Journal of Scientific and Innovative Research 2015; 4(5): 218-220
Available online at: www.jsirjournal.com

Research Article

ISSN 2320-4818
JSIR 2015; 4(5): 218-220

Received: 29-10-2015
Accepted: 24-11-2015

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Biosorption for lead (II) ions from aqueous solutions by the biomass of *Spyridia filamentosa* algal species found in Indian Ocean

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Abstract

Biosorption of heavy metals is an efficient cost effective method for removal of heavy metal ions from industrial wastewater. Studies have shown that algal species biomasses have high uptake of heavy metal ions. In this research, an adsorption property of *Spyridia filamentosa* algal species was studied on the basis of equilibrium isotherms and kinetics from batch experiments. It was found that biosorption capacities were pH dependent. The maximum adsorption capacity was found to be at 0.86 mmol/g at pH of 5. It was observed that biosorption kinetics was first within the first 30 minutes before equilibrium was obtained. The effect of light metal ions was found not to significantly affect uptake of lead (II) ions. It was as well found that *Spyridia filamentosa* biomass could purify 2.1, 1.1, 0.7 and 0.5 liters when the feed concentrations were 0.5, 1.0, 2.0 and 4.0 mM, respectively of lead (II) before breakthrough was reached. This study illustrated that that biomass of *Spyridia filamentosa* is a good biosorbent for treatment of lead (II) contained in industrial wastewater.

Keywords: Biosorption, Lead (II), Algae, *Spyridia filamentosa*, Wastewater treatment.

INTRODUCTION

Industrialization is directly related to environmental pollution with toxic metals like copper, cadmium, lead and others [1]. These metals are dangerous owing to their toxicity and non-biodegradability [2]. The undesirable effects of these heavy metal pollution can be avoided by treatment prior to discharge in the environment. This protects the environment and guarantees the quality of public health [3]. The most common methods of removal of heavy metals are: chemical precipitation, evaporation, adsorption and ion exchange. These methods are only good in situations where the concentration so heavy metals are very high however they are unsuitable in low concentrations of heavy metals this makes them expensive to apply [4]. In order to provide an alternative low cost solution to diffuse pollution problems, several biological technologies have been investigated for the removal of pollutants from waste water and biosorption has emerged as the most efficient and cost effective method for removal of toxic metals from contaminated wastewaters [3]. Biosorption is based on ability of biological materials to remove heavy metals from solutions due to their metal binding capacities by means of ion exchange, electrostatic force and precipitation [5]. In this research paper, we look at biosorption of lead (II) ions from aqueous solution by treated biomass of *Spyridia filamentosa*. The biomass was treated with a two-stage process of thermal and chemical modification. The study showed that the biomass can accumulate high amount of lead (II) from aqueous solutions and it is a suitable biosorbent for recovery of lead (II) ions.

Materials and Methods

Algea, *Spyridia filamentosa* were collected along the Tanzanian coastal areas of Indian Ocean mainly Dar es Salaam. Samples were sun dried and ground. Treatment of the algal biomass was done as follows: 20 g of algal biomass was treated with 0.2 M $CaCl_2$ solution (500 ml) for 24 hours stirring at 200 rpm. The solution pH was kept constant at pH 5.0 by using 0.1M HNO_3 or 0.1M NaOH solution when fluctuations were observed. Calcium treated biomass was washed repeatedly with distilled water in order to remove excess calcium from the algal biomass. The biomass was then heated in an oven at 60 °C for 24 hours and sieved to obtain particle size of 200–500 µm.

Adsorption Isotherm: Series of 200 ml glass vials were prepared containing lead nitrate solutions of known concentrations. 200 mg of algal biomass were added to each vial and the mixtures agitated for 24 h. The solution pH was adjusted to the required value by using 0.1M HNO_3 or 0.1M NaOH. The algal biomass was removed by using a 0.45 µm filter paper and the filtrates was analyzed for lead (II) by atomic absorption spectrometry.

Adsorption Kinetics: 1 g of algal biomass was placed in a beaker containing 500 ml of solution and agitated at 200 rpm. Samples of 1ml each were drawn from the mixture at different time intervals for analysis. The pH of the solution was as well monitored continuously adjusted with 0.1M HNO_3 or 0.1M NaOH solution whenever deviations were detected.

Fixed-bed experiments: 1g of algal biomass was packed in a glass column of 1cm in diameter. Solutions of lead (II) were pumped through the column of 1cm in diameter. Solutions of lead (II) were pumped through the column at a flow-rate of 1.5 ml/min using a pump. Effluent samples were collected for every bed volume of 6.6ml and subsequently analyzed for lead (II) concentration by using atomic absorption spectrometry.

RESULTS AND DISCUSSION

Effect of pH on Pb (II) adsorption

The amount of Pb (II) uptake increased with increase in pH, the sharpest increase was observed between pH 3 and 4. This trend continued upto pH of 5 when a plateau was reached. These results showed strong pH dependence of Pb (II) biosorption.

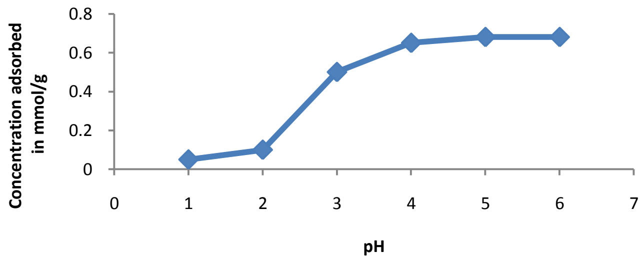

Figure 1: Amount of Pb (II) adsorbed by *Spyridia filamentosa* biomass at different pH (Dosage: 2 g/L, Concentration: 2 mM)

Studies have shown that solution pH affects biosorption of heavy metal ions. The predominant sorption of lead is Pb^{+2} and $PbOH^{+}$ which normally occurs between 4.0 to 5.5 this is the reason for sharp increase in pH observed. At pH higher than7.0 sorption recovery is reduced due to precipitation of Pb^{+2} [6].

Adsorption isotherms

The Langmuir adsorption model as in equation below was used to correlate the isotherm data obtained at constant solution pH values.

$$q = \frac{bQ_{max}\, c}{1+bc} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

Where: q is the amount of Pb (II) adsorbed at equilibrium (mmol/g), c is the Pb (II) ion concentration in solution (mM) at equilibrium, Q is the maximum adsorption capacity and b is an affinity constant. In order to determine the equilibrium parameters in the above equation can be written into a linearised form as follows:

$$\frac{c}{q} = \frac{1}{Q_{max}\, b} + \frac{c}{Q_{max}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

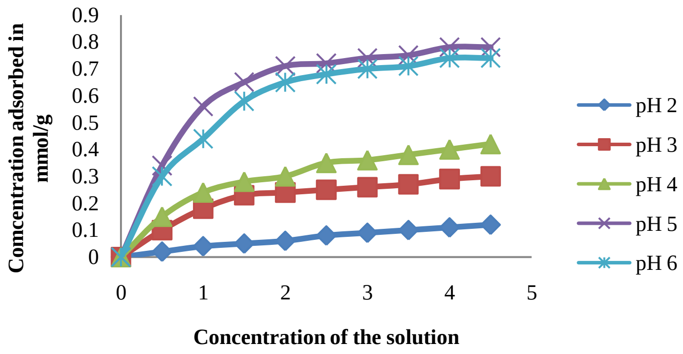

Figure 2: Adsorption isotherm of Pb (II) on to biomass of *Spyridia filamentosa* at different concentration of the bulk solution using Langmuir model (Dosage: 2 g/L, Concentration: 2 mM)

It was observed that the adsorption isotherm plots had a typical shape of L-2 isotherms, indicating a reduction in the number of active sites on the adsorbents at a high residual heavy metal concentration in the solution phase [7].

Table 1: Coefficient of sorption isotherm of Pb (II) removal by *Spyridia filamentosa*

pH	Q_{max} (mmol/g)	b	r^2
2	0.15	6.42	0.99
3	0.41	7.02	0.98
4	0.63	7.77	0.99
5	0.86	8.06	0.99
6	0.82	7.94	0.97

The parameters in linearised Langmuir equation were obtained by using a least square linear regression analysis on each set of isotherm data and presented in Table 1. The adsorption capacity Q increases with the increase in solution pH. The adsorption capacity of *Spyridia filamentosa* was found to be 0.86 mmol/g with was relatively high when compared with other adsorbents [8].

Adsorption Kinetics

Studies of kinetics of Pb (II) adsorption onto the biomass of *Spyridia filamentosa* at different initial concentrations showed that about 90% of the total soluble Pb (II) was removed from solutions within 30 min of agitation. Afterwards, no significant adsorption uptake was observed beyond, figure 3.

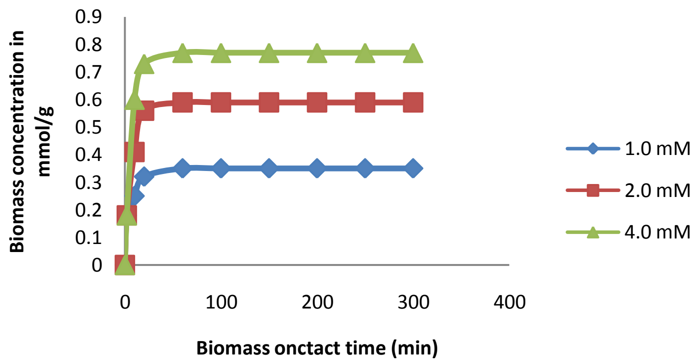

Figure 3: Adsorption kinetics of Pb (II) on *Spyridia filamentosa* biomas at different initial concentration (Dosage: 2 g/L, Agitation rate: 200 rpm and pH 5)

The possible explanation to this observation was the driving force for adsorption. The concentration difference between the bulk solution and the biomas of *Spyridia filamentosa* was high at first; this resulted to higher sorption rate. Afterwards, sorption was slowed due to slower diffusion of solute into interior of *Spyridia filamentosa* biomass [9].

Effects of light metal ions

The effect of the presence of Ca^{+2},Mg^{+2}, Na^{+} and K^{+} ions in the solution on the Pb (II) uptake was investigated, figure 4. Concentration of 10 mM of the light metal ions was used to study the effect.

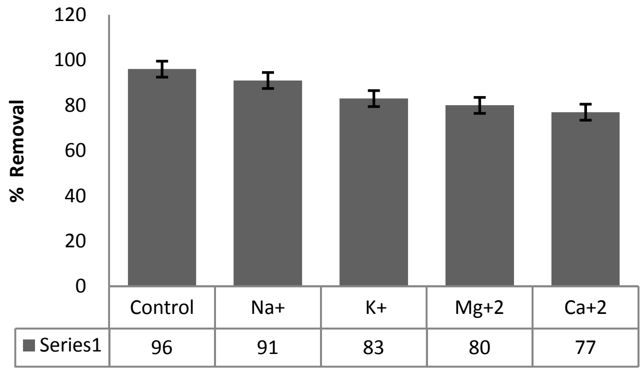

Figure 4: Removal efficiency of *Spyridia filamentosa* in the presence of light metal ions (Pb (II) concentration: 2 mM, Dosage: 2 g/L, pH: 5)

As it is in the figure above, the effect of Na^{+}, K^{+}, Mg^{+2} and Ca^{+2} reduced the removal efficiency of Pb (II) between 5% to 19% at a concentration of 10 mM. This is a significant advantage over the commercially available ion exchange resins as the binding of Ca^{+2} and Mg^{+2} to these resins often significantly reduces their efficiencies.

Fixed-bed breakthrough curves

Fixed-bed breakthrough curves at different feed concentrations of Pb (II) were done to illustrate the suitability of column operations, figure 5.

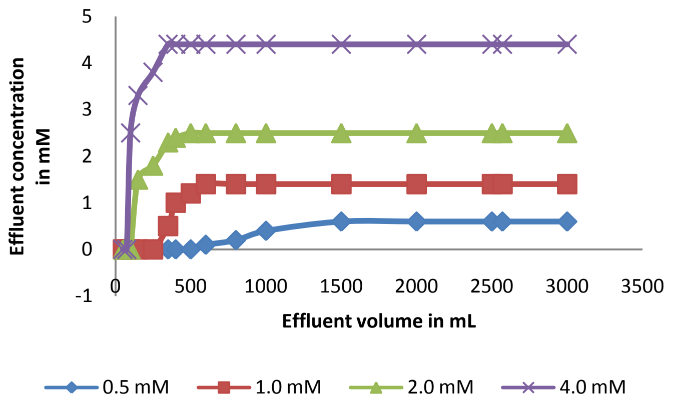

Figure 5: Fixed-bed breakthrough curves for Pb (II) removal by *Spyridia filamentosa* with different concentrations. (Experimental conditions, Dosage: 2 g, bed volume: 6.6 mL, flow rate: 1.5 mL/min)

The breakthrough curves showed S-shaped curve for column operation with favorable adsorption isotherms. It was found that adsorption column containing 1g of *Spyridia filamentosa* biomass could purify 2.1 liter of 0.5 mM lead solution before breakthrough, and it purified 1.1, 0.7 and 0.5 liter of the solutions when the feed concentrations were 1.0, 2.0 and 4.0 mM, respectively. The total uptake capacities of the fixed-bed for the different initial concentration were calculated by integrating the breakthrough curves between the breakthrough and saturation point. The adsorption capacities of column for various initial concentrations ranged between 0.76 to 0.88 mmol/g, this agreed well with the maximum value of 0.86 obtained from batch experiments.

CONCLUSIONS

The study indicated that the treated biomass of *Spyridia filamentosa* could be used as an efficient biosorbent material for the treatment of lead (II) ions bearing wastewater streams. It was found that the adsorption capacities were pH dependent. The maximum adsorption capacity was obtained to be 0.86 mmol/g at a solution pH of about 5. The kinetics of adsorption was rapid within 30 minutes. It was also observed that presence of light metals did not significantly interfere with the binding of lead (II) ions and it was established that the biomass can be used in fixed-bed operations.

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