



COMPETITIVE BIOSORPTION OF LEAD (II) IONS FROM AQUEOUS SOLUTIONS ONTO TERMINALIA CATAPPA L. LEAVES AS A COST EFFECTIVE BIOSORBENT

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Abstract: In the present study, the competitive biosorption properties of nonliving biosorbent, *Terminalia catappa* L. leaves as a cost effective biosorbent for Pb(II) ions was investigated using batch technique. FTIR analysis of the biosorbent revealed that hydroxyl, carbonyl and carboxyl groups which are involved in the uptake of lead (II) ions. SEM represents porous structure with large surface area. The effects of operational factors including solution pH, biosorbent dose, initial lead (II) ions concentration, contact time and temperature on the biosorption efficiency were studied. The optimum solution pH for Pb(II) ions adsorption by biosorbent was 6.0 with the optimal removal 82.06%. The biosorbent dose 5 mg/mL was enough for optimal removal of 79.35%. The biosorption process was relatively fast and equilibrium was achieved after 90 minutes of contact time. The experimental equilibrium biosorption data were fitted by four widely used two-parameters Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin isotherm equations. Langmuir isotherm model provided a better fit with the experimental data than Freundlich, Temkin and Dubinin-Kaganer-Redushkevich (DKR) adsorption isotherm models by high correlation coefficient value ($R^2= 0.997$). The maximum adsorption capacity determined from Langmuir isotherm was found to be 50.00 mg/g of biosorbent. Simple kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intraparticle diffusion rate mixing equation were employed to determine the adsorption mechanism. Results indicates that pseudo-second-order kinetic model ($R^2= 0.999$) was found to be correlate the experimental data strongest than other three kinetic models and this suggests that chemical biosorption process was more dominant. Thermodynamic study revealed that the biosorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. *Terminalia catappa* L. leaves were successfully used for the competitive biosorption studies of Pb(II) ions from aqueous solutions and can be applied in waste water technology for remediation of heavy metal contamination.

Keywords: Adsorption kinetics, Competitive biosorption, Lead (II) ions, *Terminalia catappa* L., Thermodynamic study.

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INTRODUCTION

Discharge of industrial effluents containing heavy metals and other toxic contaminants into the open landscapes and water bodies, which increase the environmental pollution, which is

one of the most serious issues of the country. Heavy metals are a sanitary and ecological threat. They are highly toxic, carcinogenic properties (Cimino and Caristi, 1990) and recalcitrant even at very low concentrations and they can pollute drinking water resources. One

of the most challenging environmental problems today is the removal of heavy metals from industrial waste water. Many aquatic environments face heavy metal concentrations that exceed water quality limits designed to protect the environment, animals and humans (Gin *et al.*, 2002). Research is therefore important to fully understand systems and technologies, to search for novel techniques for heavy metal removal. Additionally heavy metals recovery can also be economically interesting because of its increasing higher prices and are used in a wide variety of commercial processes. Lead is a toxic heavy metal of significant environmental and occupational concern. Lead is one of the heavy metal, considered as toxic pollutants which find its way to the water bodies through industries like metal production, phosphate fertilizers, electrical wiring, manufacture of batteries, pigments, electroplating, air conditioning tubing and plumbing. Severe lead poisoning can cause encephalopathy, with permanent damage, while moderate lead poisoning result in neurobehavioral and intelligent deficit (Chen *et al.*, 2007). The presence of lead in drinking water, even in low concentrations may cause anaemia, hepatitis and nephritic syndrome (Zulkali *et al.*, 2006). Lead can cause brain and bone damage (Wang and Chen, 2009). Therefore, the maximum concentration limit for lead ions in drinking water has been strictly regulated. According to the United States Environmental Protection Agency (USEPA) the maximum permissible limits in wastewater is 0.1 mg/L and potable water is 0.015 mg/L for lead ions. Hence, there is great interest regarding the removal of lead from waste water streams.

Various treatment processes in removal of lead from waste water has been extensively studied by many authors. A variety of suitable treatment methods can be used for removal of metal pollutants such as reverse osmosis, electro dialysis, ultrafiltration, ion exchange, chemical precipitation, phytoremediation etc. (Rich *et al.*, 1987). However, less efficiency, time consuming, disposal, high operational cost and input of chemicals often make these processes impractical and results in further environmental

damage (Han *et al.*, 2006). Treatment of industrial effluent with sorbents of biological origin is simple, comparatively inexpensive and friendly to the environment. Understanding the biosorption of heavy metals from aqueous solutions is important in water pollution control. Biosorption is an innovative technology that employs inactive and dead biomass for the removal and recovery of heavy metals from aqueous solutions (Kim *et al.*, 2008; McKay *et al.*, 1999; Romera *et al.*, 2007; Maind *et al.*, 2012; Maind *et al.*, 2013; Maind *et al.*, 2013; Bhalerao, 2011). There is a growing demand to find relatively efficient, effective cost and easily available biosorbents for the biosorption of toxic heavy metals. In recent years, there has been considerable interest in the use of agricultural by-products as a biosorbents for biosorption of lead ions such as *Caladium bicolor* (Horsell and Spiff, 2005), neem leaf (Babarinde, 2011), mango peel waste (Iqbal *et al.*, 2009), chemically modified *Moringa oleifera* tree leaves (Reddy *et al.*, 2010), processed walnut shell (Almasi *et al.*, 2012), pomegranate peel (El-Ashtoukhy *et al.*, 2008), walnut, hazelnut, almond, pistachio and apricot stone (Kazemipour *et al.*, 2008), *lagenaria vulgaris* shell (Mitic-Stojanovic *et al.*, 2011), grape stalk waste (Martinez *et al.*, 2006), rice husk (Asrari *et al.*, 2010), *Saraca indica* leaf powder (Goyal *et al.*, 2008), olive tree pruning waste (Blazquez *et al.*, 2011), teak leaves (*Tectona grandis*) (Ajmal *et al.*, 2008), *Magnifera indica* seed shell (Ajmal *et al.*, 1998), immobilized *Fucus vesiculosus* (Mata *et al.*, 2009), pre-treated biomass of phanerochaete chrysosporium (Marandi *et al.*, 2010), corn cob (Jonglertjunya, 2008), *Salvinia Natans* (Livia *et al.*, 2014), marine green algae (R P Suresh Jeyakumar *et al.*, 2014), *Sargassum myriocystum* (Sweetly *et al.*, 2014) etc. *Terminalia catappa* L. is a large tropical tree in the Leadwood tree family, belongs to the Combretaceae. Leaves of *Terminalia catappa* L. contain several flavonoids, tannins, saponins and phytosterols and can accumulate heavy metals from their external environments by means of physico-chemical and biological mechanism. *Terminalia catappa* L. leaves were selected because of a cost effective, higher

adsorption capacity, possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. The focus of this work is to study the possible use of *Terminalia catappa* L. leaves as an efficient biosorbent for removal of lead (II) ions from aqueous solutions by conducting batch experiments as a function of solution pH, biosorbent dose, initial lead (II) ions concentration, contact time and temperature. Adsorption isotherm models (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) and kinetic models (pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intraparticle diffusion rate mixing equation) were employed to understand the probable adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0).

EXPERIMENTAL

Chemicals and reagents

All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute hydrochloric acid and dilute sodium hydroxide.

Preparation of lead (II) ions solution

The stock solution of 1000 ppm of lead (II) ions was prepared by dissolving 0.1 g of lead metal (AR grade) in 100 ml of double distilled water and further desired test solutions of lead (II) ions were prepared using appropriate subsequent dilutions of the stock solution

Preparation of adsorbent

The *Terminalia catappa* L. leaves were collected and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material and water soluble impurities and water was squeezed out. Biosorbent was then dried at 50°C overnight and crushed. It was sieved to select particles 100 μ m in size will be used in all the experiments. This powder was soaked (20 g/l) in 0.1 M nitric acid for 1 hour. The mixture was filtered and the powder residue was washed with distilled water, several times to remove any acid contents. This

filtered biomass was first dried, at room temperature and then in an oven at 105°C for 1-2 hrs. For further use, the dried biomass was stored in air tight plastic bottle to protect it from moisture.

Procedure

The static (batch) method was employed at temperature (30°C) to examine the biosorption of lead (II) ions by biosorbents. The method was used to determine the biosorption capacity, stability of biosorbent, and optimum biosorption conditions. The parameters were studied by combining biosorbent with solution of lead (II) ions in 250 ml reagent bottle. The reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, centrifuged, the content was separated from the biosorbents by filtration, using Whatmann filter paper and amount of lead (II) ions in the supernatant/filtrate solutions was determined.

Estimation of lead (II) ions concentration

0.001 % w/v solution of dithizone (H_2Dz) was prepared in carbon tetra chloride (CCl_4). Known volume of sample solution containing lead (II) ions, was pipette out into 100 ml beaker, 3ml of the potassium sodium tartrate added and then adjust the pH ~8 with ammonia (1+1) and the solution transferred to 250 ml separating funnel. To the solution, dithizone (H_2Dz) in carbon tetra chloride (CCl_4) was added until no longer pink color appears. The pink color carbon tetra chloride (CCl_4) layer was separated and washed with dilute ammonia solution. The pink color solution was diluted with carbon tetra chloride (CCl_4) to the 25 ml standard measuring flask. lead (II) ions concentration was estimated by measuring absorbance of the pink color, Pb-dithizone complex at 520-nm against carbon tetra chloride (CCl_4) as a blank using a UV-visible spectrophotometer. A linear plot for standard lead (II) ions solution was obtained indicating adherence to the Beers Lambert's law in the concentration range studies and amount of lead (II) ions in the samples were estimated. The amount determined was a mean of triplicate sample analysis with standard deviation less than 5 %. The blank solution i.e. solution containing biosorbent without lead (II) ions was

tested and results shows that no any appreciable signal of intensity at wavelength 520-nm obtained.

Instrumentation and data analysis

The concentration of lead (II) ions in the solutions before and after equilibrium was determined by measuring absorbance using digital UV-visible spectrophotometer (EQUIP-TRONICS, model Eq-820). The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model Eq-610) using a combined glass electrode. The data obtained in the batch adsorption studies were used to calculate the percentage adsorption of lead (II) ions by using the mass balance relationship. The lead (II) ions concentrations adsorbed on the solid were calculated from the difference between initial lead (II) ions content (C_i) and lead (II) ions content after adsorption (C_e). The following equation was used to compute the percentage adsorption (% Ad) of lead (II) ions by the adsorbent,

$$\% \text{ Ad} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (\text{i})$$

Where C_i and C_e are the initial concentrations and equilibrium concentrations of Pb(II) ions in mg/L.

Adsorption isotherms

A series of solutions containing different initial concentrations of lead (II) were prepared and the batch adsorption studies were done at 30°C to check the applicability of the adsorption isotherms under the specified condition, the solution pH of 2.0, adsorbent dose of 5 mg/mL, an initial lead(II) concentration range 5 mg/L - 250 mg/L and contact time 150 minutes. Analysis of lead (II) content in various solutions was performed by UV-Visible spectrophotometer method. The data obtained in batch adsorption studies was used to calculate the equilibrium lead (II) adsorptive quantity by the following equation:

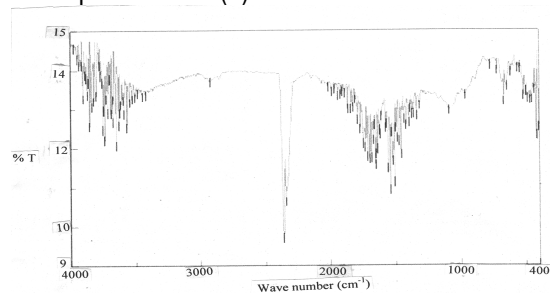
$$q_e = \frac{(C_i - C_e)}{w} \times V \quad (\text{ii})$$

Where q_e (mg metal per g dry biosorbent) is the amount of lead (II) adsorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

RESULTS AND DISCUSSION

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biomass. The biomass samples were examined using FTIR spectrometer (model:FT/IR-4100typeA) within range of 400-4000 cm^{-1} . All analysis was performed using KBr as back ground material. In order to form pellets, 0.02 g of biomass was mixed with 0.3 g KBr and pressed by applying pressure. To investigate the functional groups of biosorbent and metal loaded with biosorbent, a FTIR analysis was carried out and the spectra are shown in Figure 1 (a and b). As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The broad peak at 3421 cm^{-1} is the indicator of -OH and -NH groups. The stretching of the -OH groups bound to methyl groups presented in the signal at 2922 cm^{-1} . The peaks at 2361 cm^{-1} and 2343 cm^{-1} are stretching peaks. The peaks located at 1734 cm^{-1} and 1637 cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biomass. The peak at 1508 cm^{-1} is associated with the stretching in aromatic rings. The peaks observed at 1057 cm^{-1} are due to C-H and C-O bonds. The -OH, NH, carbonyl and carboxyl groups are important sorption sites. As compared to simple biosorbent, biosorbent loaded with lead (II) ions, the broadening of -OH peak at 3421 cm^{-1} and carbonyl group peak at 1637 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of lead (II) ions



(a)

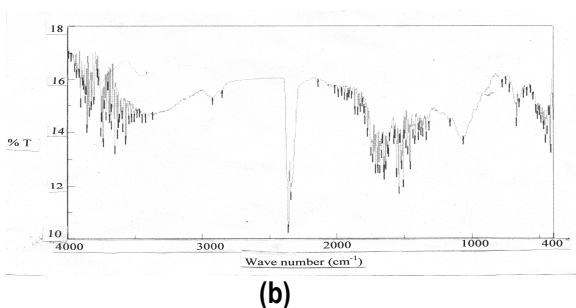
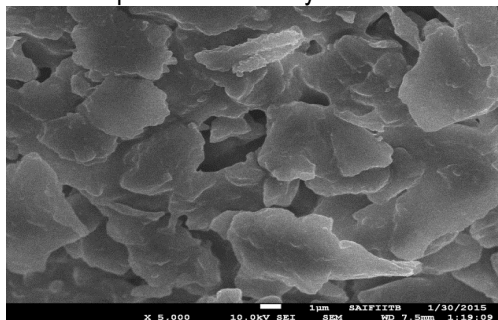


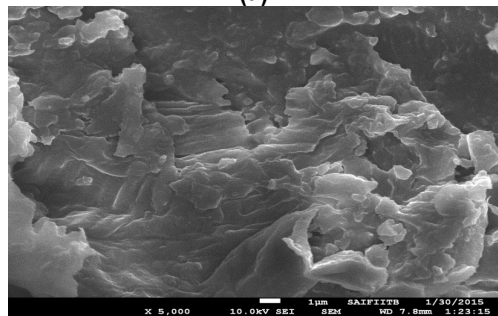
Figure 1. FTIR spectra (a) biosorbent *Terminalia catappa* L. leaves unloaded with lead (II) ions (b) biosorbent *Terminalia catappa* L. leaves loaded with lead (II) ions.

SEM analysis

The surface morphology of *Terminalia catappa* L. leaves was examined using Scanning Electron Microscopy (SEM), before and after biosorption and the corresponding SEM micrographs were obtained at an accelerating voltage at 10 kv at 5000 x magnification and are presented in Figure (a and b). At such magnification, the *Terminalia catappa* L. leaves particles showed rough areas of surface within which micropores were clearly identified.



(a)



(b)

Figure 2. SEM analysis (a) biosorbent *Terminalia catappa* L. leaves unloaded with lead (II) ions (b) biosorbent *Terminalia catappa* L. leaves loaded with lead (II) ions.

Effect of pH

The pH is considered as a very important parameter in biosorption process. The functional groups responsible for binding of metal ions in the biosorbent, affected by pH. It also affects the competition of metal ions that gets biosorb to active sites of biosorbent. pH influences the chemical structure of the lead (II) ions in aqueous solution, hence influencing its bioavailability (Ozacar, 2005). The biosorption capacity of the lead (II) ions depends on the pH of the adsorption medium, which influences electrostatic binding of lead (II) ions to corresponding functional groups. The optimization of pH was done by varying the pH in the range of 2-10 for lead (II) ions and pH trend observed in this case is shown in Figure 3. It was found that biosorption increased by increasing pH and at pH 5-6 the biosorption process was maximum with 82.06 % and then slightly decreases and practically constant till pH 10. The lesser biosorption at lower pH was due to lesser surface sites are available for sorption. The pH 6 was chosen for all further biosorption studies.

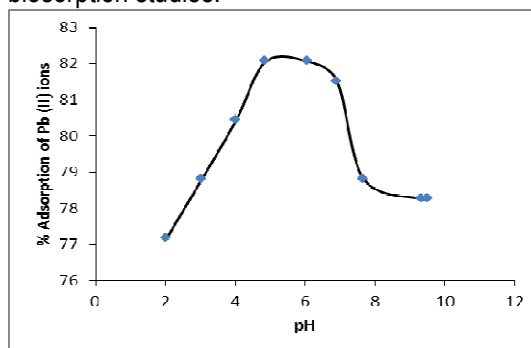


Figure 3. Effect of pH on lead (II) ions biosorption *Terminalia catappa* L. leaves (biosorbent dose concentration: 5 mg/ml, lead (II) ions concentration: 10 mg/L, contact time: 90 minutes, temperature: 30°C.

Effect of biosorbent dose

The effect of biosorbent dose of biosorption of metal ions onto biosorbent which is an important parameter was studied while conducting batch adsorption studies. The biosorption capacity of lead (II) ions on to *Terminalia catappa* L. leaves by varying adsorbent dose from 1.0 mg/ml to 20 mg/ml is as shown in Figure. 4. From the results it was found that biosorption of lead (II) ions

increases with increase in adsorbent dosage and is highly dependent on adsorbent concentration. Increase in adsorption by increase in adsorbent dose is because of increase of ion exchange site ability, surface areas and the number of available biosorption sites (Naiya et al., 2009). The point of saturation for *Terminalia catappa* L. leaves was found at 5 g/L of biosorbent dose with 79.35 % of removal efficiency. The decrease in efficiency at higher biosorbent concentration could be explained as a consequence of partial aggregation of adsorbent which results in a decrease in effective surface area for metal uptake. The biosorbent dose 5 mg/ml was chosen for all further studies.

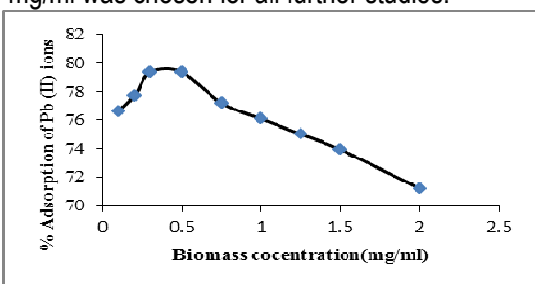


Figure 4. Effect of biosorbent dose concentration on lead (II) ions biosorption by *Terminalia catappa* L. leaves (pH: 6, lead (II) ions concentration: 10 mg/L, contact time: 90 minutes, temperature: 30°C).

Effect of initial lead (II) ions concentration

The effect of initial lead (II) ions concentration from 5 mg/L-300 mg/L on the removal of lead (II) ions from aqueous solutions at biosorbent dose 5 mg/ml and at optimum pH 6.0 at 30°C temperature was studied. On increasing the initial lead (II) ions concentration, the total Pb(II) ions uptake increased appreciably 65.22% to 87.31% at lead (II) ions concentration ranges from 5 mg/L- 300 mg/L.

Effect of contact time

Contact time plays an important role in affecting efficiency of biosorption. Contact time is the time needed for biosorption process to achieve equilibrium when no more changes in biosorptive concentration were observed after a certain period of time. The contact time which is required to achieve equilibrium depends on the differences in the characteristics properties of the biosorbents. In order to optimize the contact time for the maximum uptake of lead (II) ions,

contact time was varied between 5 minutes–180 minutes on the removal of lead (II) ions from aqueous solutions in the concentration of lead (II) ions 10 mg/L, biosorbent dose 5 mg/ml, optimum pH 6.0 and 30°C temperature. The results obtained from the biosorption capacity of lead (II) ions onto *Terminalia Catappa* L. leaves showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of lead (II) ions onto *Terminalia catappa* L. leaves showed that the biosorption increases with increases in contact time until it reached equilibrium. The optimum contact time for biosorption of lead (II) ions onto *Terminalia catappa* L. leaves was 90 minutes with 74.45 % removal. The rapid uptake of lead (II) ions is due to the availability of ample active sites for biosorption. A further increase in the contact time has a negligible effect on the biosorption capacity of Pb(II) ions biosorption. So a contact time of 90 minutes was fixed for further experiments.

Adsorption isotherms

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm (Langmuir, 1918): The Langmuir equation, which is valid for monolayer biosorption onto a surface of finite number of identical sites, is given by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \text{(iii)}$$

Where q_m is the maximum biosorption capacity of biosorbent (mg/g). b is the Langmuir biosorption constant (L mg⁻¹) related to the affinity between the biosorbent and biosorbate. Linearized Langmuir isotherm allows the calculation of biosorption capacities and Langmuir constants and is represented as:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \quad \text{(iv)}$$

The linear plots of $1/q_e$ vs $1/C_e$ is shown in Figure 5(a). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m , b and regression

coefficient (R^2) are listed in Table 1. Maximum biosorption capacity of biosorbent (q_m) is found to be 50 mg/g of biosorbent which is higher than the other biosorbents used by many authors.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation:

$$R_L = \frac{1}{1 + bC_i} \quad (v)$$

Where b is the Langmuir constant and C_i is the maximum initial concentration of lead (II). The value of separation parameters R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.0273-0.5846 for concentration of 5 mg/L -250 mg/L of Cr (VI). They are in the range of 0-1 which indicates favorable biosorption.

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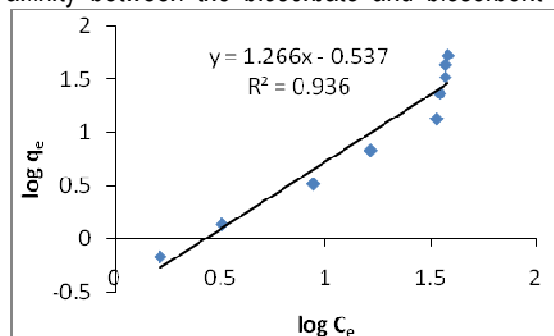
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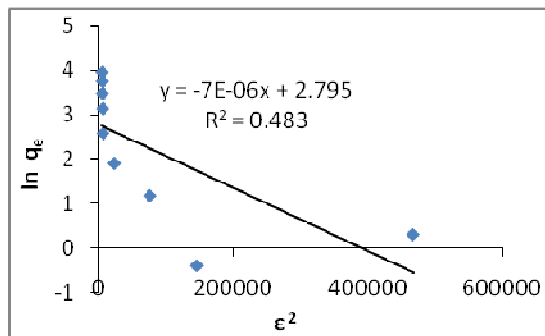
Where b is the Langmuir constant and C_i is the maximum initial concentration of lead (II) ions. The value of separation parameters R_L provides important information about the nature of biosorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.2904-0.9608 for concentration of 5 mg/L - 300 mg/L of lead (II) ions. They are in the range of 0 to 1 which indicates favorable biosorption (Malkoc and Nuhoglu, 2005). Biosorption can also be interpreted in terms of surface area coverage against initial metal ion concentration and separation factor. Langmuir model for surface area of biosorbent surface has been represented in the following equation:

$$\ln \frac{q_e}{1 - q_e} = \frac{\Theta}{1 - \Theta} \quad (vii)$$

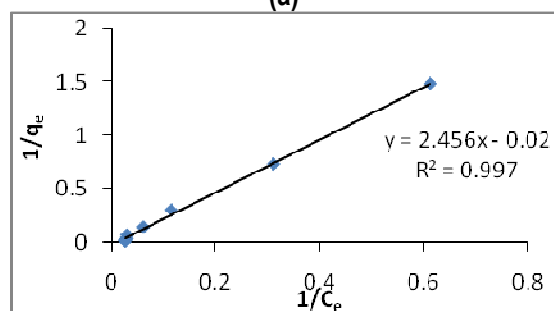
Where Θ is the surface area coverage. The Θ was found to be 0.0391-0.7095 for concentration of 5 mg/L -300 mg/L of lead (II) ions.



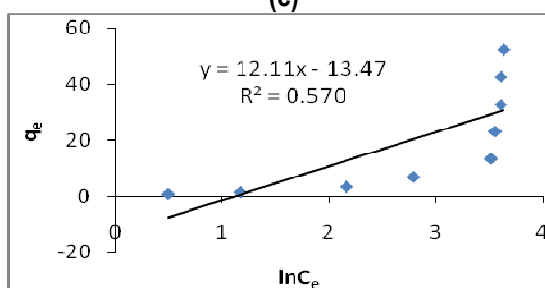
(a)



(c)



(b)



(d)

Figure 5. Adsorption isotherm models (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for biosorption of lead (II) ions by Terminalia Catappa L. leaves

(pH: 6.0, biosorbent dose concentration: 5 mg/mL, contact time: 90 minutes, temperature: 30°C).

Freundlich adsorption isotherm (Freundlich, 1906): Freundlich equation is represented by:

$$q = KC_e^{1/n} \quad \text{(viii)}$$

Where K and n are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively.

Linearized Freundlich adsorption isotherm was used to evaluate the biosorption data and is represented as:

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad \text{(ix)}$$

Equilibrium data for the biosorption is plotted as $\log q_e$ vs $\log C_e$, as shown in Figure 5b. The two constants n and K are calculated from the slope ($1/n$) and intercept ($\log K$) of the line, respectively. The values of K , $1/n$ and regression coefficient (R^2) are listed in Table 1. The n value indicates the degree of non-linearity between solution concentration and biosorption as follows if $n = 1$, then biosorption is linear; if $n < 1$, then biosorption is chemical process; if $n > 1$, then biosorption is a physical process. A relatively slight slope and a small value of $1/n$ indicate that, the biosorption is good over entire range of concentration. The n value in Freundlich equation was found to be 1.8621. Since $n > 1$, this indicates the physical biosorption of Pb(II) ions onto *Terminalia catappa* L. leaves. The higher value of K (918.450) indicates the higher biosorption capacity of the biosorbent.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm (Dubinin and Radushkevich, 1947): Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as:

$$\ln q_e - \ln q_m - \beta \varepsilon^2 \quad \text{(x)}$$

Where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean sorption energy and ε is the polanyi potential, which is calculated from the following relation:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad \text{(xi)}$$

Equilibrium data for the biosorption is plotted as $\ln q_e$ vs ε^2 , as shown in Figure 5c. The two constants β and q_m are calculated from the slope (β) and intercept ($\ln q_m$) of the line, respectively. The values of biosorption energy E was obtained by the following relationship.

$$E = \frac{1}{\beta} \quad \text{(xii)}$$

The values of q_m , β , E and regression coefficient (R^2) are listed in Table 1. The mean free energy gives information about biosorption mechanism, whether it is physical or chemical biosorption. If E value lies between 8 KJ/mol and 16 KJ/mol, the biosorption process take place chemically and $E < 8$ KJ/mol, the biosorption process of the physical in nature (Olivieri and Brittenham, 1997). In the present work, E value (0.262 KJ/mol) which is less than 8 KJ/mol, the biosorption of lead (II) ions onto biosorbent is of physical in nature.

Temkin adsorption isotherm (Temkin and Pyzhev, 1940): Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad \text{(xiii)}$$

Where b_T is the Temkin constant related to heat of sorption (J/mol) and A_T is the Temkin isotherm constant (L/g). Equilibrium data for the adsorption is plotted as q_e vs $\ln C_e$, as shown in Figure 5d. The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot \ln A_T$) of the line, respectively. The values of A_T , b_T and regression coefficient (R^2) are listed in Table 1.

Table 1. Adsorption isotherm constants for biosorption of lead (II) ions by Terminalia Catappa L. leaves

Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
q_m	b	R^2	K	$1/n$	R^2	q_m	β	E	R^2	A_T	b_T	R^2
50.00	0.0081	0.997	18.450	0.537	0.936	16.362	-7 E-6	0.2672	0.483	3.0413	208.021	0.570

Adsorption kinetics

As aforementioned, a lumped analysis of adsorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the

pseudo-first-order equation (Lagergren, 1898) (b) the pseudo-second-order equation (Mckay et al., 1999) (c) Elovich equation (Chien and Clayton, 1980) (d) Weber and Morris intraparticle diffusion

rate equation (Weber and Morris, 1963) are presented below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{(xiv)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(xv)}$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad \text{(xvi)}$$

$$q_t = k_i t^{0.5} + c \quad \text{(xvii)}$$

Where q_e (mg/g) is the solid phase concentration at equilibrium, q_t (mg/g) is the average solid phase concentration at time t (min), k_1 (min^{-1}) and k_2 (g/mg/min) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of α (mg/g/min) and β (g/mg) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. k_i (mg/g/min^2) is the intraparticle diffusion rate constant, c is intercept. If the biosorption follows the pseudo-first-order rate equation, a plot of $\ln(q_e - q_t)$ against time t should be a straight line. Similarly, t/q_t should change lineally with time t if the biosorption process obeys the pseudo-second order rate equation. If the biosorption process obeys Elovich rate equation, a plot of q_t against $\ln t$ should be a straight line. Also a plot of q_t against $t^{0.5}$ changes lineally the biosorption process obeys the Weber and Morris intraparticle diffusion rate equation. Biosorption of lead (II) ions on to biosorbent was monitored at different specific time interval. The lead (II) ions uptake was calculated from the data obtained. From the lead (II) ions uptake was plotted against time to determine a suitable kinetic model, the biosorption data was fitted into pseudo-first-order rate equation, pseudo-second-order rate equation, Elovich equation and the Weber and Morris intraparticle diffusion rate equation. The pseudo-first-order equation was plotted for $\ln(q_e - q_t)$ against t (Figure. 6a). The values of q_e and k_1 values were calculated from the slope (k_1) and intercept ($\ln q_e$) of this plot and shown in Table 2. Pseudo-first-order kinetic model showered the correlation value ($R^2 = 0.7320$) being lower than the correlation coefficient for the pseudo-second-order equation. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the adsorbent and the ions biosorbed onto it (Septum et al., 2007). The pseudo-second-order equation was plotted for t/q_t against t (Figure 6b). The values of q_e and k_2 are calculated from the slope ($1/q_e$) and intercept ($1/k_2$)

q_e^2) of the plot and values are shown in Table 2. Pseudo-second-order kinetic model showered the strongest correlation ($R^2 = 0.9990$). This suggests that lead (II) ions adsorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical adsorption is the rate-limiting step. Pb(II) ions react chemically with the specific binding sites on the surface of biosorbent. The Elovich equation was plotted for q_t against $\ln t$ (Figure 6c). The values of β and α are calculated from the slope ($1/\beta$) and the intercept ($\ln(\alpha\beta)/\beta$) of the plot and values are shown in Table 2. The Elovich equation has been used to further explain the pseudo-second-order equation with the assumption that the actual adsorption surface is energetically heterogeneous. Elovich equation showed a correlation value ($R^2 = 0.9110$) being lower than the correlation coefficient for the pseudo-second-order equation. Therefore, this could be used to explain that the adsorption surface is energetically heterogeneous (Thomas and Thomas, 1997). The intraparticle diffusion rate equation was plotted for q_t against $t^{0.5}$ (Figure. 6(d)). The value of k_i and c are calculated from the slope (k_i) and intercept (c) of the plot and values are shown in Table 2. The Weber and Morris intraparticle diffusion rate equation showed a correlation value ($R^2 = 0.9120$) being lower than the correlation coefficient for the pseudo-second-order equation. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intraparticle pore diffusion is not only rate-limiting step (Weber and Morris, 1963). The plot of intraparticle diffusion rate equation showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of biosorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption (Panday et al., 1986).

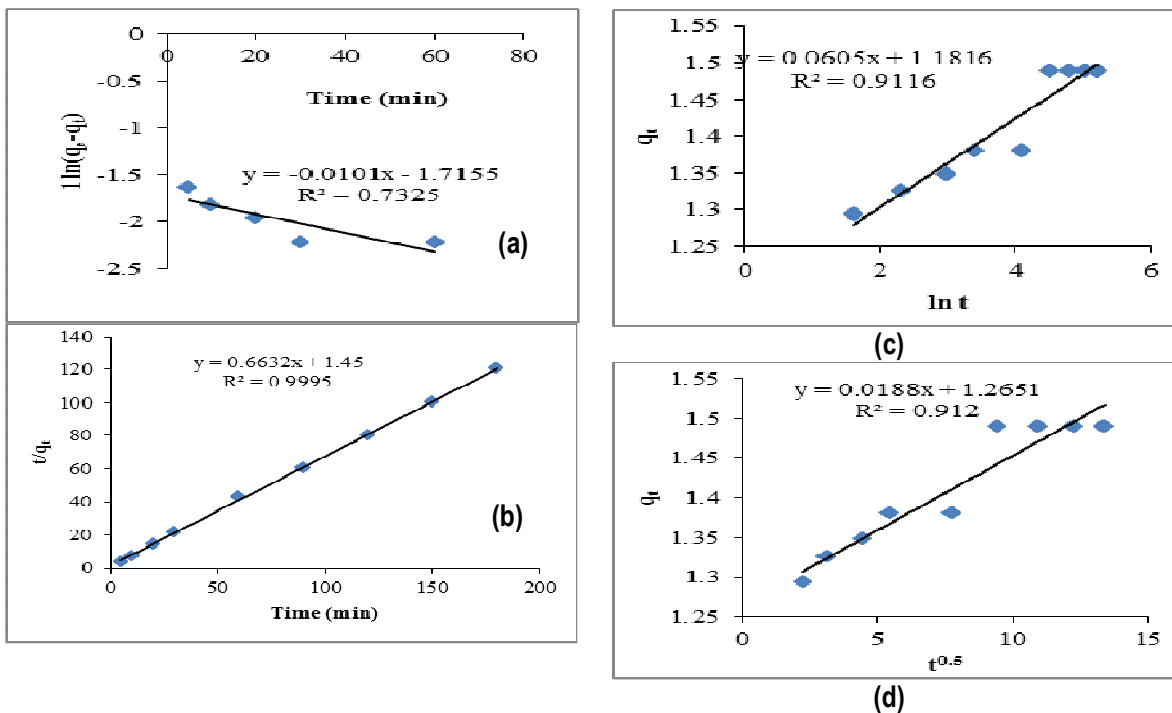


Figure 6. Adsorption kinetic models (a) pseudo-first-order equation, (b) pseudo-second-order equation, (c) Elovich equation and (d) Weber and Morris intra-particle diffusion rate equation, for biosorption of lead (II) ions by *Terminalia Catappa* L. leaves. pH: 6.0, biosorbent dose concentration: 5 mg/mL, lead (II) ions concentration: 10 mg/L, Temp: 30°C.

Table 2. Adsorption kinetic data for biosorption of lead (II) ions by *Terminalia catappa* L. leaves

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra particle diffusion model		
q_e	K_1	R^2	q_e	K_2	R^2	a	β	R^2	K_i	c	R^2
5.556	0.010	0.732	1.5082	0.3031	0.999	2.1189 E7	16.666	0.911	0.018	1.265	0.912

Thermodynamic study

The effect of temperature on removal of lead (II) ions from aqueous solutions in the lead (II) ions concentration 10 mg/L and biosorbent dose 5 mg/ml with optimum pH 6.0 was studied. Experiments were carried out at different temperatures from 30°C-70°C. The samples were allowed to attain equilibrium. Sorption slightly increases from 30°C-50°C. The equilibrium constant (Catena and Bright, 1989) at various temperatures and thermodynamic parameters of biosorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad \text{(xviii)}$$

$$\Delta G^0 = -RT \ln K_c \quad \text{(xix)}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad \text{(xx)}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \text{(xxi)}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration of lead(II) ions in solution (mg/L) and C_{Ae} is the lead (II) ions concentration biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0 , ΔH^0 and ΔS^0 are changes in standard, Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K), T is the temperature (Kelvin). The values of ΔH^0 and ΔS^0 were determined from the slope ($\Delta H^0/R$) and the intercept ($\Delta S^0/R$) from the plot of $\ln K_c$ versus $1/T$ (Figure 7).

Table 3. Thermodynamic parameters of biosorption of Lead(II) ions by *Terminalia catappa* L. Leaves

T (K)	Kc	$-\Delta G^0$ (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)
303	2.6078	2.414	8.268	34.284
313	2.9149	2.783		
323	3.1818	3.108		

The values of equilibrium constant (K_c), standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) calculated in this work were presented in Table 3. The equilibrium constant (K_c) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intraparticle diffusion. The standard Gibbs free energy (ΔG^0) is small and negative and indicates the spontaneous nature of the biosorption. The values of ΔG^0 were found to decrease as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of ΔH^0 was positive, indicating the endothermic nature of the biosorption of lead (II) ions onto *Terminalia catappa* L. leaves. The positive values of ΔS^0 shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

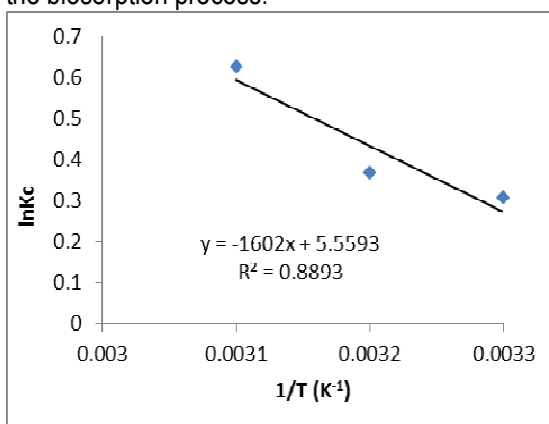


Figure 7. Determination of thermodynamic parameters for biosorption of lead (II) ions by *Terminalia catappa* L. leaves (pH: 6.0, biosorbent dose concentration: 5 mg/ml, lead (II) ions concentration: 10 mg/L, contact time: 90 minutes).

CONCLUSION

The present investigation reveals that *Terminalia catappa* L. leaves can be an inexpensive, excellent biosorbent for the removal of lead (II) ions from aqueous solutions. The optimal parameters such as solution pH, biosorbent dose, initial lead (II) ions concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of lead (II) ions onto *Terminalia catappa* L. leaves. The maximum lead(II) ion loading capacity (q_e) of *Terminalia catappa* L. leaves was found to be 50.00 mg g⁻¹ with perfect fit to

Langmuir isotherm model and follows pseudo-second order kinetics. The thermodynamic study confirmed that reaction of biosorption of lead (II) ions onto *Terminalia Catappa* L. leaves is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that *Terminalia catappa* L. leaves has considerable biosorption capacity, available in abundant, non-hazardous material could be used as an effective indigenous material for treatment of wastewater stream containing lead (II) ions. The FTIR study of biosorbent showed that the possibility of availability of functional groups such as hydroxyl, carbonyl, carboxyllick. The SEM represents porous structure with large surface area.

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