African Journal of Biotechnology Vol. 8 (3), pp. 507-514, 4 February, 2009
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2009 Academic Journals

Full Length Research Paper

Equilibrium modeling and pH-dependence of the adsorption capacity of *Vitex doniana* leaf for metal ions in aqueous solutions

Benevolent Orighomisan Atolaiye[1]*, Jonathan Oyebamiji Babalola[2], Matthew Ayorinde Adebayo[3] and Matthew Oluleke Aremu[1]

[1]Department of Chemistry, Nasarawa State University, Keffi, Nigeria.
[2]Department of Chemistry, University of Ibadan, Ibadan, Nigeria.
[3]Department of Chemical Sciences, Ajayi Crowther University, Oyo, Nigeria.

Accepted 22 December, 2008

This study involved the examination of biomass, *Vitex doniana* leaf powder, in the adsorption of heavy metals from water. The water samples were obtained from two sources in Nasarawa town in Nasarawa State, Nigeria; River Tammah (one of the two major river sources of water for drinking, domestic, irrigation and other agricultural uses in the town) and the confluence of two rivers called "Magami". Batch pH profile experiment for lead and iron indicated that metal ion binding capacity of the biomass increased as pH increased, but was the reverse for magnesium ions. Optimum uptake for lead and iron occurred at pH 7.0 - 7.8 for lead and 7.8 for Iron in water from river Tammah. Optimum uptake occurred at the same pH ranges for both Lead and Iron in water sample from Magami. In both cases optimum desorption occurred for magnesium ions. At room temperature and with good equilibrium the adsorption capacities of *V. doniana* leaf powder for lead and iron ions were 99.98 and 86%, respectively. *V. doniana* leaf powder therefore showed good binding capacity for lead and iron but was not efficient for magnesium.

Key words: Biomass, *Vitex doniana*, binding capacity, pH-dependence, water treatment.

INTRODUCTION

Pollution is the unsought, unexpected and unforeseen consequences of the entire phenomena of civilization (WHO, 1972). Pollution occurs when a substance having deleterious effects on one or more aspects of water quality is present in water as a result of human activity (Adeniyi et al., 2008). Pollution induces or causes objectionable conditions in any water source, affecting adversely the uses to which the water thereof may be put (Klein, 1962).

Heavy metals have been defined based on the specific density of metals (greater than 4 or 5 gl^{-1}), having atomic weights between 63,546 and 200, 590 (Sagakuchi and Nakajima, 1991). Living organisms require trace amounts of some heavy metals such as cobalt, copper, iron, manganese, molybdenum, vanadium, strontium and zinc. Excessive levels of such essential metals however can be detrimental to the organism. Other heavy metals such as lead and cadmium have no vital or beneficial effect on organisms and their accumulation over time in the body of mammals can cause serious illness (Ahalya et al., 2005). The presence of heavy metal ions in waste waters has generated considerable concern in recent years because of their toxicity to aquatic organisms at trace concentrations. Unlike organic pollutants, heavy metals are non-biodegradable, so they persist for long in their host organism, constituting long term problem. It is noted that water pollution is as a result of the pollutants such as organic wastes, domestic sewages, inorganic chemicals and heavy metals effects on water (Charles, 1972).

All heavy metals exist in surface waters in colloidal, particulate and dissolved phases, although dissolved concentrations are generally low. The colloidal and particulate metal may be found in hydroxides, oxides, sili-

---

*Corresponding author. E-mail: misan1965@yahoo.co.uk. Tel: +2348036190301.

cates or sulphates or adsorbed to clay, silica or organic matter. It has been reported that the behaviour of metals in natural water is a function of the substrate sediment composition, the suspended sediment composition and the water chemistry. Sediment composed of fine sand and silt will generally have higher levels of adsorbed metals than will quartz, feldspar and dendrital carbonate-rich sediment. Metals also have a high affinity for humic acids, organo-clays and oxides coated with organic matter (Connel et al., 1984). Heavy metals in surface water systems can be from natural or anthropogenic sources. Excess metal levels in surface water may pose a health risk to humans and to the environment. Pollution due to heavy metals is an issue of great environmental concern. Heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu) and nickel (Ni) pose serious health hazards through entry into the food chain by anthropogenic pathways (Vasudevan et al., 2003).

It has been discovered that lead can substitute for calcium because of size and charge similarities and can therefore be included in bone. Children are generally susceptible to lead because the developing skeletal system requires high calcium level. Lead that is stored in bone is not harmful, but if high level of calcium is ingested later, the lead in the bone may be replaced by calcium and mobilized. When free in the system, lead may cause nephrotoxicity, neutrotoxicity and hypertension. Cadmium has been reported to interfere with the metallothionein ability to regulate zinc and copper concentration in the body. Metallothionein is a protein which binds to excess essential metals to render them unavailable. When cadmium induces metallothionein activity, it binds to copper and zinc, disrupting the homeostasis levels (Kennish, 1992).

USEPA (1987) confirmed that mercury poses a great risk to humans, especially in the form of methyl mercury. When mercury enters water it is often transformed by microorganisms into the toxic methyl mercury form. Symptoms of acute poisoning are pharyngitis, gastroenteritis, vomiting, nephritis, hepatitis and circulatory collapse. Chronic poisoning is usually a result of industrial exposure or a diet consisting of contaminated fish (mercury is the only metal that will bioaccumulate). Chronic poisoning may cause liver damage, neural damage and teratogenesis.

According to Viessman and Hammer (1985), it was reported that arsenic ingestion can cause severe toxicity through ingestion of contaminated food and water. Ingestion causes vomiting, diarrhea and cardiac abnormalities. They also reported that the presence of abundant chromium anions in water is generally a result of industrial waste. The chronic adverse health effects are respiratory and dermatologic.

Lead and its compounds may enter the environment during mining, smelting, processing and use as in batteries, cables, pigments, gasoline additives, steel products and solder to water distribution pipes, in seams of cans used to store foods, some traditional remedies, bottles used for alcoholic beverages, ceramic glazes and crystal table ware. The effect of lead on the hemopoiethic system results in decreased hemoglobin synthesis and possibly hemolysis (WHO, 1995).

Applications of Iron go from food containers to family cars, from screw drivers to washing machines, from cargo ships to paper staples. Iron may cause conjuctivities, choroidities and rentinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of Iron oxide fumes or dusts may result in development of benign pneumoconiosis called sclerosis. Inhalation of excessive concentrations of Iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens (Lenntech, 2001).

Magnesium has become increasingly important as a structural substance. Its alloys are used in many motorcycle parts, milk of magnesia suspension (magnesium hydroxide in water) and as antacid and laxative (Kemdirin et al., 1989). At threshold concentrations for some aquatic organisms, animals begin to demonstrate a lack of muscular control, reduced feeling and reproductive rate and eventually death occurs (Australia, 2002).

Traditional technologies for heavy metal removal including ion exchange and precipitation are frequently inefficient and/or expensive when applied for removal of metal ions in low concentrations. Biosorption, the passive, non-metabolic mediated process of metal ion binding by living or dead biomass has a great potential to reach these objectives (Sandau et al., 1996). It is a process that utilizes inexpensive biomass to sequester toxic heavy metals and is found to be particularly useful for the removal of contaminants from industrial effluents (Yu et al., 2003). Biosorption is proven to be quite effective at removing metal ions from contaminated solution in a low cost and environmentally friendly manner (Volesky, 1990). The major advantages of biosorption over conventional treatment methods include; low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional cost required, regeneration of biosorbent and the possibility of metal recovery (Kratochvil and Volesky, 1998). Living and dead microbial cells are able to remove heavy metal ions from solution. Bacteria (Strandberg et al., 1981), fungi (Sag and Kutsal, 1995), marine algae, sea weeds (Matheickal et al., 1997) have been evaluated for their heavy metal uptake capacities and suitability to be used in the development of biosorbents and are found to be comparable to those of synthetic ion exchange resin.

This study evaluated the efficiency of biomass *Vitex doniana* leaves in the adsorption of heavy metals from water, batch laboratory pH-dependence, equilibrium effect and binding capacity of the leaves at room temperature. The biosorption performance was evaluated by its uptake capacity for lead, iron and magnesium ions which exhibited highest concentrations in solution (Atolaiye et al., 2006; Atolaiye and Aremu, 2007). *V. doniana* is a species of the plant family *verbenaceae*; it is called “dinya” in

Table 1. Mean metals concentrations in water sample from river Tammah in mgl^{-1}.

	Pb	Fe	Mg	Zn	Mn	Cu
Mean	4.24	2.14	5.84	0.22	0.22	0.64
S.D	± 0.01	± 0.01	± 0.01	± 0.03	± 0.03	± 0.02
C.V%	0.23	0.47	0.17	13.64	13.64	3.13

S.D = Standard deviation, C.V = Coefficient of variation.

Table 2. Mean metals concentrations in water sample from Magami in mgl^{-1}.

	Pb	Fe	Mg	Zn	Mn	Cu
Mean	3.974	1.50	5.80	0.18	0.21	0.67
S.D	± 0.02	± 0.01	± 0.01	± 0.03	± 0.03	± 0.02
C.V%	0.50	0.67	0.17	16.67	14.29	2.99

S.D = Standard deviation, C.V = Coefficient of variation.

hausa and “orunla” in Yoruba.

MATERIALS AND METHODS

Sample collection and treatment

Fresh leaves of biomass *V. doniana* were obtained from Nasarawa town in Nigeria. The fresh biomass was washed with excess running tap water and then deionized water. The leaves were then macerated into small sizes, air-dried at room temperature for 24 h and milled into fine powder with an electric blender. The milled sample was filtered using a sieve with mesh size 200 µm and stored at 37°C in a dessicator for later use.

Water samples were collected from the two river sites (river Tammah and Magami) at 9.00 h Greenwich Mean Time (GMT) and at a temperature of 27°C. The fresh water samples were collected at three different points; the bank, middle and the deep end, placed in HCl-leached plastic containers, into a refrigerator at 18°C until the time of use. The actual pH of the water at each site was determined using fresh water samples collected into unleached plastic containers the same day.

Sample analyses

The pH of water samples from the two sample sites was determined in the main chemistry laboratory of the Nasarawa State University, Keffi, Nigeria using a Lutron PH-201 model pH meter. The adsorbent experiment was carried out at 27°C, room temperature to study batch laboratory pH profile, equilibrium effects and binding capacity of the leaves biomass for lead, iron and magnesium ions in aqueous solution. This was done by exposing 65 ml of each water sample to 1.0 g of *V. doniana* leaf powder measured using a Mettler AE100 balance. The mixtures were shaken thoroughly using an electric stirrer equilibrated at room temperature and allowed to stand for a contact time of 24 h. The pH of each water sample was adjusted to the required values; 6.8 - 8.4, similar to the range used by the Water Works Department in Nasarawa town where both sample sites are located. The pH range 6.8 - 8.4 is also similar to that of the World Health Organization accepted standard for drinking water. Adjustments were made using 2 M sodium hydroxide to increase or 2 M hydrochloric acid to decrease the pH of the untreated water samples. Columns were set up using the biomass *V. doniana* leaf powder as stationary phase while water samples which had been kept in contact with the biomass was used as mobile phase. The filtrates were collected into 500 ml conical flasks and labeled according to their pH. The pH values were varied from 6.8 - 8.4 with an increment of 0.2. Filtrates and plain water control from the two water samples from both water sites were paired into different containers, labeled according to pH values and taken for heavy metal analyses using SOLAR 969 Atomic Absorption Spectrophotometer.

Statistical analysis

All results for both sample sites were expressed as final or residual concentrations (C_f) of metals’ ions in solution. In the determination of biosorption capacity, biosorption metal uptake (q) was calculated for water from each sample site using the sorption system mass balance:

$$q = V(C_i-C_f)/S$$

Where V = volume of solution, S = amount of dry biosorbent, C_i = initial metal concentration and C_f = final metal concentration. C_f is the metal concentration at equilibrium.

RESULTS AND DISCUSSION

Results obtained in this research were expressed in terms of the mean metals concentrations in water samples, mean metal residual concentrations in solution (C_f) in mgL^{-1}, concentrations of metals adsorbed by biomass from solution (C_i - C_f) in mgL^{-1}, concentrations of metals accumulated per gram of biosorbent in mgg^{-1} and percentage adsorption of biomass for metals at various pH. Table 1 showed the mean metals concentrations in water samples from river Tammah. Table 2 showed mean metals concentrations in water sample from Magami. Values of mean metals concentrations were higher for Pb, Fe, Mg, Zn and Mn in water from river Tammah than in water sample from Magami, the confluence of two major rivers in Nasarawa town of Nigeria. The metal concentration for Cu in Magami were

Table 3. Mean metals residual concentrations in the water sample from River Tammah (C_f) in mgl^{-1}.

pH	Pb	Fe	Mg
5.6	0.0074 ± 0.0003	0.3498 ± 0.01	20.009 ± 0.20
6.8	0.0035 ± 0.00024	0.2564 ± 0.015	18.509 ± 0.15
7.0	0.0000 ± 0.00	0.1978 ± 0.007	18.211 ± 0.13
7.2	0.0000 ± 0.00	0.1897 ± 0.008	18.050 ± 0.17
7.4	0.000 ± 0.00	0.1871± 0.005	17.829 ± 0.10
7.6	0.000 ± 0.00	0.867 ± 0.01	17.020 ± 0.22
7.8	0.000 ± 0.00	0.1710 ± 0.006	16. 997 ± 0.14
8.0	0.0012 ± 0.0002	0.1996 ± 0. 013	17.610 ± 0.18
8.2	0.0007 ± 0.0002	0.1810 ± 0.02	14.009 ± 0.12
8.4	0.0004 ± 0.0001	0.1799 ± 0.01	12.509 ± 0.10

Table 4. Mean metal residual concentrations in water sample from Magami in mgl^{-1}.

pH	Pb	Fe	Mg
5.6	0.0014 ± 0.0003	0.3176 ± 0.007	19.799 ± 0.25
6.8	0.0000 ± 0.00	0.2048 ± 0.00 1	18.844 ± 0.12
7.0	0.0000 ± 0.00	0.1894 ± 0.006	18.704 ± 0.15
7.2	0.0000 ± 0.00	0.1799 ± 0.002	18.209 ± 0.10
7.4	0.0000 ± 0.00	0.1777 ± 0.006	18.219 ± 0.13
7.6	0.0000 ± 0.00	0.1737 ± 0.001	17.990 ± 0.21
7.8	0.0000 ± 0.00	0.1611 ± 0.004	17.710 ± 0.17
8.0	0.0006 ± 0.0001	0.1748 ± 0.008	16.760 ± 0.14
8.2	0.0000 ± 0.00	0.1711 ± 0.002	16.551 ± 0.15
8.4	0.0004 ± 0.00005	0.1441 ± 0.002	14.449 ± 0.10

however higher than in river Tammah.

Tables 3 and 4 depict the mean metal residual concentrations in water samples from river Tammah and Magami respectively in mgl-^{1}. From both results, at the original pH of both water samples from both river sites, (5.6), the mean metals residual concentration was highest for Mg and lowest for Pb in river Tammah and Magami. For this study, only the three metals with highest mean metals concentrations (Mg > Pb > Fe) in both water samples were considered. For both water samples, according to the results in Tables 3 and 4, the mean concentrations of the metals remaining in the water samples decreased with increase in pH; adsorption was not consistent from pH 8.0 and above.

The concentrations of metals adsorbed from solution (mgl^{-1}) are shown in Tables 5 and 6 for water samples from river Tammah and Magami. In both water samples, nearly all lead present in solution before contact with *V. doniana* biomass were adsorbed from solution, more than half the quantity of iron in solution were adsorbed while there was desorption for magnesium. Adsorption efficiency or capacity of biomass increased with increase in pH; in water sample from river Tammah, before contact with *V. doniana* leaf powder, 4.24 mgl^{-1} of Pb were in solution and after exposure to the biomass, between 4.2365 and 4.2396 mgl^{-1} (pH 6.8 - 8.4) were adsorbed from solution. The 2.14 mgl^{-1} of iron in solution before contact with biomass decreased after contact with the biomass; 1.8836 - 1.9601mgl^{-1} was adsorbed from solution, which showed increase in adsorption with increase in pH. Table 5 showed that though there was desorption for magnesium, the values obtained for metal concentration adsorbed from solution was found to increase as pH increased (-12.669 to -6.669 mgl^{-1}). In water sample from Magami, adsorption of lead and iron were found to increase with increase in pH while magnesium showed desorption as shown in Table 6. Desorption in magnesium decreased with increase in pH.

Tables 7 and 8 show the concentrations of metals accumulated per gram of biosorbent in mgg^{-1} for water samples from river Tammah and Magami in Nasaraawa town. In both water samples, at all pH values concentrations of lead adsorbed were nearly constant which showed that biomass *V. doniana* leaf was very efficient in the adsorption of lead from solution. The concentration of iron adsorbed from solution increased from pH 6.8 to 7.8 (0.1224 - 0.1280 mgg^{-1}), the trend was the same for water sample from Magami (0.0842 - 0.0870 mgg^{-1}).

Table 5. Concentrations of metals adsorbed from River Tammah water sample (C_i - C_f) in mgl^{-1}.

pH	Pb	Fe	Mg
5.4	4.2326	1.7902	-14.169
6.8	4.2365	1.8836	-12.669
7.0	4.2400	1.9422	-12.371
7.2	4.2400	1.9503	-12.210
7.4	4.2400	1.9529	-11.989
7.6	4.240	1.9533	-11.180
7.8	4.2400	1. 9690	-11.159
8.0	4.2388	1.9404	- 11.770
8.2	4.239	1.9590	- 8.169
8.4	4.2396	1.9601	- 6.669

Table 6. Concentrations of metals adsorbed from Magami water sample (C_i – C_f) in mgl^{-1}.

pH	Pb	Fe	Mg
5.6	3.972	1.1824	13.999
6.8	3.9740	1.2952	13.044
7.0	3.9740	1.3106	12.904
7.2	3.9740	1.3201	12.409
7.4	3.9740	1.3223	12.419
7.6	3.9740	1.3263	12.190
7.8	3.9740	1.3389	11.910
8.0	3.9734	1.3252	10.960
8.2	3.9740	1.3289	10.751
8.4	3.9736	1.3559	8.649

Table 7. Concentrations of metal accumulated per g of the biosorbent from river Tammah water sample in mgg^{-1}.

pH	Pb	Fe	Mg
5.6	0.2751	0.1164	-0.9210
6.8	0.2754	0.1224	-0.8235
7.0	0.2756	0.1262	-0.8041
7.2	0.2756	0.1268	-0.7937
7.4	0.2756	0.1269	-0.7793
7.6	0.2756	0.1270	-0.7267
7.8	0.2756	0.1280	- 0.7252
8.0	0.2756	0.1261	-0.7651
8.2	0.2756	0.1273	-0.5309
8.4	0.2756	0.1274	-0.4335

Table 8. Concentrations of metals accumulated per g of the biosorbent (q) from Magami water sample in mgg^{-1}.

pH	Pb	Fe	Mg
5.6	0.2582	0.0769	-0.9099
6.8	0.2583	0.0842	-0.8479
7.0	0.2583	0.0852	-0.8388
7.2	0.2583	0.0858	-0.8066
7.4	0.2583	0.0859	-0.8072
7.6	0.2583	0.0862	-0.7924
7.8	0.2583	0.0870	-0.7742
8.0	0.2583	0.0861	-0.7124
8.2	0.2583	0.0864	-0.6988
8.4	0.2583	0.0881	-0.5622

Tables 9. Percentage adsorption of metals (%ad.) from river Tammah water sample at various pH.

pH	Pb	Fe	Mg
5.6	99.83	88.65	-242.62
6.8	99.92	88.02	-216.93
7.0	100	90.76	-211.83
7.2	100	91.14	-209.08
7.4	100	91.26	-205.29
7.6	100	91.28	-191.44
7.8	100	92.01	-191.04
8.0	99.97	90.67	-201.54
8.2	99.98	91.54	-139.88
8.4	99.99	91.59	-114.20

% ad. = [(Ci – C_f)/C_i] x 100.

Adsorption of magnesium increased with increasein pH, though there was a general trend of desorption for magnesium in both water samples (-0.8235 to -0.4335 mgg^{-1} and -0.8388 to -0.5622 mgg^{-1} for water samples from river Tammah and Magami, respectively).

Percentage adsorption of metals from both water samples; river Tammah and Magami are shown in Tables 9 and 10, respectively. At pH 6.8 - 8.4 in water sample from river Tammah there was 99.92 - 99.99% adsorption for lead, 88.02 - 92.01% for iron at pH 6.8 - 7.8 with a decrease at pH 8.0 and -216.93 to -114.20% for Mg at pH 6.8 - 8.4. In water sample from Magami, percentage adsorption of lead from solution was 100% at all pH values with little exceptions at pH 8.0 and 8.4 (99.98 and 99.99%, respectively). Adsorption for iron increased from pH 6.8 - 7.8; 86.35 - 89.26% with little variations at pH 8.0 - 8.2; 88.35 - 88.59% and then increasing to 90.39% at pH 8.4. Desorption was the trend in the case of Mg at all pH values (-224.90 to -149.12%); desorption decreased as pH increased.

The values of mean metals concentrations in river Tammah and Magami as shown in Tables 1 and 2 were in agreement with previous work done by Atolaiye et al. (2006, 2007). All mean metals concentrations of metals in both water samples agree with the maximum permissible value of the World Health Organisation standards (WHO, 2003) except for Pb whose value was higher. The WHO maximum standard values are as follows; Pb = 0.01 mgl^{-1}, Fe = 3 mgl^{-1}, Mg = 20 mgl^{-1}, Cu = 2.0 mgl^{-1}, Mn = 0.4 mgl^{-1}. Mg had the highest concentrations in both water

Table 10. Percentage adsorption of metals (% ad.) from Magami water sample at various pH.

pH	Pb	Fe	Mg
5.6	99.96	78.83	-241.36
6.8	100	86.35	-224.90
7.0	100	87.37	-222.48
7.2	100	88.01	-213.95
7.4	100	88.15	-214.12
7.6	100	88.42	-210.17
7.8	100	89.26	-205.34
8.0	99.98	88.35	-188.97
8.2	100	88.59	-185.36
8.4	99.99	90.39	-149.12

% ad. = [(Ci – C_f)/C_i] x 100.

samples; river Tammah and Magami. Mg had been reported to contribute to both carbonate and non-carbonate hardness in water usually at a concentration much lower than that of calcium components, therefore excessive concentrations of Mg are undesirable in domestic water because of the problem of scale formation (Ademoroti, 1981).

Tables 3 and 4 showing the mean metals residual concentrations of Pb, Fe and Mg in mgl^{-1} of water samples from the two sites showed that Pb had the least residual concentration in both water samples at all pH values after exposure to *V. doniana* leaf powder. At the actual pH values of both water sites (5.6) before adjustments to the desired working pH values, Pb also had the least residual metal concentration in both water samples. The values of mean metals residual concentrations of all metals in both water samples fall within the WHO standard for maximum permissible value in drinking water. Mg recorded desorption rather than adsorption in both water samples and at all pH.

Tables 5 and 6 showing the concentrations of metals adsorbed from solution from both sample sites showed that values for Mg in both water samples were negative, thus implying desorption. In both water samples nearly all Pb present (100%) in solution was adsorbed by *V. doniana* leaves, between 83.65 to 91.59% of Fe was adsorbed and -216.93 to -114.20% of Mg from water sample from river Tammah. The pattern appeared very similar in water sample from Magami. Removal of Pb by sorption processes had been studied by several workers using tree fern (Ho et al., 2002), soil bacterium (Alexandra et al., 1996), waste brewery biomass (Marques et al., 1999), peat moss (Ho and Mckay, 2000) and different kinds of marine biomass (Raize et al., 2004; Klimmek et al., 2001). It had been shown that biosorption processes have shown high effectiveness in reducing the concentration of Pb ions in aqueous solutions.

Tables 7 and 8 depict metal uptake of biosorbent from water samples from river Tammah and Magami, respectively. Metal uptake increased for Pb in river Tammah from pH 6.8 - 7.8 and from 8.2 - 8.4 and was highest between 7.0 and 7.8. For Fe, metal uptake increased from pH 6.8 to 7.8, was maximum at 7.8. There was variation between pH 8.0 and 8.4. For Mg, metal uptake increased also from pH 6.8 to 8.4 though result showed desorption overall. Peak values of metal uptake of biosorbent from water from both sample sites were found to be at pH 7.0 to 7.8 (0.2756 mgg^{-1}) and also at 8.2 to 8.4 for Pb, 7.8 (0.1280 mgg^{-1}) for Fe and 5.6 (-0.9210 mgg^{-1}) for Mg. Compared to lead sorption which had a steady sorption at pH 7.0 - 7.8 (0.2756 mgg^{-1}), iron sorption by biosorbent showed significant variation with changes in pH. The values obtained for lead were close to those obtained for Magami (0.2583 mgg^{-1}). It was evident from this study that the biosorbent exhibited maximum metal uptake capacity for lead at pH range 7.0 - 7.8 and iron at 7.8. Instead of increase in metal uptake capacity for Mg there was desorption. pH had been reported to be an important parameter on biosorption of metal ion from aqueous solutions (Gong et al., 2005), therefore *V. doniana* leaf which presents a high content of ionizable group (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides could be assumed to be made at least in theory, very liable to the influence of pH. When the pH increasesd, the ligands such as carboxylate groups in the leaf were assumed to be exposed, increasing the negative charge density on the biomass surface and so increased the attraction of metallic ions with positive charge and allows biosorption onto the cell surface (Kumar et al., 2006).

Tables 9 and 10 show that *V. doniana* (dinya) adsorbed nearly 100% of Pb at pH 6.8 – 8.4, 86 - 90% of Fe within the same range and for Mg, a percentage adsorption range of -149 to -225% (or percentage desorption of 149 to 225%) at pH 6.8 – 8.4. However, this value of lead was comparable with that of Umit et al. (2006); 93 - 100% in environmental samples by membrane filtration while that of iron, 86 - 92% was lower than this. The percentage adsorption of lead using sea weed was 90%. From this study, percentage adsorption of iron by *V. doniana* was 86 – 90%. Iron adsorption percentage fell within the percentage range obtained by Kumar and Kaladharan (2006) for the removal of metals from a multi – metal ion solution (50 - 97%).

Biosorption studies

The equilibrium biosorption can be described for this study using the Langmuir equation;

$$q = q_{max}\, bC_f/(1 + bC_f)$$

q is the metal uptake (mgg^{-1}), q_{max} is the monolayer adsorption capacity of adsorbent (mgg^{-1}), b is Langmuir's constant (mg^{-1}) and C_f is the final or equilibrium metal concentration in solution (mgl^{-1}). This equilibrium model was developed to predict the influence of pH on biosorption. The results obtained in the study of the water samples from river Tammah and Magami confirmed the significant role of pH in the metal sorption process. At pH 6.8 – 8.4 carboxylic groups were considered to be the predominant active sites to bind Lead and Iron. From pH > 7.0 hydroxyl groups may have contributed to metal adsorption. For pH > 8.4 though, the result may fluctuate because of the possibility of hydroxide participation. From the study it was seen that *V. doniana* leaves was a better adsorbent at pH < 8.0.

Biosorption equilibrium

Comparing Tables 2 and 4 there was a gradual increase in adsorption for Fe with increase in pH until equilibrium was attained while for Pb, there was nearly 100% adsorption right from the first working pH (6.8). This is observable from the constant values observed for milligram of metal accumulated per gram of biosorbent (q); 0.2583 mgg^{-1}. The uptake capacity increased with the solution pH. This was also the pattern observed when Tables 7 and 9 were compared, suggesting an increase in metal uptake by biomass *V. doniana* leaves with increase in pH. Comparison of Tables 7 and 9 showed a gradual increase of adsorption for Fe until equilibrium, or a plateau was attained while for Pb there was a sharp increase. The uptake capacity increased with the solution pH. The same result was obtained by Vitor et al. (2006). There was a gradual decrease or desorption for Mg until a plateau was attained. An equilibrium concentration of Pb, Fe and Mg was reached at a range of about 0.000 mgl^{-1} ± 0.00 to 0.0007 mgl^{-1} ± 0.0002, 0.1871 mgl^{-1} ± 0.005 and 17.02 mgl^{-1} ± 0.22, respectively for *V. doniana* leaves. The maximum metal adsorption of lead and iron was observed in the biosorption as well as desorption for magnesium. The results of the final or residual metal concentrations after a contact time of 24 h were 0.0074 mgl^{-1} ± 0.0003 for lead, 0.3498 mgl^{-1} ± 0.01 for iron and 20.009 mgl^{-1} ± 0.2 for magnesium for the actual pH of the river (river Tammah) and for pH 6.8 to 8.4, 0.000 mgl^{-1} ± 0.00 to 0.0035 mgl^{-1} ± 0.00024 for lead, 0.1710 mgl^{-1} ± 0.006 to 0.2564 mgl^{-1} ± 0.015 for iron and 12.509 mgl^{-1} ± 0.1 to 18.509 mgl^{-1} ± 0.15 for magnesium, the percentage adsorption was between 99.92 to 100%, 88.02 to 92.01% and -114.20 to -216.93%, respectively. A similar result was obtained by Vitor et al. (2006) in kinetics and equilibrium modeling of lead uptake by algae *Gelidium* and algal waste from agar extraction industry. For Mg, there was a gradual decrease or desorption until equilibrium was attained.

An equilibrium concentration of Pb, Fe and Mg was reached at a range of about 0.000 mgl^{-1} ± 0.00 to 0.0006 mgl^{-1} ± 0.0001, 0.1777 mgl^{-1} ± 0.006 to 0.1799 mgl^{-1} ± 0.002 and 18.209 mgl^{-1} ± 0.10 to 18.219 mgl^{-1} ± 0.13, respectively, for *V. doniana* leaves.

In the biosorption experiment, the maximum metal adsorption was observed in the case of lead followed by iron and desorption observed in the case of magnesium. The result showed the effectiveness of the biomass by the percentage adsorption of metals from water samples from both river sites; between 99.98 to 100%, 86.35 to 90.39% and -149.12 to -224.90%, respectively for Pb, Fe and Mg. It was evident from the study that the biosorbent exhibited maximum metal uptake capacity for lead at pH range 7.0 - 7.8 and iron at 7.8. Instead of metal uptake capacity to have increased for Mg there was desorption.

V. doniana leaf presented a high content of ionizable group (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides which made it at least in theory very liable to the influence of pH. As the pH increased, the ligands such as carboxylate groups in the leaf were exposed this caused an increase in the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface (Kumar et al., 2006).

The values obtained for iron were close to those obtained by Odusanya (2007); 0.1279 mgg^{-1} using *Basella alba* (Spinach) and also to values obtained for the metals in this research work but were much lower than that obtained by Kumar et al. (2006); 0.1543 mgg^{-1} using *Tectona grandis* leaf.

Conclusion

This study showed that the mean metals concentrations of water from the two sample sites; river Tammah and Magami fell within the World Health Organization (WHO) maximum permissible values except for that of lead whose values in both water sources were higher. *V. doniana* leaf was found to be an effective biosorbent for the adsorption of heavy metals (lead and iron) from water samples. There was desorption for magnesium. The uptake of lead and iron increased with increase in pH and had its highest adsorption between pH 7.4 to 7.8 for the two sample sites. Metal uptake fluctuated for pH > 8.0. Adsorption isotherm could be well fitted by the Langmuir equation. This study therefore showed that *V. doniana* leaf was effective in the removal and accumulation of lead and iron from aqueous solutions but was not effective in the removal of magnesium.

REFERENCES

Ademoroti CMA (1981). Application of continuous monitoring to river management. Proceedings of the second national conference of water pollution. Niger. J. Water Resour. 1: 167-176.

Adeniyi AA, Yusuf KA, Okedeyi OO (2008). Assessment of the exposure of two fish species to metals pollution in the Ogun river catchments, Ketu, Lagos, Nigeria. Environ. Monit. Assess. 137: 1573-2959 (Online).

Ahalya N, Ramachondra TV, Kanamadi RD (2005). Biosorption of heavy metals. Centre for Economics Science, Median Institute of Science, Banglore. pp. 1-50.

Alexandra C, Plette C, Benedectti MF, Riemsdijk WHV (1996). Competitive binding of protons, calcium, lead, and zinc to isolated cell walls of a gram-positive soil bacterium. Environ. Sci. Technol. 30: 1902-1910.

Atolaiye BO, Aremu MO (2007). Bioaccumulation of some trace elements in the body parts of fish species associated with soil sediments and water from "Magami" confluence in Nasarawa State, Nigeria. Elect. J of Environ. Agric. Food Chem. 6(5) 2001-2008.

Atolaiye BO, Aremu MO, Shagye D, Pennap GRI (2006). Distribution and concentration of some mineral elements in soil sediment, ambient water and the body parts of *Clarias gariepinus* and *Tilapia quineensis* fishes in river Tammah, Nasarawa State, Nigeria. Curr. World Environ. 1(2): 95-100.

Australia Environment Annual Report Online (2002).

Charles EW (1972). Biol. Water Pollut. Contr. Ecol. 53 (2): 371-372.

Gong R, Ding YD, Liu H, Chen Q, Liu Z (2005). Lead biosorption by intact and pretreated Spirulina maxima biomass. Chemosphere, 58: 125-130.

Ho YS, McKay G (2000). Batch sorber design using equilibrium and contact time data for the removal of lead. Water Air Soil Pollut. 124: 141-153.

Kendirim EC, Ejike C, Anadis DI (1989). Niger. J. Biotechnol. 6: 16.

Klein LA (1962). River pollution Vol II. Causes and effects. Lond. J Water Pollut. Control Fed. I: 120.

Klimmek SK, Wilke A, Bunke G, Buchholz R, Stan HJ (2001). Comparative analysis of the biosorption of cadmium, lead, nickel and zinc by algae. Environ. Sci. Technol. 35:4283-4288.

Kratochvil D, Volesky B (1998). Advances in the biosorption of heavy metals. Trends Biotechnol. 16: 291-300.

Kumar VV, Kaladharan P (2006). Biosorption of metals from contaminated water using sea-weed. Curr Sci. 90(9): 1263-1266.

Kumar YP, King P, Prasad VSRK (2006). Equilibrium and kinetics for the biosorption system of copper (II) ion from aqueous solutions using *Tectona grandis* leaves powder. J Hazard Mater. B13: 1211-1217.

Lenntech (2001). Water treatment and air purification. Netherland J Environ Agency Online. Vol 4: 26-29.

Matheickal JT, Feltham J, Yu Q (1997). Cu(II) binding by marine algae. *Ecklonia radita* biomaterial. Environ. Technol. 18: 25-34.

Odusanya AA (2007). The biosorption of lead ions from waste water using leaf of *Talinum triangulare* and *Basella alba*.B.Sc Thesis, University of Ibadan.

Raize O, Argaman S, Yannai S (2004). Mechanisms of biosorption of different heavy metals by brown marine macroalgae. Biotechnol. Bioeng. 87: 451-458.

Sag Y, Kutsal T (1995). Biosorption of heavy metals by *Zoogloea ramigera*: Use of adsorption isotherms and a comparison of biosorption characteristics. Chem. Eng. J. Biochem. Eng. J. 60: 181-188.

Sagakuchi T, Nakajima A (1991). Accumulation of heavy metals by microorganisms. In: Smith RW, Mistra M (editors), Mineral Bioprocessing. The minerals, Metals and Materials Society.

Sandau E, Sandau P, Pulz O (1996). Heavy metal sorption by microalgae. Acta. Biotechnol. 16: 227-235.

Strandberg GW, ShumateII SE, Parrot JR (1981). Microbial cells as biosorbemts of heavy metals: Accumulation of uranium by *Saccharomyces cerevisae* and *Pseudomonas aeruginosa*. Appl. Environ. Microbiol. 41: 237-245.

Umit D, Astihan AK, Mustafa S, Latif E (2006). Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations. J. Hazard Mater. 145(3): 459-464.

US EPA (1987). Practical handbook of soil, vadose zone and ground water. (Phytoremediation of contaminated ground water). p. 565.

Vasudevan P, Padmavathy V, Dhingra SC (2003). Kinetics of biosorption of cadmium on baker's yeast. Biotechnology, 89(3): 271-287.

Viessman P, Hammer U (1999). In: The national academies press (editors), Arsenic in Drinking Water. Commission on Life Sciences. 11 Risk Characterisation.

Vitor JPV, Gotalia MSB, Rui ARB (2006). Kinetics and equilibrium modeling of lead uptake by algae *Gelidium* and algal waste from agar extraction industry. J. Hazard Mater. 143: 396-408.

Volesky B (1990). In CRC Press, Florida (editors), Biosorption and biosorbents. pp. 3-6.

WHO (1972). Health hazards to human environment, World Health Organisation.

WHO, Geneva (1995). WHO Environmental Health Criteria. pp. 165: Inorganic lead.

World Health Organisation (WHO) (2003). Drinking water quality criteria. Geneva.

Yu B, Zhang Y, Shukla A, Shukla SS, Doris KL (2003). The removal of heavy metal from aqueous solutions by sawdust adsorption – removal of copper. J. Hazard. Mater. B80: 33-42.