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Continuous Biosorption Of Arsenic By *Moringa Olefera* In A Packed Column

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Abstract: Biosorption of As (V) by *Moringa oleifera* seed powder using a batch system and a continuous upflow mode in a fixed bed column was studied. Batch adsorption experiments were performed as a function of pH, biosorbent dose, contact time, volume of the solution and initial metal concentration. The biodsorption isotherms obtained fitted well into the Freundlich and Langmuir isotherms. The dynamic removal of arsenic by powdered seed of the *Moringa oleifera* was studied in packed column. The effect of bed height (4 and 8 cm) and flow rate (2ml/min and 5 ml/min) on biosorption process was investigated and the experimental breakthrough curves were obtained. Results showed that by increasing the bed height and decreasing the flow rate, the breakthrough and exhaustion times increased. The break-through time was considered as a measure of the column performance. The maximum break-through time of 320 min was achieved at the operating condition of 2 ml/min influent flow rate and bed height of 8 cm.
Keywords- Continuous biosorption, *Moringa oleifera,* Packed column, breakthrough curves.

1. Introduction

Arsenic, the king of poisons, is known to be detrimental to human beings and animals, causing several neurological [1], dermatological [2], gastro-intestinal [3] and cardio renal diseases [4], besides the fact that it is considered to be carcinogenic [5]. The problem of high levels of arsenic in drinking water over distributed areas of the world has received lot of attention of late. Taking the case of West Bengal alone, at least 200,000 people have been poisoned by the presence of As in the tube well water they consume. In these regions the typical concentration of As is around *2000 mg/*l, while according to latest WHO standards, nothing above *10 µg/l* can be safe for human consumption.

Most commonly used techniques for removal of Arsenic in wastewaters are membrane filtration, ion exchange, solvent extraction, chemical precipitation, reverse osmosis, electro dialysis, electrocoagulatation and adsorption [6-12]. However, these methods are associated with several disadvantages such as unpredictable metal ion removal, high material costs and the generation of toxic sludge that is often more difficult to manage. Most of these conventional techniques are ineffective below dilute yet lethal concentrations of *50 µg/l.* The use of biosorbents for the removal of toxic pollutants or for the recovery of valuable resources from aqueous wastewaters is one of the most recent developments in environmental or bioresource technology [13-16]. The major advantages of this technology over conventional ones include not only its low cost, but also its high efficiency, the minimization of chemical or biological sludges, the ability to regenerate biosorbents, and the possibility of metal recovery following adsorption [16]. *Moringa oleifera* (drumstick), a cosmopolitan tropical, drought tolerant tree, available throughout the year, has been well documented for its various pharmacological importances, viz. its antihypertensive [17] analgesic [18], and anti-inflammatory effects [19]. The powdered seed of the plant *Moringa oleifera* has coagulating properties [20-21] that have been used for various aspects of water treatment such as turbidity, alkalinity, total dissolved solids and hardness.

P. Sharma et al. studied the removal and recovery of arsenic from aqueous solution using shelled *Moringa oleifera Lamarck* seed powder. The sorption was found to occur due to amino acid-arsenic interactions, as revealed by Fourier transform infrared spectrometry [22].

In the present investigation a, the performance of locally available, low-cost and ecofriendly plant biomass such as powdered seed of the *Moringa oleifera* for biosorption of Arsenic was studied. Batch adsorption experiments were performed as a function of pH, biosorbent dose, contact time, volume of the solution and initial metal concentration. In addition, the present study employed an up-flow packed column to investigate Arsenic removal as a function of bed height and flow rate.

2. Materials and Methods

2.1 Biosorbent preparation

Moringa oleifera seeds were dried in sunlight for 3 days. Drumstick seeds were washed in 70% alcohol and allowed to dry by placing in Hot Air Oven (Serwell instrument) at 55°C for 24hrs. The Seeds were powdered in mortar and pestle and sieved through 44 mm mesh (Symmetric systems and control).

2.2 Biosorption studies

Batch biosorption experiments were conducted in cleaned and labeled 250 ml Borosil Erlenmeyer flasks containing the solutions of $Na_2HAsO_4.7H_2O$ (Loba Chemi) as functions of biomass dosage (0.5–3.0 g), contact time (20–120 min),metal concentration (10–100mg/L), pH (2–4.5), and Volume of test solution(100 to 300mL). After pH adjustments, a known quantity of dried biosorbent was added and the test solutions were agitated on shaker under magnetic stirring (Remi) at a constant temperature at a constant speed of 1,000 rpm until the equilibrium conditions were reached. The suspension is allowed to settle (10 min). The residual biomass adsorbed with metal ions is filtered using Whatman 42 filter paper (Ragavendra Scientific). Filtrates are collected and subjected for metal ion estimation using atomic absorption spectroscopy (GBC Advanced scientific Instruments).The metal concentrations before and after adsorption were recorded. The percent metal sorption by the sorbent was computed using the equation: Percent Sorption = Co—Ce/Co·100, where Co and Ce are the initial and final concentration of metal ions in the solution.

2.3 Continuous Column Studies

A packed bed column made of glass with an internal diameter of 30mm and a height of 100 mm is used for the study. To enable a uniform inlet flow of the solution into the column glass beads are placed to attain a height of 1 cm. A stainless sieve followed by glass wool is provided at the bottom of the column and glass beads at the top to support the packing. A known quantity of biomass is placed in the column to yield the desired adsorbent bed height of 4cm and 8cm. Arsenic solutions of known initial concentration are fed upward inside the column by a peristaltic pump (Murhopye scientific company) to get the desired flow rates. Two such columns were prepared, two of packing height 4 cm and two others of packing height 8 cm.

3. Results and Discussion

3.1 Effect of biosorbent dosage

The efficiency of biosorbent was studied at different biosorbent dosages for the percent removal As (V). The experiments were conducted at constant initial metal concentration (25 mg/L), initial volume of solution (200ml), contact time (60min) respectively, pH (2.5) with varying biosorbent dosages (0.5–3g). With increasing of biosorbent dosage, the removal of As (V) increases. Highest uptake was observed at 2g biomass for As (V) (64.57%). Increase in As(V) removal with biosorbent dosage can be attributed to increased surface area and the availability of more biosorption sites.. However, no significant increment in the biosorption tendency was observed on further increasing the biomass dosage from 2g onwards (Fig 1).

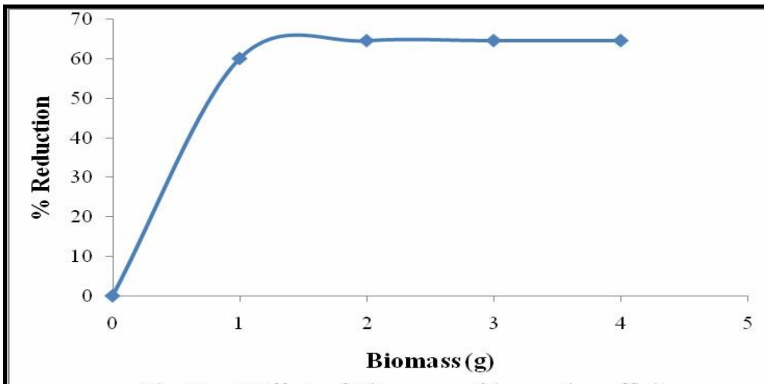


Fig No :1 Effect of Biomass on biosorption efficiency

3.2 Effect of metal concentration on biosorption

The sorption behavior of As(V) on *Moringa Oleifera* seed powder,carried out in the range of metal concentration (5– 30 µg/mL). Biosorption of As(V) on the biomass increased with increasing concentration of the metal ion reaching to an optimal level (25 µg/mL).{ 65.09%} and after that percent biosorption remained constant(Fig 2).

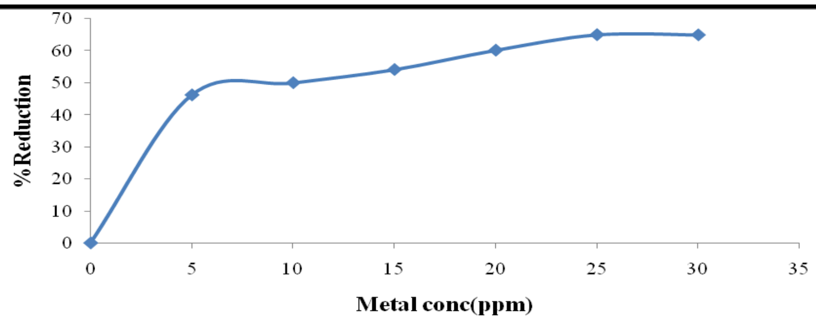


Fig No :2 Effect of on Metal conc on Reduction efficiency

3.3 Effect of pH on As(V) sorption

The percentage biosorption of As(V) ion on *Moringa Oleifera* seed powder increases as the pH of the solution increased from 2.5 to 4.5. The pH profile for the As (V) biosorption on seed powder shows that metal biosorption is a function of pH, exhibiting maximum sorption at pH 2.5(63.53%). There was no significant difference in sorption behavior with further increase in pH up to 4.5(Fig 3).

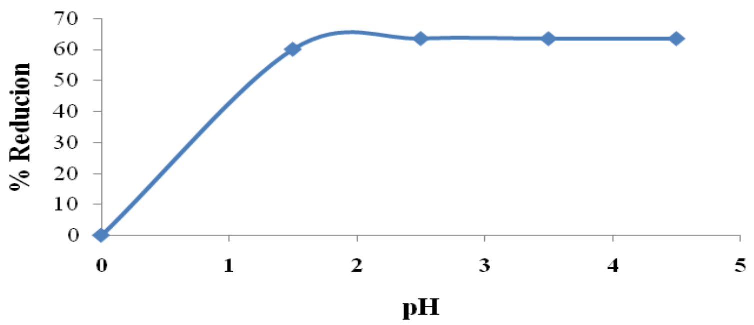


Fig No :3 Effect of pH on Reduction efficiency

3.4 Effect of volume on As(V) biosorption

Percent biosorption of As(V) on *Moringa Oleifera* seed powder was observed under similar experimental conditions in different set of volumes (100–300 mL) of the test solution. Maximum biosorption was obtained in the volume (200 mL) of the test solution. It shows that the ratio of sportive surface of the seed powder to total metal ion on availability is optimum, exhibiting maximum percentage removal (62.08%) of As(V) (Fig 4).

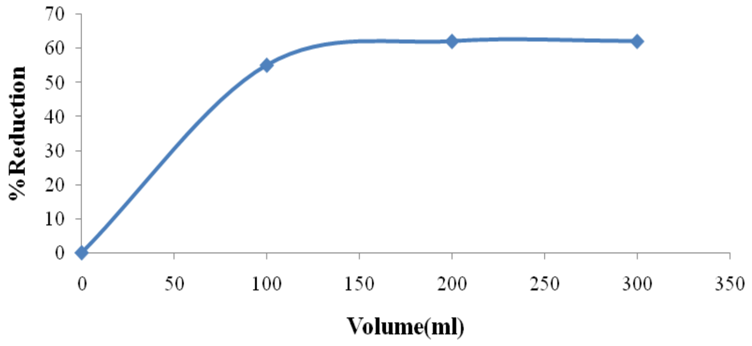


Fig No :4 Effect of Volume on biosorption efficiency

3.5 Effect of contact time

The effect of changing contact time on biosorption, while keeping the biosorbent dosage (2g), pH (2.5) and initial volume of solution (200mL). The removal As(V) by biosorbent increased with increasing contact time and attains a maximum value at 60 min (60.20%) and thereafter, it remains almost constant. After the equilibrium time, no more As(V) were removed (Fig 5).

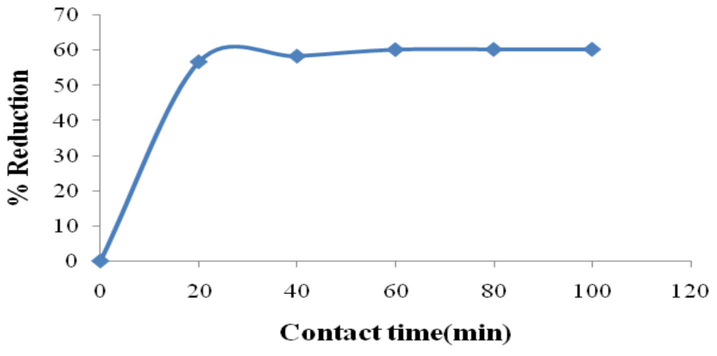


Fig No 5 : Effect of Contact time on Reduction efficiency

3.6 Adsorption Isotherm

The langmiur isotherm was applied for the adsorption equilibrium for the adsorption equilibrium of As(V) using following equation.

$$1/q_e = (1/q_{max}\, b)\, 1/C_e + (1/q_{max}) \quad (1)$$

Where q_e is the maximum sorption uptake per unit mass of adsorbent in mg/g, C_e is the equilibrium concentration of heavy metal ions in mg/L and b is the Langmuir constant of biosorption and desorption rate. q_{max} and b are Langmuir constants related to maximum uptake of the metal uptake adsorption capacity and the energy of adsorption respectively calculated from the intercept and slope of the plots and found to be q_{max} = 2.4 and b = 0.038 (Fig 6).

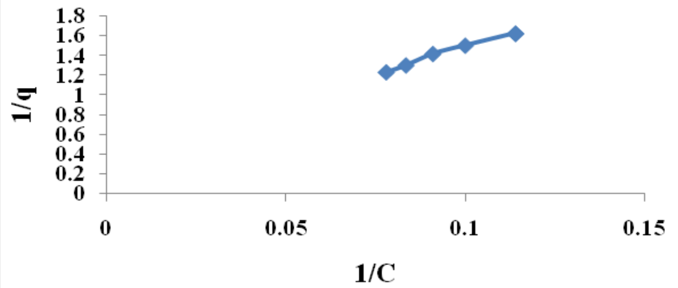


Fig No 6 : Langmuir isotherm (1/q v/s 1/C)

3.7 Freundlich Isotherm:

The linear form of the Freundlich equation is represented by

$$log\ q_e = log\ K_f + 1/n\ log\ C_e \qquad (2)$$

Where q_e is the uptake of the metal per unit weight of the biosorbent, C_e is equilibrium concentration of metal ion in solution (mg/g), K_f and n are Freundlich constants and have been calculated from intercept and slope of the plots and found to be K_f= 1.6.3 and n = 1.47 (Fig 7).

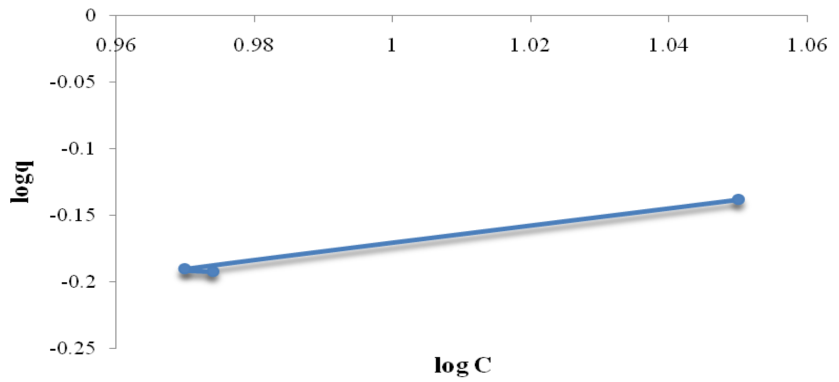


Fig 7 : Checking for conformity with Freundlich Adsorption Isotherm for Arsenic

The experimental data obtained from the batch studies were found to obey Langmuir and Freundlich Isotherm models. From the nature of the graph it is confirmed that the biosorption of the As(V) on *Moringa Oleifera* seed powder follows the Langmuir and Freundlich Isotherm models.

Column studies

3.8 Effect of flow rate on breakthrough curves

Effect of feed flow rates on breakthrough curves at bed height of 4cm and 8cm are studied. The breakthrough curves obtained exhibits the biosorbent is exhausted at a faster rate for higher flow rate irrespective of bed height (4cm and 8 cm).At a flow rate of 2ml/min of As (V) solution for bed height of 4 cm and 8 cm, it was found that the break through point was 300 and 320 min, the saturation time was around 440 and 540 min. (Fig 10 and Fig 11)

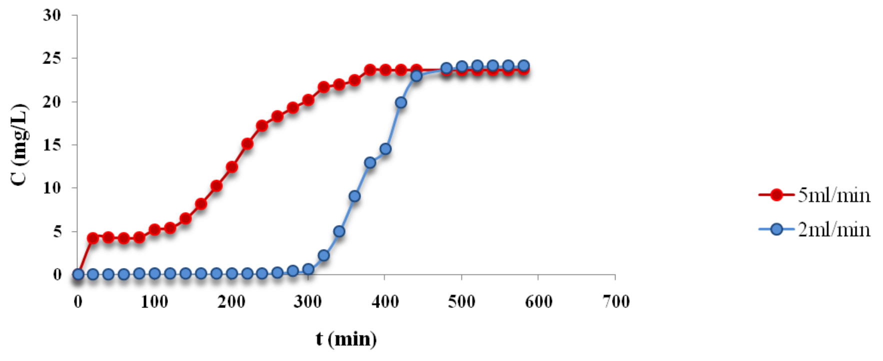


Fig 8 : Continuous column studies of Arsenic for column height 4cm (flow rate 5ml/min and 2ml/min).

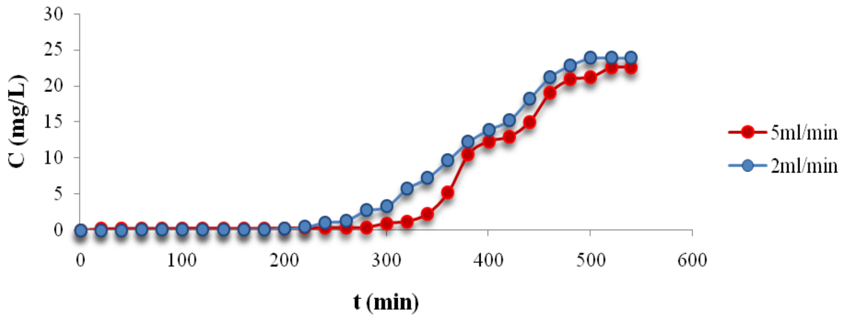


Fig 9 : Continuous column studies of Arsenic for column height 8cm (flow rate 5ml/min and 2ml/min).

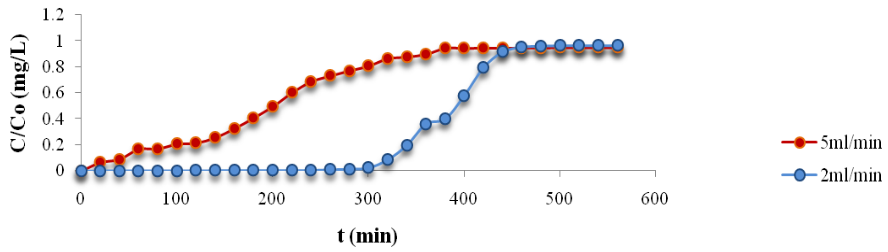
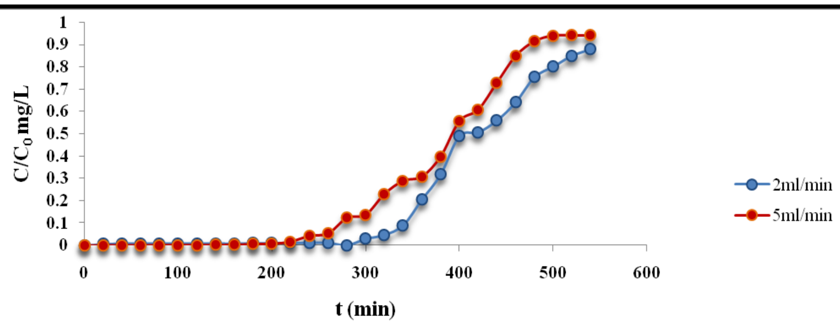


Fig 10 : Breakthrough curve of Arsenic for column height 4cm (flow rate 5ml/min and 2ml/min).



It's clear from breakthrough curves obtained, that as the flow rate increases the time of breakthrough point decreases. This is because the residence time of solute in the bed decreases. Therefore there is no enough time for biosorption equilibrium to be reached which results in lower bed utilization and the b iosorbate solution leaves the column before equilibrium.

3.9 Effects of bed height

The bed height is one of the major parameter in the design of fixed bed biosorption column. The experimental breakthrough curves obtained for different bed height of biomass (4 and 8 cm) at constant flow rate and constant initial concentration. At smaller bed height the C/Co increases more rapidly than at higher bed height. Furthermore at smaller bed height the bed is saturated in less time compared with the higher bed height It is clear that increasing bed height increases the breakthrough time and the saturation time of the As(V) solution in the bed.

4. Conclusion.

The *Moringa oleifera Lamarck* seed powder was used as biosorbent for the removal of As(V). Effects of biosorbent dosage pH, volume of solution, metal ion concentration and contact time on the biosorption of As(V) were studied. The Langmuir isotherm and Freundlich isotherms of the biosorption process were investigated. The obtained results showed that biosorbent dosage, pH, volume of solution, metal ion concentration and contact time highly affected the biosorption of As(V). Adsorption isotherms like Langmuir isotherms and Freundlich isotherms were plotted are found to be favourable. Column studies indicated that bed height and flow rate affected the biosorption characteristics of *Moringa oleifera Lamarck* seed powder, with highest bed height and lowest flow rate resulted in better metal uptake. Comparing the batch and column experiments, packed column effectively exploited the biomass metal binding capacity rather than batch mode.

Nomenclature

q_e = maximum sorption uptake per unit mass of biosorbent (mg/g).

C_e = the equilibrium concentration of heavy metal ions (mg/L).

q_{max} and b = Langmuir constants related to biosorption capacity (mg/g) and the energy of biosorption (L/mg) respectively.

Freundlich Isotherm:

q_e = The uptake of the metal per unit weight of the biosorbent (mg/g)

C_e = Equilibrium concentration of Cd(II) ion in solution (mg/L),

K_f and n = Freundlich constants related to the adsorption capacity and adsorption intensity

respectively.

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