Use of Alginate-*Moringa oleifera* Beads on Cu (II) and Cd (II) Adsorption from Aquatic Systems

Monalisa Franco, Jesus Beltran-Heredia, and Jose Euclides Stipp Paterniani

Abstract—**In this paper, we present the results of Cu (II) and Cd (II) removal by alginate immobilized *Moringa oleifera* beads. The beads were separated in two fractions, dried and soaked ones. Equilibrium and kinetic experiments were conducted to determine maximum adsorption capacity under various experimental conditions. A sorption capacity of 67.0 mg.g^{-1} was obtained using 10 units of dried beads on 20 mg.L^{-1} Cu (II) and of 60.0 mg.g^{-1} was obtained using 15 units of dried beads on 23 mg.L^{-1} Cd (II). In conclusion, alginated – *Moringa oleifera* beads show to be an efficient adsorbent on aquatic system, with more than 90% of efficiency of removal. And biosorbent regeneration demonstrated to be efficient and maintained its adsorption capacity for seven cycles.**

Index Terms—**Adsorption, heavy metals, natural coagulant, *Moringa oleifera.***

I. INTRODUCTION

Biosorption is a process that provides the removal of metal ions by living or dead biomass as an option for the chemical products that are used on this process. Moreover, the use of natural compounds represents a potentially cost effective way of treatment of heavy metals from aquatic systems

Lots of biosorbents have been tested, including fungal biomass, bacteria, water hyacinth, agricultural waste, aquatic weeds and other biomaterials [1].

Among these products we can find lots of paper that describes the use of *Moringa oleifera* on the process of metal uptake [1]-[4].

The seeds of *Moringa oleifera* are normally used for turbidity removal, in the mean time they have been recognized as a promising low-cost adsorbent for the removal of heavy-metal ions. Much of the work on the *Moringa oleifera* has been centered on the use of the powdered form of the seeds on the metal removal [2]-[5].

The use of the seeds in powdered form presents some difficulties associated with separation of biomass after adsorption, mass loss after regeneration and small particle size which make it difficult to use in column applications.

Therefore, modification of raw biomass can improve the sorption capacity. The modification can be achieved by physical processes (including autoclaving, steam and thermal drying), chemical processes (pretreatment with acid, alkali or other chemicals) and chemical entrapment of the biomass to form membranes, beads, pellets or granular biosorbents [6].

As an option, Alginate has been applied in preparation of beads for biosorption. The idea is entrap the biomass and prevent its loss while substrates and products are allowed to pass through the support material [7]. Alginate is a polyelectrolyte material commonly present in gel form. It possesses properties such as a relatively inert aqueous environment, encapsulation process free of solvents, ability to control the porosity with single coating, procedures to make a favorable matrix for entrapment of organic and inorganic compounds [8].

The metal removal by alginate immobilized *Moringa oleifera* beads is an improvement of powdered form application of *Moringa oleifera* seeds.

To study the use of these beads we tested equilibrium, kinetic sorption of alginate-*Moringa oleifera* beads for Cu (II) and Cd (II) adsorption and biosorbent regeneration.

Adsorption isotherms are studied by varying the adsorbent dosage for a fixed metal concentration or by varying the metal concentration for fixed adsorbent dose. And they are used to estimate the adsorption capacity of the biosorbent. Langmuir and Freundlich isotherm models are commonly used on the metal biosorption by Moringa oleifera seeds.

The kinetic study describes the adsorbate uptake over the time. So is possible to decide the minimum residence time of the adsorbate in the solid-liquid interface and reactor dimensions [9]. On this study, Lagergren, Ho and Elovich were used as kinetics models to identify the mechanism reaction of biosorption process.

The main objective of this study was to investigate the effectiveness of M. oleifera seed for the removal of Copper and Cadmium.

It is part of the effort to use low-cost natural materials in order to make treatment systems more affordable, particularly in developing countries.

II. MATERIAL AND METHODS

A. Moringa Oleifera Treatment

Moringa oleifera seeds were collect in Campinas State University, Campinas, São Paulo, Brazil. They were sent to Extremadura University and maintained at room temperature until used.

At the time of using, shelled seeds were crushed by a domestic blender. The powder was sieved at fraction of 0.5 mm and stored in closed flask at room temperature.

B. Preparation of Alginate – Moringa Oleifera Beads

The procedure was based on a method used by reference [10]-[11]. A 2% polymer solution was prepared by dissolving 0.5 g of sodium alginate in 25 ml of deionised water and then

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agitated for 24 hours at 300 rpm to make a homogenous polymer solvent mixture. 0.25 g of biomass powder was then blended with 25 ml of 10% w/v sodium alginate solution to make beads.

Spherical beads were prepared by dropping the mixed solution into a 0.1 M calcium chloride solution. Beads were formed by drop-wise gravity from a pipette. The beads were hardened by placing them in 2% calcium chloride solution for 24 hours.

Then the beads were washed in distilled water by agitation at 100 rpm in a beaker for 30 min, discarding the solution, and then repeating the process 3 times.

After removing residual water with paper towels, the beads were separated in two fractions: one of them was maintained soaked in distilled water (named seeds C) and the second fraction was dried gradually at room temperature (named as seeds A). Both were then used for further experiments.

C. Equilibrium Adsorption

In all sets of experiments a fixed volume of metal ion solution, 50mL was added to pre determinated units of beads in 250 mL flasks at 20 ±℃.

The mixtures were then agitated at 100 rpm for 24 hours to ensure that equilibrium was attained. The metal solution was collected and analyzed for Cu and Cd by spectrophotometric method.

Equilibrium data was collected from 5 ppm, 7 ppm, 20 ppm and 25 ppm initial concentration of Cu and Cd. The number of beads varied from 5 beads to 35 beads.

Adsorption capacity was calculated using Equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where: V is the volume of metal in solution (L), C_o and C_e are the initial and equilibrium concentrations respectively (m g.L^{-1}), m is the weight of the biomass used, q_e is the amount of metal ions sorbed per gram of biomass (mg.g^{-1}).

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for designing purposes. In order to investigate the sorption isotherm, this study used two models: Langmuir and Freundlich.

Langmuir and Frendlich plots were drawn for the experimental data of the amount of Cd (II) and Cu (II) biosorbed per unit mass (mg.g^{-1}) versus equilibrium solution concentration of Cu (II) and Cd (II)

The theoretical Langmuir isotherm is often used to describe sorption of a solute from a liquid solution as:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \tag{2}$$

where Ce is the equilibrium solute concentration (mg.L^{-1}); qe is the amount of metal ion sorbed (mg.g^{-1}); qm is qe for a complete monolayer (mg g^{-1}); K_l is sorption constant (L.mg^{-1}).

The Freundlich isotherm assumption is that different sites with several adsorption energies are involved in adsorption, described as:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F (mg.g^{-1}) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption respectively.

D. Kinetics of Adsorption

In all sets of experiments a fixed volume of metal ion solution, 50 mL was added to 35 units of beads in 250 mL flasks at 20 ±℃. The mixtures were then agitated at 100 rpm. To check on the variation of concentration with time, 1 mL of metal solution were sub-sampled at 15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min, 240 min, 300 min, 330 min and 1440 min respectively. The same procedure was repeated for both metals – Cu^{+2} and Cd^{+2}.

Adsorption capacity at time t was calculated using Equation (2):

$$q_t = \frac{(C_o - C_t)V}{m} \tag{4}$$

where C_t is the concentration of metal (aq) at time t (mg.L^{-1}).

The kinetics of the alginate-*Moringa oleifera* beads and metal ion interactions was tested with different kinetic models including Lagergren (pseudo-first order), Ho (pseudo-second-order) and Elovich models.

The pseudo-first order kinetic model equation is written as equation (5)

$$q = q_e - q_e e^{-K_l t} \tag{5}$$

where K_l is a Lagergren constant known as speed constant; q_e is the amount of metal ions sorbed per gram of biomass (mg.g^{-1}) in equilibrium; q is the concentration of metal (mg.g^{-1}) at time t (min).

The equation (6) presents the pseudo-second-order kinetic model equation:

$$q = \frac{t}{\frac{1}{K_h q_e^2} + \frac{t}{q_e}} \tag{6}$$

In (6), q_e is the maximum adsorption capacity (mg.g^{-1}) and K_h (g. mg^{-1}.min^{-1}) is the adsorption rate constant of pseudo-second order.

The Elovich model is written as equation (7):

$$q = \frac{1}{\beta_e}\ln(\alpha_e . \beta_e) + \frac{1}{\beta_e}\ln t \tag{7}$$

where α_e is the speed of adsorption (mg.g^{-1}.min^{-1}); β_e is the constant of desorption (g.mg^{-1}); t is time (min).

E. Biosorbent Regeneration

To investigate the effect of regeneration of Alginate – *Moringa oleifera* beads 0.1 M calcium chloride acidified to pH 3 was used. The beads were stirred for 24 hours and then washed with 10 mL of distilled water The sorption capacity for each cycle was then noted for 7 regeneration cycles.

F. Metal Concentration Analysis

Metal concentration analysis was carried out by a spectrophotometric method. 1mL of sample was put into a 25-mL flask. 5mL of borate buffer (sodium borate and sodium carbonate in equal quantities, pH 10) and 2mL of 4-(2-pyridyl-azo)-resorcinol (PAR) were added, and mixture were diluted to the mark with water. Then the solution was mixed and after 20min absorbance at 505nm in a 1-cm optical glass cell was measured. Calibration was prepared with appropriate standards [12].

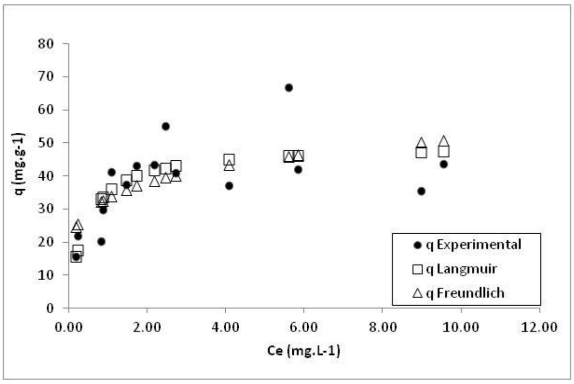

Fig. 1. Application of Langmuir and Frendlich models on Cu (II) removal with dried beads.

III. RESULTS AND DISCUSSION

A. Isotherm Models

The isotherm studies were carried out for 24h of contact time. We studied this process by varying the adsorbent dosage for a fixed metal concentration. Experimental data obtained for Cu (II) adsorption by dried Alginate – *Moringa oleifera* beads (A) were evaluated using the Langmuir and Freundlich models and the adsorption parameters present R^2 as 0.84 and 0.79 for Langmuir and Freundich models, respectively. For soaked Alginate – *Moringa oleifera* beads (C), these results were 0.86 for Langmuir model and 0.91 for Freundlich model. For Cu (II) the maximum adsorption capacity was 67.7 $mg.g^{-1}$ using dried beads. The use of soaked beads for its high weight promoted less adsorption capacity, around 1.4 $mg.g^{-1}$.

Adsorption isotherm data for Cd (II) using A beads are shown on Fig. 1. The values of R^2 are 0.97 for Langmuir and 0.98 for Freundlich model. For C, the soaked beads, Langmuir model present R^2 as 0.89 and Freundlich model present r 0.90. The maximum adsorption capacity for Cd (II) was 60 $mg.g^{-1}$ when dried beads were tested. When soaked beads were used this value was around 1.4 $mg.g^{-1}$.

This results show to be slightly better than the values presented by [13]. The authors used alginate (dried beads) from *L. digitata* without *M. oleifera* and the adsorption capacity presented was 55 $mg.g^{-1}$ for equilibrium concentration around 20 – 25$mg.L^{-1}$ for Cu (II) and Cd (II) in metal binding experiments.

B. Kinetic Models

Kinetic studies were carried out for initial metal concentration of 25$mg.L^{-1}$ and contact time of 24h using dried and soaked beads.

The results indicate that about 50% of the adsorption occurred in the first two hours

As the Fig. 3 shows, for Cu (II) the kinetic of soaked beads is faster than the kinetic of dried ones. However after 24 hours dried beads present greater efficiency of removal, 90%, while soaked present 85%. With dried beads the final amount of Cu (II) was around 2.6 $mg.L^{-1}$, the final amount with soaked beads were 3.8 $mg.L^{-1}$.

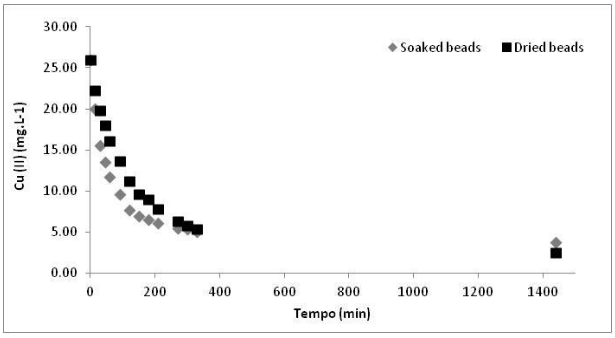

Fig. 3. Kinetics of Cu (II) with dried and soaked beads.

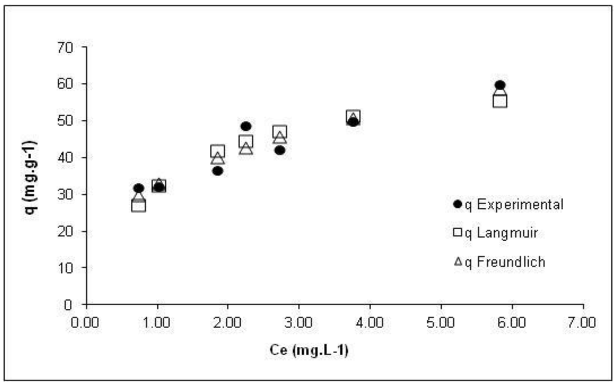

Fig. 2. Application of Langmuir and Frendlich models on Cd (II) removal with dried beads.

The same behavior was presented by kinetics studies of Cd: kinetic of soaked beads is faster than the kinetic of dried ones and after 24 hours, dried beads present greater efficiency of removal. With dried beads the final amount of Cd (II) was around 1.0 $mg.L^{-1}$ (96% of removal), the final amount with soaked beads were 1.6 $mg.L^{-1}$ (93% of removal).

Based on the value of R^2, it can be stated that the data fit best to the Ho models. The Table I presents the values of R^2 of Lagergren, Ho and Elovich on the removal of Cd (II) and Cu (II). The Fig. 2 confirms that the data fit best to the Ho models.

TABLE I: KINETIC PARAMETER "R" OF KINETICS MODELS APPLICATION FOR CADMIUM (II) REMOVAL WITH DRIED AND SOAKED BEADS

	Lagergren		**Ho**		**Elovich**	
	Cu	**Cd**	**Cu**	**Cd**	**Cu**	**Cd**
Dried beads	0.995	0.993	0.998	0.999	0.974	0.984
Soaked Beads	0.989	0.993	0.998	0.999	0.938	0.900

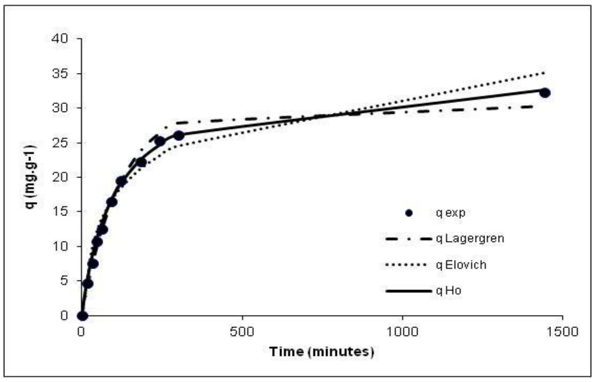

Fig. 4. Application of Lagergren, ho and Elovich models on Cd (II) removal with 35 units of dried beads.

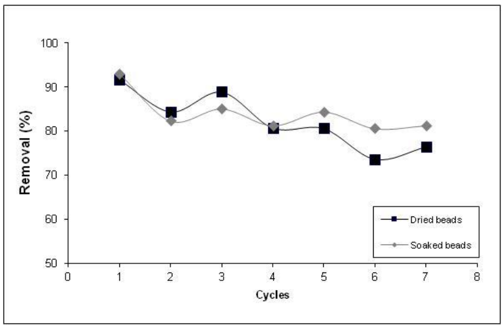

Fig. 5. Adsorption efficiency from regeneration beads for Cu (II) – dried and soaked beads.

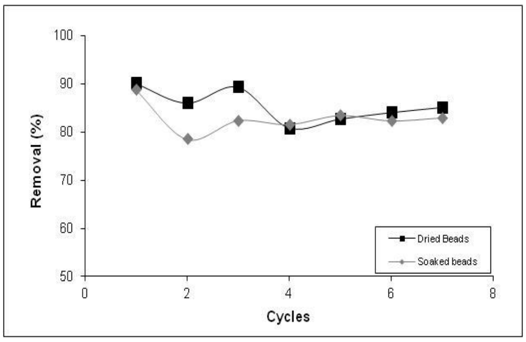

Fig. 6. Adsorption efficiency from regeneration beads for Cd (II) – dried and soaked beads

TABLE II: VARIATION OF SORPTION CAPACITY AFTER DESORPTION CYCLES (g/mg)

Cycles		1	2	3	4	5	6	7
Cu	Dried Beads	30.3	27.9	29.4	26.70	26.7	25.1	26.1
	Soaked beads	1.6	1.4	1.4	1.4	1.4	1.4	1.4
Cd	Dried Beads	30.4	29.0	30.2	27.3	27.9	28.4	28.7
	Soaked beads	1.5	1.4	1.4	1.4	1.4	1.4	1.4

C. Biosorbent Regeneration

The Table II shows the results of reuse of the beads on adsorption considering bead performance in 7 regeneration cycles. The change in adsorption capacity deteriorated from the first to the second cycle in all cases. [9] comments that "the slight drop could be attributed to losses in mass of the beads as fine loosely held biomass surface during regeneration cycles".

Cu and Cd present better adsorption capacity when dried beads were used and the beads present good sorption after seven cycles after use and regeneration. However the adsorption efficiency slightly decreased from cycle to cycle. From figures 5 and 6 we can analyze that soaked beads present more constant adsorption efficiency, around 82% for Cd and Cu.

The use of 0.1 M calcium chloride acidified to pH 3 promoted a efficient beads regeneration above 90% in all cases.

IV. CONCLUSION

This paper presents a study conducted to assess the adsorption properties and capacity of dried and soaked beads form alginate-*Moringa oleifera* for Cu (II) and Cd (II)

Form this study we conclude that: Cu (II) and Cd (II) was effectively removed by both adsorbents, over 90% of removal. The isotherm models that fits best is Freundlich model. The kinetic model that fits best to the results is Ho model. The use of 0.1 M calcium chloride on regeneration process were found to be efficient desorbing agent.

However, more investigation is required on structural properties of the biosorbent, influence of pH, temperature and application in a continuous process of water treatment.

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