We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Application of *Luffa Cylindrica* in Natural form as Biosorbent to Removal of Divalent Metals from Aqueous Solutions - Kinetic and Equilibrium Study

Innocent O. Oboh, Emmanuel O. Aluyor and Thomas O. K. Audu

University of Benin,
Nigeria

1. Introduction

Environmental pollution due to the discharge of heavy metals from various industries, including metal plating, mining, painting and agricultural sources such as fertilizers and fungicidal sprays are causing significant concern because of their toxicity and threat to human life, especially when tolerance levels are exceeded (Gupta et al., 2009).

The species with the most toxicological relevance found in the industrial effluents are the heavy metals. These species are bio-accumulative and not biodegradable over time (Abdel-Ghani et al., 2009).

Activated carbon is the most employed adsorbent for heavy metal removal from aqueous solution (Mohan et al., 2005). However, the extensive use of activated carbon for metal removal from industrial effluents is expensive (Babel and Kurniawan, 2003), limiting its large application for wastewater treatment. Therefore, there is a growing interest in finding new alternative low-cost adsorbents for metal removal from aqueous solution, such as: microorganisms (Martins et al., 2006; Klen et al., 2007), and residuals of agricultural products (Basil et al., 2006; Lima et al., 2007).

The greatest demand for metal sequestration today comes from the need to immobilize the metals released to the environment (or mobilized) by and partially lost through human technological activities. It has been established that dissolved metals (particularly heavy metals) escaping into the environment pose a serious health hazard (Kuyucak and Volesky, 1990). They accumulate in living tissues throughout the food chain, which has humans at its top, multiplying the danger. Thus, it is necessary to control emissions of heavy metals into the environment.

Urban and industrial wastewaters with toxic metal ions are a serious environmental problem (Santhy and Selvapathy, 2004). Metals have a high degree of toxicity, which can be deleterious for both the human beings and the environment. Inorganic micro pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a carcinogenic effect (Cimino, et al., 2000).

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Graeme and Pollack, 1998). There are 35 metals that concern us because of

occupational or residential exposure; 23 of these are the heavy elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Life Extension, 2009).

Generally, heavy metals inflict toxicity by forming highly stable ligands as giant molecular complexes with the organic compounds in the body. The bioaccumulated heavy metal bounded with the organic compound modifies the biological organic molecule which in many occasions losses their ability to function properly, consequently, resulting in malfunction, change major constituents of the affected cells, and in some instances, the cell dies. At the death of the cell, the normal functions of the body systems are interfered and common symptoms are manifested depending on the organ affected (David and Norman, 1986).

In the present study, the following heavy metals namely: lead, copper, zinc and nickel were investigated.

a. Lead can contaminate the environment through natural geochemical and anthropogenic processes. The anthropogenic sources of lead to the environment include coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities and the utilization of fossil fuels (King et al., 2007). Various plant materials viz. rice husk, maize cobs, coconut and seed hull, saw dust, maize leaf and olive pomace have been studied for Pb removal from water bodies. An investigation dealt with the abatement of Pb (II) ions from aqueous system using *Saraca indica* leaf powder (SILP). The manuscripts also reported the applicability of leaf biomass for Pb (II) metal ion recovery and regenerate the exhausted biosorbent thereby making the process more economical, beneficial and cost effective (Goyal et al., 2008).

b. Copper metal contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of computer heat sinks, Copper plumbing, as well as biostatic surface, as a component in ceramic glazing and glass colouring (Tumin et al., 2008). Copper is regularly used in agricultural chemicals for mildew prevention, and as algicides in water treatment of industrial waters. It is also used as a preservative for wood, leather, and fabrics. Workers in, or those living near mines, smelters, metal fabrication and manufacturing plants, wood treatment plants, phosphate fertilizer plants, and waste water plants may also experience excessive copper exposure (Jolley et al., 2003). Probably the most likely route of excessive copper intake for most people will be through drinking water. Although high copper concentrations are rare in most water sources, all water is aggressive toward copper, brass and bronze plumbing fixtures to some extent. In some cases the water will dissolve some of the copper, especially when it sits for long in pipes. Soft water is more aggressive than hard water, because hard water will often lay down a protective scale layer that keeps the water from direct contact with the pipe (Jolley et al., 2003).

c. Nickel metal contamination exists in natural deposits; industrial processes that use nickel catalysts, such as coal gasification, petroleum refining, and hydrogenation of fats and oils. They have also been identified in residual fuel oil and in atmospheric emissions from nickel refineries. Nickel is toxic and relatively widespread in the environment. It is used in a wide variety of industries such as plating and cadmium–nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys, and find its way to the aquatic environment through wastewater discharge. Therefore, a systematic study on the removal of nickel from wastewater is of considerable significance from an environmental point of view (Singh, 2008).

d. Although zinc occurs naturally, most zinc find its way into the environment because of human activities. Mining, smelting metals (like zinc, lead and cadmium) and steel

production, as well as burning coal and certain wastes can release zinc into the environment. High level of zinc in soil may result from the improper disposal of zinc-containing wastes from metal manufacturing industries and electric utilities. Drinking water that flows through metal pipes coated with zinc also are sources of zinc exposure. Zinc is often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal waste water treatment plants and is not biodegradable and travels through the food chain via bioaccumulation. Therefore, there is significant interest regarding zinc removal from waste waters since its toxicity for humans is 100-500 mg/day. World health organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/l (Rakesh et al., 2010).

Loofa sponge is a lignocellulosic material composed mainly of cellulose, hemicelluloses and lignin (Rowell et al., 2002). The fibers are composed of 60% cellulose, 30% hemicelluloses and 10% lignin (Mazali and Alves, 2005). The fruits of *L. cylindrica* are smooth and cylindrical shaped (Mazali and Alves, 2005). *L. cylindrica* is a sub-tropical plant, which requires warm summer temperatures and long frost-free growing season when grown in temperate regions. It is an annual climbing which produces fruit containing fibrous vascular system. It is a summer season vegetable. It is difficult to assign with accuracy the indigenous areas of *Luffa* species.

They have a long history of cultivation in the tropical countries of Asia and Africa. Indo-Burma is reported to be the center of diversity for sponge gourd. The main commercial production countries are China, Korea, India, Japan and Central America (Bal et al., 2004).

The structure of *Luffa cylindrica* for example, is cellulose based (Rowell et al., 2002; Mazali and Alves, 2005), and the surface of cellulose in contact with water is negatively charged. Metal compounds used in this study will dissolve to give the cationic metal and this will undergo attraction on approaching the anionic *Luffa cylindrica* structure (Ho et al., 2002). On this basis, it is expected that a metal cation will have a strong sorption affinity for *Luffa cylindrica*.

The study investigated time dependence and concentration dependence studies on the sorption of some selected divalent metal ions on the seeds and sponge mixture of *Luffa cylindrica*. The data obtained from the batch concentration studies were fit into Langmuir, Sips, Redlich-Peterson and Freundlich adsorption isotherms to establish mechanism for the biosorption process. The kinetics of the biosorption process was established by fitting the data from the time dependency study into pseudo-first order, Avrami (Fractional order), Intra-particle diffusion and pseudo-second order kinetic models.

2. Materials and methodology

2.1 Preparation of *Luffa cylindrica*
The plant materials (sponge and seeds) were dried at room temperature for a period of three days. The biosorbent was screened to obtain a geometrical size of 0.25 - 0.5mm. The ground seed and sponge were mixed at a ratio of 1:1.

2.2 Preparation of aqueous solutions
Stock solutions of Nickel, Lead, Copper, and Zinc were prepared with distilled water and Nickel (II) tetraoxosulphate (VI), Lead (II) trioxonitrate (V), Copper (II) tetraoxosulphate (VI) and Zinc chloride respectively. All working solutions were obtained by diluting the stock solutions with distilled water. The pH of the effluent was adjusted to 5. The concentration of metal ions in effluent was analyzed by Atomic Absorption Spectrophotometer. A duplicate was analyzed for every sample to track experimental error and show capability of reproducing results (Marshall and Champagne, 1995).

2.3 Scanning electron microscope and elemental analysis

The microstructures, composition, and morphology of *Luffa cylindrica* the biosorbent material was analysed by means of scanning electron microscopy (SEM). A Philips scanning electron microscope (ESEM XL30) equipped with energy dispersive X-ray spectrometer (EDX) was used to analyse the various elemental composition found in the powders.

2.4 Fourier transform infra red analysis

Fourier transform infrared spectroscopy (FTIR) of the adsorbent was done by using an FTIR spectrometer (Model FTIR 2000, Shimadzu, Kyoto, Japan). About 150 mg KBr disks containing approximately 2% of *Luffa cylindrica* sample was prepared shortly before recording the FTIR spectra in the range of 400 – 4000.0 cm^{-1} and with a resolution of 4 cm^{-1}. The resulting spectra were average of 30 scans.

2.5 Surface area

The surface area of the *Luffa cylindrica* sample was determined using Flowsorb 2300 manufactured by Micrometrics Instrument Corporation, USA. Krypton gas was used in conducting single-point surface area measurements. Liquid nitrogen was used in setting the adsorption of nitrogen gas by the samples. The *Luffa cylindrica* was degassed at 100ºC for 30 minutes and were then cooled to liquid nitrogen temperature. The surface area of the sample under measurement was then read from the display-meter. The value of the surface area recorded was then converted to specific surface area (m^2/g) by dividing the reading on the display by the weight of the *Luffa cylindrica* sample.

2.6 Biosorption experiment

The experiments were carried out in the batch mode for the measurement of adsorption capabilities. The bottles with 500ml capacity were filled with 50ml of the synthetic wastewater, and 1g of dried plant materials (ground). The bottles were shaken for a predetermined period of 2h at room temperature in a reciprocating shaker 300 rpm. The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer (AAS).

The amount of the metal ion sorbed and percentage of removal of metal ion by the biosorbent were calculated by applying the Equations (1) and (2), respectively:

$$q = \frac{(C_0 - C_f)}{m} . V \tag{1}$$

$$\% \, \text{Removal} = \frac{(C_0 - C_f)}{C_0} . 100 \tag{2}$$

where *q* is the amount of metal ion sorbed by the biosorbent (mg/g); C_0 is the initial ion concentration put in contact with the biosorbent (mg/L), C_f is the final concentration (mg/L) after the batch biosorption procedure, *V* is the volume of aqueous solution (L) put in contact with the biosorbent and m is the mass (g) of biosorbent.

Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study
199

2.7 Kinetic and equilibrium studies

The kinetic equations, which are, Avrami (Lopes et al., 2003), pseudo first-order (Largegren, S., 1898), pseudo-second order (Ho, Y.S., Mckay, G.M., 1999), Elovich (Ayoob et al., 2008) and intra-particle diffusion model (Weber Jr. and Morris, 1963) are given in Table 1.

Kinetic model	Equation
Pseudo-first-order (Largegren, S., 1898)	$q_t = q_e \cdot \left[1 - \exp\left(- \mathrm{k_p} . t\right)\right]$
Pseudo-second-order (Ho, Y.S., Mckay, G.M., 1999)	$\dfrac{\mathrm{t}}{\mathrm{q_t}} = \dfrac{1}{\mathrm{kq_e^2}} + \dfrac{1}{\mathrm{q_e}} \mathrm{t}$
Elovich (Ayoob et al., 2008)	$q_t = \dfrac{1}{\beta} \ln(\alpha\beta) + \dfrac{1}{\beta} \ln t$
Avrami (Lopes et al., 2003)	$q_t = q_e \cdot \left(1 - \exp\left[- \left(\mathrm{k_{AV}} . t\right)\right]\right)$
Intra-particle diffusion (Weber Jr.and Morris, 1963)	$q_t = k_{id}\sqrt{t} + C$

Table 1. Kinetic adsorption models

The isotherm equations which are, Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906). Sips (Sips, 1948) and Redlich–Peterson (Redlich and Peterson, 1959) are given in Table 2.

Isotherm	Equation
Langmuir (Langmuir,1918)	$Q_e = \dfrac{x}{m} = \dfrac{K_L C_e}{1 + aC_e}$
Freundlich (Freundlich, 1906)	$Q_e = K_F C_e^{1/n}$
The Redlich-Peterson (Redlich and Peterson, 1959)	$Q_e = \dfrac{K_j C_e}{1 + \alpha_L C_e^{\beta}}$
Sips (Sips,1948)	$Q_e = \dfrac{abC_e^n}{1 + aC_e^n}$

Table 2. Equilibrium isotherm models

2.8 Evaluation of the kinetic and isotherm parameters

In this work, the kinetic and equilibrium models were fitted employing the non-linear fitting method, using the non-linear fitting facilities of the software NLREG version 6.5.

3. Results and discussion

3.1 Results

Specific surface area - BET (m²/g)	0.28
Total Surface area (m²/g)	1.1895
Pore Diameter Range (µm)	1051.309204 to 0.003577

Table 3. Physical properties of the *Luffa cylindrica* biosorbent

Elements	Weight%	Atomic%
C	79.33	86.91
O	12.25	10.07
P	00.95	00.40
S	00.75	00.31
Cl	01.58	00.59
K	03.86	01.30
Ca	01.29	00.42

Table 4. Elemental composition of the *Luffa cylindrica* biosorbent

(a) Subfigure A

(b) Subfigure B

(c) Subfigure C

(d) Subfigure D

(e) Subfigure E

(f) Subfigure F

(g) Subfigure G

(h) Subfigure H
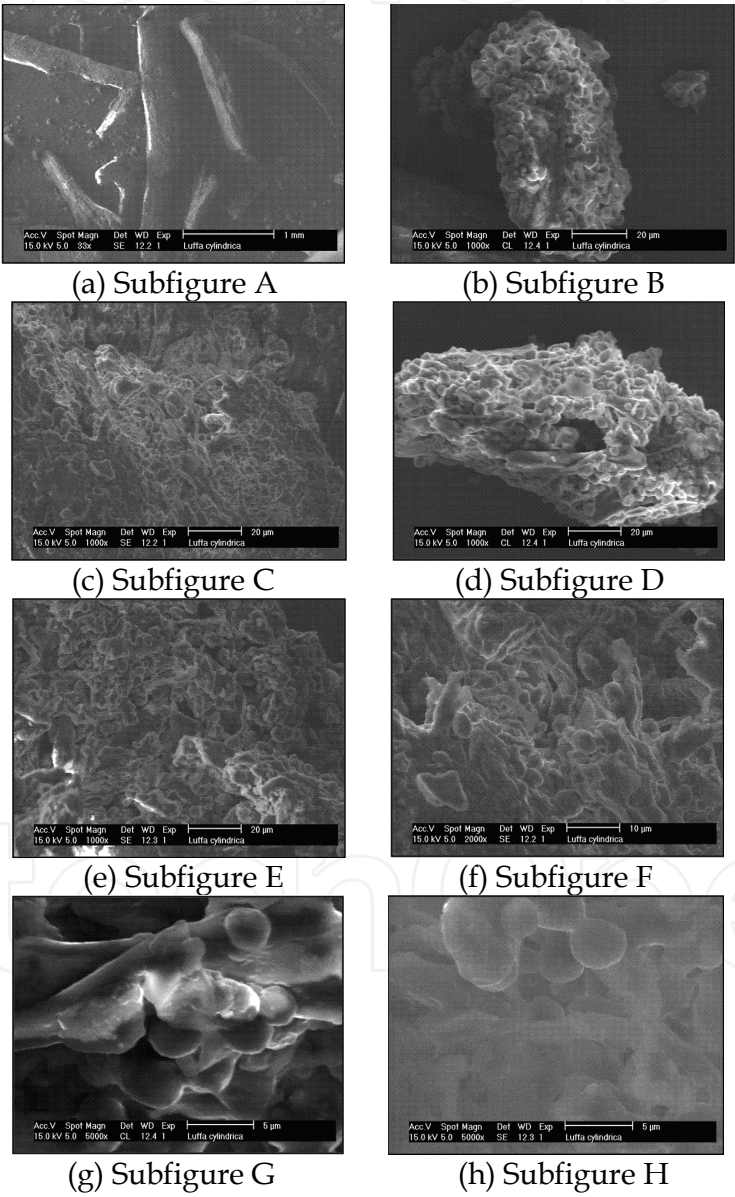
Fig. 1. Scanning electron microscopy of *Luffa cylindrica* seeds and sponge mixture biosorbent: (A) transversal view of the mixture of seed and sponge 33×; (B, C, D, E) transversal view of the mixture of seed and sponge 1000×; (G, H) transversal view of the mixture of seed and sponge 5000×.

Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study
201
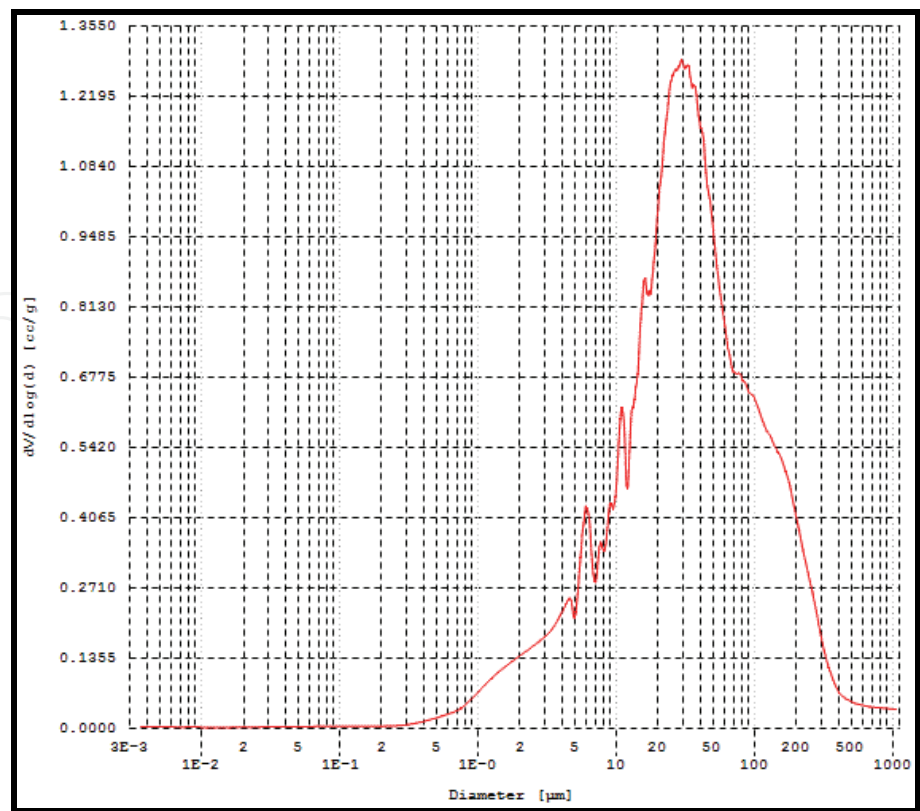
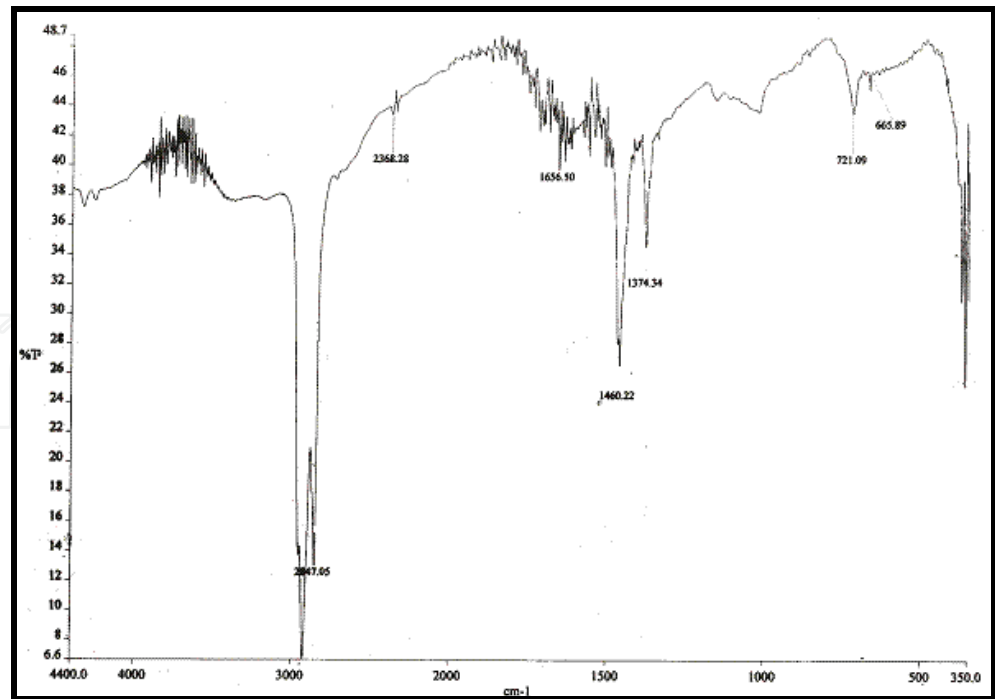Fig. 2. A plot showing the pore size distribution of the biosorbent - *L. cylindrica*

Fig. 3a. FTIR spectrum of the mixture of seed and sponge of *L. cylindrica* biosorbent before biosorption.
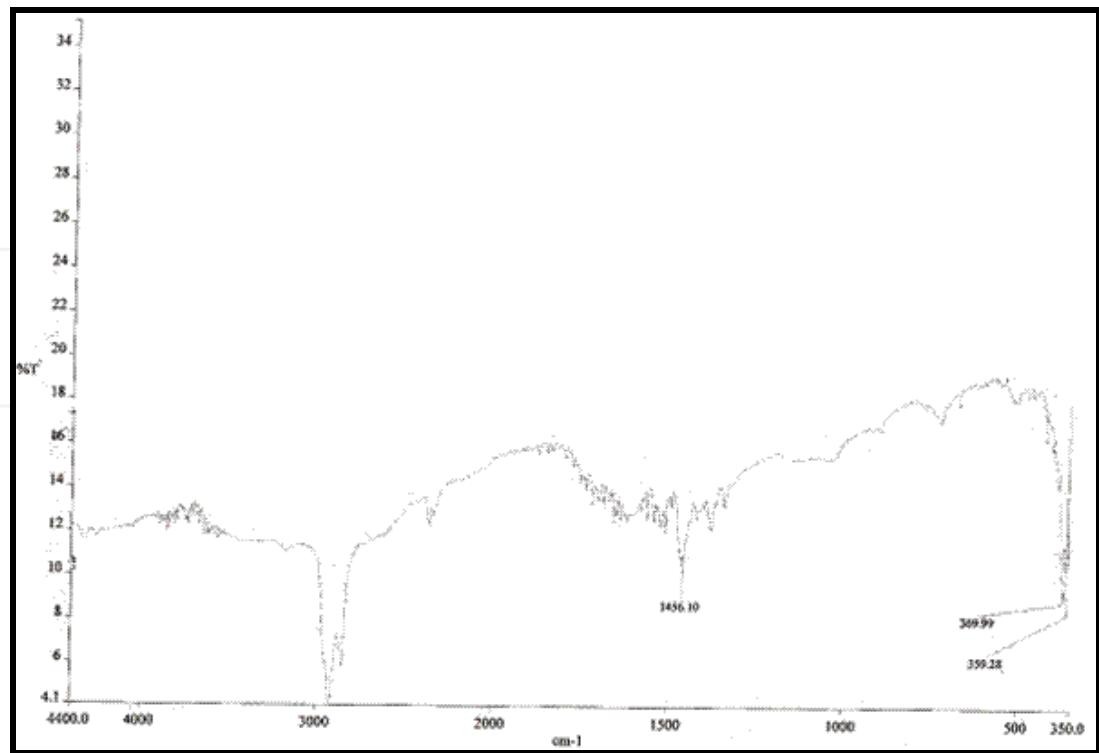
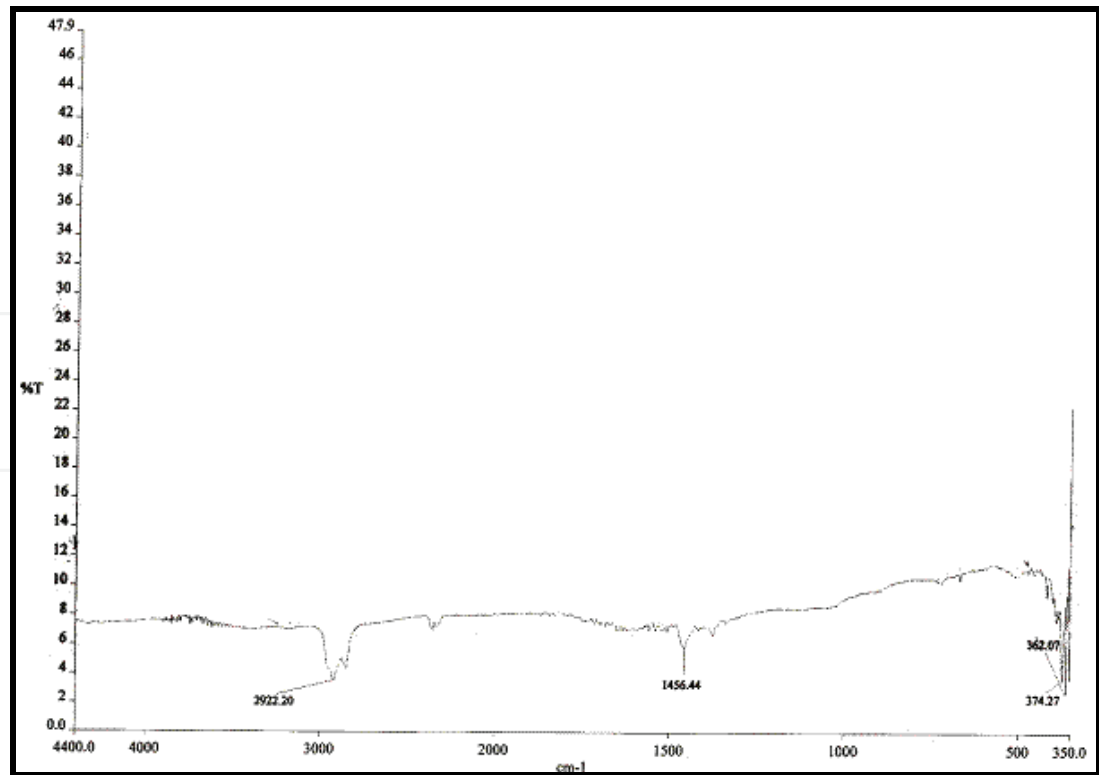Fig. 3b. FTIR spectrum of the mixture of seed and sponge of *L. cylindrica* biosorbent after biosorption of Ni²⁺ions .

Fig. 3c. FTIR spectrum of the mixture of seed and sponge of *L. cylindrica* biosorbent after biosorption of Cu²⁺ions.
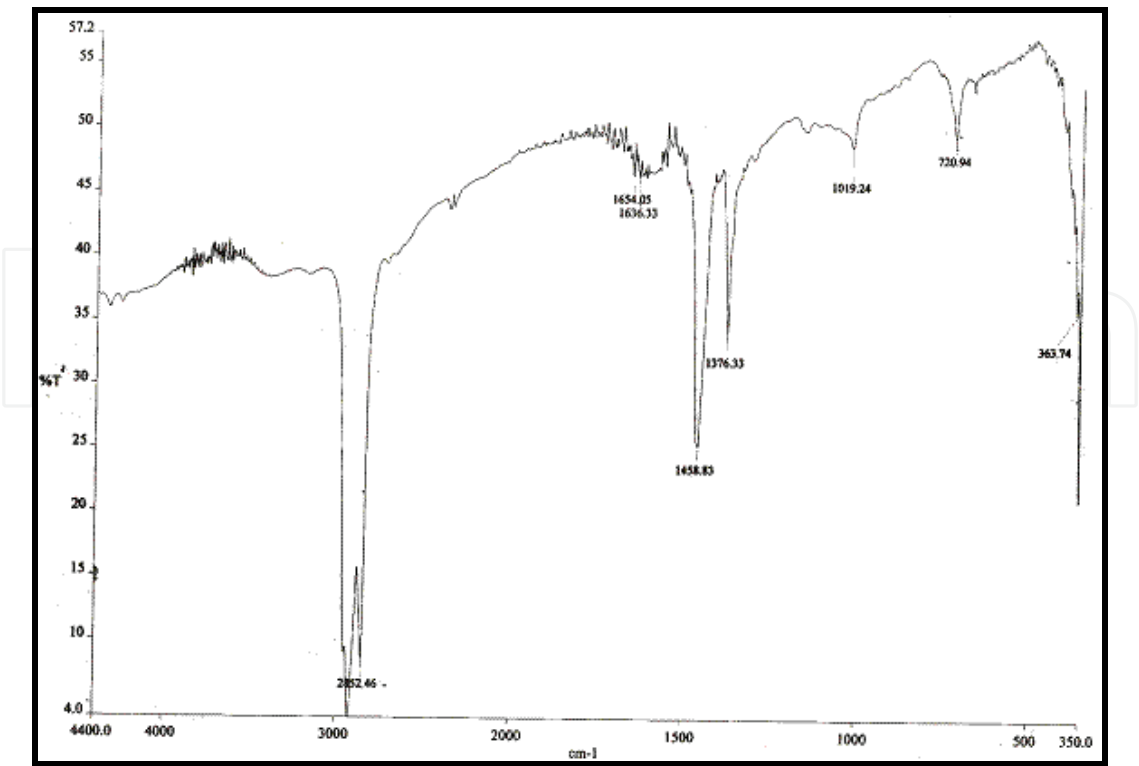
Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study
203

Fig. 3d. FTIR spectrum of the mixture of seed and sponge of *L. cylindrica* biosorbent after biosorption of Pb^{2+}ions.
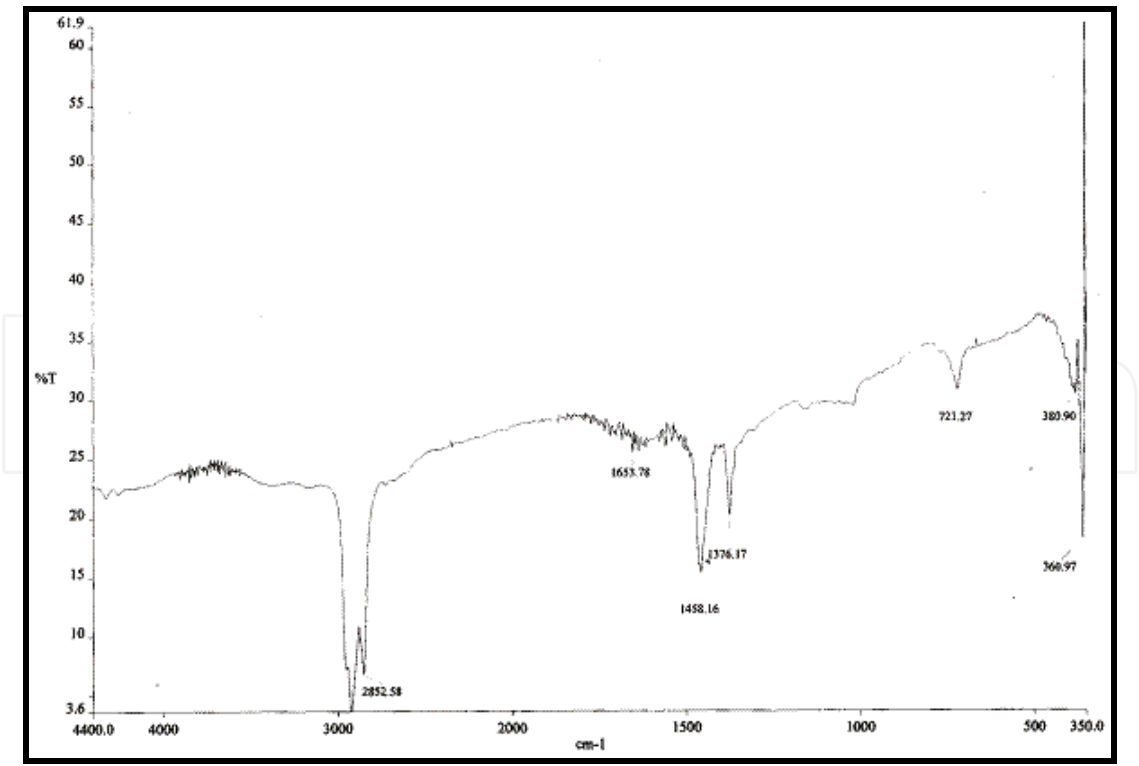

Fig. 3e. FTIR spectrum of the mixture of seed and sponge of *L. cylindrica* biosorbent after biosorption of Zn^{2+}ions.
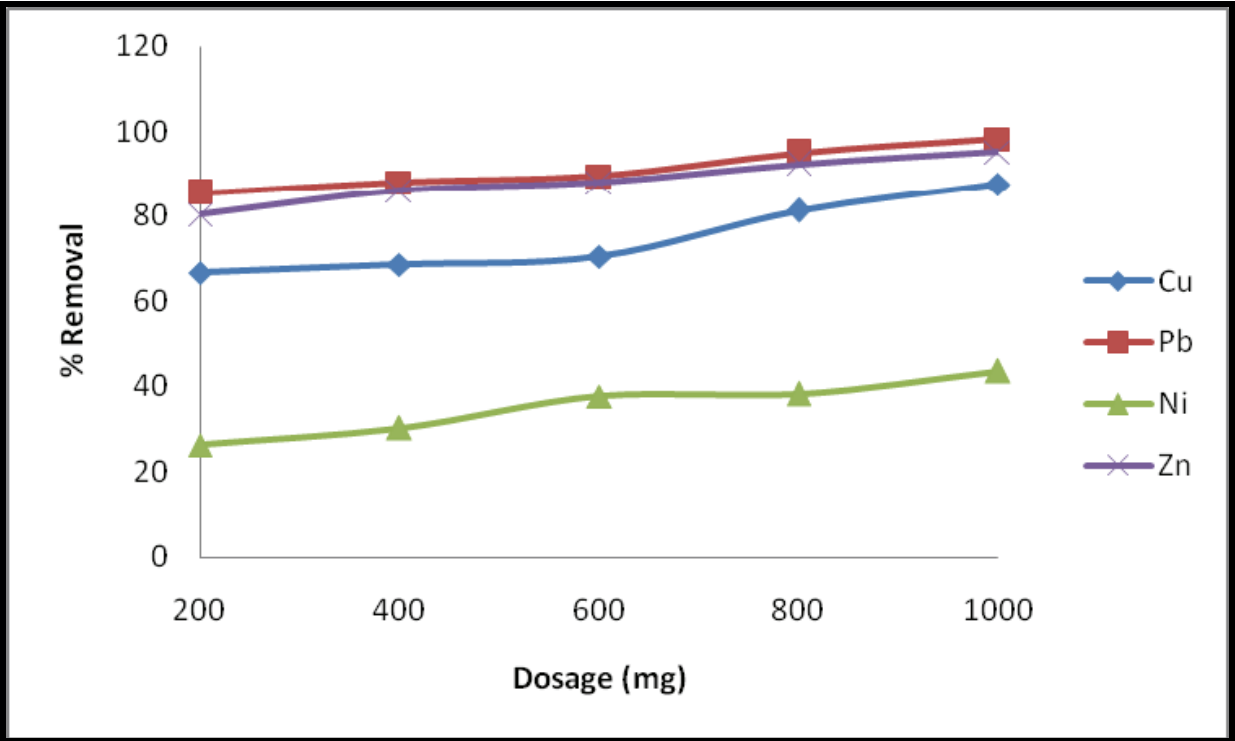
Fig. 4. % Removal of heavy metal ions from aqueous solutions (50 ml, pH 5.0) with increasing dosage of the heavy metals using *L. cylindrica* (1.0 g) as biosorbent for 2h.
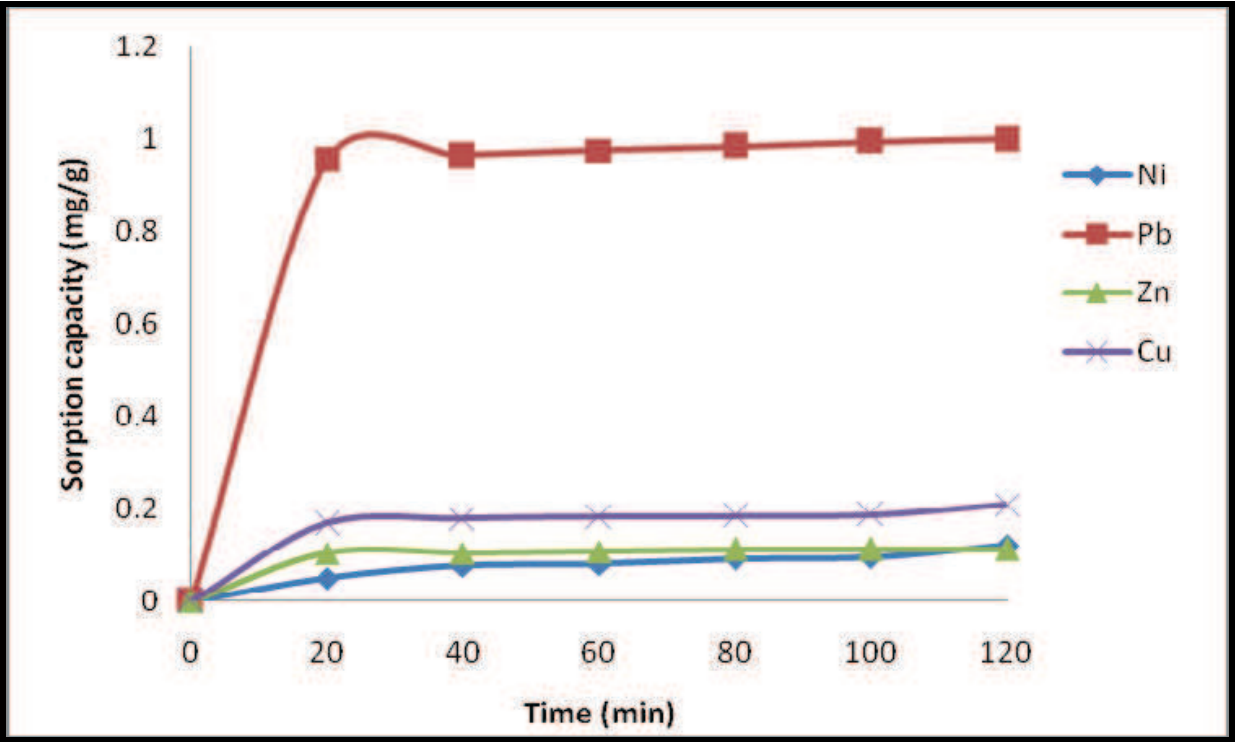

Fig. 5. Time dependent study of the sorption of lead, copper, zinc and nickel on *L. cylindrica* seeds and sponge mixture using 1.0 g biosorbent dose. Initial lead, Nickel, Copper and Zinc concentrations were 20.0, 4.0, 5.0 and 2.5 mg/L respectively with pH 5.0.

Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study
205

Kinetic model	Parameters	Metal ions (M^{2+})			
		Cu	Pb	Zn	Ni
Pseudo-First order	q_e (mg/g)	0.1886	0.9843	0.1100	0.1141
	k_{e1} (g/mg min)	0.1044	0.1720	0.1364	0.0240
	r^2	0.9819	0.9991	0.9947	0.9556
Pseudo-Second order	q_e (mg/g)	0.2002	1.0004	0.1138	0.1490
	k_{e2} (g/mg min)	1.1300	0.9183	3.7011	0.1522
	r^2	0.9883	0.9997	0.9977	0.9666
Intra-particle diffusion	k(mg/g min$^{0.5}$)	0.0168	0.0824	0.0094	0.0102
	C (mg/g)	0.0419	0.2691	0.0278	0.0026
	r^2	0.7933	0.6989	0.7401	0.9752
Elovich	α (mg/g min)	10.2050	1.292E+13	7649.602	0.0070
	β (g/mg)	56.7641	38.7968	167.0520	29.3910
	r^2	0.7375	0.9704	0.8709	0.9054
Avrami	K_{av}(min^{-1})	0.3228	0.5434	0.3374	-0.1163
	n_{av}	0.3235	0.5434	0.4042	-0.2064
	q_e(mg/g)	0.1886	0.9794	0.1099	0.1141
	r^2	0.9819	0.9983	0.9947	0.9556

Table 5. Kinetic model rate parameters obtained using the nonlinear methods.

Isotherm	Parameters	Metal ions (M^{2+})			
		Cu	Ni	Pb	Zn
Langmuir	Q_{max}	2.26E+04	8.20E+03	1.36E+05	2.89E+04
	K_L	1.4580	7.01E-06	8.32E-06	3.00E-05
	r^2	0.4922	0.3518	0.6571	0.8576
Freudlich	K_F	0.2519	0.0015	0.2544	1.3655
	n	0.5897	0.2121	0.3846	0.6801
	r^2	0.5381	0.9231	0.7189	0.9212
Sips	Q_{max}	1.19E+04	1.59E+03	7.90E+04	1.14E+04
	K_s	0.5897	9.51E-07	3.22E-06	1.20E-04
	n	2.11E-05	0.2120	0.3845	0.6801
	r^2	0.5381	0.9231	0.7189	0.9212
Redlich-Peterson	A_{rp}	-0.5421	-0.2936	-0.2525	-1.0178
	K_{rp}	0.0458	0.0117	0.3875	0.5072
	g	1.0000	1.0000	1.0000	1.0000
	r^2	0.7449	0.9632	0.8218	0.9539

Table 6. Equilibrium isotherm parameters obtained using the nonlinear methods.

3.2 Discussion

Table 3 show the surface area and pore diameter range for the biosorbent used for this study. The Specific surface area using the BET method was 0.28m²/g and the Pore diameter range was between 1051.309204 to 0.003577μm. As observed, the surface area for the seed and sponge mixture of *L. cylindrica* is relatively low, with pore diameter values in agreement with those found for typical mesoporous materials (Hamoudi and Kaliaguine, 2003).

Table 4 shows the elemental composition of *Luffa cylindrica* that was analysed by means of scanning electron microscopy (SEM). The *Luffa cylindrica* sample showed a very high percentage of carbon.

Scanning electron microscopy (SEM) of the *Luffa cylindrica* biosorbent was taken in order to verify the presence of macropores in the structure of the fiber. In the micrographs presented Figure 1 (A - J) is observed the fibrous structure of *Luffa cylindrica*, with some fissures and holes, which indicated the presence of the macroporous structure. These, should contribute a little bit to the diffusion of the Ni (II), Pb (II), Cu (II) and Zn (II) to the *Luffa cylindrica* biosorbent surface. The small number of macroporous structure is confirmed by the low specific surface area of the biosorbent (see Table 3). As the biosorbent material presents few numbers of macroporous structure, it adsorbed low amount of nitrogen, which led to a low BET surface area (Passos et al., 2006; Vaghetti et al, 2003; Arenas et al., 2004; Passos et al., 2008). Therefore the major contribution of the Ni (II), Pb (II), Cu (II) and Zn (II) uptake can be attributed to micro- and mesoporous structures (see Figure 1 (A-J)).

The pore size distribution of the *Luffa cylindrica* sample was obtained by Mercury intrusion method, and it is shown in Figure 2. The distribution of average pore diameter curve presents a maximum with an average pore diameter of about 30 μm. The amount of pores seen in the *Luffa cylindrica* biosorbent decreases for average pore diameters ranging from 30 to 1000 μm. On the other hand, the amount of average pores ranging from 3.0E-03 to 30 μm is predominant. Therefore, this biosorbent can be considered mixtures of micro- and mesoporous materials (Passos et al., 2006; Vaghetti et al, 2003; Arenas et al., 2004; Passos et al., 2008).

Figure 4 show the percent removal of Ni²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ ions from the aqueous solution using *Luffa cylindrica* seeds and sponge mixture. The highest percent removal for the dosage of 1000 mg of the biosorbent was 98.2 for Pb²⁺and was followed by 95.2, 87.6 and 43.5 for Zn²⁺, Cu²⁺ and Ni²⁺ ions respectively.

Figures 3 a - e show the FTIR spectral. The functional groups on the binding sites were identified by FTIR spectral comparison of the free biomass with a view to understanding the surface binding mechanisms. The significant bands obtained are shown in Figure 3 a - e. Functional groups found in the structure include carboxylic, alkynes or nitriles and amine groups (Pavia et al., 1996).

The stretching vibrations of C-H stretch of -CHO group shifted from 2847.05 to 2922.20, 2852.58, 2852.46 and 2852.43 cm⁻¹ after Cu²⁺ , Zn²⁺, Pb²⁺ and Ni²⁺ions biosorption. The assigned bands of the carboxylic, amine groups and alkynes or nitriles vibrations also shifted on biosorption. The shift in the frequency showed that there was biosorption of Cu²⁺, Zn²⁺, Pb²⁺ and Ni²⁺ ions on the *L. cylindrica* biosorbent and the carboxylic and amine groups were involved in the sorption of the Cu²⁺ , Zn²⁺, Pb²⁺ and Ni²⁺ions.

Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study
207

Adsorption kinetic study is important in treatment of aqueous effluents as it provides valuable information on the reaction pathways and in the mechanism of adsorption reactions.

In this study nonlinear kinetic equations were preferred to the linear equations, since there are always errors associated with linearization (Mohan et al., 2005; Kumar, 2007; Kumar, 2007). Therefore large errors in kinetic and equilibrium parameters could be obtained, if a not suitable linear equation is utilized (Mohan et al., 2005; Kumar, 2007; Kumar, 2007). In addition, the nonlinear kinetic equations have successfully been employed to obtain these adsorption parameters with excellent accuracy for different adsorbates and adsorbents (Kumar, 2007; Kumar, 2007; Arenas et al., 2007; Jacques, et al., 2007; Jacques, et al., 2007; Lima et al., 2007; Lima et al., 2008).

The kinetic study carried out showed that the sorption was best described by all the models used. The experimental data for all the metal ions studied fitted very well to the Pseudo-second order model then followed by Pseudo-first order, Avrami, Elovich and Intra-particle diffusion models. This was shown in Table 5. It was observed that Pb^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+}ions had regression values (r^2) for Pseudo-second-order as 0.9997, 0.9977, 0.9883 and 0.9666 respectively. Both Pseudo first order, Pseudo-second order and Avrami models had values higher than that of Elovich and Intra-particle diffusion models which had a values of 0.7401, 0.7933, 0.6989 and 0.9752 for Zn^{2+}, Cu^{2+} , Pb^{2+} and Ni^{2+}ions respectively. Thus it can be concluded that sorption kinetics using *Luffa cylindrica* seed and sponge mixture as biosorbent followed the Pseud-first-order, Pseudo-second-order and Avrami kinetic models. Hence, the pseudo-second-order model is better in explaining the observed rate. This suggests that sorption of the metal ions involve two species, in this case, the metal ion and the biomass (Herrero et al., 2008). These results are in accordance with similar researches carried out (Ho et al., 2004; Kumar et al., 2006; Lodi et al., 1998) with several natural sorbents.

The time profile for the various metal ions studied on *L. cylindrica* is presented in Figure 5. The rate of Zn^{2+}, Cu^{2+}, Pb^{2+} and Ni^{2+}ions removal was rapid in the first 20 minutes and it decreased progressively afterwards. It was observed that the biosorption process reached equilibrium after 120 minutes.

The observed fast biosorption kinetics was consistent with the biosorption of metal involving non-energy mediated reactions, where metal removal from solutions is due purely to physico-chemical interactions between biomass and metal solution. This fast metal uptake from solution indicates that binding might have resulted from interaction with functional groups on the cell wall of the biosorbent rather than diffusion through the cell wall of the biomass this is in agreement with results that have been reported in many studies using different biosorbents on the uptake of different heavy metals (Kumar et al., 2006; Pan et al., 2006; Bueno et al., 2008).

The fitting of data to Redlich-Peterson, Sips, Langmuir and Freundlich isotherms suggest that biosorption of Pb (II) ions onto the biosorbent could be explained by Redlich-Peterson isotherm with correlation coefficient of 0.8218 as outlined in Table 6. The biosorption of Zn (II) ions onto the biosorbent could be explained by all the isotherms studied with correlation coefficients of 0.8576, 0.9212, 0.9212 and 0.9539 for Langmuir, Freundlich, Sips and Redlich-Peterson isotherms respectively. The biosorption of Ni (II) ions onto the biosorbent could be explained by Freudlich, Sips and Redlich-Peterson isotherms with correlation coefficients of

0.9231, 0.9231 and 0.9632 respectively. The biosorption of Cu (II) ions could be explained by Redlich-Peterson isotherm with the correlation coefficient of 0.7449. Because experimental q_e values were lower than that of Q_{max}, considering the reported approaches in the literature (Hall et al., 1996; Ozer and Ozer, 2003), it may be suggested that biosorption takes place as monolayer phenomena and that *L. cylindrica* biomass was not fully covered by the metal ions.

4. Conclusion

The removal of metal ions from aqueous solution is of importance both environmentally and for water re-use. The *Luffa cylindrica* seeds and sponge mixture has been presented here as a good alternative biosorbent for Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} ions removal from aqueous solution. This biosorbent has the ability to sorb the Ni^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} ions at the solid/liquid interface, when the sample were suspended in water at a pH of 5.0 and a contacting time of 2h to saturate the available sites located on the biosorbent surface. Out of the five kinetic models used to adjust the sorption, the best fit was the Pseudo-second order model and for the isotherm the best fit was Redlich-Peterson isotherm for Ni (II) ion biosorption onto *L. cylindrica* seeds and sponge mixture biosorbent.

5. References

Abdel-Ghani, N. T., Ahmad K. H., El-Chaghaby, G. A. and Lima, E. C. (2009). Factorial experimental design for biosorption of iron and zinc using Typha domingensis phytomass. Desalination 249: 343–347.

Arenas, L. T., Lima, E. C., dos Santos Jr., A. A., Vaghetti, J. C. P., Costa, T. M. H., Benvenutti, E.V. (2007). Use of statistical design of experiments to evaluate the sorption capacity of 1,4-diazoniabicycle[2. 2. 2] Octane/silica chloride for Cr (VI) adsorption, Colloid Surf. A. 297, pp. 240–248.

Arenas, L. T., Vaghetti, J. C. P. Moro, C. C. Lima, E. C. Benvenutti, E. V. Costa, T. M. H. (2004). Dabco/silica sol–gel hybrid material. The influence of the morphology on the $CdCl^2$ adsorption capacity, Mater. Lett. 58, pp. 895–898.

Ayoob, S. Gupta, A. K. Bhakat, P. B. Bhat, V. T. (2008). Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules, Chem. Eng. J. 140, 6–14.

Babel, S., Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97, 219–243.

Bal K. J., Hari B. K. C., Radha K., Ghale G. M., Bhuwon R.S., Madhusudan P.U.(2004) Descriptors for Sponge Gourd [*Luffa cylindrica* (L.) Roem.], NARC, LIBIRD & IPGRI.

Basil JL, Ev RR, Milcharek CD, Martins LC, Pavan FA, dos Santos, Jr. AA, Dias SLP, Dupont J, Noreña CPZ, Lima EC (2006). Statistical Design of Experiments as a tool for optimizing the batch conditions to Cr (VI) biosorption on *Araucaria angustifolia* wastes. J Hazard Mater; 133: 143-153.

Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study

209

Bueno, B. Y. M., Torem, M. L., Molina, F., de Mesquita, L. M. S. (2008).Biosorption of lead(II), Chromium(III) and copper(II) by R. opacus: Eqilibrium and kinetic studies. Miner.Eng. 21, 65-75.

Cimino, G., Passerini, A. and Toscano, G., (2000). Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell. Water Res., 34 (11), 2955-2962.

David, W. O. and Norman, H. N. (1986). Principles of Modern Chemistry. Saunders Golden Sunburts Series Printed by the Dryden Press. 383 Madison Avenue, New York. N. Y.10017. USA.

Freundlich, H. M. F. (1906). Über die adsorption in lösungen, Zeitschrift für Physikalische Chemie (Leipzig) 57A, 385–470.

Goyal, P., Sharma, P., Srivastava, S, Srivastava, M. M. (2008). *Saraca indica* leaf powder for decontamination of Pb: removal, recovery, adsorbent characterization and equilibrium modeling, International Journal of Enviornmental Science and Technology, Vol. 5, No. 1, pp. 27-34.

Gupta, N., Prasad, M., Singhal, N. and Kumar, V. (2009). Modeling the Adsorption Kinetics of Divalent Metal Ions onto Pyrophyllite Using the Integral Method. Ind. Eng. Chem. Res., 48 (4), 2125-2128.

Graeme, K. and Pollack C., Jr (1998). Heavy metal toxicity, Part I: Lead and metal fume fever. Journal of Emergency Medicine, Volume 16, Issue 2, Pages 171-177.

Hall, K. R. Egleton, L. C. Acrivos, A., Vemeulen, T. (1966). Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. Ind. Eng. Chem. Fund. 5, 212-223.

Hamoudi, S., Kaliaguine, S.(2003). Sulfonic acid-functionalized periodic mesoporous organosilica. Micropor. Mesopor. Mater. 59, p. 195-204.

Herrero, R. Lodeiro, P. Rojo, R. Ciorba, A. Rodriguez, P. Sastre deVicente, M.E.(2008). The efficiency of the red alga Mastocarpus stellanua for remediation of cadmium pollution. Bioresour. Technol. 99, 4138-4146.

Ho, Y. S., Chui, W. T., Hsu, C. Huang, C. (2004). Sorption of lead ions from aqueous solution using tree fern as a sorbent. Hydrometallurgy. 73, 55-61.

Ho Y. S., Huang C. T. Huang H.W. (2002).Equilibrium sorption isotherm for metal ions on tree fern.Process Biochemistry 37, 1421-1430.

Ho, Y. S., Mckay, G. M. (1999). Pseudo-second order model for sorption process, Proc. Biochem. 34,451–465.

Jacques, R. A., Bernardi, R., Caovila, M., Lima, E. C., Pavan, F. A., Vaghetti, J. C. P., Airoldi, C. (2007). Removal of Cu(II) Fe(III) and Cr(III) from aqueous solution by aniline grafted silica gel, Sep. Sci. Technol. 42, pp. 591–609.

Jacques, R. A., Lima, E.C., Dias, S.L.P., Mazzocato, A.C., Pavan, F.A. (2007).Yellow passion fruit shell as biosorbent to remove Cr(III) and Pb(II) from aqueous solution, Sep. Purif. Technol. 57, pp. 193–198.

Jolley, O. D., O'Brien, G. and Morrison, J. (2003).Evolution of Chemical Contaminant and Toxicology Studies, Part 1 - An Overview, South Pacific Journal of Natural Science, Vol 21, 1-5.

King, P., Rakesh, N., Beenalahari,Y., Kumar, Y.P., Prasad, V.S.R.K. (2007). Removal of lead from aqueous solution using *Syzygium cumini L.*: Equilibrium and Kinetic studies. J. Harzad. Mater. 142: 340 – 347.

Klen, M. R. F., Ferri, P., Martins, T. D., Tavares, C. R. G. and Silva, E. A. (2007) Equilibrium study of the binary mixture of cadmium–zinc ions biosorption by the *Sargassum filipendula* species using adsorption isothermsmodels and neural network, Biochem. Eng. J. 34,136–146.

Kumar, K. V. (2007). Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, Dyes Pigment 74, pp. 595–597.

Kumar, K. V. (2007). Pseudo-second order models for the adsorption of safranin onto activated carbon: comparison of linear and non-linear regression methods, J. Hazard. Mater. 142, pp. 564–567.

Kumar, Y. P, King, P. Prasad, V.S. (2006). Equilibrium and kinetic studies for the biosorption system of copper(II) ion from aqueous solution using *Tectona grandis* L. f. leaves powder, J. Hazard. Mater. 137, 1211-1217.

Kuyucak, N.; Volesky, B. In Biosorption of Heavy Metals; Volesky, B., ed.; CRC Press: Boca Raton, FL, 1990, pp. 173-198.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40, 1361–1403.

Largegren, S, (1898). About the theory of so-called adsorption of soluble substances, Kungliga Suensk Vetenskapsakademiens Handlingar 241,1–39.

Life Extension. Heavy metal toxicity.
http://www.lef.org/protocols/prtcls-txt/t-prtcl-156.html.
Assessed on the 7th of November, 2009.

Lima, E. C., Royer, B., Vaghetti, J. C. P., Brasil, J. L., Simon, N. M., dos Santos Jr., A. A., Pavan, F. A., Dias, S. L. P., Benvenutti, E. V. and da Silva, E. A. (2007). Adsorption of Cu (II) on *Araucaria angustifolia*wastes: determination of the optimal conditions by statistic designof experiments, J. Hazard. Mater. 140, 211–220.

Lima, E. C., Royer, B., Vaghetti, J. C. P., Simon, N. M., da Cunha, B. M., Pavan, F. A., Benvenutti, E. V., Veses, R. C., Airoldi, C. (2008). Application of Brazilian-pine fruit coat as a biosorbent to removal of reactive red 194 textile dye from aqueous solution. Kinetics and equilibrium study, J. Hazard. Mater. 155, pp. 536 – 550.

Lodi, A., Solisio, C., Converti, A. Borghi, M. (1998). Cadmium, zinc, copper, silver and chromium (III) removal from wastewaters by *Sphaerotilus natans*. Bioprocess Biosyst. Eng. 19, 197-203.

Lopes, E. C. N. dos Anjos, F. S. C. Vieira, E. F. S. Cestari, A. R. (2003). An alternative Avrami equation to evaluate kinetic parameters of the interaction of Hg (II) with thin chitosan membranes, J. Colloid Interface Sci. 263 , 542–547.

Marshall, W. E. and Champagne, T. E. (1995). Agricultural Byproducts as Adsorbents for Metal ions in Laboratory Prepared Solutions and in Manufacturing Wastewater, Journal of Environmental Science and Health, Part A: Environmental Science and Engineering. Vol. 30, No. 2, 241 – 261.

Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals
from Aqueous Solutions - Kinetic and Equilibrium Study
211

Martins, B. L., Cruz, C. C. V., Luna, A. S. and Henriques, C. A. (2006). Sorption and desorption of Pb^{2+} ions by dead *Sargassum* sp. biomass, Biochem. Eng. J. 27, 310 - 314.

Mazali I. O. Alves O. L. (2005). Morphosynthesis: high fidelity inorganic replica of the fibrous network of loofa sponge (*Luffa cylindrica*). Anais da Academia Brasileira de Ciências, Vol. 77, No. 1, p. 25-31.

Mohan, D., Singh, K. P., Singh, V. K. (2005). Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind. Eng. Chem. Res. 44, 1027–1042.

Ozer, A., Ozer, D. (2003).Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats. J. Harzad. Mater. 100: 219-229.

Pan, J., Ge, X., Liu, R., Tang, G.H. (2006). Characteristic features of Bacillus cereus cell surfaces with biosorption of Pb (II) ions by AFM and FT-IR. Colloids Surf., B. 52, 89-95.

Passos, C. G. Lima, E. C. Arenas, L. T. Simon, N. M. da Cunha, B. M. Brasil, J. L. Costa, T. M. H. Benvenutti, E. V. (2008). Use of 7-amine-4-azahepthylsilica and 10-amine- 4-azadecylsilica xerogels as adsorbent for Pb (II). Kinetic and equilibrium study, Colloids Surf. A .316, pp. 297–306.

Passos, C. G. Ribaski, F., Simon, N. M., dos Santos Jr., A. A., Vaghetti, J. C. P., Benvenutti, E. V. , Lima, E. C. (2006). Use of statistical design of experiments to evaluate the sorption capacity of 7-amine-4-azahepthylsilica and 10-amine- 4-azadecylsilica for Cu (II) Pb (II) and Fe (III) adsorption, J. Colloid Interface Sci. 302, pp. 396–407.

Pavia, D. L., Lampman, G. M., Kriz, G. S. (1996). Introduction to Spectroscopy, 2nd edn., Saunders Golden Sunburst Series, New York.

Rakesh N., Kalpana P., Naidu T. V. R and Venkateswara Rao M. (2010). Removal of Zinc Ions from Aqueous Solution by Ficus Benghalensis L.: Equilibrium and Kinetic Studies. International Journal of Engineering Studies. Volume 2, Number 1, pp. 15–28.

Redlich, O., Peterson, D.L. (1959). A useful adsorption isotherm, J. Phys. Chem. 63, 1024–1027.

Rowell R. M., James S. H., Jeffrey S. R. (2002). Characterization and factors effecting fibre properties, In Frollini E, Leao, AL, Mattoso LHC, (ed.), Natural polymers and agrofibres based composites. Embrapa Instrumentacao Agropecuaria, San Carlos, Brazil pp.115-134.

Santhy, K. and Selvapathy, P., (2004). Removal of heavy metals from wastewater by adsorption of coir pith activated carbon. Sep. Sci. Technol., 39 (14), 3331- 3351.

Sherrod, P. NLREG version 6.5 (Demonstration) copyright © 1992-2008.

Singh, S., Verma, L. S., Sambi, S. S., Sharma, S. K.. Adsorption Behaviour of Ni (II) from Water onto Zeolite X: Kinetics and Equilibrium Studies. Proceedings of the World Congress on Engineering and Computer Science 2008(WCECS 2008), October 22 - 24, 2008, San Francisco, USA.

Sips, R. (1948). On the structure of a catalyst surface, J. Chem. Phys. 16, 490–495.

Tumin, N. D., Chuah, A. L., Zawani, Z., Abdul Rashid, S. (2008). Adsorption of Copper from aqueous solution by *Elais guineensis* kernel activated carbon. Journal of Engineering Science and Technology Vol. 3, No. 2, 180 – 189.

Vaghetti, J. C. P. Zat, M., Bentes, K. R. S., Ferreira, L. S., Benvenutti, E. V., Lima, E. C. (2003). 4-Phenylenediaminepropylsilica xerogel as a sorbent for copper determination in waters by slurry-sampling ETAAS, J. Anal. Atom. Spectrom. 18, pp. 376–380.

Weber Jr. W. J., Morris, J. C. (1963). Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civil Eng. 89, 31–59.

Waste Water - Treatment and Reutilization

Edited by Prof. Fernando Sebastián GarcÃa Einschlag

The steady increase in industrialization, urbanization and enormous population growth are leading to production of huge quantities of wastewaters that may frequently cause environmental hazards. This makes waste water treatment and waste water reduction very important issues. The book offers a collection of studies and findings concerning waste water treatment, minimization and reuse.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Innocent O. Oboh, Emmanuel O. Aluyor and Thomas O. K. Audu (2011). Application of Luffa Cylindrica in Natural form as Biosorbent to Removal of Divalent Metals from Aqueous Solutions - Kinetic and Equilibrium Study, Waste Water - Treatment and Reutilization, Prof. Fernando Sebastián GarcÃa Einschlag (Ed.), ISBN: 978-953-307-249-4, InTech, Available from: http://www.intechopen.com/books/waste-water-treatment-and-reutilization/application-of-luffa-cylindrica-in-natural-form-as-biosorbent-to-removal-of-divalent-metals-from-aqu

INTECH
open science | open minds