EXPERIMENTAL INVESTIGATION ON THE USE OF NATIVE BIOMASS AS BIOSORBENTS FOR METAL POLLUTANT REMOVAL

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ABSTRACT

Waste water treatment is a permanent task. Many novel techniques have emerge in recent years and one of them is using biomass in removing heavy-metals. In this research screening and preliminary optimization experiments have identified different types of abundant biomass which can accumulate heavy metals such as Fe^{3+}, Co^{3+}, Cu^{2+} and Cr^{3+} from effluent. Cystoseira Myrica has a high uptake of Cr^{3+} while Sargassum Polycystum has been found to have a high uptake of Fe^{3+}. Observed biosorption kinetics shows rapid initial stage, followed by slower second stage and the amount of material adsorbed increases linearly as its concentration in the solutions increases.

INTRODUCTION

Background

In recent years, major efforts have been undertaken to develop waste water treatment techniques which are effective at removing both organic and inorganic contaminants so that waste water discharges, and water quality standards can be met [1]. This is becoming an even more of concern as the need for recycling of industrial waste water, and recovery and concentration of useful metals.

Biosorption of heavy metals by microbial cells is recognised as a potential alternative to existing technologies for the recovery of heavy metals from industrial waste streams and natural waste waters [2].

While research on novel techniques using immobilized biomass continue elsewhere [3], it may worthwhile for Africa to look at the potential of the abundant native biomass for use as biosorbents which are cheap but effective.

Mechanism for metal uptake

Biosorptive potential of biomass is attributed to either biosorptive uptake by non-living biomass or bio-accumulation by living cells. In facts, both mechanisms may occur Simultaneously, albeit at different rates [3]. In this work, biosorptive uptake using non-living (inactive) biomass is chosen for investigation because no toxicity problems may be encountered in non-living biomass and the process is not governed by physiological constraints. The use of inactive biomass also eliminates the possibility of biodegradation as a removal process [4]. Furthermore, there is evidence from literature [5] that, with respect to equilibrium, biosorption occurs to the same extent in living cells as in dead cells.

EXPERIMENTAL

Preparation of Material

Identification of species

Six different types of seaweeds specimens used in the study identified with the help of Department of Botany, University of Dar es Salaam as *Ulva Racticulata (I), Ulva fasciata (II), Crystoseira Myrica (III), Sargassum Polycystum (IV), Gracilaria Grassa (V), and Amansia Species (VI)* (numbers in brackets indicates coding used in this work).

The seaweeds used in the study were picked by hand during low tides, packed in plastic bags and rinsed thoroughly with fresh water to remove surface salts and debris. The rinsed algae were then dried in an oven at temperature of 100°C and then ground in a mortar to the size of about 60 US mesh and stored in stoppered flasks. Activated carbon (80 US mesh) used for comparison was obtained from purchased stock in Chemical Engineering Laboratory.

AAS Calibration

Concentration measurements were done using an Atomic Absorption Spectrometer (AAS Pelkin Elmer Model 3100 - Flame ionizer type). The use of AAS requires calibration curve for each metal of interest to be developed. Standard solutions of metals of interest (Cr^{3+}, Cu^{2+}, Co^{3+} and Fe^{3+}) were prepared at concentrations 1, 3, 5, 7, and 10 ppm. The AAS was then programmed to read concentration directly in ppm. During measurements, the filtrate was diluted to within the standard concentration selected. Detail of calibration may be found elsewhere [6].

Adsorption Experiments

An aqueous solution containing 20%w.w. of the element of interest was prepared. 50mls of aqueous solution was measured and put in 250ml flask. 2g of powdered adsorbent was added in the solution and then shaken thoroughly. The mixture was kept at 30°C for 24 hours in a gantry shaker at medium intensity mixing. Samples were taken for analysis after very hour, in the first 5 hours and after 24 hours the mixture was filtered and the filtered and the residual metal in the filtrate was analyzed using AAS.

Time Course of Adsorption

50 mls of aqueous sample of metal of interest is contacted with 2g of the corresponding adsorbent. The mixer was then placed in a gantry shaker and mixed at medium intensity. Samples were analyzed for free metal after the every 30 minutes using AAS.

Contact Density

50 mls of aqueous solution of the metal of interest was mixed with 0.5, 2, 4, 6, 8, and 10g of adsorbent separately. The sample was then shaken for 30 minutes in gantry shaker and residual metal concentration measured using AAS.

RESULTS AND DISCUSSION

Screening Experiments

From screening results in Figs. 1 through 4, shows that there is a significant difference in the biosorptive capacities of the different samples for the various aqueous species contacted. Fig. 1 shows that there is potential for Fe^{3+} removal by most of the native biomass tested. But in further experimentation in this study *Sargassum Polycystum (IV)* showed higher potential for Fe^{3+} removal by giving the lowest residual metal content during the first two to three hours of contacting. From fig. 2, *Cystoseira Myrica (III)* shows higher potential for chromium removal since it gives a minimum residual metal (comparable to activated carbon). Fig. 3 shows that *Cystoseira Myrica* and *Sargassum Polycystum* gives an appreciable reduction in residual concentration of copper ions in solution. From Fig. 4, we see again that *Sargassum Polycystum* gives an appreciable reduction of Co^{3+} ions from aqueous solution.

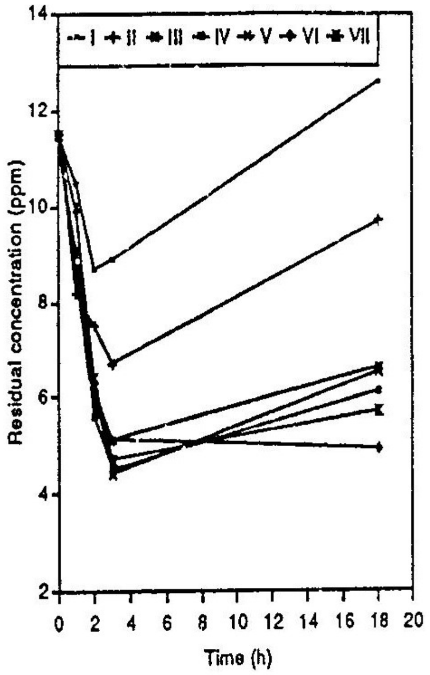
Time Course of Adsorption and Contact Density

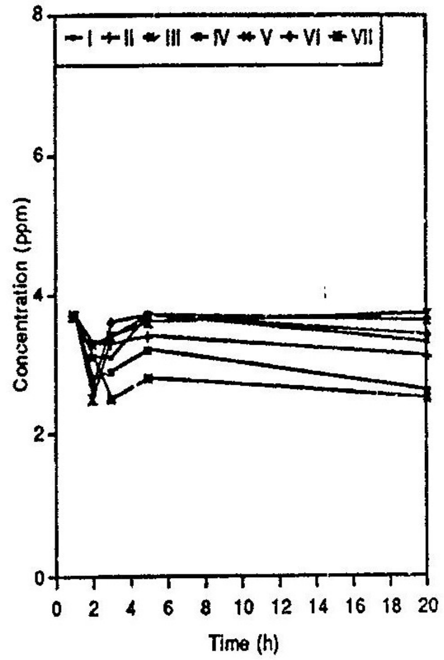
Fig. 5 shows that *Cystoseira Myrica* has a rapid uptake of Cr^{3+} and Cu^{2+} during the first 30 minutes of contact. Biosorption then continues slowly, and reaches equilibrium after two hours for the case of chromium while copper uptake increases slowly up to 7.5 contact hours. *Sargassum Polycystum* shows a rapid uptake of Fe^{3+} during the first 30 minutes of contact, followed by a period of slow uptake, reaching equilibrium before 2 contact hours have passed.

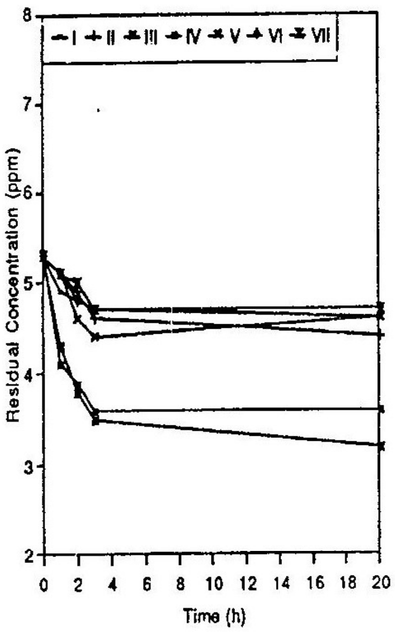
In Fig. 6 it is shown that *Cystoseira Myrica* has rapid Cu^{2+} uptake when contacted in 50 mls, 8ppm/6g adsorbent and biomass loading of 6g in 50mls, 8ppm Fe^{3+} with *Sargassum Polycystum* as adsorbent is optimal.

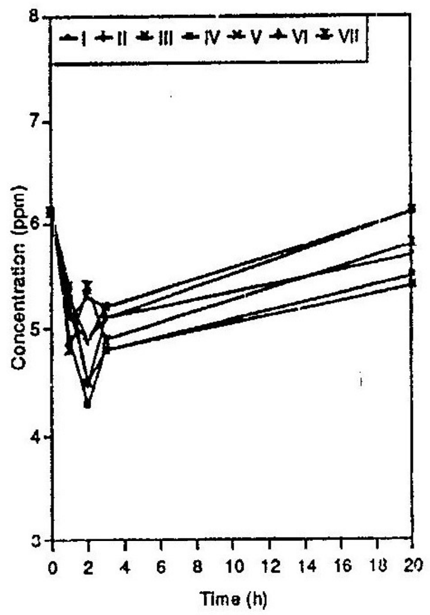
Effect of External Metal Concentration

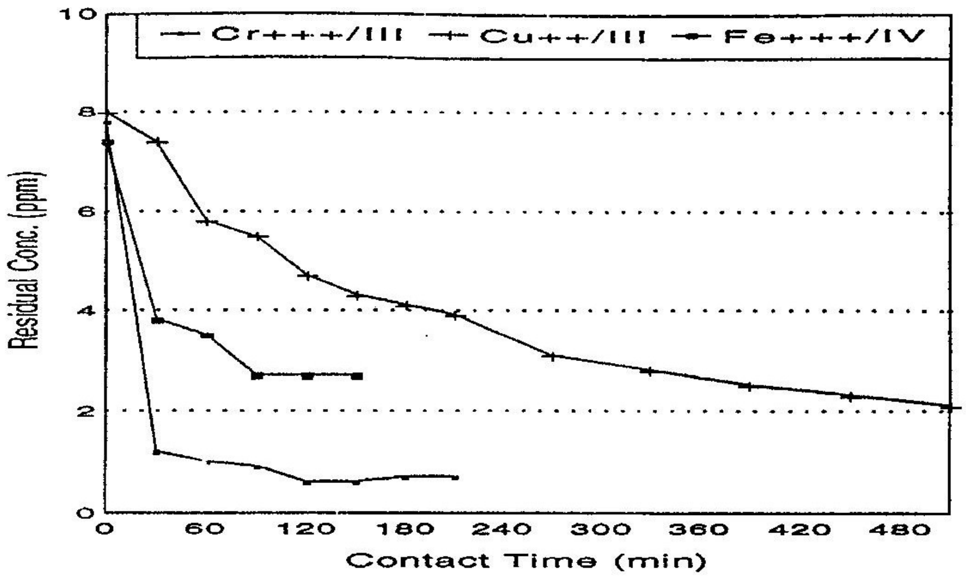
Fig. 7 shows that when the concentration of metals in the solution was increased keeping mass of adsorbents constant the amount of metal adsorbed per gram of adsorbent increases linearly. The trend is similar to the results reported by Freer et at (1989) for Uranium adsorption by Pinus Radiata D. Don.

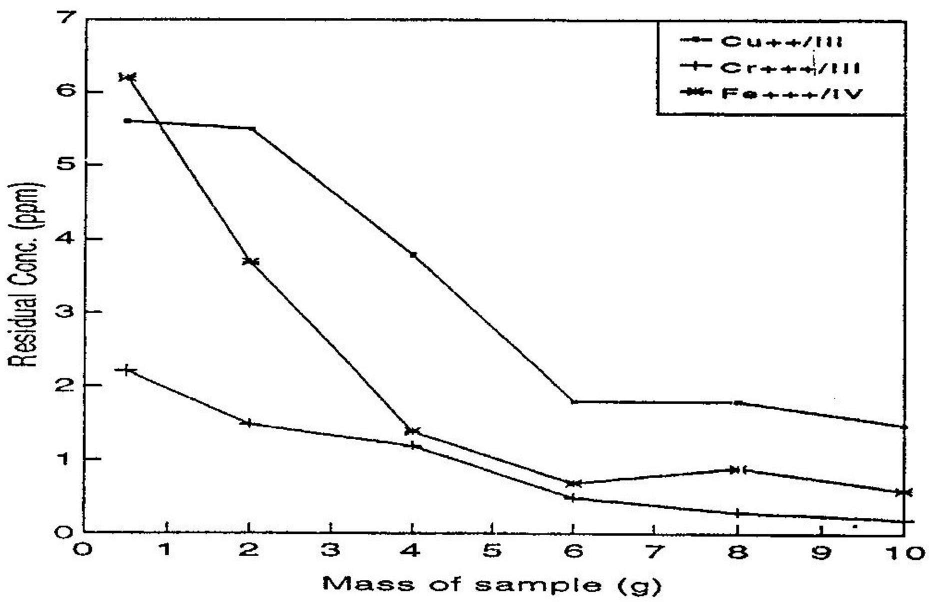

I II III IV V VI VII
Residual concentration (ppm)
Time (h)

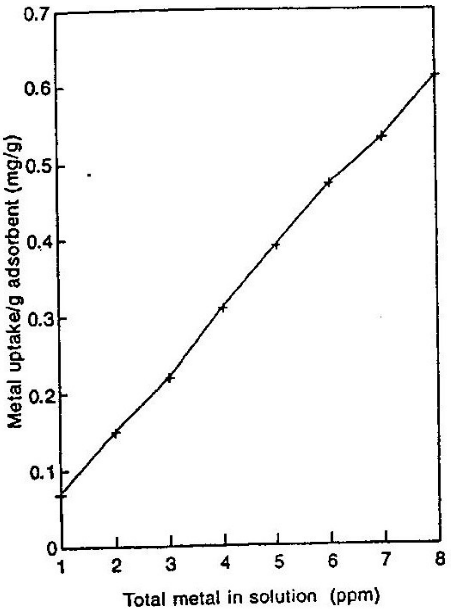

I II III IV V VI VII
Concentration (ppm)
Time (h)

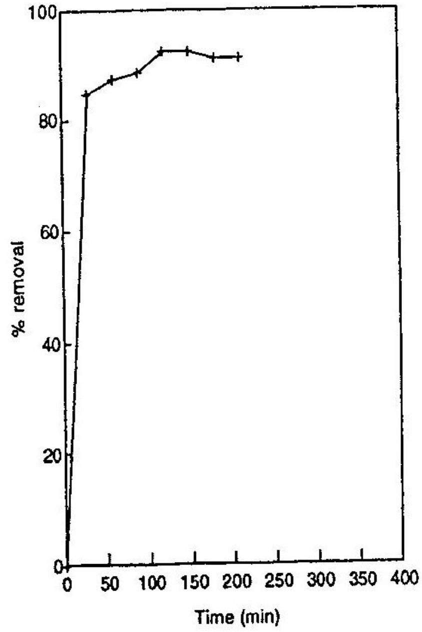

I II III IV V VI VII
Residual Concentration (ppm)
Time (h)

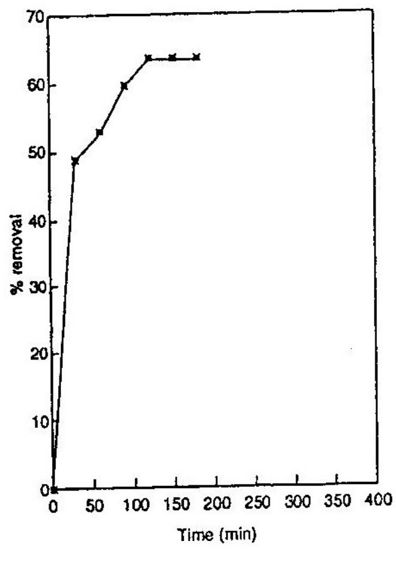

I II III IV V VI VII
Concentration (ppm)
Time (h)

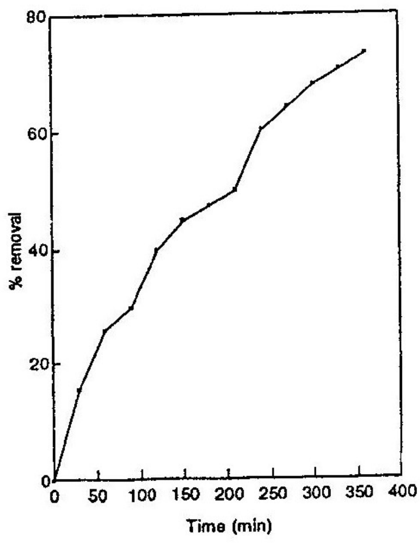

Cr+++/III
Cu++/III
Fe+++/IV
Residual Conc. (ppm)
Contact Time (min)
0
60
120
180
240
300
360
420
480
0
2
4
6
8
10


Cu++/III
Cr+++/III
Fe+++/IV
Residual Conc. (ppm)
Mass of sample (g)
0
1
2
3
4
5
6
7
8
9
10
0
1
2
3
4
5
6
7


Metal uptake/g adsorbent (mg/g)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1 2 3 4 5 6 7 8
Total metal in solution (ppm)


% removal
100
80
60
40
20
0
0 50 100 150 200 250 300 350 400
Time (min)


% removal
70
60
50
40
30
20
10
0
0 50 100 150 200 250 300 350 400
Time (min)


% removal
80
60
40
20
0
0 50 100 150 200 250 300 350 400
Time (min)

Removal Efficiency.

Figs. 8 to 10 shows the percentage removal for metal/adsorbent systems identified by this study as potential for biosorptive investigations. Removal of Chromium ions up to 87% can be achieved using *Cystoseira Myrica* can reach to about 70% if contact time extend to seven hours using. Depending on the type of reactor/contacting mode which will be applied (subjected to further investigations), these systems are found to be suitable.

CONCLUSION AND SIGNIFICANCE

The uptake of metals is rapid in the first minutes, followed by a slow uptake in after a few hours, reaching to an equilibrium point beyond which the rate of desorption is greater than adsorption. These findings are similar to those obtained for other biosorption systems using immobilised biomass [2] and add to the speculation that the initial biosorptive stage follows second order kinetics.

Metal uptake increases with contact time. Further experiments need to be done to optimize PH, temperature and optimum contact mode. This may lead to pilot plant design of equipment for metal removal from wastewaters containing metals of interest. As these results are only preliminary, a detail study of the adsorbents selected and a wider range of optimization needs to be done. From the preliminary results it is concluded two types of biomass has been identified which has great potential for biosorption in the native form, namely *Cystoseira Myrica* and *Sargassum Polycystum.*

Advantages of using Biomass in Africa is obvious since they are abundant available and are not yet exploited in any way. In the second stage of our research, also, we will look on the possibility of regenerating the biomass for re-use or other means of depositing the used biomass.

REFERENCES

1. L.C. Russell, *Handbook of Advance Wastewater Treatment.* 2 ed, 1978
2. T. Mario, and A. A. Deuschmann, Investigation on Engineering Parameters for the use of Immobilized Particles in Biosorption,

Jour. Chem. Tech. Biotechnol., vol. 48, 1990, pp 29 - 39.

3. M Tsezos, Z. Wang, Study of the Kinetics of Hazardous Pollutants Adsorption and Desorption by Biomass: mechanistic consideration., *Jour. Chem. Tech. Biotechnol.* vol. 50, 1991, pp 507 - 521.
4. G.L. Baungman, D.F. Paris, R.E. Hodson, Microbial Bioconcentration of Organic Pollutants from Aquatic Systems: A Critical Review, *CRC Cr. Rev. Microbiol.*, vol. 8, 1981, pp 205 - 208.
5. M. Tsezos, J. Bell, Comparison of the Biosorption and Desorption of Hazardous Organic Compounds by Live and Dead Biomass, in *Water Research*, vol. 23, 1989, pp 561 - 568.
6. Atomic Absorption Manual Accompany Model 3100 - Pelkin Elmer.
7. J. Freer, J. Baeza, H. Malurana, G. Palma, N. Duran, Removal and Recovery of Uranium by modified Pinus Radiata Barks, *Jour. Chem. Tech. Biotechnol.*, vol. 46, 1989, pp 41 - 49.
8. T.P. Mushi, The Removal of Metal Pollutant from Industrial Effluent by Natural Sorbents, Final Year Project, (Unpublished), Chemical and Process Engineering Dept., University of Dar es Salaam, 1992.

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