Trends in

Applied Sciences Research

ISSN 1819-3579

Academic
Journals Inc.

www.academicjournals.com

Trends in Applied Sciences Research 1 (1): 83-90, 2006
ISSN 1819-3579
© Academic Journals Inc., USA

Selective Biosorption of Heavy Metal Ions from Aqueous Solutions by Pre-Treated Nigerian Fresh Water Algae

James M. Okuo, S.B. Sanni and S.U. Aigbedion
Department of Chemistry, Faculty of Physical Sciences,
University of Benin, Benin City, Nigeria

Abstract: Fresh water algae (spirogyra) was obtained from ponds and ditches around Ugbowo in Benin metropolis, Nigeria and used to adsorbed Cr^{6+} and Cu^{2+} ions from aqueous solutions. The amounts of metal ions adsorbed were determined by Atomic Absorption Spectrophotometric (AAS) method. The effect of pH and light metal ions were also monitored. The optimum pH of adsorption for the two metal ions was found to be 4. The range of Cr^{6+} and Cu^{2+} ions adsorbed at pH 4 was between 0.46-4.47 and 0.38-4.06 mM, respectively. The algal specie selectively adsorbed more of Cr^{6+} ion when compared with Cu^{2+} ion as validated by the Freundlich isotherms and that Cr^{6+} ion was three folds adsorbed as much as Cu^{2+} ion. The Cr^{6+} ion has a relatively light antagonistic effect in the uptake of Cu^{2+} ion while the presence of light metal ions has a lesser significant effect on Cr^{6+} and Cu^{2+} ions adsorption.

Key words: Selective biosorption, fresh water algae, heavy metal ions, freundlich isotherms

---

Introduction

Pollution of the environment by toxic heavy metals arises primarily as a result of industrial processes, agricultural run-off and sewage discharge which have continually degraded the ecosystem. The continual discharge of these heavy metals into our environment have been a source of concern to the Nigerian Government, since these pollutants cause severe damage to human kidney, liver and the nervous system.

The common methods for the removal of these heavy metal ions from waste water are chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Rich and Cherry, 1987). However, identifying practical and cost effective means of removing such contaminants at very low concentrations is much more difficult particularly when it involves selective removal of a particular pollutant. Processes that are otherwise suitable at high concentrations are often either ineffective or cost prohibitive when applied to dilute wastes with heavy metal concentrations of less than 100 mg L^{-1} (Volesky, 1990).

Several researchers have shown that Biosorption technology using algae, yeast, fungi pseudomonas and bacterial as biosorbents for toxic metal removal from waste waters have prove to be highly efficient (Volesky, 1986; Kratochvivl, 1998; Darnall *et al*., 1986; Holan *et al*., 1993; Aderhold *et al*., 1996; Kuyucak and Volesky, 1989; Volesky, 1987, 1994; Volesky and Holan, 1995). The use of biosorbents of biological origin have emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies (Tsezos and Volesky,

---

Corresponding Author: James M. Okuo, Department of Chemistry, Faculty of Physical Sciences, Uninersity of Benin, Benin, Nigeria

1981; Townsley *et al*., 1986; Rome and Gadd, 1987; Macaskie, 1990; Costa and Leite, 1991; Rao *et al*., 1993, Shumate and Strandberg, 1985; Eccles, 1990; Macaskie, 1990; Teszos and Deutschmann, 1992; Okuo and Ozioko, 2001; Okolo and Okuo, 2004; Okuo, 2005). Recent biosorption experiments have focused attention on waste materials, which are by-products or the waste materials from large-scale industrial operations. For example, the waste mycelia available from fermentation processes, olive mill residues (Pagnanelli *et al*., 2002; Hussein *et al*., 2001; Hussein *et al*., 2003), activated sludge from sewage treatment plants (Hammaini, 2003), biosolids (Norton, 2003), aquatic macrophytes (Keskinkan, 2003). These studies on Biosorption of heavy metal ions were concentrated on the use of biomass to treat solutions containing only the heavy metal of interest without considering the interference of other metals in the adsorption process.

The fresh water algae used for this study is widely available in this part of the world, particularly the Southern part of the Country with an annual rainfall of 276.86 cm. This algal specie can also be grown easily in the laboratory. The drainage system in Benin metropolis is very unkempt. The disheveled nature of the drainage system is responsible for the stagnation of run-off water and formation of ponds and ditches along motor ways where this specie thrives. This algal specie together with other wastes disposed off indiscriminately into the drains caused the obnoxious odour the inhabitants experienced in the wet season. The biomass can gainfully be employed in treatment of waste water laden with heavy metals. Report on the use of fresh water algae for selective adsorption of heavy metal ions is also uncommon in this part of the world. Therefore, this study describes the competitive adsorption of heavy metal ions from aqueous solutions which can be applied to the treatment of effluents from industries.

Materials and Methods

The algae samples (spirogyra) used for this study were collected between August and September, 2005, from stagnant ponds and ditches around Ugbowo area, Benin City, Nigeria, using thoroughly rinsed 500 mL beaker. The collected sample was emptied into a clean one liter flat bottomed flask and taken to the Department of Botany, University of Benin, Benin City, Nigeria, for identification, sub cultured and inoculation. The Chu (1942) modified algal growth medium method was used for the inoculation process. Thereafter, a sample was taken for microscopic examination to determine which species are present. A further sub culturing was carried out from the new culture until a pure culture of only the spirogyra specie used for the experiment was obtained. The spirogyra specie was taken to Chemistry Department, University of Benin, Benin City for the adsorption experiment.

For the equilibrium studies, a series of flasks were prepared containing metal ion solutions (50 mL) of known concentrations varying from 0.5 to 4.5 mM. Each of these flasks contained the two metal ions (Cr^{6+} and Cu^{2+}) solution with the same concentration and pH. About 5 g of the pre-treated algae (dry weight) were added to the flasks, sealed with cotton wool and agitated on a rotatory shaker for 36 h. The pH controlled experiments were conducted by adjusting the pH of the solutions with 0.1 M HNO_3 or 0.1 M NaOH before and after the addition of the dried algae using pH meter. The experiment was performed at room temperature of 27-28°C. The biomass was removed by filtration through a what man membrane filter of 0.45 μm pore in a filtration chamber. The filtrates were then analyzed for heavy metal ion concentrations using Perkin Elmer atomic absorption spectrophotometer (Buck Scientific Model-200A/210) with double beam background corrector. Air acetylene flame and graphite furnace (Perkin Elmer HGA 500) and a hollow cathode lamp were used. All chemicals and reagents including those of the heavy metal solutions i.e., $CuSO_4$ and $Na_2Cr_2O_7 \cdot 2H_2O$ were of analar grade.

The effect of light metal ions (K^+ and Na^+) was monitored using 2 g L^{-1} biosorbents in a series of flasks containing heavy metal ions solution ($Cr^{6+} + Cu^{2+}$) of known concentration varying from 0.5 to 4.6 mM at pH 4. The mixtures were agitated on a rotatory shaker for the same number of hours until equilibrium was established. Blank samples without light metal ions were used as controls.

Results and Discussion

The data presented in Table 1 and 2 revealed the values of Q_{max} (The amount of Cr^{6+} and Cu^{2+} ions adsorbed at different pH) and K in Fig. 1 biosorption process indicated that the presence of Cu^{2+} ion with Cr^{6+} ion have a relatively light antagonistic effect in the uptake of Cu^{2+} ion. In the same vein, the presence of light metal ion (Table 3) has a light significant effect on Cu^{2+} and Cr^{6+} ions uptake. The implication of the result obtained in Table 3 is that the presence of light metal ions in the removal of heavy metal ions from industrial effluents is less significant in biosorption systems.
Q is obtained from the formula

$$Q = V(C_i\text{-}C_f)/m,$$

Where, Q is the metal ion uptake (mM metal ion per gram of biosorbent), V the liquid sample volume (mL), C_i the initial concentration of the metal ions in solution (mM/L), C_f the equilibrium concentration of the metal ions in solution (mM) and 'm' the amount of added biosorbent on dry mass basis in gram.

Table 1: Effect of concentrations and pH on the removal of heavy metal ions by pre-treated biomass

	Amount adsorbed (Q_{max})									
Initial concentration	pH 1		pH 2		pH 3		pH 4		pH 5	
(Mm)	Cr^{6+}	Cu^{2+}	Cr^{6+}	Cu^{2+}	Cr^{6+}	Cu^{2+}	Cr^{6+}	Cu^{2+}	Cr^{6+}	Cu^{2+}
0.5	0.10	0.20	0.20	0.31	0.28	0.42	0.45	0.38	0.44	0.37
1.5	0.80	0.32	0.93	0.83	1.12	0.94	1.44	1.21	1.42	1.21
2.5	1.40	0.92	1.31	1.08	1.83	1.35	2.41	2.08	2.31	2.03
3.5	1.29	1.10	1.51	1.28	2.14	1.88	3.32	3.10	3.08	3.06
4.5	1.50	1.31	1.18	1.51	2.85	2.09	4.47	4.06	4.10	4.03

Table 2: Effect of light metal ions (K+ and Na+) on heavy metal ions removal by pre-treated biomass at pH 4

Initial concentration (mM)	Cr^{6+} ion Equilibrium concentration	Amount adsorbed (Q_{max})	Cu^{2+} ion Equilibrium concentration	Amount adsorbed (Q_{max})
0.5	0.09	0.41	0.18	0.32
1.5	0.10	1.40	0.49	1.11
2.5	0.44	2.06	0.54	1.96
3.5	0.50	3.00	0.56	2.94
4.5	0.47	4.03	0.50	4.00

Table 3: Logarithms of the amount adsorbed per unit mass of the biomass and equilibrium concentration of Cr^{6+} and Cu^{2+} ions biosorption at pH 4

	Cr^{6+} ion				Cu^{2+} ion		
Q (mM g^{-1})	C_e (mM)	D = log (Q/C_e)	% adsorbed	Q (mM g^{-1})	C_e (mM)	D = log (Q/C_e)	% adsorbed
1.90	0.05	-0.21	90.00	0.24	0.12	0.65	76.00
3.60	0.06	-0.45	96.00	0.80	0.29	1.81	80.67
6.02	0.09	-0.74	96.40	2.30	0.42	-0.97	83.20
8.30	0.18	-1.22	94.49	2.75	0.40	-1.08	88.57
11.17	0.03	-0.68	99.93	0.32	0.44	1.37	90.22

C_e = Equilibrium concentration after sorption
D = Distribution coefficient of the heavy metal ions.

The effect of concentrations on the removal of heavy metal ions at different pH (Table 1) showed that adsorption increases with the solution pH. However, maximum adsorption was attained at pH 4. At pH 5 there was decease in the rate of adsorption. For instance, the amount of Cr^{6+} ion adsorbed at pH 4 ranged 0.45-4.47 mM as compared with that of pH 5 which is between 0.44-4.10 mM. This might be attributed to the commencement of precipitation reaction which occurs at pH 5-6 as suggested by Matheickal and Yu (1998).

In explaining the dependence of adsorption of heavy metal ions by biosorbents on pH, it is pertinent to consider the ionic states of the cell wall functional groups as well as heavy metal solution chemistry at various pH values. Matheickal and Yu (1998) reported the presence of Cr^{6+} and Cu^{2+} ions in their free ionic forms at pH values of less than 5. The extent of heavy metal ions biosorption also depends on the protonation or deprotonation of the cell wall polymer functional groups relative to their pKa. The cell wall of fresh water algae are chiefly compose of three kinds of polymers: cellulose, alginic acid and the heterogeneous fucose containing sulphated polysaccharides called fucans (Clayton, 1981). These polymer functional groups act as binding sites for the metal ions. At low pH, the protonation of the functional groups gives an overall positive charge to the polymer molecules and consequently reduce adsorption of positively charged heavy metal ions. Increase in pH reduces the electrostatic repulsion and exposing more ligands carrying negative charges. This will ultimately leads to increase in adsorption which might be responsible for the optimum adsorption obtained at pH 4.

The Freundlich isotherms have approximate straight lines which indicate that adsorption process follows the Freundlich isotherm (Fig. 1 and 2).

$$n = \frac{1}{\text{Slope}} = \frac{1}{0.735} = 1.36$$

Intercept = log K
K = Antilog (1.45) = 28.18

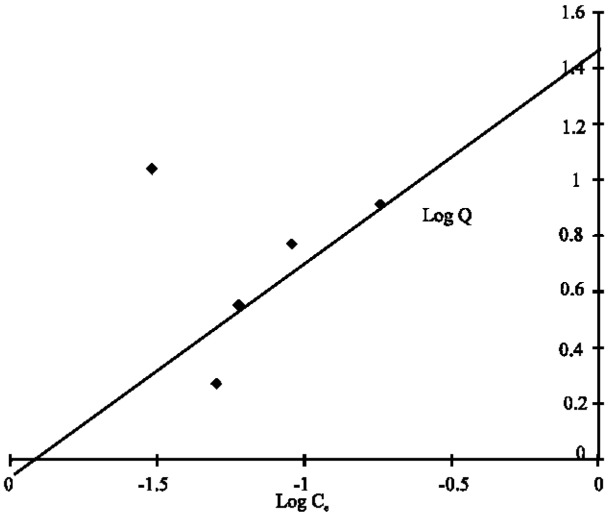

Fig. 1: Freundlich isotherm Cr (VI) ion biosorption at pH 4

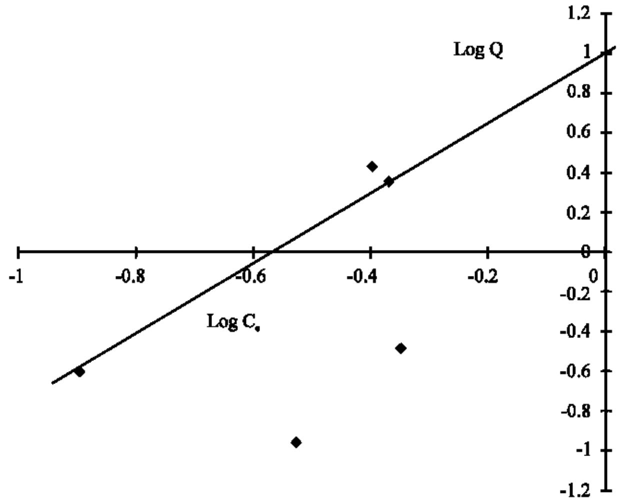

Fig. 2: Freundlich isotherm Cu(II) ion biosorption at pH 4

$$n = \frac{1}{\text{Slope}} = \frac{1}{1.25} = 0.80$$

Intercept = log K

K = Antilog (1.0) = 10.0

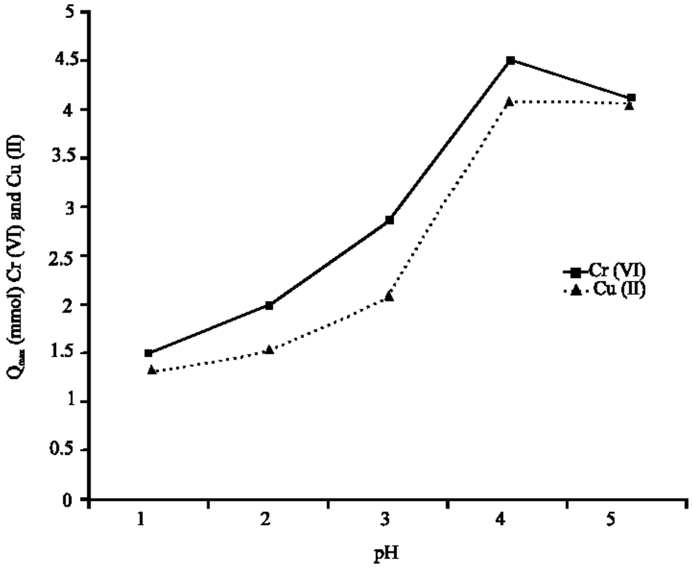

Fig. 3: Q_{max} [Cr(VI) and Cu(II) ions] versus pH

The Freundlich isotherm takes the form

$$Q = KC^n_e$$

This is found to be adequate for adsorption over a considerable range of concentrations (C), 'Q' is the amount of adsorbate adsorbed per unit mass of fresh water algae from a solution of concentration C, K and n are constants for the given adsorbent and adsorbate. Taking the logarithms of the above equation gives

$$\log Q = \log K + n \log C_e$$

A plot of log Q against log C_e gives a straight line, K is the intercept and 1/n is the slope. The values of K obtained for Cr^{6+} and Cu^{2+} ions are 28.18 and 10.00, respectively (Fig. 1 and 2). These values showed that Cr^{6+} ion is approximately three folds adsorbed as much as Cu^{2+} ion. This might be due to the fact that Cr^{6+} ion is better hydrated than Cu^{2+} ion. In addition, Cr^{6+} ion is highly stable both in solid and in aqueous solutions and has a tendency to form complexes such as hex aqua $[Cr(H_2O)_6]$. This stability is related to the high crystal field stabilization energy of its d^3 electronic configuration. This might be responsible for the enhanced adsorption of Cr^{6+} ion onto the polymeric functional groups present in the fresh water algae. Copper has a noble character and relatively unreactive. It does not react with water and forms no complexes with water (Lee, 1996).

The distribution coefficient of Cr^{6+} and Cu^{2+} ions ranged between-0.68 to-0.21 and-1.08 to 1.37 while the percent adsorbed ranged between 90.00-99.93% and 76.00-90.22%, respectively. The difference in the values of D for the two metal ions is quite large. The value of D is very significant in the treatment of industrial effluents loaded with toxic heavy metal ions. D allows the number of cycles of equilibrium sorption processes required to reduce the level of heavy metal ions in solution to be attained. Cr^{6+} ion with negative values of D would be easily removed from effluents containing Cr^{6+} and Cu^{2+} ions. Hence Cr^{6+} ion is selectively favored in the adsorption processes.

Conclusions

The study showed that abundantly and cheaply available fresh water algae can be use for the development of efficient biosorbent materials for heavy metal ions recovery from industrial effluents. The algal specie selectively removed more of Cr^{6+} ion than Cu^{2+} ion.

Industrial effluents which contain large amount of light metal ions such as K^+ and Na^+ ions that often reduce the binding capacity of commercial exchange resin can be treated with fresh water algae since the biosorbent has much higher relative affinities for the heavy metal ions than for light metal ions. This biosorbent appears to be well suitable for the treatment of effluents or waste waters from industries with low levels of these metal ions studied.

References

Alderhold, D., C.J. Williams and R.G.J. Edyveen, 1996. The removal of heavy metal ions by seaweeds and their derivatives. Bioresour. Technol., 58: 1-6.

Arica, M.Y., 2003. Comparative biosorption of mercuric ions from aquatic systems by immobilized live and heat inactivated *Trametes versicolor* and *Pleurotus sajur-caju*. Environ Sci. Technol., 33: 2213-7

Chu, S.P., 1942. Cultivation of algae in the laboratory: Introduction to Algae Structure and Reproduction, Bold, H.E. and A.E. Wynne, (Eds.). Prentice-Hall, Englewood Cliff, New Jersey, pp: 571-577.

Clayton, M.N., 1981. Phaeophyta, In: Clayton, M.N., King and R.J. (Eds.) Marine Botany-An Australian Perspective. Longman Cheshire, Melbourne, Australia, pp: 105-137.

Costa, A.C.A. and S.G.C. Leite, 1991. Metal biosorption by sodium alignate immobilized *Chlorerella homospharea.* Biotechnol. Lett., 13: 559-562.

Darnall, D.W., B. Greene, M. Hosea, R.A. McPherson, M. Henzl and M.D. Alexander, 1986. Recovery of Heavy Metals by Immobilized Algae. In: Thompson R. (Ed.), Trace metal removal from aqueous solutions. The Royal Society of Chemistry, London, pp: 1-25.

Eccles, H., 1990. Biosorption of heavy metals: A scientist's dream or a commercial reality. J. Chem. Technol. Biotechnol., 49: 330-334.

Hammaini, A., 2003. Simultaneous uptake of metals by activated sludge. Minerals Eng., 16: 723-729

Holan, Z.R., B. Volesky and I. Prasetyo, 1993. Biosorption of cadmium by biomass of marine algae. Biotechnol. Bioeng., 41: 818-825.

Hussien, H., R. Krull, S.I. Abou El-Ela and D.C. Hempel, 2001. Interaction of the different heavy metal ions with immobilized bacterial cultured degrading xenobiotic wastewater compounds. In: Confernce Proceeding: International Water Association World Water Conference. (15th-19th October, Berlin Germany).

Hussien, H., S. Farag and H. Moawad, 2003. Isolation and characterization of *Pseudomonas* resistant to heavy metals contaminants. Arab J. Biotechnol., 7: 13-22.

Keskinkan, O., 2003. Heavy metal absorption characteristics of a submerg aquatic plant (*Myriphyllum nicatum*). Process Biochem., pp: 1-5.

Kratochvivl, D., 1998. Biosorption of heavy metals. Water Res., 32: 2760-2768.

Kuyucak, N. and B. Volesky, 1988. Biosorbent for recovery of metals from industrial solutions. Biotechnol Left., 10: 137-142.

Kuyucak, N. and B. Volesky, 1989. The mechanism of cobalt biosorption. Biotechnol. Bioeng., 33: 823-831.

Lee, J.D., 1996. Concise Inorganic Chemistry, Blackwell Science Ltd., Osney Mead, Oxford Oxzoel, pp: 723-821.

Macaskie, L.E., 1990. An immobilized cell bioprocess for removal of heavy metals from aqueous flows. J. Chem. Technol. Biotechnol., 49: 330-334.

Matheickal, J.T. and Q. Yu, 1998. Biosorption of lead (II) and copper (II) from aqueous solution by pre-treated biomass of Australian marine algae. Bioresource Technol., 69: 223-229.

Norton, L., 2003. Biosorption of zinc from aqueous solutions using biosolids. Adv. Environ., 6: 2342-2348

Okuo, J.M. and A.C. Ozioko, 2001. Adsorption of lead and mercury ions on chemically treated periwinkle shells. J. Chem. Soc. Nig., 26: 60-65.

Okolo, P.O. and J.M. Okuo, 2004. Heavy metal ions adsorption by chemically treated coconut husk, shells and palm kernel fibre. Intl. J. Chem. Indian, 14: 185-194.

Okuo, J.M., 2005. Removal of heavy metal ions by blended periwinkle shells. Global J. Pure and Applied Sci., (Accepted).

Pagnanelli, F., L. Toro and F. Veglio, 2002. Olive mill solid residues as heavy metal sorbent material: A preliminary study. Waste Manage., 22: 901-907

Rao, C.R.N., L. Iyengar and C. Venkobachar, 1993. Sorption of copper (II) from aqueous phase by waste biomass. J. Environ. Eng. Division, ASCE., 61: 369-377.

Rich, G. and K. Cherry, 1987. Hazardous Waste Treatment Technologies. Puduan Publishers, New York.

Rome, L. and G.M. Gadd, 1987. Copper adsorption by *Rhizopus arrhizus Cladospoium resinaea and Penicillium italicum.* Applied Microbiol., 26: 84-90.

Townsley, C.C., I.S. Ross and A.S. Atkins, 1986. Biorecovery of metallic residues from various industrial effluents using filamentous fungi. Process Metallurgy, 4: 279-289.

Shumate, E.S. and W.G. Strand berg, 1985. Accumulation of metals by microbial cells. Comprehensive Biotechnol., 13: 235-247.

Tsezos, M. and B. Volesky, 1981. Biosorption of uranium and thorium. Biotechnol. Bioeng., 24: 385-401.

Tsezos, M. and A.A. Deutschmann, 1992. The use of mathematical model for the study of important parameters in immobilized biomass biosorption. J. Chem.Technol. Biotechnol., 53: 1-12.

Volesky, B., 1986. Biosorbent materials. Biotechnol. Bioeng. Symp., 16: 121-126.

Volesky, B., 1987. Biosorbents for metal recovery. Trends in Biotechnol., 5: 96-101.

Volesky, B., 1990. Biosorption of Heavy Metals. CRC Press, Boca Raton, USA.

Volesky, B., 1994. Advances in biosorption of metals: selection of biomass types. FEMS. Microbiol. Rev., 14: 291-302.

Volesky, B. and Z.R. Holan, 1995. Biosorption of heavy metals. Biotechnol Prog., 11: 235-250.