ISSN 0126-2807

Journal of Applied Sciences in Environmental Sanitation

Volume 6, Number 3: 269-277, September, 2011
© T2011 Department of Environmental Engineering
Sepuluh Nopember Institute of Technology, Surabaya
& Indonesian Society of Sanitary and Environmental Engineers, Jakarta
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International peer-reviewed journal

Research Paper

BIOSORPTION OF AQUEOUS SOLUTIONS OF LEAD ON *XYLOPIA AETHIOPICA* (ETHIOPIAN PEPPER)

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Received: 18th April 2011; Revised: 10th June 2011; Accepted: 10th June 2011

Abstract: The biosorption of Pb on *Xylopia aethiopica* was studied at 25°C. The effect of pH on the biosorption of heavy metal Pb was studied. It was found that increase in pH increases the biosorption of Pb by *Xylopia aethiopica*. The maximum uptake capacity for Pb is 7.69 mg g^{-1}. The biosorption isotherm of *Xylopia aethiopica* was determined. The Langmuir and Freundlich models give good fit (R^2 = 0.99 and R^2 = 1.00 respectively).The values of $1/n$ is 0.97 for the adsorbate, Pb, which indicate favourable biosorption. The results of this study indicate the possibilities that exist in the clean-up of the environment with the use of natural resources.

Keywords: Lead, *Xylopia aethiopica*, Freundlich isotherm, Langmuir isotherm

INTRODUCTION

The deleterious effect of heavy metals on the environment cannot be over–emphasized. Metals such as Cd, Hg, Pb, Cr, Ni, Cu, Zn, and Co are, at elevated concentrations, detrimental to human health and ecosystem stability [1]. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations [2, 3].

Heavy metal pollution of the environment may come from industrial sources such as metal plating, electroplating, mining, ceramic, batteries, pigment manufacture and automobile [4,5,6]. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings [7]. Some of the methods used in the removal of heavy metals are the following: chemical oxidation or reduction, evaporative recovery, incomplete removal of metals, chemical precipitation as sulphides and hydroxides, lime coagulation, ion exchange, reverse osmosis, chemical precipitation and filtration, and pre-concentration. These methods have several disadvantages including high-energy requirements, incomplete removal of metals and high capital investment and running costs [8]. Thus there is need for the development of methods that are not only cost effective but can also be easily implemented [9].

Biosorption by inexpensive biomaterials promises to be an excellent alternative. Biosorption is an emerging and cost effective method that uses biological materials to remove metals from solution through biosorption. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [10]. 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 nutrient requirement, regeneration of biosorbent and the possibility of metal recovery [11].

Some biosorbents used included materials such as cork and yohimbe bark wastes [12], *Rhizopus nigricans* [13], duck weed *Wolffia globosa* [14], lignocellulosic substrate extracted from wheat bran [15], wheat shell [16], rice bran [17], shelled *Moringa oleifera* Lamarck seed powder [18], Okra [19], rice husk and modified rice husk [20], Coir [1], *Enteromorpha prolifera* [6], *Scenedesmus quadricauda* [21] and barley straw [22].

*Xylopia aethiopica (*Ethopian pepper) is an evergreen aromatic tree, growing up to 20 m high. The pods are opened and discarded while the peppers removed from it are kept for consumption. The aim of this study was to evaluate the efficiency of *Xylopia aethiopica* pod powder as a biosorbent in the removal of heavy metal (Pb).

MATERIALS AND METHODS

Sample preparation

The *Xylopia aethiopica* pods were obtained from a local market in Nigeria. It was then washed with distilled water and dried for a period of 4 weeks. It was grinded using mortar and pestle. *Xylopia aethiopica was* sieved with a 2mm seive and kept in a clean plastic bottle.

Effect of pH

The effect of pH on the biosorption of Pb was carried out within the range that would not be influenced by the metal precipitated [23]. The effect of pH on biosorption of heavy metals by *Xylopia aethiopica was* carried out by preparing 50mg l^{-1} solution of Pb.

The solutions were conditioned in the pH range 2 - 7 using aqueous solutions of 1M HCl and 1M NaOH in order to determine the maximum experimental pH at which adsorption will occur. The pH was determined using Jenway pH meter (3505). The Erlenmeyer flasks containing the mixture were left in a shaker (Stuart Orbital Shaker SSL1) for 12 h at 25^{o}C. The *Xylopia aethiopica* was removed from the solution by filtration and the residual Pb concentrations in the solution were analyzed using atomic absorption spectrophotometer (Perkin – Elemer AAS3110). Subsequent biosorption studies were performed at pH 7.

Batch equilibrium studies

Biosorption isotherms were performed in a set of Erlenmeyer flasks (250 ml) where solutions of Pb (200 ml) with different initial concentrations (50–200 mgl^{-1}) were placed in these flasks. Equal mass of 0.1 g of *Xylopia aethiopica* prepared from *Xylopia aethiopica* pods was added to Pb solutions and kept in an isothermal shaker (25± 1°C) for 12 h to reach equilibrium of the solid-solution mixture. Similar procedure was followed for another set of Erlenmeyer flask containing the same metal concentration without *Xylopia aethiopica* to be used as a blank. The pH was adjusted to 7 by adding either few drops of diluted hydrochloric acid or sodium hydroxide (1M). The flasks were then removed from the shaker. The samples were filtered using Whatman 540 mm filter paper prior to analysis in order to minimise interference of the *Xylopia aethiopica* fines with the analysis. The concentration of Pb in the supernatant solution after and before biosorption was determined using an atomic absorption spectrophotometer (Perkin – Elemer AAS3110). Each experiment was duplicated under identical conditions. The amount of biosorption at equilibrium, q_e (mg g^{-1}), was calculated by

$$q_e = \frac{(C_o - C_e)}{W} V \qquad (1)$$

where C_o is the initial metal ion concentration (mg/l) and C_e is the residual metal ion concentration in solution at equilibrium (mg/l), V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Effect of solution pH on biosorption

The pH of the system controls the biosorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of the lead ions in solutions. In the present work, biosorption of Pb on *Xylopia aethiopica* was studied over the pH range of 2 – 7 at constant Pb concentrations of 50mg/l.

The effect of pH on the biosorption at equilibrium of both Pb is presented in Fig.1. The percentage Pb biosorbed increases from pH 2-4 and then became almost constant at pH 4 to 6. It then increases sharply from pH 6 to 7. *Xylopia aethiopica* biosorbed Pb at pH range 2-7.This result confirms the earlier report that the biosorption of metal is pH-dependent [23]. If the initial pH was too high, lead ions precipitate out and this defeats the purpose of employing the biosorption process. The result suggests that maximum biosorption was obtained at pH 7. Consequently, all the other experiments were carried out at pH 7. At low pH the biosorption capacity for all metal ions is low, because large quantity of hydrogen ions competes with metal ions at sorption sites. As the pH increases more negatively charged cell surface become available thus enhancing greater metal uptake [24]. Thus initial pH would play an important role in the removal of Pb and Ni from aqueous solution using *Xylopia aethiopica* . Similar results were obtained in the biosorption of Pb by Okra [19].The maximum adsorption capacity for Pb occurred at pH 5.0 for *Penicillum simplicissimum* [25], pH 3.6 for algae *Gellidium* [26] and pH 4.0 for Gram negative capsulated and noncapsulated bacteria [27].

Biosorption isotherms

One of the important physicochemical aspects for the evaluation of the biosorption process as a unit operation is the equilibria of the biosorption. Equilibrium studies give the capacity of the adsorbent [28].

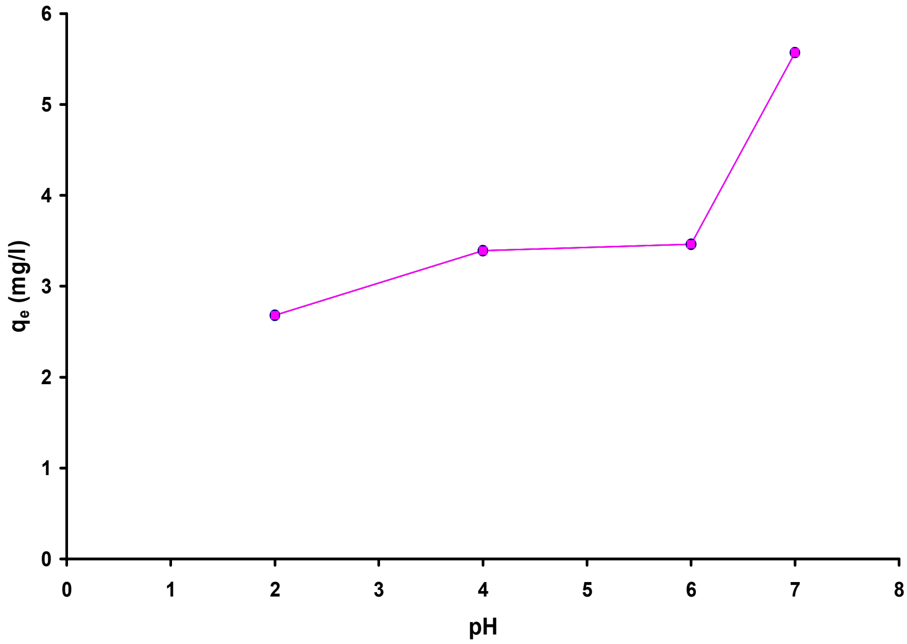

Fig. 1: The effect of pH on equilibrium of Pb ions biosorption capacity on *Xylopia aethiopica* at 25°C and initial metal concentration of $50 mgl^{-1}$.

The biosorption isotherm indicates how the biosorption molecules distribute between the liquid phase and the solid phase when the biosorption process reaches an equilibrium state [29]. The analysis of equilibrium biosorption data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purposes [30]. Biosorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich [31,32]. The Langmuir isotherm assumes monolayer biosorption onto a surface containing a finite number of biosorption sites of uniform strategies of biosorption with no transmigration of adsorbate in the plane of surface [33]. The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [33]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Langmuir isotherm. The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \qquad (2)$$

where C_e is the equilibrium concentration of the adsorbate (Pb) (mg/l), q_e, the amount of adsorbate biosorbed per unit mass of adsorbent ($mg\ g^{-1}$), and Q_o and b are Langmuir constants related to monolayer biosorption capacity and affinity of biosorbent towards adsorbate, respectively. When C_e/q_e was plotted against C_e, straight line with slope $1/Q_o$ was obtained (Fig. 2), indicating that the biosorption of heavy metal (Pb) on *Xylopia aethiopica* follows the Langmuir isotherm. The Langmuir constants 'b' and 'Q_o' were calculated from this isotherm and their values are given in Table 1. From Fig. 2 the Langmuir isotherm fitted well for Pb (R^2= 0.99).

Table 1 Langmuir and Freundlich isotherm for lead biosorption on *Xylopia aethiopica* at 25°C

Langmuir isotherm	*Pb*
Q_o(mg/g)	7.69
b (l/mg)	0.096
R^2	0.99
R_L	0.018
Freundlich isotherm	
k_f(mg/g)	0.74
$\frac{1}{n}$ (l/mg)	0.97
R^2	1.00

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of *Xylopia aethiopica* surface, i.e. each molecule of *Xylopia aethiopica* has equal biosorption activation energy. The results also demonstrate the formation of monolayer coverage of Pb molecules at the outer surface of *Xylopia aethiopica* .

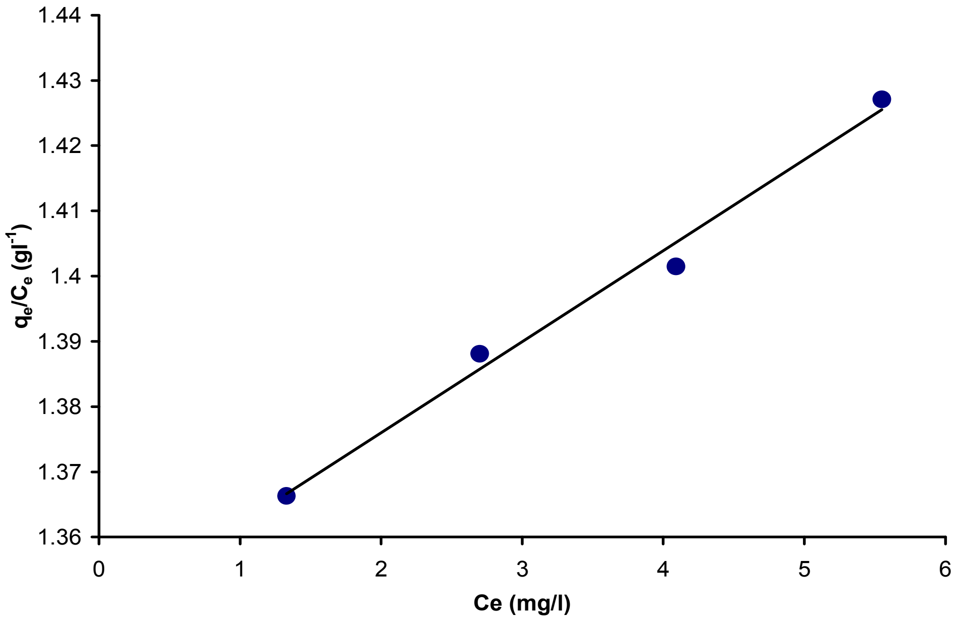

Fig. 2: Langmuir isotherm for the sorption of Pb on *Xylopia aethiopica at 25°C*

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) described by Weber and Chakkravorti [34], which is defined by:

$$R_L = \frac{1}{(1 + bC_o)} \qquad (3)$$

where b is the Langmuir constant and C_o the highest metal concentration (mg l^{-1}).The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$) favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found to be 0.018 for Pb respectively. This confirmed that *Xylopia aethiopica* is favourable for biosorption of Pb under conditions used in this study.

Freundlich isotherm. The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

where q_e is the amount biosorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (Pb) and K_f and n are Freundlich constants where n gives an indication of how favourable; where n gives an indication of how favourable the biosorption process is and K_f is the biosorption capacity of the adsorbent, *Xylopia aethiopica*. K_f can be defined as the biosorption or distribution coefficient and represents the quantity of Pb biosorbed onto biosorbent for a unit equilibrium concentration. The slope $1/n$ ranging between 0 and 1 is a measure of biosorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [30]. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is indicative of cooperative biosorption [33].

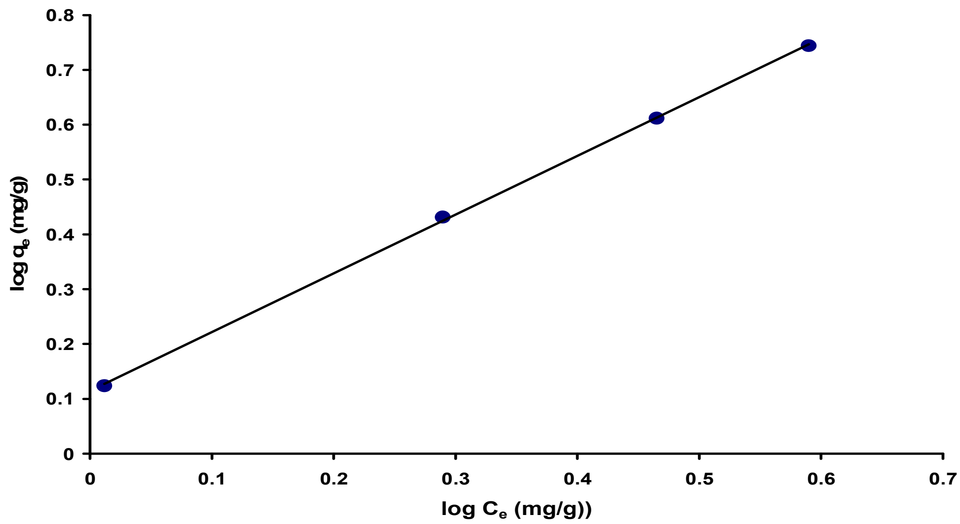

Fig. 3: Freundlich isotherm for the sorption of Pb on *Xylopia aethiopica* at 25°C.

The plot of log q_e versus log C_e gives straight lines with slope '$1/n$' (Fig.3), which shows that the biosorption of heavy metal, Pb, also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_f and n) were calculated and recorded in Table 1. Table 1 shows the values of the parameters of the two isotherms and the related correlation coefficients. As seen from Table1, The Langmuir ($R^2 = 0.99$) and Freundlich ($R^2 = 1.00$) models give a good fit. As also illustrated in Table 1, the value of $1/n$ is 0.97 for the adsorbate, Pb, which indicates favourable biosorption [35]. The maximum uptake capacity of *Xylopia aethiopica* is 7.69 mg/g for Pb.

Table 2 shows the comparison of the uptake capacities of *Xylopia aethiopica* with other biosorbents for lead.This differences in maximum biosorption capacity of *Xylopia aethiopica* and that of others could be due to the differences in the functional groups present in the various biosorbents, differences in particle size as well as differences in temperature and pH at which maximum biosorption occurred [22].

Table 2: Comparison of the maximum monolayer adsorption of lead on various adsorbents

Adsorbents	Maximum monolayer adsorption capacity (mg g^{-1}) Pb	Temperature (^oC)	Reference
Xylopia aethiopica	7.69	25	This study
Phaeodactylum spp.	1.49	-	[36]
Porphyridium spp.	0.32	-	[36]
Sagassum spp.	1.16*	21	[37]
Fucus vesiculosus	1.02*	-	[38]

* Adsorption capacity in mmol/g

CONCLUSION

The biosorption of Pb on *Xylopia aethiopica at 25^oC* was studied. It has been considered that this biosorbent has acceptable biosorption capacity towards the investigated metal ion. The pH of the aqueous solution strongly affects the biosorption capacity. *Xylopia aethiopica* biosorbed Pb at pH range 2-7.It was concluded that the biosorption was favoured by an increase of pH to an experimental value of 7. The biosorption isotherms were used for a mathematical description of biosorption of metal ions onto *Xylopia aethiopica.* The Langmuir (R^2 = 0.99) and Freundlich (R^2 = 1.00) models give good fits. The results of this study indicate the possibilities that exist in the clean-up of the environment with the use of natural resources.

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