0, 0.15, 0.30, 0.60 and 0.90 g). Mercury adsorption experiment was done similarly using the conditions described above but with 16 minutes of shaking.

Procedure for column utilization (Breakthrough curve)
The column used has a diameter of 2 cm and a length of 44 cm. It was packed uniformly with 1.0 g of green ***Enteromorpha*** algae powder. The mercury solution (300 ppm) at pH 7.0 was drained through the column at a constant rate 2.5 mL/min. Collected aliquots of similar volume were collected repeatability from the column and analyzed for mercury [**25**]. The same experiment was repeated using sweeden wood for column packing. It was also repeated by packing with algae residue collected after reflux.

Adsorption Isotherms

The adsorption of metal onto algae materials occurs at algae/solution interface. This phenomenon could take place via electrostatic attraction between **(i)** the charged metal and the charged biomass molecules, **(ii)** dipole type interaction between uncharged biomass molecule with the metal, **(iii)** π-interaction with the metal and **(iv)** a combination of all the above [**26**]. If the adsorption process involves charge sharing or charge transfer, a coordinate type bond will be formed and the process is termed chemisorption [**26-33**].

The adsorption of metal ion onto the surface of biomass is regarded as a substitutional adsorption process between the metal in the aqueous phase ($M_{(aq.)}$) and the water molecules adsorbed onto the biomass surface ($H_2O_{(s)}$) [**34**].

$$M_{(aq.)} + x\ H_2O_{(s)} \rightarrow M_{(s)} + x\ H_2O_{(aq.)} \quad (1)$$

where x is the size ratio and is simply the number of water molecules replaced by one molecule of metal adsorbate. A number of mathematical relationships representing adsorption isotherms that characterize the dependence of the surface coverage function "θ" on the metal concentration have been suggested to fit the various experimental data. The simplest theoretical equation is that due to Langmuir and is given by the equation [**35**]:

$$\frac{\theta}{1 - \theta} = K C \quad (2)$$

where θ is the surface coverage, K is the equilibrium constant of the adsorption reaction and C is the metal concentration in bulk of the solution.

A number of mathematical expressions have thus been developed to take into consideration some of the non-ideal effects. The most used expressions are Frumkin [**36**], Hill de Boer [**37**], Parsons [**38**], Temkin [**36**], Flory-Huggins [**39**], Bockris-Swinkels [**40**] adsorption isotherms, kinetic-thermodynamic model [**41**] and Freundlich equation [**42**].

Frumkin Adsorption Isotherm:

$$\left[\frac{\theta}{1 - \theta}\right] \exp\left[-\ 2\ a\ \theta\right] = K\ C \tag{3}$$

where **a** is a molecular interaction parameter depending on the molecular interactions in the adsorption layer and on the degree of heterogeneity of the surface. It can have both positive and negative values and is a measure of the steepness of the adsorption isotherm. The more positive the value of a, the steeper is the adsorption isotherm. This has been interpreted to imply that the ions-molecules interactions with positive "a" value cause an increase in the adsorption energy with the increase of θ value. **K** is the equilibrium constant of the adsorption isotherm.

Hill de Boer Adsorption Isotherm:

$$\left[\frac{\theta}{1 - \theta}\right] \exp\left[\frac{\theta}{1 - \theta}\right] \left[-\ 2\ a\ \theta\right] = K\ C \tag{4}$$

Parsons Adsorption Isotherm:

$$\left[\frac{\theta}{1 - \theta}\right] \exp\left[\frac{2 - \theta}{(1 - \theta)^2}\right] \exp\left[-\ 2\ a\ \theta\right] = K\ C \tag{5}$$

Temkin Adsorption Isotherm:

$$a\ \theta = \ln K\ C \tag{6}$$

Flory-Huggins Adsorption Isotherm:

$$\frac{\theta}{x\,(1 - \theta)^x} = K\ C \tag{7}$$

Bockris-Swinkels Adsorption Isotherm:

$$\frac{\left[\dfrac{\theta}{(1 - \theta)^x}\right]^{\left[\theta + x\,(1 - \theta)^{x-1}\right]}}{x^x} = K\ C \tag{8}$$

Kinetic-thermodynamic model:

$$\log \frac{\theta}{1 - \theta} = \log K' + y \log C \quad (9)$$

where K' is a constant and related to the binding constant, K, by the following relationship:

$$K = K'^{\left(\frac{1}{y}\right)} \quad (10)$$

where **y** is the number of metal ions occupying one active site and **1/y** represents the number of active sites of the surface occupied by one metal ion. It is of importance to realize that values of **1/y** greater than unity imply the formation of multilayers of metal on the surface of biomass. While values of **1/y** less than unity, means that a given metal ion will occupy more than one active site. Large values of the binding constant means better removal efficiency of a given metal ion, i.e., stronger electrical interaction between the double layer existing at the phase boundary and the adsorbing metal. Small values of the binding constant, however compromise that such interactions by the adsorbing metal and the metal surface are weaker, denoting that the metal ions are easily removable by the solvent molecules from the surface.

Freundlich equation:

$$q = K(C)^{1/n} \quad (11)$$

where **q** is the maximum metal uptake and **C** is the initial ion concentration in ppm, **K** and **n** are the Freundlich constants that are characteristics of the system. **K** and **n** are the indicators of the adsorption capacity and adsorption intensity respectively.

Results and Discussion

Infrared spectroscopy

FTIR spectra of Enteromorpha algae shows strong stretch at 3395 cm^{-1} due to –NH of amino group, strong stretch at 1646.5 cm^{-1} and a weaker ones at 1436 cm^{-1} due to carboxylate group, and strong bending vibration at 1105 and 1158 cm^{-1} due to C-O of ether and alcoholic group respectively, **Fig. 1 [43, 44].** FTIR spectra of Enteromorpha algae with adsorbed mercury, also shows many peaks similar to free algae, **Fig. 1**. However the peak due to –NH stretch has been shifted to lower wave number 3291 cm^{-1}. The bands at 1651 cm^{-1} due to carboxylate shows a little shift to higher wave number and a variation in the shape of the peak compared to free algae, also the peak at 1105 disappears in the case of algae with biosorbed mercury. Both indicate the involvement of carboxylate and ester groups in the binding with mercury, **[43, 44]**.

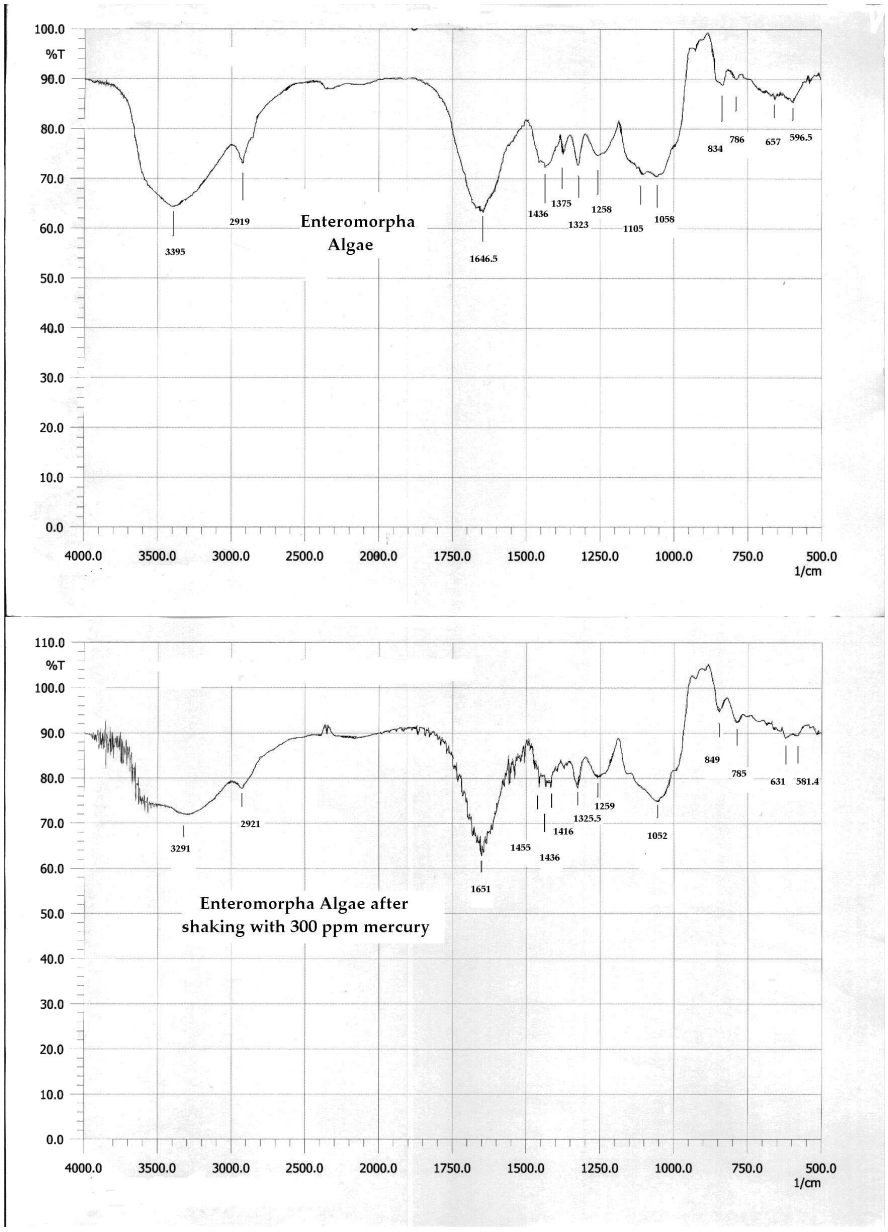

Figure 1: FTIR spectra of Enteromorpha algae with or without adsorbed mercury

Metal uptake

The effect of mass of algae on metal uptake was studied in batch system for 200 ppm initial mercury concentration, pH 7.5 and residence time 24 h. There was a steep increase in the biosorption of mercury as the mass of algae increased from 0.09 g to 0.30 g. The optimum mass of algae 0.30 g corresponds to a maximum metal uptake of 85 % (capacity 14.21 mg/g) for a volume reaction of 25 mL mercury (200 ppm), **Fig. 2**. With higher biomass level ranging from 0.35 to 1.0 g there were no significant increases in the metal uptake.

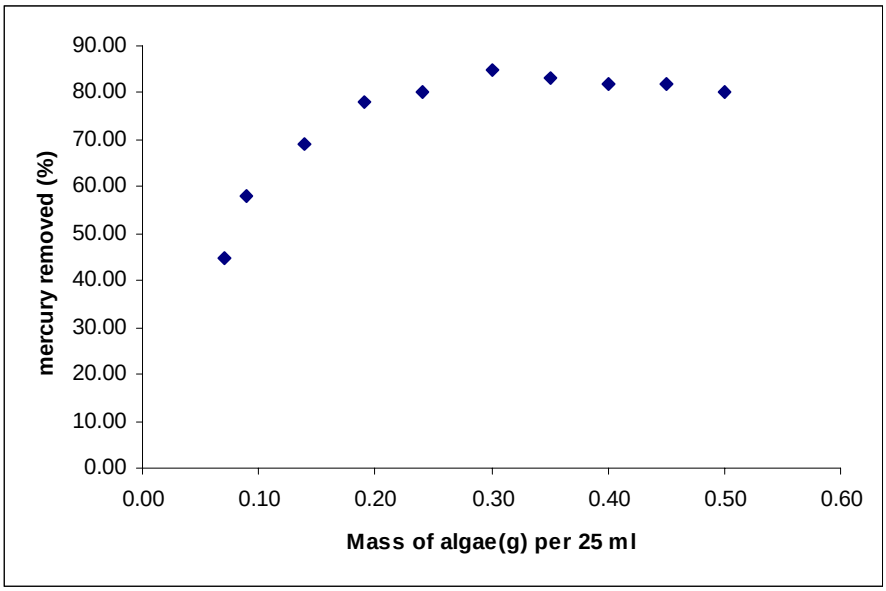

Figure 2: Effect of mass of Enteromorpha algae on metal uptake for a 25 mL of mercury (200 ppm) solution.

The standard mercury solution (200 ppm) was prepared in three medium: 1) acetate buffer to cover a pH range 2.0-7.0, 2) phosphate buffer to cover a range 8.0-10.0 and 3) HCl or NaOH to cover a pH 2.0-8.0. The data of metal uptake by 0.30 g algae in a 25 mL standard mercury solution are presented in **Fig. 3-5** respectively for different pH media. It was found that as the pH of the solution increases above 2.0, mercury binding increases until an optimum pH 7.0 1) using sodium acetate or phosphate buffer, corresponding to a metal uptake 84 % (capacity 13.71 mg/g algae) and 2) using HCl/NaOH solutions, corresponding to a metal uptake of 80 % (capacity 13.37 mg/g algae). The results of the IR suggests that to some extent the carboxyl group (-COOH) as well as $-NH_2$ group are responsible for the binding of the mercuric ion. This gives us an insight into the mechanism of the binding involved within the biomass. At lower pH (< 4), the carboxyl group retains their proton reducing the probability of metal binding to any positively charged ion such as ammonium group present. Whereas at higher pH (> 4), the carboxyl groups are deprotonated and become negatively charged and the ammonium groups become neutral, this can help attraction of positively charged metal ion to these two biomass material groups so that binding can occurs. Thus metal ion binding to the biomass is essentially an ion exchange mechanism which involves electrostatic interaction between the negatively charged groups in the cell wall and metallic cation [**45, 46**]. At pH lower than 4, there is still significant binding of mercury to biomass, less than 50 %. These suggest that at these low pH values, other groups such as ester present in the biomass play a role in binding. At pH higher than 7.0 (pH 8-10), there is a dramatic decrease in metal uptake, **Fig. 4 & 5**. This can be attributed to the hydrolysis of mercury and decrease in the availability of free mercuric ion responsible for binding [**47**, **48**].

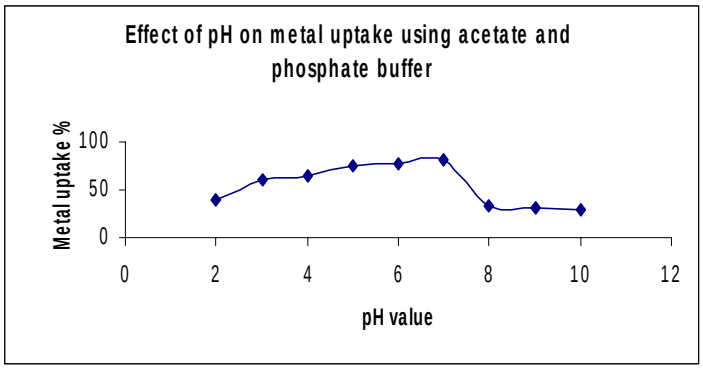

Figure 3: Effect of pH on % metal uptake using acetate buffer medium pH 2-7, and phosphate buffer pH 8-10, for 0.30 g algae per 25 mL Hg solution 200 (ppm).

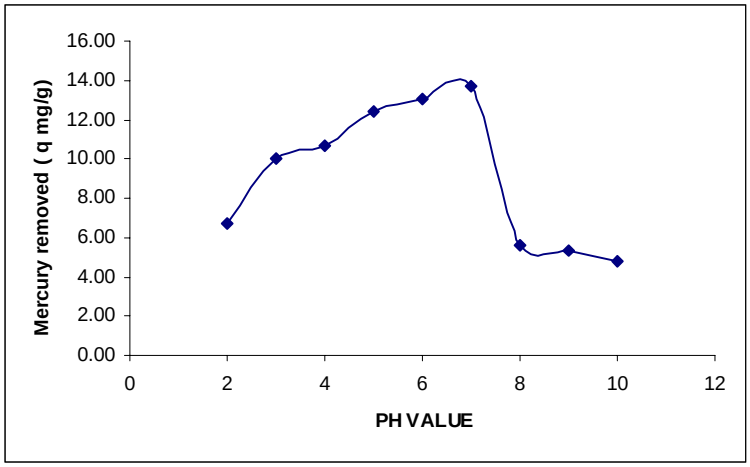

Figure 4: Effect of pH on metal uptake using acetate buffer medium pH 2-7., and phosphate buffer pH 8-10, for 0.30 g algae per 25 mL Hg solution 200 (ppm).

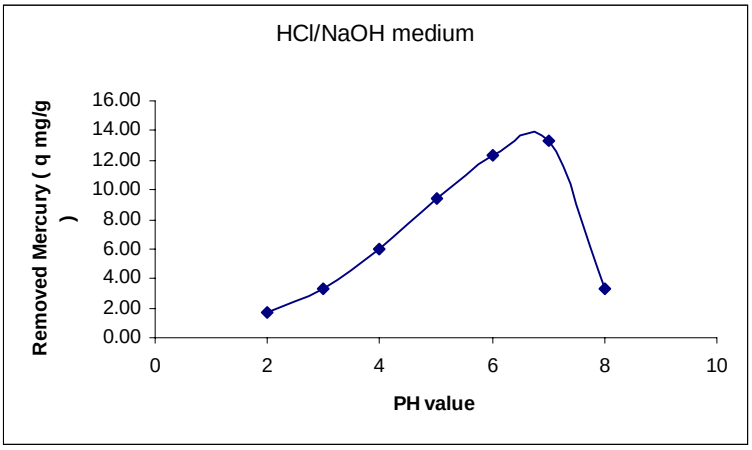

Fig. 5. Effect of pH on metal uptake using HCl/NaOH medium for 0.30 g Enteromorpha algae per 25 mL Hg solution 200 (ppm).

The experiment of effect of mercury concentration on metal uptake was done in batch system concentrations of 0.3 g at optimum pH 7.0 (using sodium acetate buffer) for a residence time of 24 hrs and different mercury concentrations in the range 10 - 500 ppm, **Fig. 6**. There was a sharp increase in biosorption as the mercury concentration increases from 10 to 300 ppm algae and reaches a maximum at 400 ppm mercury corresponding to a percentage metal uptake of 77 % and a metal uptake capacity of 25.7 mg/g algae. For mercury solution greater than 400 ppm, the algae become saturated.

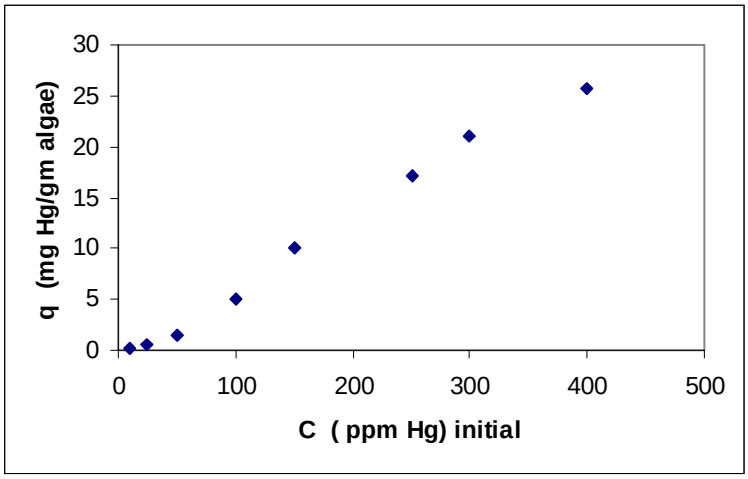

Figure 6: Equiibrium isotherms for mercury (II) adsorption by Enteromorpha algae. Algae mass of 0.3 g in 25 mL Hg(II) solution.

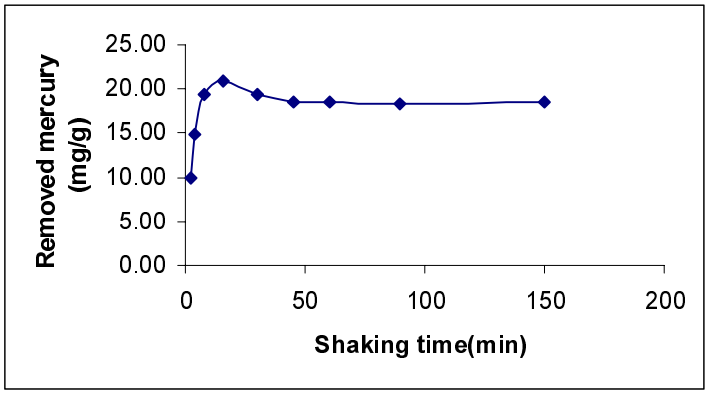

Figure 7: Effect of shaking time on metal uptake

Effect of shaking time on metal uptake was studied with 0.30 g algae in 25 mL mercury solution 300 (ppm) at optimum pH 7.0 using sodium acetate buffer, and variable shaking time (2, 4, 8, 16, 30, 45, 60, 90 min) at 200 r.p.m, **Fig. 7**. This experiment shows that the algae have bound most of the metal after 16 min, and that equilibrium was reached after maximum metal uptake 83.50 % (capacity 20.88 mg/g algae). This result is in parallel with those previously obtained with different algae and fungi for heavy metal uptake **[45, 46].**

In column experiment for the determination of breakthrough curve of mercury using column packed uniformly with 1.0 g of Enteromorpha algae powder at pH 7.0. Aliquots of 25 mL were collected from the column and analyzed for mercury**, Fig. 8**. This experiment showed that 43.28 mg of mercury was removed after passage of 275 mL solutions of mercury (300 ppm) **Table 1**. The mercury uptake capacity is comparable with other worker with different algae [**47**, **49**]

Also this experiment was repeated using Sweden powder wood with same conditions **Fig. 9**, showing a 31.45 mg mercury uptake with total volume of 275 mL, Table 2.

While repetition using algae residue after reflux gave a 33.99 mg of mercury uptake with a total of 275 mL Table 3. Fig 10, Shows saturation of the column after passage of 8-11 aliquots of 25 mL 300 ppm mercury.

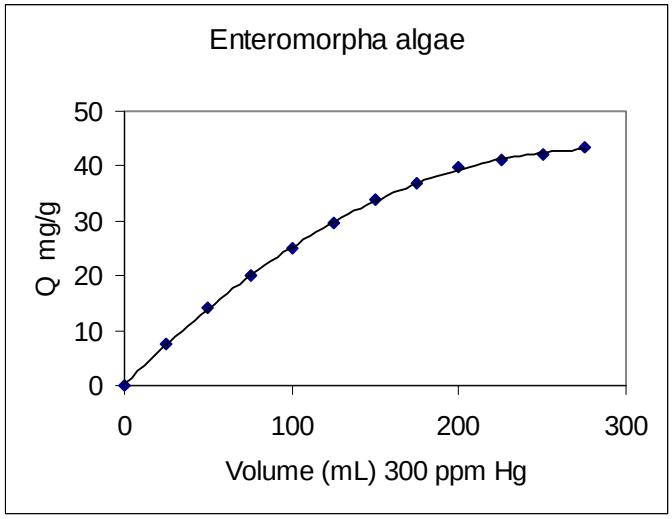

Figure 8: Breakthrough curve: capacity of 1 gram of marine algae (Enteromorpha) at pH 7 and flow rate 2.5 mL/min with 300 ppm mercury solution (partical size 0.5 mesh)

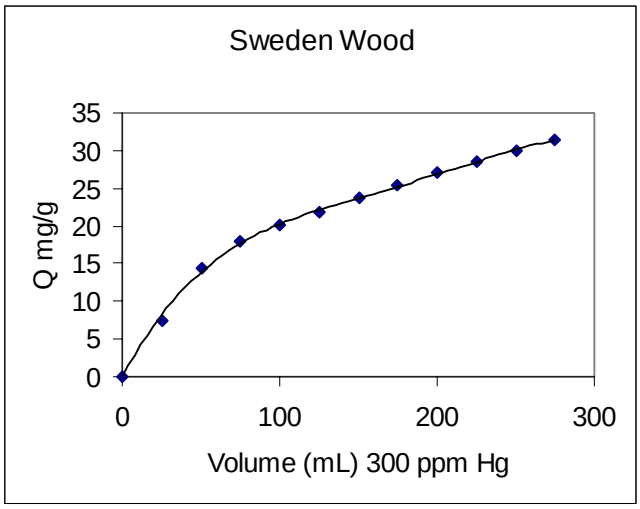

Figure 9: Breakthrough curve: capacity of 1 gram of Sweden Wood powder at pH 7 and flow rate 2.5 mL/min with 300 (ppm) mercury solution (partical size 0.5 mesh).

Table 1. Capacity for a column filled with 1 g algae after passage of a 300 ppm Hg solution

Volume (mL)	$Q_{mg/g}$
0	0
25	7.5
50	14.3
75	20.09
100	24.88
125	29.47
150	33.86
175	36.85
200	39.64
225	41.02
250	42.2
275	43.28

Table 2. Capacity for a column filled with 1 g wood after passage of 300 ppm Hg solution

Volume (mL)	$Q_{mg/g}$
0	0
25	7.5
50	14.5
75	17.89
100	20.12
125	21.9
150	23.68
175	25.36
200	26.99
225	28.47
250	29.95
275	31.43

Table 3. Capacity for a column filled with 1 g wood after passage of 300 ppm Hg solution

Volume mL	$Q_{mg/g}$
0	0
25	5.9
50	11.19
75	16.18
100	20.47
125	23.36
150	25.54
175	27.42
200	29.05
225	30.63
250	32.31
275	33.99

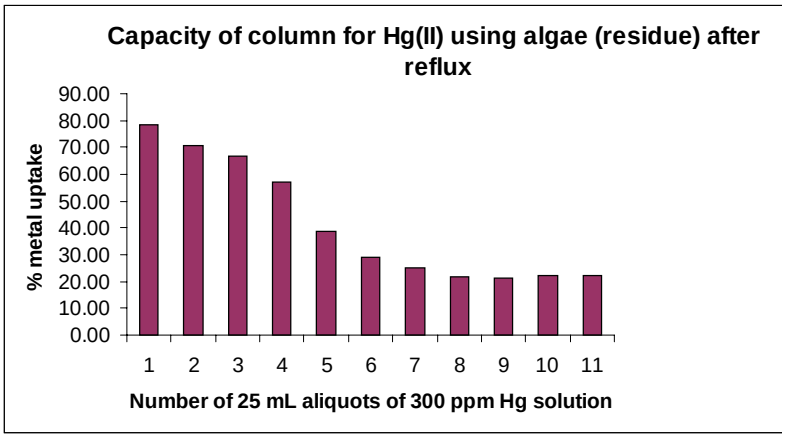

Figure 10: Saturation of the column after passage of 8-11 aliquots of 25 mL 300 ppm mercury for a column filled with 1 g Enteromorpha algae residue after reflux.

Adsorption Isotherm Calculations

It is reported that Freundlich model was applicable in biosorption studies of mercury with Chlamydomonas reinhardtii algae [**47**]. In this study, it was found that Freundlich model (Equation 11, Fig. 11) was the most suitable isotherm fit the obtained data and describing well the adsorption behavior of mercury onto Enteromorpha algae. The biomass concentration is 3.64 mg (dry weight) /mL using 300 ppm mercury solution at a flow rate 2.5 mL/min. The obtained parameters have the following values: (K = 4.984 x 10^{-3}, n = 0.999). The results suggest that the metal ions are adsorbed through one active center and occupy active sites on algae surface. K is related to the standard free energy of adsorption $\Delta G^{o}_{ads.}$ by:

$$K = \frac{1}{55.5}\exp\frac{-\Delta G^{o}_{ads.}}{RT}$$

Thus, the calculated $\triangle G^{o}_{ads}$ value is 3.184 kJ/mol.

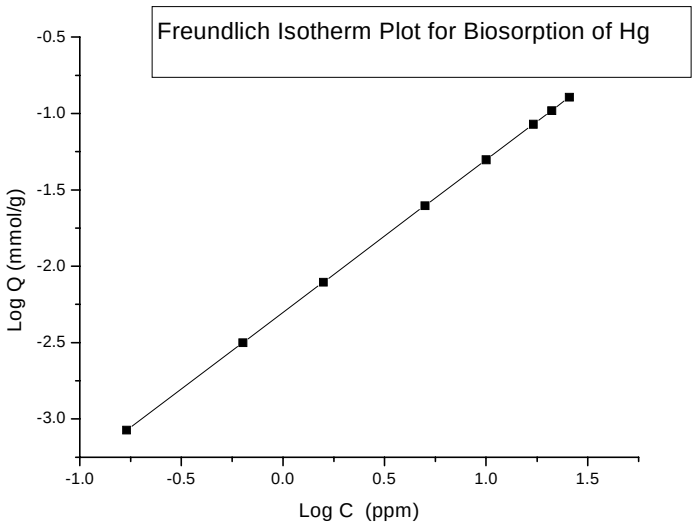

Figure 11: Adsorption of mercury onto Enteromorpha algae using Freundlich adsorption isotherm.

Thermal analysis

The results of thermogravimetric analysis of free algae and algae with biosorbed mercury are shown in **Fig. 12 and 13** respectively. The algae materials were heated to 800 ^{0}C, where all relevant weight loss were complete. The % mass loss at each temperature for Enteromorpha algae are: 12.82 % (65^{o}C), 36.3% (217^{o}C), 21.58 (448^{o}C), 25.8 % (717.2^{o}C) while the % mass loss and temperature for algae with biosorbed mercury are:

14.82 % (68^{o}C), 44.33 % (222^{o}C), 22.35 % (450^{o}C), 16.17 % (650^{o}C).

The two TGA curve reveal difference between loss in weight with temperatures for both materials, with greatest difference occurring at 220^{o}C where free algae shows a loss of 36.4 % while algae with biosorbed mercury shows a loss of 44.3 %. The 7.9 % difference between the two could be attributed to the adsorbed amount of mercuy. In addition, this process is exothermic in both cases.

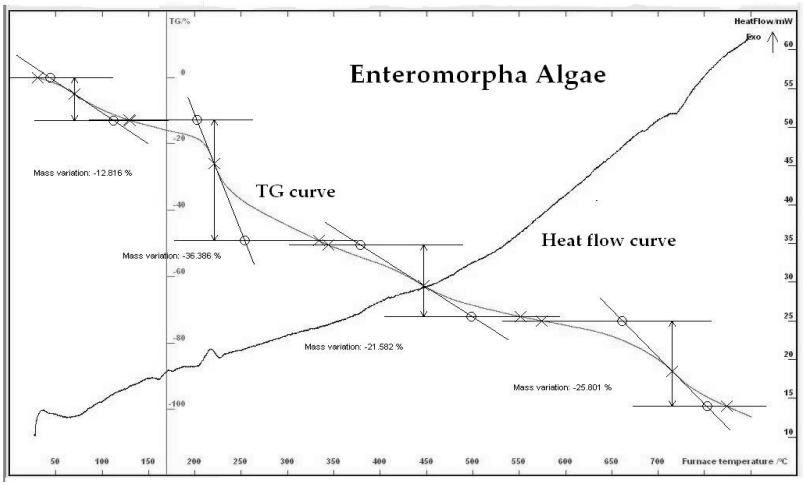

Figure 12: Thermal analysis of Enteromorpha algae

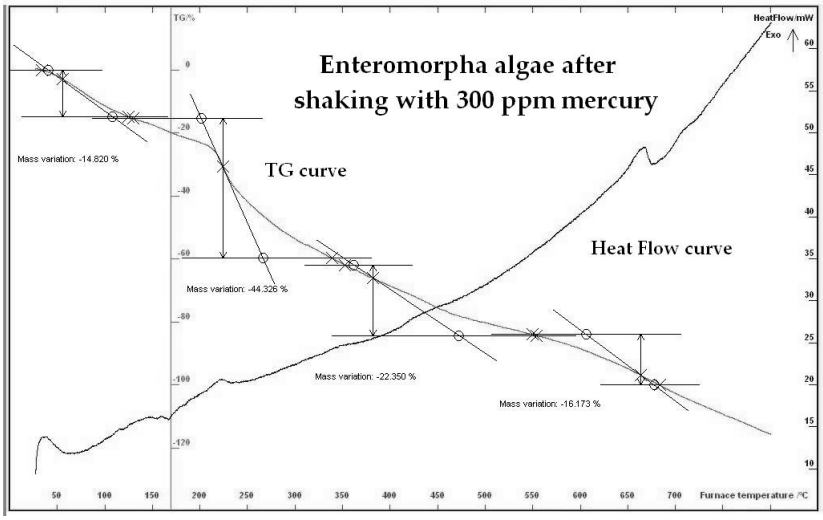

Figure 13: Thermal analysis of Enteromorpha algae with adsorbed mercury

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