

Removal of Pb(II) from Aqueous Solutions using *Calotropis Procera* Roots in a Fixed-Bed Column

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Abstract: The biosorption of lead was investigated with a biomass of *Calotropis procera* roots, in a fixed-bed column. The effect of operating parameters such as inlet metal ion concentration, amount of biomass packed and flow rate on the sorption characteristics of *Calotropis procera* roots was investigated. The data confirmed that the total amount of sorbed Pb(II) and equilibrium Pb(II) uptake decreased with increasing flow rate and increased with increasing inlet lead concentration, and amount of biomass packed. The breakthrough data obtained for lead was adequately described by the Thomas adsorption model. The amounts of metal adsorbed per unit weight of biosorbent were 2.83mgg⁻¹, 2.79mgg⁻¹ and 2.23mgg⁻¹ respectively. The adsorbed metal ions were easily eluted from column using 0.05N nitric acid. Results indicated that lead was efficiently recovered by the biomass.

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1. Introduction

Natural waters have been found to be contaminated with several heavy metals arising mostly from mining wastes and industrial discharges (Dönmez and Aksu, 2001; Patterson, 1977). The presence of heavy metals in the environment is of major concern because of their toxicity, bio-accumulating capacity, threat to human life and the environment (Volesky, 1994; Volesky, 1995). Heavy metals are among the conservative pollutants that are not subject to bacterial attack or other break down or degradation process and are permanent addition to the marine environment (El-Nady and Atta, 1996). As a result of this, their concentrations often exceed the permissible levels normally found in soil, water ways and sediments. Hence they can profoundly disrupt biological processes.

The discharge of heavy metals into surface waters has become a matter of concern in Pakistan over the last two decades. These contaminants are introduced into surface waters through various industrial operations (Kratochvil and Volesky, 1998).

Lead, cadmium and mercury are examples of heavy metals that have been classified as priority pollutants by the U.S Environmental Agency (U.S EPA) (Keith and Telliard, 1979).

Pb(II) is toxic metal contaminant in water. According to Pakistan standards the maximum discharge limits for Pb(II) in wastewater are

respectively 0.5mgL⁻¹. Maximum limit in drinking water is 0.05mgL⁻¹ (Jnr. Horsfall and Spiff, 2005).

As required by EPA, maximum concentration of Pb(II) in sewage sludge applied to agriculture land is 420mgL⁻¹ (Brady and Ray, 1999).

Pb(II) is a heavy metal which forms complexes with oxo-groups in enzymes to affect virtually all steps in the processes of hemoglobin synthesis and porphyrin metabolism (Ademorati, 1996). Toxic levels of Pb(II) in human beings have been associated with encephalopathy seizures and mental retardation (Schumann, 1990).

Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, matches and explosives. In order to solve the problem of heavy metals pollution in the eco system it is important to bring pragmatic solutions to the issue. The techniques presently in existence for removal of heavy metals from wastewater are relatively expensive involving either elaborate and costly equipment or high costs of operation with ultimate disposal problems (Tsoumbaris and Tsoukali-Papadopoulou, 1994; Bossrez et al., 1997). In view of these reasons, development of a more cost effective remediation process using biological system for removal of heavy metal ions from wastewater is necessary.

Biosorption or bioremediations consists of a group of applications which involve the detoxification of hazardous substances instead of transferring them from one medium to another by

means of microbes and plants. This process is characterized as less disruptive and can be often carried out on site, eliminating the need to transport the toxic materials to treatment sites (Bossrez et al., 1997).

Biomaterials previously investigated include sago waste (Quek et al., 1998), Cyanidium caldarium sunflower (Sun and Weixing, 1998), Spagnum peat moss (YU and Kaewsarn, 1999), cassava waste (Jnr. Horsfall and Spiff, 2003), Fluted pumpkin waste and *Caladium bicolor* (Jnr. Horsfall and Spiff, 2005), for the removal of metal ions from aqueous solutions.

The sorption capacity parameters obtained from a batch experiment is useful in providing information about effectiveness of metal biosorbent system. However, the data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficiently long for the attainment of equilibrium (Cloutier et al., 1985). Hence there is a need to perform equilibrium studies using column.

The objective of the present work is to adsorb Pb(II) ions from aqueous solution by *Calotropis procera* roots using fixed bed column. The important design parameters such as flow rate of fluid, bed height, concentration of metal solution have been investigated. The data obtained in column studies was used to calculate maximum solid phase concentration of metals on beads and the adsorption rate constant using the kinetic model developed by Thomas (1948). The expression by Thomas for an adsorption column is given as follows (Reynolds and Richards 1996).

$$\frac{C_e}{C_o} \approx \frac{1}{1 + \exp\left(\frac{k}{Qq_oM - C_oV}\right)}$$

Where, C_e = effluent solute concentration (mgL^{-1}); C_o = Influent solute concentration (mgL^{-1}); k = Thomas rate constant ($\text{mLmin}^{-1}\text{mg}^{-1}$); q_o = maximum solid phase concentration of solute (mgg^{-1}); M = mass of the adsorbent (g); V = throughput volume (mL); and Q = volumetric flow rate (mLmin^{-1}). The Thomas model is also applicable to the design of ion exchange columns (Reynolds and Richards, 1996). The Thomas equation constant k and q_o values can be obtained from the columns data and can be used in the design of full-scale adsorption bed. The Thomas equation was linearized and fitted to the breakthrough data to obtain k and q_o . The linearized form of Thomas equation used is as follows.

$$\log\left(\frac{C_o}{C_e} - 1\right) = \frac{kq_oM}{Q} - \frac{kC_oV}{Q}$$

2. Experimental

2.1. Prepration of biomass

Calotropis procera roots were collected from local environment of Old Kahna near Lahore. These roots were washed with distilled water to remove any soil or debris. The washed samples were oven dried at a temperature of 333K for two days. Dried roots were ground and sieved to 100 mesh sizes. This biomass was stored in air tight glass bottles to protect it from humidity.

2.2. Prepration of metal solution:

Analytical grade Pb(II) stock solution of 1000 mgL^{-1} ($\text{Fe} \pm 0.5\%$) as $(\text{PbNO}_3)_2$ in approximately 1M HNO_3 supplied by Applichem was used for the study. This was further diluted to get solutions of various known concentrations of lead.

2.3. Column studies

The sorption process was carried out in a glass column. The column was 3.5 cm internal diameter, with 0.4cm wall thickness and 15cm in height. In a typical experiment the lead solution of a known concentration was pumped in downward direction by a peristaltic pump at a fixed flow rate to the filled with known bed height of adsorbent. The particle size of adsorbent used in the experiment was 10 mesh size. The experiments were carried out to study the effect of bed height, flow rate of pollutant solution ($4\text{-}9 \text{ mL/min}$), and concentration of pollutant ($30\text{-}50 \text{ mgL}^{-1}$). The sample of metal solution from the downstream of the column was collected at different intervals of time and analyzed using flame atomic absorption spectrometer (FAAS). The samples were analyzed and collected until equilibrium was reached in the column.

3. Results and discussion:

Adsorption of lead by *Calotropis procera* roots were presented in the form of breakthrough curves. In these curves concentration ratio C/C_o was plotted against time reported that the breakthrough curve become less sharp when the mass transfer rates were decreased. Since mass transfer rates were infinite, the breakthroughs were diffused and S-shape.

3.1. Effect of amount of biosorbent packed.

Breakthrough profile of lead adsorption for different amount of biosorbent packed at a given flow rate indicates that the uptake of lead increased with increase in amount of biosorbent from 4g to 8g [Fig 1]. This was reflected from the breakthrough with a biosorbent amount of 4g; the biosorbent gets saturated early compared to other biosorbent amount. The breakthrough time was also increased with an

increase in biosorbent amount packed (Pradip and Sharma, 1991).

3.2. Effect of concentration of pollutant:

The breakthrough profiles for the adsorption of lead at different initial concentration are shown in Fig 2. Uptake of lead decreased with the increase in lead concentration of the lead solution. The biosorbent gets saturated early at high concentration (50mgL^{-1}). This implies that the breakthrough time decreased with the increase in initial lead concentration, thus showing that the acceleration in lead ion concentration reduced the metal/biosorbent ratio and the metal uptake, i.e. metal adsorption per unit of biosorbent, as long as the biosorbent was not saturated.

3.3. Effect of flow rate

When the effect of flow rate was studied, the results showed that the uptake of lead decreased with the increase in flow rate [Fig. 3]. It was also found that the biosorbent gets saturated early at higher flow rate (9 mlmin^{-1}). The breakthrough capacity of biosorbent was found to decrease with flow rate and was in agreement with the literature (Praveen and Bhatia, 1994). This behavior was due to low quantity of lead ions passing through the column thus

reducing the efficiency of metal uptake by *Calotropis procera* roots. As the volumetric throughput and velocity through the bed decrease, the depth of adsorption one decreases because there is more time for adsorption on each layer.

3.4. Thomas kinetic modeling:

The column data of adsorption of lead for different amount of biomass packed (4g, 6g and 8g) was fitted to the linearized form of the Thomas model shown in equation 2. From linearized Thomas equation plots, the k and q_0 were calculated and are shown in Table 1. The linearized equation adequately described the breakthrough data as evident from the R^2 values obtained by the model fit and correlation was found to be statistically significant (from t-test) at 95% confidence level. The amounts of metal ion adsorbed per unit weight of biosorbent for different amount of biomass packed were 2.83mgg^{-1} , 2.79mgg^{-1} and 2.23mgg^{-1} respectively. Thomas equation for different amount of biomass showed that there was a positive relationship for the data & sorption data. The q_0 for Pb(II) sorption on *Calotropis procera* roots decreased from 2.83 to 2.23mgg^{-1} with the increase in adsorbent dose. This was due to metal concentration shortage in solution at high dose rates.

Table 1: Thomas model equations for adsorption of Pb(II) onto *Calotropis procera* roots for different amount of biomass packed.

| Amount of q_0 (mg/g) biomass packed (g) | Regression equation | R^2 | $k(\text{mL/minmg})$ | |
|---|-----------------------|-------|----------------------|--------|
| 4 2.8265 | $y = 2.135 - 0.034x$ | 0.988 | 1.133 | |
| 6 2.7885 | $y = 1.766 - 0.019x$ | 0.964 | 0.633 | |
| 8 | $y = 1.858 - 0.0188x$ | 0.946 | 0.626 | 2.2260 |

Correlation was found to be statistically significant (by t-test) at 95% confidence interval.

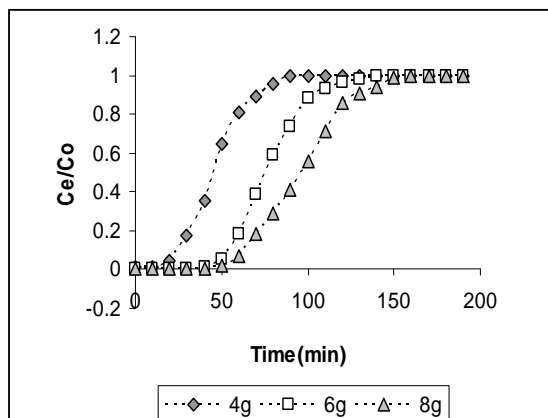


Fig 1: Breakthrough curves for Pb(II) sorption by *Calotropis procera* roots packed bed with different amount of biomass. Average flow rate 6ml/min, influent lead concentration 30mgL⁻¹.

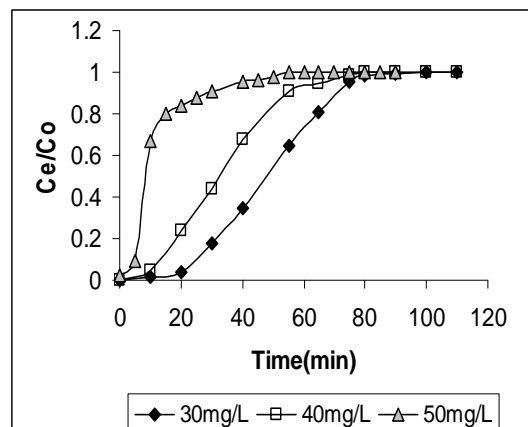


Fig 2: Breakthrough curves for Pb(II) sorption by *Calotropis procera* roots packed bed with different influent Pb(II) concentration. Average flow rate 6ml/min, biomass packed 6g.

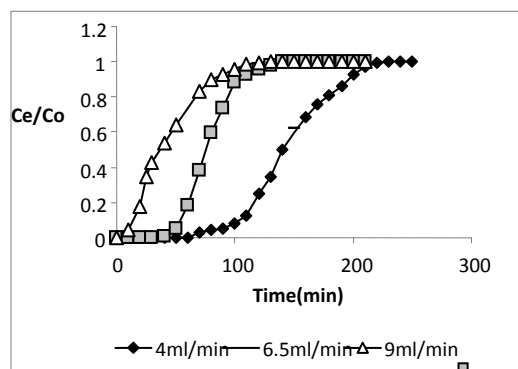


Fig3: Breakthrough curves for Pb(II) sorption by *Calotropis procera* roots packed bed at different influent flow rate. Influent Pb(II) concentration: 30mgL⁻¹, biomass packed: 6g.

Conclusion:

Calotropis procera roots can be successfully used for Pb(II) removal from aqueous Column studies showed that the adsorption of Pb(II) onto *Calotropis procera* roots depends on flow rate and inlet feed Pb(II) concentration. Process adopted is simple and economically viable.

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