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Research Article

Biosorption of Lead Ions from Aqueous Solution Using *Ficus benghalensis* L.

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Ficus benghalensis L., a plant-based material leaf powder, is used as an adsorbent for the removal of lead ions from aqueous solution using the biosorption technique. The effects of process parameters such as contact time, adsorbent size and dosage, initial lead ion concentration, and pH of the aqueous solution on bio-sorption of lead by *Ficus benghalensis* L. were studied using batch process. The Langmuir isotherm was more suitable for biosorption followed by Freundlich and Temkin isotherms with a maximum adsorption capacity of 28.63 mg/g of lead ion on the biomass of *Ficus benghalensis* L. leaves.

1. Introduction

The removal of toxic metal ions and the recovery of valuable ions from wastewaters, soils, and waters are important in economic and environmental problems. Heavy metals and other metal ions exist as contaminants in aqueous waste streams of many industries, such as tanneries and mining. Some metals associated with these activities are Pb, Hg, Cr, and Cd. Toxic metals are released into the environment in a number of ways. Coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities, and the utilization of fossil fuels are just a few examples. Some of these metals accumulate in living organisms and cause various diseases and disorders.

Heavy metals such as lead, mercury, arsenic, copper, zinc, and cadmium are highly toxic when adsorbed into the body [1]. They can cause accumulative poisoning, cancer, brain damage, and so forth. Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semipermanent brain damage in young children [2]. Lead has the ability to replace calcium in the bone to form sites for long-term release, hence, the imminent need to remove these toxic metals from waters and wastewaters. The permissible limit of lead in wastewater as set by the Environment protection Agency is 0.1 mg/L, whereas in drinking water it is 0.05 mg/L [3]. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents, and cost effectiveness [4].

Earlier studies demonstrated that the living systems could often be unreliable because of many associated problems in maintaining active microbial populations under highly variable conditions of wastewaters [5]. Therefore, some types of biomass are often chosen to serve as biosorbents to remove heavy metals [5–8]. Biosorption, a term that describes the removal of heavy metals by passive binding to nonliving biomass from an aqueous solution, is considered as an alternative to conventional methods of metal recovery from solutions. Although freely suspended biomass may have better contact with adsorbate during biosorption process, the suspended biomass is normally not the practical form for direct use in the removal of heavy metals. Since cell immobilization can enhance its stability, mechanical strength, reusability, and the ease of treatment, the process has been well used to remove toxic heavy metals [5, 9–11].

The effectiveness of biosorption for the removal of heavy metals has been shown in a number of studies. However, only

when the cost of the biosorption process can compete with the existing technologies will it be accepted commercially. Kuyucak [12] indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process. Therefore, low-cost biomass becomes a crucial factor when considering practical application of biosorption. Sari and Tuzen [13] performed biosorption characteristics of Cd(II) ions using the red alga (*Ceramium virgatum*) and found that the red alga is an effective and alternative biomass for the removal of Cd ions from aqueous solution. Anayurt et al. [14] performed equilibrium, thermodynamic, and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution using macrofungus (*Lactarius scrobiculatus*) biomass and concluded that the recovery of the metal ions from this biomass was found higher than 95% using 1 M HCl and 1 M HNO_3.

The present work investigated the potential use of untreated *Ficus benghalensis* L. biomass as metal sorbent for the removal of lead from aqueous solution. *Ficus benghalensis* L. (also known as Bodhi tree, peepul, and sacred fig) is native to southeast Asia, southwest China, India, and the Himalayan foothills. The tree is a large broadleaf evergreen tree with wide-spreading branching that grows to 60–100′ tall with trunk size as much as 9′ in diameter. This tree is semideciduous to deciduous in native monsoon climates. Tree seed (often deposited by birds) may germinate in upper tree crevices, producing dangling, nonparasitic, aerial roots that grow to the ground, root in the soil, and produce trunks. *Ficus benghalensis* L. was chosen as a biosorbent because of its availability if needed at a large scale and the relative lack of information about its sorption ability. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, adsorbent concentration, and adsorbent size were evaluated. The equilibrium adsorption data were evaluated by Langmuir, Freundlich, and Temkin isotherm models. The kinetic data were correlated by first- and second-order kinetic models.

2. Materials and Methods

2.1. Preparation of Biosorbent. The *Ficus benghalensis* L. (Indian banyan tree) leaves were collected and washed with deionized water several times to remove dirt and they were dried. The dried leaves were powdered using a domestic grinder to the particle size of 75–212 μm and used as biosorbent without any pretreatment for lead adsorption.

2.2. Chemical. $Pb(NO_3)_2$, HCl, and NaOH were of AR grade and purchased from Merck (Mumbai, Maharashtra, India). Lead ions were prepared by dissolving their corresponding nitrate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and NaOH.

2.3. Characterization of Biosorbent. The elemental analysis of the biosorbent was performed using PerkinElmer ELAN 5000 inductively coupled plasma-mass spectroscopy (ICP-MS) instrument. Surface area, pore volume, and average pore diameter of powdered biomass were measured using an ASAP 2000 Micromeritics system. The sample was degassed for 2 h under vacuum, and the BET area, pore volume, and pore diameter were determined.

2.4. Biosorption Experiments. Biosorption experiments were performed at room temperature (30 ± 1°C) in a rotary shaker at 180 rpm containing 30 mL of different lead concentrations using 250 mL Erlenmeyer flasks. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g biomass of *Ficus benghalensis* L. leaves, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (AAS) (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with 0.45 μm filter paper. The AAS was operated using air-acetylene flame at a wave length of 283.5 nm with slit width of 0.5 nm and cathode lamp current of 5 mA to determine the absorption of Pb metals. The amount of metal adsorbed by *Ficus benghalensis* L. leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = \left(C_0 - C_f\right)\frac{V}{M}, \tag{1}$$

where q is the metal uptake (mg/g); C_0 and C_f, the initial and final metal concentrations in the solution (mg/L), respectively; V, the solution volume (mL); and M, the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1 N HCl and 0.1 N NaOH. All the experiments were repeated five times, the average values have been recorded, and the statistical error was given in the figures. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

The Langmuir [15] sorption model was chosen for the estimation of maximum lead sorption by the biosorbent. This model is based on the hypothesis that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules and can be expressed as follows:

$$q = \frac{Q_{\max} b C_{\text{eq}}}{1 + bC_{\text{eq}}}, \tag{2}$$

where $Q_{\max}$ indicates the monolayer adsorption capacity of adsorbent (mg/g), and the Langmuir constant b (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as follows:

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}C_{\text{eq}}}. \tag{3}$$

The Freundlich [16] model is represented by

$$q = KC_{\text{eq}}^{1/n}, \tag{4}$$

where K (mg/g) is the Freundlich constant related to the adsorption capacity of adsorbent, and $1/n$ is the Freundlich exponent related to the adsorption intensity (dimensionless).

For fitting the experimental data, the Freundlich model was linearized as follows:

$$\ln q = \ln K + \frac{1}{n} \ln C_{\text{eq}}. \quad (5)$$

The Temkin isotherm [17] has generally been applied in the following form:

$$q = \frac{RT}{b_T} \ln \left(A_T C_{\text{eq}} \right), \quad (6)$$

where A_T (L/mg) is the Temkin isotherm energy constant, and b_T is Temkin constant related to the heat of sorption.

2.5. Biosorption Kinetics. The kinetic studies were carried out by conducting batch biosorption experiments with initial lead concentrations of 20, 40, 60, 80, and 100 mg/L. Biosorbent is separated by filtration, and the supernatant was used for analysis. Samples were taken at different time periods and analyzed for their lead concentration.

3. Results and Discussion

3.1. Characterization of the Biosorbent. Table 1 presents the elemental analysis of biosorbent *Ficus benghalensis* L. measured by ICP-MS. The biosorbent *Ficus benghalensis* L. mainly constitutes of carbon, oxygen, and hydrogen along with traces of other elements. The surface area of the biomass confirmed its porous nature. The surface area and elemental analysis of biosorbent are presented in Table 2.

3.2. Batch Biosorption Experiments. Batch biosorption experiments were carried out by varying the parameters, and the effect of contact time, pH, metal ion concentration, and the adsorbent dosage has been studied.

3.2.1. The Effect of Contact Time. The data obtained from the biosorption of lead ions on the *Ficus benghalensis* L. showed that a contact time of the 20 min was sufficient to achieve equilibrium, and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed lead concentrations at the end of 20 min were given as the equilibrium values, that is, q_e (mg/g) and C_{eq} (mg/L) (Figure 1). Other adsorption experiments were conducted at this contact time of 20 min. As shown in Figure 1, the biosorption process took place in two stages: the first rapid stage in which about 90% biosorption was achieved in 10 min, and a slower second stage, with equilibrium attained in another 5 to 10 min. During the first stage of biosorption, initial accumulation of metal takes place due to the availability of the large surface area. The penetration of metal molecules to the inner active sites of the biosorbent takes place in the second slower stage. This was confirmed as a decrease in pH was observed at the end of the experiments which might be due to the release of H^+ ions as result of ion exchange between Pb^{2+} and proton.

Table 1: Elemental analysis of biosorbent *Ficus benghalensis* L.

Element	Percentage (%)
C	49.22
O	37.85
H	8.14
N	0.98
S	0.11
Ca	0.75
Al	0.29
Na	0.22
K	0.14
Fe	0.03
Mg	0.02
Others	2.25

Table 2: Textual characteristics of biosorbent *Ficus benghalensis* L.

	BET surface area (m^2/g)	Total pore volume (cc/g)	Average pore diameter (nm)
Ficus benghalensis L.	7.21	0.07	120.7

3.2.2. Effect of pH. *Ficus benghalensis* L. presented a high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall of polysaccharides, which made it very susceptible to the influence of the pH [18]. The effect of pH on biosorption was shown in Figure 2, and it indicated that the uptake of lead increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in the literature for different biomass systems [19–21]. At pH values lower than 2.0, lead removal was inhibited possibly as a result of the competition between hydrogen and lead ions on the sorption sites. This leads to an apparent preponderance of hydrogen ions, which restricted the approach of metal cations. This can be explained by the passive transport mechanism: metal ions diffuse to the surface of biomass where they bind to active sites on the cell surface formed with various chemical groups such as carboxylate, hydroxyl, amino, and phosphate that exhibit affinity for metal ions [22]. According to the surface complexation theory, the increase in metal removal as pH increases can be explained on the basis of a decrease in the competition between proton and metal species for surface sites and by the decrease in the surface charge [19]. As the pH increased, the ligands such as carboxylate groups in *Ficus benghalensis* L. would be exposed increasing the negative charge density of the biomass surface, which in turn increased the attraction of metallic ions with positive charge, and allowing the biosorption onto the cell surface. Based on the shift of pH value in the biosorption process, it may be concluded that ion exchange was the dominant mechanism during the sorption process.

In this study, the lead cations at pH 6 (approximately) were expected to interact more strongly with the negatively-charged binding sites in the adsorbent. As a result, the optimum pH for lead adsorption was found to be 6, and hence the other adsorption experiments were performed at this pH value.

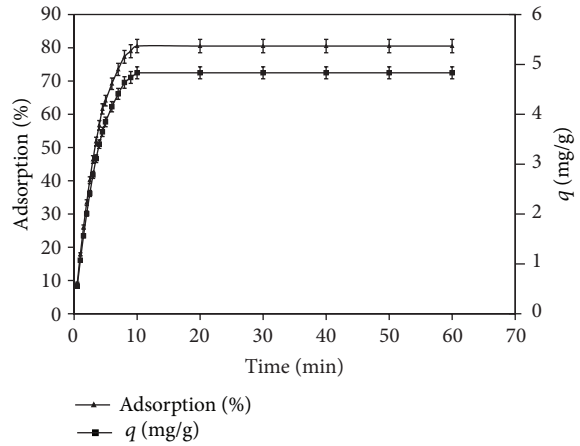


Figure 1: Effect of contact time on the biosorption of lead by *Ficus benghalensis* L. for 20 mg/L of metal, 0.1 g/30 mL of biosorbent concentration, and solution pH of 6.0.

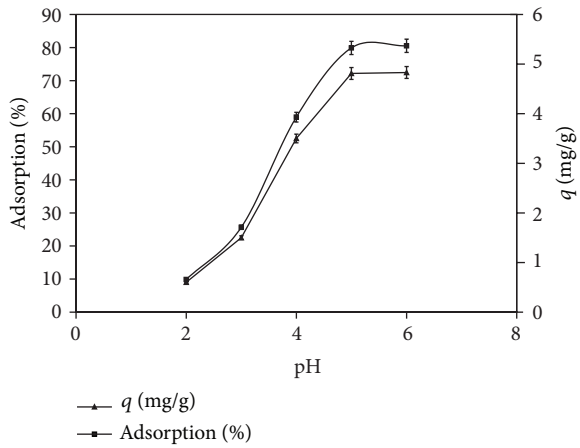


Figure 2: Effect of pH on lead biosorption by *Ficus benghalensis* L. for 20 mg/L of metal and 0.1 g/30 mL of biosorbent concentration.

3.2.3. Effect of Metal Ion Concentration. Figure 3 showed the effect of metal ion concentration on the adsorption of lead by *Ficus benghalensis* L. The metal uptake increased and the adsorption percentage of lead decreased with an increase in metal ion concentration. This increase (5.53–21.77 mg/g) was a result of the increase in the driving force that is a concentration gradient. However, the adsorption percentage of lead ions on *Ficus benghalensis* L. has decreased from 80.51 to 67.86%. Though an increase in metal uptake was observed, the decrease in adsorption percentage may be attributed to the lack of sufficient surface area to accommodate much more metal available in the solution. The percentage of adsorption at higher concentration levels showed a decreasing trend whereas the equilibrium uptake of lead showed an opposite trend. At lower concentrations, all lead ions present in the solution could interact with the binding sites and thus the percentage of adsorption was higher than that at higher lead ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites.

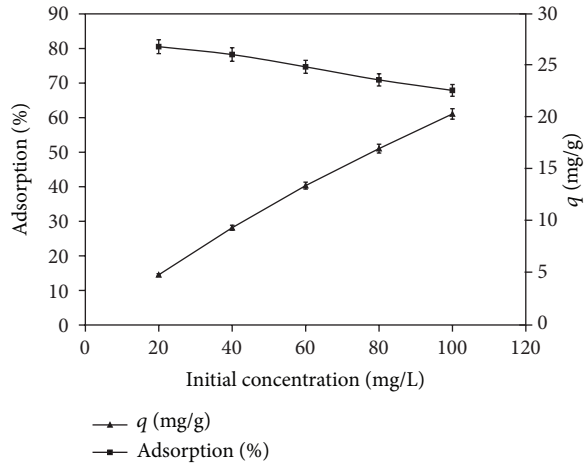


Figure 3: Effect of metal concentration on the biosorption of lead by *Ficus benghalensis* L. at 0.1 g/30 mL of biosorbent concentration and solution pH of 6.0.

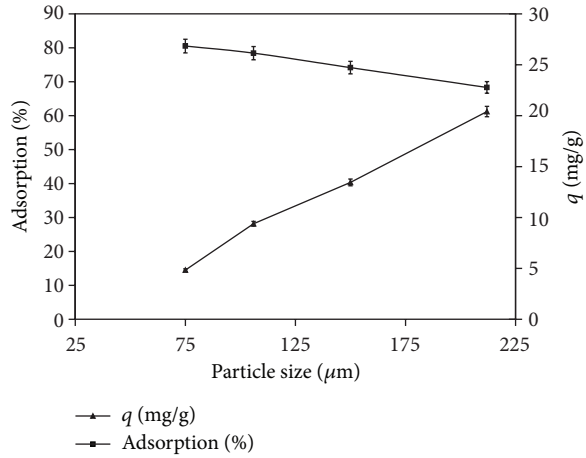


Figure 4: Effect of *Ficus benghalensis* L. particle size on biosorption of lead for 20 mg/L of metal, 0.1 g/30 mL of biosorbent concentration, and solution pH of 6.0.

3.2.4. Effect of Adsorbent Size. The effect of different adsorbent particle sizes on removal percentage of lead was investigated, and the results were shown in Figure 4. It was noted that the adsorption of lead on *Ficus benghalensis* L. decreased from 80.51 to 68.32% with the increased particle size from 75 to 212 μm at an initial concentration of 20 mg/L. The smallest size obtained was 75 μm due to the limitation of available grinder configuration. This was due to the fact that decreasing the average particle size of the adsorbent increased the surface area, which in turn increased the number of sites available leading to an increase in adsorption.

3.2.5. Effect of Adsorbent Dosage. The effect of adsorbent dosage on the removal percentage at equilibrium conditions was studied, and it was observed (Figure 5) that the amount of lead adsorbed varied with varying adsorbent dosage. The amount of lead adsorbed increased with an increase in

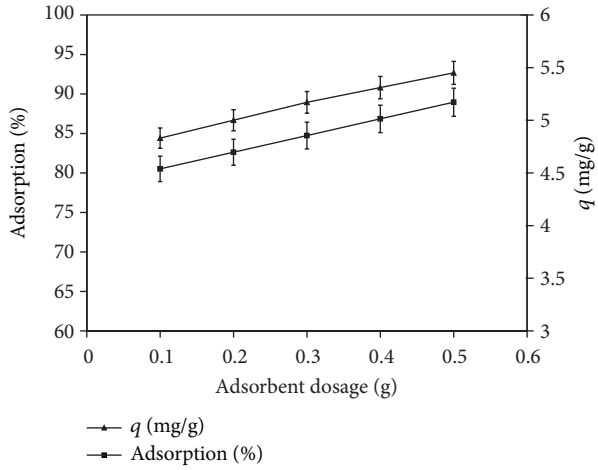


Figure 5: Effect of *Ficus benghalensis* L. dosage on biosorption of lead for 20 mg/L of metal concentration and solution pH of 6.0.

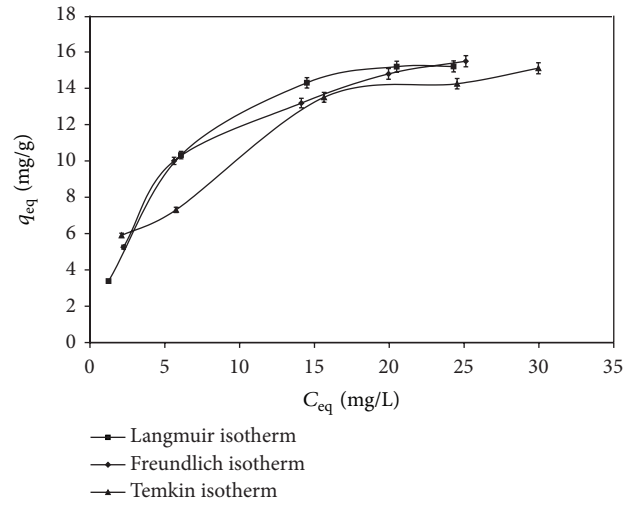


Figure 6: Langmuir, Freundlich, and Temkin isotherms plot for lead biosorption at 0.1 g in 30 mL of biosorbent concentration and solution pH of 6.0.

the adsorbent dosage from 0.1 to 0.5 g. The percentage of lead removal increased from 80.51 to 88.95% for an increase in adsorbent dosage from 0.1 to 0.5 g, respectively, at initial concentration of 20 mg/L. The increase in the adsorption of the amount of solute was obvious due to the increase in the amount of adsorbent, which in turn increased the number of sites available leading to an increase in adsorption. Similar trend was also observed by Bhattacharyya and Sharma [23] for the removal of lead using *Azadirachta indica* as adsorbent.

3.3. Biosorption Equilibrium. The equilibrium biosorption of lead on the *Ficus benghalensis* L. is established when the concentration of sorbate in bulk solution is in dynamic balance with that on the liquid-sorbent interface. The relationships between the concentrations of biosorbed metal and metal in solution at a given temperature are known as biosorption isotherms. In the present work, the Langmuir, Freundlich, and Temkin models described the equilibrium data. Equilibrium concentration, C_e, and equilibrium capacity, q_e, were determined in each case and displayed in Figure 6. The data obtained after linear regression analysis in each case was plotted and shown in Figures 7, 8, and 9. From these figures, it can be observed that the data is well fitted with the Langmuir model to the experimental data. This indicates that biosorption of lead on FRLs occurred in a monolayer. The values of the Langmuir, Freundlich, and Temkin models constants are listed in Table 3.

3.4. Kinetics of Adsorption. The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. In Figure 1, the adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeded at a slower rate till equilibrium, and finally the steady state was obtained after equilibrium. The saturation time was found to be 20 min based on the initial metal concentrations. The kinetics of the adsorption data was

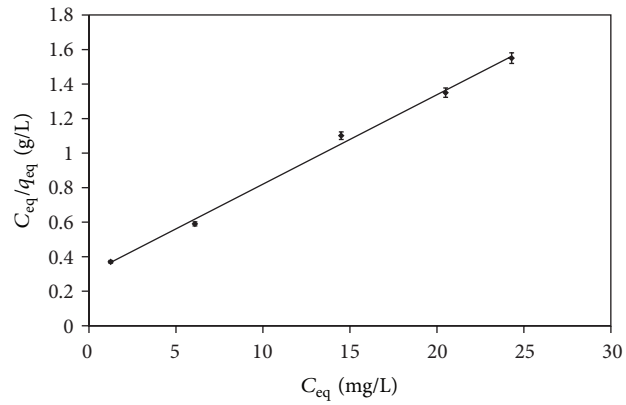


Figure 7: Langmuir biosorption isotherm for lead at 0.1 g in 30 mL of biosorbent concentration and solution pH of 6.0.

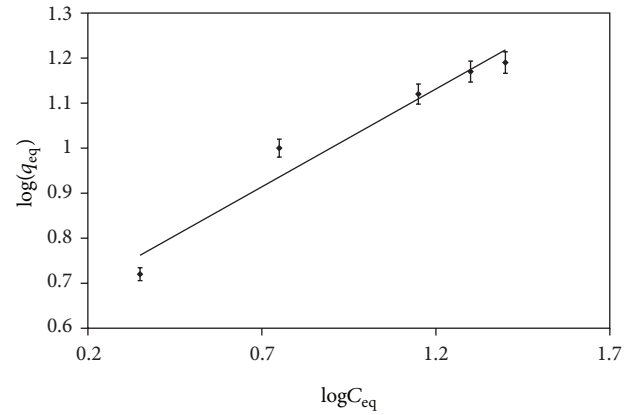


Figure 8: Freundlich biosorption isotherm for lead at 0.1 g in 30 mL of biosorbent concentration and solution pH of 6.0.

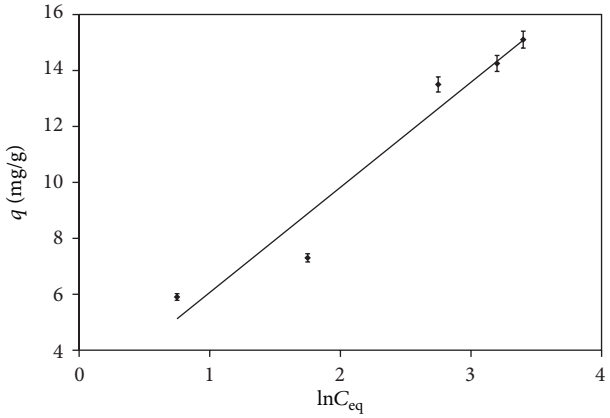


Figure 9: Temkin biosorption isotherm for lead at 0.1 g in 30 mL of biosorbent concentration and solution pH of 6.0.

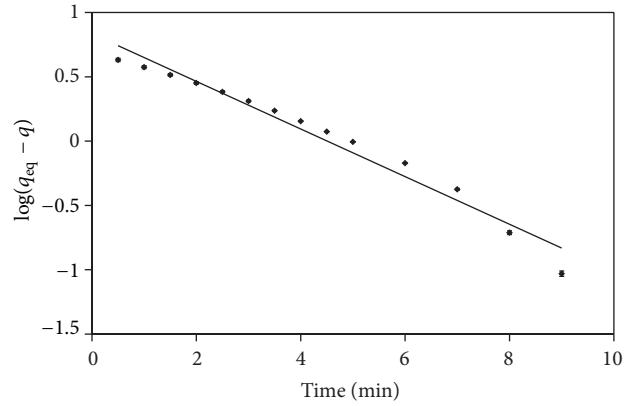


Figure 10: Pseudo-first-order biosorption of lead by *Ficus benghalensis* L. for 20 mg/L of metal, 0.1 g/30 mL of biosorbent concentration, and solution pH of 6.0.

Table 3: Langmuir, Freundlich, and Temkin isotherm constants and correlation coefficients.

Langmuir	
Q (mg/g)	28.636
b (L/mg)	0.1213
R^2	0.9979
Freundlich	
K_f	4.5552
n	2.0125
R^2	0.9545
Temkin	
A_T	1.4091
b_T	392.37
R^2	0.9473

analyzed using two kinetic models, pseudo-first- and pseudo-second-order kinetic models. These models correlated solute uptake, which was important in predicting the reactor volume.

3.4.1. The Pseudo-First-Order Equation. The pseudo-first-order equation of Lagergren is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t), \tag{7}$$

where q_e and q_t are the sorption capacities (mg/g) at equilibrium and at time t, respectively. k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). Integration of (7) with the boundary conditions $q_t = 0$ when $t = 0$ and $q_t = q_t$ at $t = t$ resulted in the following:

$$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} t. \tag{8}$$

The pseudo-first-order rate constant k_1 was obtained from the slope of the graph between $\log(q_e - q_t)$ versus time t (Figure 10). The calculated k_1 values and their corresponding linear regression correlation coefficients were shown in Table 4. The linear regression correlation coefficient value R_1^2 was found to be 0.9695, which indicated that this model did not predict the adsorption data, and hence could not be considered as a true representative of the kinetic model.

3.4.2. The Pseudo-Second-Order Equation. If the rate of sorption follows second-order kinetics, the pseudo-second-order chemisorption kinetic rate equation is expressed as follows [28]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \tag{9}$$

where k is the rate constant of pseudo-second-order sorption (g/(mg min)). For the boundary conditions $q_t = 0$ when $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of (9) becomes

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t, \tag{10}$$

where t is the contact time (min) and q_e (mg/g) is the amount of the solute adsorbed at equilibrium. Equation (10) does not require assigning any value for effective q_e. If pseudo-second-order kinetics is applicable, the graph t/q_t against t should show a linear relationship, from which q_e and k can be determined from the slope and interception of the plot. The data were plotted in Figure 11. The advantages of (10) were that there was no need to know any parameter beforehand.

The pseudo-second-order rate constant k_2, the calculated q_e value, and the corresponding linear regression correlation coefficient value R_2^2 were given in Table 4. At an initial lead concentration of 20 mg/L, the linear regression correlation coefficient R_2^2 value was higher. The higher R_2^2 value confirms that the adsorption data were well represented by pseudo-second-order kinetic model. The pseudo-second-order kinetics model applicability suggested that adsorption of lead on the *Ficus benghalensis* L. was based on chemical reaction involving the exchange of electrons between biosorbent and metal.

Table 4: Kinetic constants for lead onto *Ficus benghalensis* L.

Initial concentration (mg/L)	Pseudo-first-order			Pseudo-second-order		
	Rate constant k_1 (min^{-1})	Amount of lead absorbed on adsorbent, q_e (mg/g)	Correlation coefficient R_1^2	Rate constant k_2 (min^{-1})	Amount of lead absorbed on adsorbent, q_e (mg/g)	Correlation coefficient R_2^2
20	0.6032	9.532	0.9695	0.1165	5.535	0.9996

Table 5: Comparison of maximum adsorption capacities for lead adsorption to different adsorbents.

Adsorbent material	Adsorption capacity (mg/g)	pH	Reference
Na-Montmorillonite	3.6	5.0	Abollino et al. [8]
Crushed concrete fines	33.0	5.5	Coleman et al. [24]
Coir	8.6	5.5	Kathrine and Hansen [25]
Barley straw	5.3	5.5	Kathrine and Hansen [25]
Peat	11.7	5.5	Kathrine and Hansen [25]
Coniferous bark	7.4	5.5	Kathrine and Hansen [25]
Fontinalis antipyretica	14.7	5.0	Martins et al. [26]
Aspergillus niger 405	4.7	5.0	Filipovic-Kovacevic et al. [27]
Ficus benghalensis L.	28.6	6.0	Present study

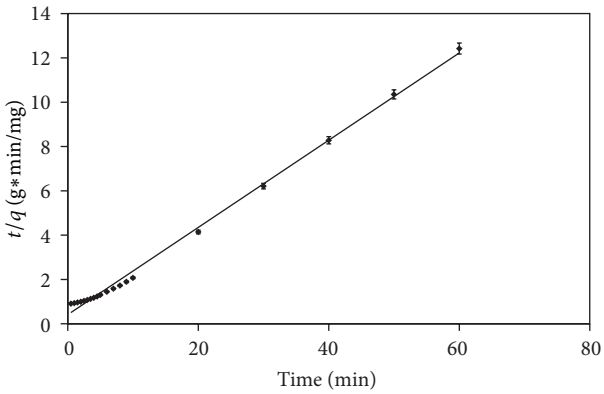


Figure 11: Pseudo-second-order biosorption of lead by *Ficus benghalensis* L. for 20 mg/L of metal, 0.1 g/30 mL of biosorbent concentration, and solution pH of 6.0.

3.5. Comparison of Ficus benghalensis L. with Other Sorbents. Table 5 summarizes the comparison of the maximum biosorption capacities of various sorbents. This comparison shows that *Ficus benghalensis* L. has higher biosorption capacities than Na-Montmorillonite [8], coir, barley straw, peat, coniferous bark [25], *Fontinalis antipyretica* [26], and *Aspergillus niger* 405 [27]. Crushed concrete fines [24] have higher biosorption capacity than *Ficus benghalensis* L. Cellulose, hemicelluloses, pectin, and lignin in the cell walls of *Ficus benghalensis* L. biomass are the most important sorption sites compared to other sorbents. Leaves have chlorophyll, carotene, anthocyanin, and tannin which contribute to metal biosorption as they contain hydroxyl, carboxylic, carbonyl, amino, and nitro groups which are important sites for metal sorption [29]. The easy availability and cost effectiveness of *Ficus benghalensis* L. biomass are additional advantages which make it a better biosorbent for treatment of lead wastes.

4. Conclusions

The present study showed that the *Ficus benghalensis* L. was an effective biosorbent for the adsorption of lead ions from aqueous solution. The easy availability of *Ficus benghalensis* L. biomass and their cost effectiveness are additional advantages, which make it a better biosorbent for treatment of lead wastes. The effect of process parameters like pH, metal ion concentration, adsorbent dosage, and adsorbent size had considerable effect on the process equilibrium. The uptake of lead ions by *Ficus benghalensis* L. was found to increase by increasing the metal ion concentration and the adsorbent dosage and decrease by increase the adsorbent size. The metal uptake was also noted to increasing by increasing the pH up to 6. The adsorption isotherms could well represent the Langmuir equation followed by Freundlich equation. The biosorption process could be best described by pseudo-second-order kinetics.

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