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Adsorption isotherm studies of Zn (II) ions from aqueous solution using citric acid modified Tamarind pod shell (*Tamarindus indica* L.)

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Abstract
The need to clean-up heavy metal contaminated environment cannot be over emphasized. This paper describes the adsorption isotherm studies of Zn (II) ions from aqueous solution using tartaric acid modified Tamarind pod shell (*Tamarindus indica* L.). Tamarind pod shell (*Tamarindus indica* L.) was found to be an excellent adsorbent for the removal of these metal ions. The amount of metal ions adsorbed increased as the initial concentration increased. Also, tartaric acid modification enhanced the adsorption capacity of Tamarind pod shell (*Tamarindus indica* L.) probably due to the chelating ability of tartaric acid. Among the four adsorption isotherm tested, Freundlich adsorption isotherm fitted well with its good correlation coefficient. Experimental data were analyzed by kinetic parameters such as pseudo-first order, pseudo-second order models, Elovich and Weber & Morris intra-particule diffusion. Results clearly indicate that pseudo-second order kinetic model by its good correlation coefficient value which is very close to the unity. Thermodynamic study revealed that the adsorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. Tamarind pod shell (*Tamarindus indica* L.) used successfully for removal of chromium (VI) and zinc (II) from aqueous solutions can have been good scope in future for industrial wastewater treatment.

Keywords: Tamarind pod shell (*Tamarindus indica* L.), Adsorption isotherm, Adsorption kinetics, tartaric acid.

1. Introduction
Environmental pollution and its harmful effect on ecology have been studied intensively during last decade years. Problems of the pollutants removal from wastewater were increased with fast industrialization. These waste waters are produced large volumes and must be absolutely treated before discharge. Heavy metals are very harmful for humans, animals and plants. Global and local agencies have therefore established certain limits on the quantities of heavy metals being discharged into environment. Rapid industrial development has cause pollution to the environment. As a result of the activities of the mining industry, pulp, and paper industry, textile industry, metal plating, agricultural industries trigger increased levels of heavy metals in the water caused by waste discharged into waters (Metcalf et al., 2003; Tiwari et al., 2015).
Numerous methods have been employed to remove zinc (II) ions from wastewater, including precipitation, coagulation, ion exchange, membrane filtration, and electrolysis (Wahby et al., 2011; Lin et al., 2010). But the high cost of the materials these method are not generally use. Therefore now day's very innovative and cost effective methods are used for the removal toxic substance from waste water (Rakesh kumar et al., 2012). Bio-sorption of heavy metal from aqueous solution is an efficient technology in industrial waste water treatment (Gorstal et al., 2003; Pino et al., 2006; Chandra et al., 2003). This new technology has been loosely grouped together under the term biosorptions (Sumathi et al., 2005). The recent studies has showed that heavy metals can be removed using a variety of low cost bio mass has been studied by various workers for controlling pollutions from the diverse sources in different part of the world (Karp et al.,2004). They include agricultural materials rice brown, soya

beans and cotton seed hulls, crop milling wastes ground net husk, maize cop meal, coir, jute and saw dust (Shukla et al., 2005). The most convenient means of determining metal uptake ability is through a batch reaction process. In the present study by citric acid modified tamarind pod shell (*Tamarindus indica* L.) offer local substitute for existing commercial adsorbent materials.

2. Materials and Methods

A. Chemical and reagent

All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water will be used for all experimental work including the preparation of zinc (II) standard solution. The zinc (II) standard solution was prepared by using their respective compounds. The desired pH of the metal solution was adjusted with the help of dilute hydrochloric acid and dilutes sodium hydroxide.

B. Preparation of Zinc (II) standard solution

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

C. Collection and preparation of biomass

Tamarind pod shells were collected from the local market pune and Mumbai. The collected biomaterial is washed extensively in running water and deionized water to remove the dirt and other impurities. The dirt-free Tamarind pod shells were dried in the shade. Then the Tamarind pod shells were crushed using mixture grinder. Then the Tamarind pod shells powder were sieved using 100 µm Mesh and fine biomass was stored in air tight glass bottles to protect it from moisture.

D. Modification of biosorbent

About 25 g grinded tamarind pod shell powder was mixed with 17.5 m L of 1.2 M citric acid (CA). The mixture was stirred until homogenous and dried at 60°C in oven for 24 hours. Again it was kept in oven at 120°C for 2 hours. The treated tamarind pod shell powder was subsequently washed with distilled water and dried for 40 hours in oven at 50°C. The final product was labelled as citric acid modified tamarind pod shell (*Tamarindus indica* L.).

E. Instrumentation

The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode. The concentration of zinc (II) in the solution before and after equilibrium was determined by measuring absorbance using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) technique. Biosorbent was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and X-ray diffraction (XRD).

1) 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 biosorbent. The biomass samples were examined using FTIR spectrometer (model: FT/IR-4100 type A) 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.

2) Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis: The Scanning Electron Microscope (SEM) was used to see the porosity of the biosorbent. The samples were covered with a thin layer of gold and an electron acceleration voltage of 10 KV was applied and then Scanning Electron Micrograph was recorded.

3) Characterization of biosorbent by X-ray diffraction analysis (XRD) analysis: X-ray diffraction (XRD) was used for the qualitative and quantitative determination of solid samples of biosorbent. It works on the principle that X-ray diffraction pattern is unique for each sample. This pattern from XR-D was compared with a known compound and the chemical compound was identified.

F. Experimental procedure

The static (batch) method was employed at temperature (30^0C) to examine the biosorption of zinc (II) by biosorbent. The method was used to determine the biosorption capacity, stability of biosorbent and optimum biosorption conditions. The parameters were studied by combining biosorbent with zinc (II) solution in 250 ml separate reagent bottles. 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 biosorbent by filtration, using Whatmann filter paper and amount of zinc (II) in the filtrate solutions was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The following equation was used to compute the percent removal (% Adsorption) of zinc (II) by the biosorbent,

$$\%\ \mathrm{Ad} = \frac{(C_i\text{-}C_e)}{C_i} \times 100 \qquad \textbf{(1)}$$

Where *Ci* and *Ce* are the initial concentrations and equilibrium concentrations of the zinc (II) in mg/L.

The equilibrium adsorptive quantity (qe) was determined by the following equation,

$$\boldsymbol{q_e = \frac{(C_i - C_e)}{w} \times V} \qquad \textbf{(2)}$$

G. Desorption study

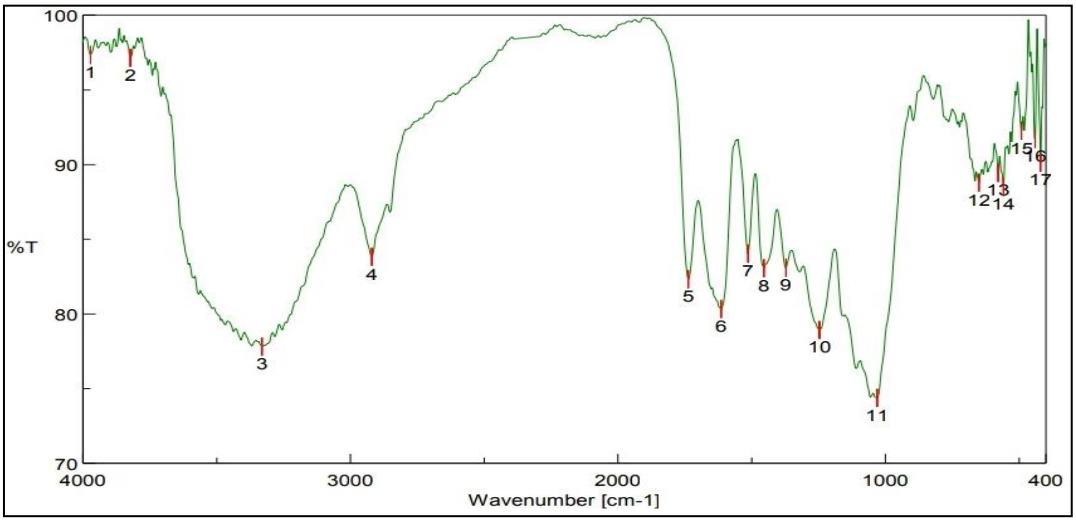
To evaluate desorption efficiency; zinc (II) loaded biosorbent was dried after equilibrium sorption experiments. The dried biosorbent was contacted with 0.1 M nitric acid (HNO_3), 0.1 M hydrochloric acid (HCl) and 0.1 sulphuric acid (H_2SO_4) separately for 2 hours to allow zinc (II) to be release from biosorbent. The samples were separated from the biosorbents by filtration, using Whitman filter paper and amount of and zinc (II) in the filtrate solutions was determined by ICP-AES to find out desorption efficiency. Desorption efficiency was calculated from the amount of metal adsorbed on the biosorbent and the final metal concentration in the biosorption medium.

$$\textbf{\textit{Desorption efficiency}}\ (\%) = \frac{\text{released metal ions in mg/L}}{\text{initially adsorbed metal ions in mg/L}} \times 100 \qquad \textbf{(3)}$$

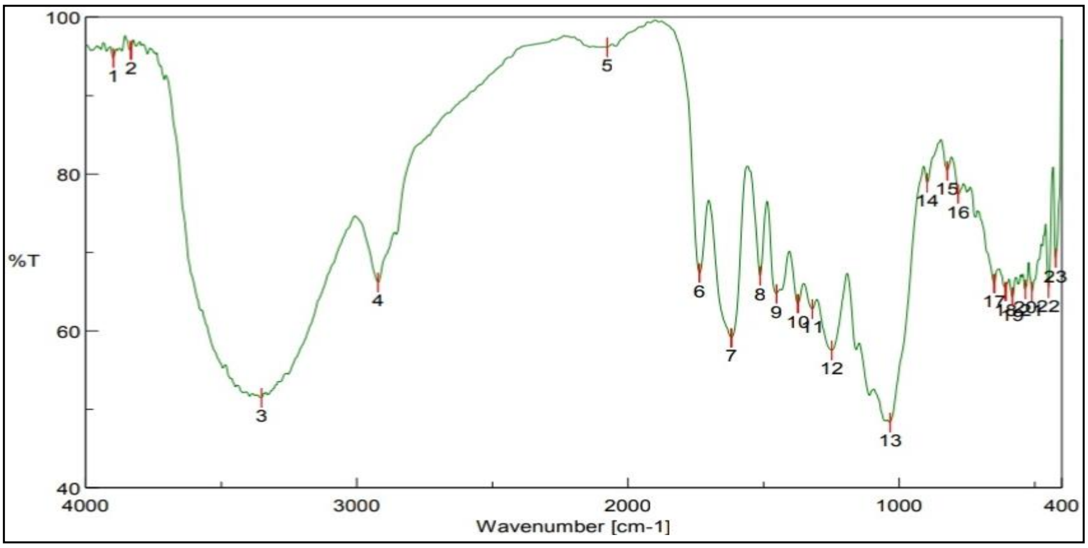
3. Results and Discussion

A. Characterization of biosorbent by Fourier Transform Infrared (FTIR) spectroscopy

FTIR spectra of citric acid modified tamarind pod shell, as seen in the figure unloaded biosorbent displays a number of biosorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3330 cm^{-1} is the indicator of -OH and -NH groups. The peaks located at 1736 cm^{-1} and 1614cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biosorbent. The peaks observed at 1030 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 zinc (II) the broadening of -OH peak at 3350 cm^{-1} and carbonyl group peaks at 1736 cm^{-1} and 1618cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of zinc (II) ions.



(a)

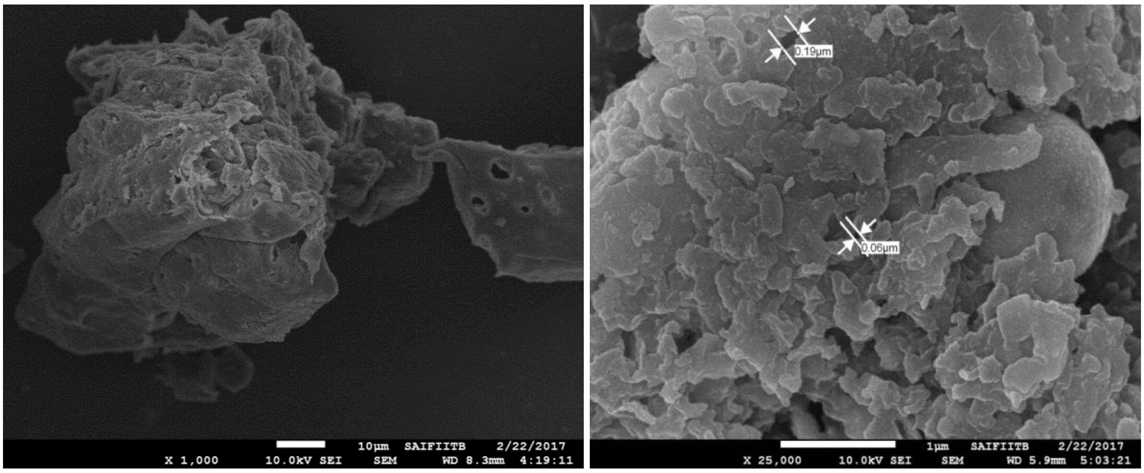


(b)

Fig 1: FTIR spectra (a) Biosorbent citric acid modified tamarind pod shell unloaded with zinc (II) (b) Biosorbent citric acid modified tamarind pod shell loaded with zinc (II)

B. Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The surface characteristics, structure and particle size distribution of citric acid modified tamarind pod shell before and after biosorption was examined using Scanning Electron Microscope (SEM). Citric acid modified tamarind pod shell confirmed that they have large number of pores on the surface with cracks and crevices. The SEM clearly demonstrated that there is more uniformity after biosorption on metal ions in comparison to before biosorption. It was evident from the micrographs that the biosorbents presents an unequal structure before metal adsorbed. The number of canals in the biosorbents was higher in the initial case. The metal ions adsorbed on the cell wall matrix and created stronger cross linking and uniformity on the surface of biosorbents.



(a) (b)

Fig 2: Scanning Electron Microscope (SEM) analysis (a) Biosorbent citric acid modified tamarind pod shell unloaded with zinc (II) (b) Biosorbent citric acid modified tamarind pod shell loaded with zinc (II)

C. X-ray diffraction analysis (XRD) analysis

X-ray diffraction is a non-destructive technique used to provide detailed information on the crystallographic structure of materials. This method offers several advantages e.g., non-destructive, high accuracy, capability to detect single crystals, polycrystalline or amorphous materials. The XRD profile of the citric acid modified tamarind pod shell shows typical diffraction peaks. Broad peaks were obtained instead of sharp peaks indicating the sample was poorly crystalline. The XRD spectra of loaded zinc (II) exhibit strong peaks at 2θ value 25.58º, 24.08º, and 45.7º equivalent to 232.33, 289.462 and 169.2262, respectively. In addition, several other low intensity peaks corresponding to other crystalline phases have also been observed. After biosorption of zinc (II), the porous structures of the biosorbents decreased. These causes low intensity XRD peaks. Hence crystalline phases should have been reduced. It was also observed that after chemical modification the ability to form hydrogen bonds has decreased and the adsorbent becomes amorphous. Resulting zinc (II) finally gets absorbed by biosorbent.

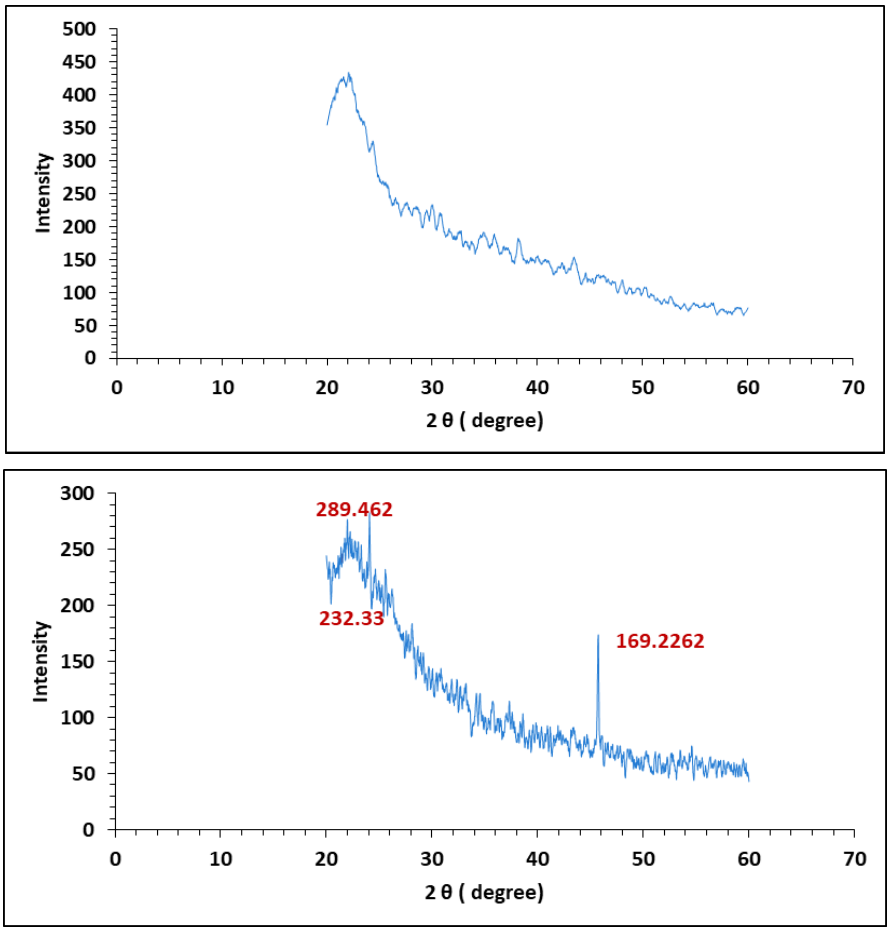


Fig 3: X-ray diffraction analysis (XR-D) study (a) Biosorbent citric acid modified tamarind pod shell unloaded with zinc (II) (b) Biosorbent citric acid modified tamarind pod shell with loaded with zinc (II)

D. Effect pH

The Batch equilibrium studies at different pH are studied from the range 2-9. They are presented in Figure 4. The solution pH is one of the important variables governing biosorption materials by sorbents. It is found that the uptake of zinc (II) ions by biomass depend on pH. There is a steep increase up to pH 6 after that there is a gradual decrease, as seen in the graph. It is interesting to note that absorption of zinc (II) ion at pH 6 is very high. The result shows adsorption of biomass depends on pH of medium. So pH 6 is optimized for this batch equilibrium studies.

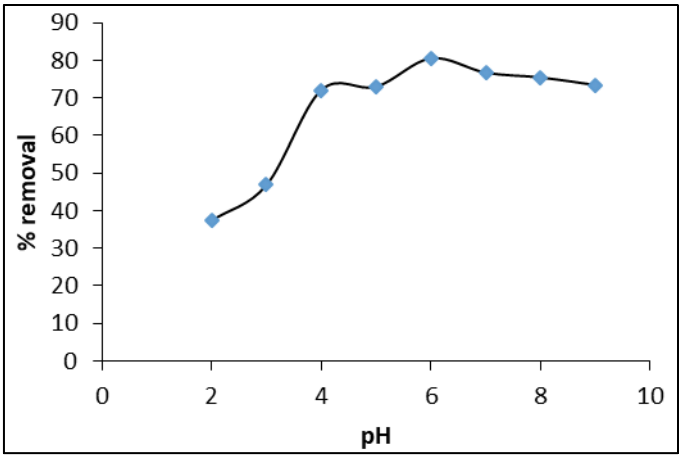


Fig 4: Effect of pH on zinc (II) biosorption by citric acid modified tamarind pod shell (Biosorbent dose concentration: 5 g/L, zinc (II) concentration: 5 mg/L, contact time: 120 minutes, temperature: 30^0C, agitation rate: 120 rpm)

E. Effect of biosorbent dose

The effect of biosorbent dose on the zinc (II) biosoption is studied by keeping all other parameters constant ranging from 1 g/L to 15 g/L. This range of biosorbent dose is used to determine the suitable quantity of biomass for maximum sorption. The graph is plotted for percentage removal efficiency against biosorbent dose is shown in the figure 5. It is evident from the graph that an adsorbent dose 5.0 g/L is sufficient to removal of zinc (II) metal by the biomass. From the observations it is interesting to note that further increment in sorbent did not cause significant improvement in the sorption.

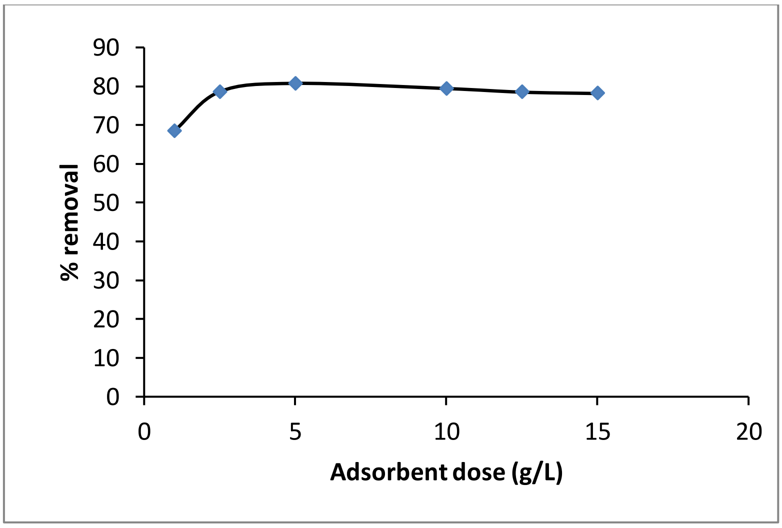


Fig 5: Effect of biosorbent dose concentration on zinc (II) biosorption citric acid modified tamarind pod shell (pH: 6, initial zinc (II) concentration: 5 mg/L, contact time: 120 minutes, agitation rate: 120 rpm, temperature: 30°C)

F. Determination of Equilibrium time

Equilibrium time is maximum time taken by the sorption experiment to achieve equilibrium after which no further metal uptake is adsorbed. The graph is plotted for the biomasses and is shown in the Figure 6. It can be noticed from the graph that the contact time significantly affects the metal uptake. The metal sorption increases sharply for the biomass individually in the first 90 min and then equilibrium approached according to the result. From the observation it is concluded that 90 min are sufficient for the sorption to attain equilibrium for citric acid modified tamarind pod shell.

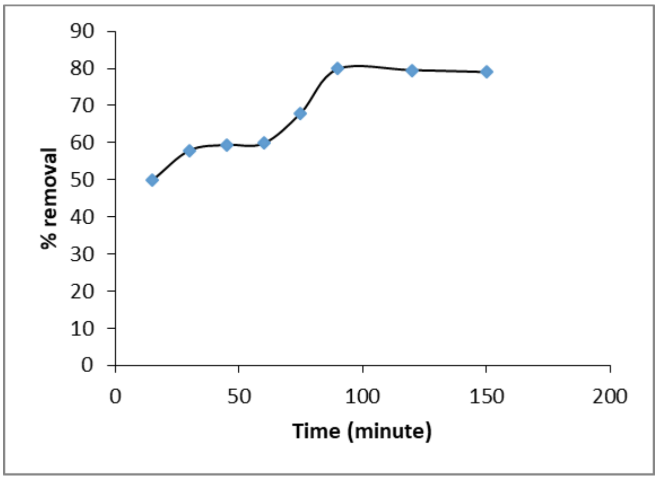


Fig 6: Effect of contact time on zinc (II) biosorption by citric acid modified tamarind pod shell (pH: 6, biosorbent dose concentration: 5 g/L, initial zinc (II) concentration: 5 mg/L, agitation rate: 120 rpm, temperature: 30^0C)

G. Effect of Initial metal ion Concentration

The rate of sorption is function of initial concentration of metal ion which makes it an important factor to be considered for effective biosorbent. The initial metal ion concentrations provide driving force overcome mass transfer ions between aqueous and solid phase. The initial concentrations are changed in the range of 5 mg/L to 250 mg/L by keeping all other parameters constant. The results are shown in the figure 7. The sorption capacity increases with increasing initial metal ion concentration for zinc (II) for biomass.

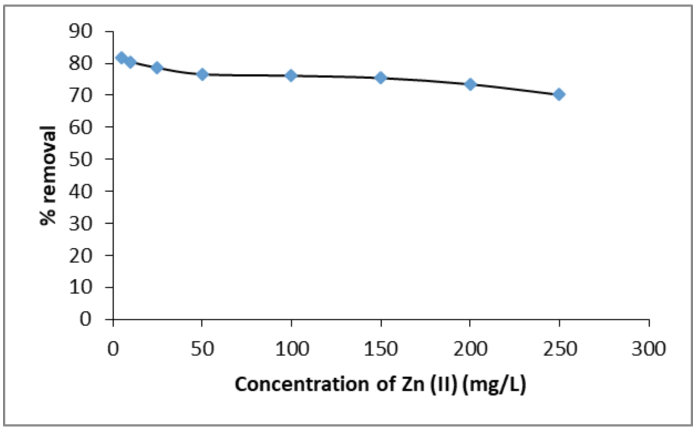


Fig 7: Effect of initial zinc (II) concentration on zinc (II) biosorption by citric acid modified tamarind pod shell (pH: 6, biosorbent dose concentration: 5 g/L, contact time: 120 minute, agitation rate: 120 rpm, temperature: 30^0C)

H. Effect of temperature

The effect of temperature on removal of zinc (II) from aqueous solutions using citric acid modified tamarind pod shell was studied at different temperatures from 20^0C-40^0C. The influence of temperature is depicted in Figure 8. Maximum sorption was seen at 30^0C with percentage removal 80.54%.

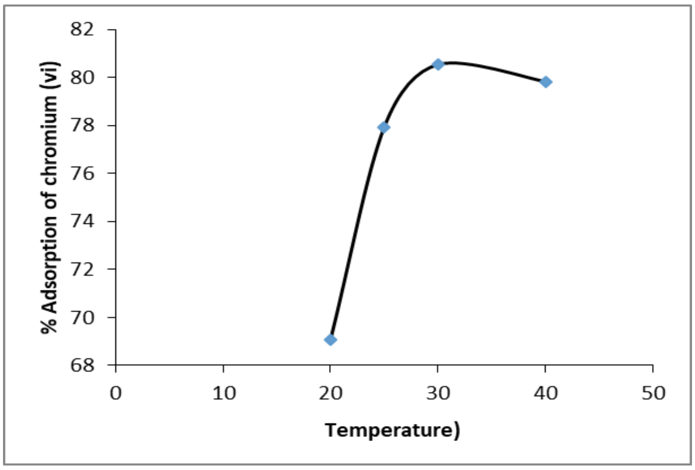


Fig 8: Effect of temperature on zinc (II) biosorption using citric acid modified tamarind pod shell (pH 6.0, biosorbent dose concentration: 5 g/L, agitation rate: 120 rpm, initial zinc (II) concentration: 5 mg/L, contact time: 120 minutes.)

I. Effect of agitation rate

The effect of agitation rate on removal of zinc (II) from aqueous solutions at biosorbent dose 5 g/l and at optimum pH 6 at 30^{0}C was studied at different agitation rate such as 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200rpm. The efficiency was highest at 120rpm with percentage removal 80.54%. So, 120 rpm was chosen for all further biosorption studies.

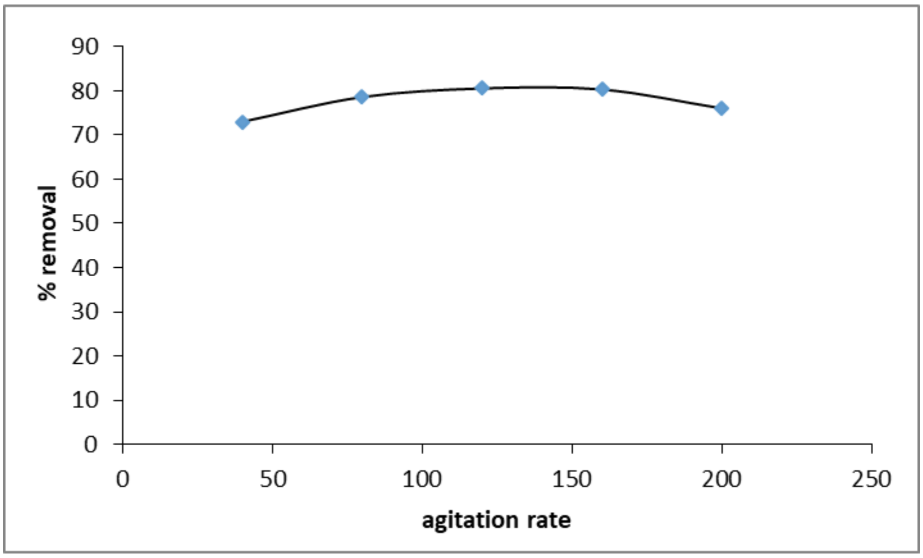


Fig 9: Effect of agitation rate on zinc (II) biosorption by citric acid modified tamarind pod shell (pH: 6, biosorbent dose concentration: 5 g/L, initial zinc (II) concentration: 5 mg/L, contact time: 120 minute, temperature: 30^{0}C)

J. Desorption study

In application of real wastewater, desorption of heavy metal ions in the biosorbent is important process. Citric acid modified tamarind pod shell was the most effective waste biosorbent with desorption efficiency 55.27% (0.1 M hydrochloric acid), 85.87% (0.1 M nitric acid)and 65.04% (0.1 M sulphuric acid). Nitric acid has shown highest desorbed capacity of zinc (II) followed by hydrochloric acid and sulphuric acid from citric acid modified tamarind pod shell.

K. Adsorption isotherm models

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. Adsorption isotherms data for biosorption of zinc (II) by citric acid modified tamarind pod shell is shown in;

i. Langmuir adsorption isotherm

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by;

$$q_e = \frac{q_m\, b\, C_e}{1+bC_e} \quad \textbf{(4)}$$

Where q_m is the maximum biosorption capacity of biosorbent (mg g^{-1}). 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:

$$\frac{1}{q_e} = \frac{1}{q_m\, b\, C_e} + \frac{1}{q_m} \quad \textbf{(5)}$$

The linear plots of 1/q vs 1/C_e is shown in Figure 10 (a). The two constants b and q_m are calculated from the slope (1/q_m·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 38.4615 mg per g for citric acid modified tamarind pod shell. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using

$$R_L = \frac{1}{1+bC_i} \quad \textbf{(6)}$$

Where b is the Langmuir constant and C_i is the maximum initial concentration of zinc (II). The value of separation parameters *RL* provides important information about the nature of adsorption. The value of *RL* indicated the type of Langmuir isotherm separation factor or dimensionless equilibrium parameters, *RL* expressed as in the following equation: to be irreversible (*RL* = 0), favorable (0 <*RL*< 1), linear (*RL* = 1) or unfavorable (*RL*>1). The *RL* was found to 0.1454 to 0.8948 for concentration of 5 mg/L-250 mg/L of zinc (II). They are in the range of 0-1 which indicates favorable biosorption (Malkoc et al., 2005).

ii. Frenudlich adsorption isotherm (Freundlich 1906):

Freundlich equation is represented by:

$$\mathbf{q_e = KC_e^{1/n}} \quad \textbf{(7)}$$

Where K and n are empirical constants incorporating all parameters affecting the adsorption process such as, sorption capacity and sorption intensity respectively. Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad \textbf{(8)}$$

Equilibrium data for the adsorption is plotted as log q vs log C_e, as shown in Figure 10 (b). 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 adsorption as follows: if n = 1, then adsorption 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 1.0395. Since n<1, this indicates the chemical process biosorption of zinc (II) ions onto citric acid modified tamarind pod shell. The higher value of K (0.9044) indicates the higher adsorption capacity for the citric acid modified tamarind pod shell.

iii. Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm (Dubinin and Radushkevich 1947):

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

$$\boldsymbol{ln q_e} = \ln \boldsymbol{q_m} - \boldsymbol{\beta}\, \varepsilon^2 \qquad \textbf{(9)}$$

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

$$\varepsilon = \boldsymbol{RTln}\ (\mathbf{1} + \frac{\mathbf{1}}{\boldsymbol{Ce}}) \qquad \textbf{(10)}$$

Equilibrium data for the adsorption is plotted as $\ln q_e$ vs ε^2, as shown in Figure 10 (c). 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 adsorption energy E was obtained by the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \qquad \textbf{(11)}$$

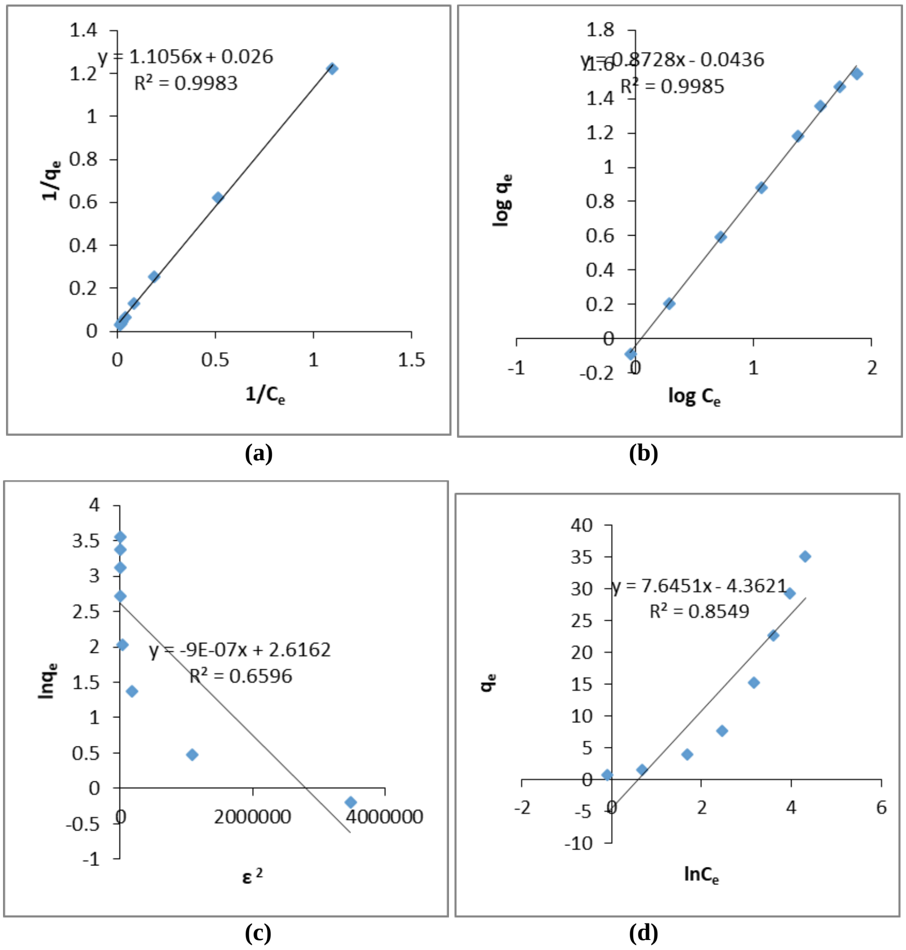
The E value was found to be 0.7553 KJ mol^{-1}. The mean free energy gives information about biosorption mechanism whether it is physical or chemical biosorption. If E value lies between 8 KJ mol-1 and 16 KJ mol-1, the biosorption process take place chemically and E > 8 KJ mol-1, the biosorption process of the physical in nature (Olivieri et al., 1997). In the present work, E value (0.7553 KJ mol^{-1}) which is less than 8 KJ mol-1, the biosorption of zinc (II) onto citric acid modified tamarind pod shell is of physical in nature (Sawalha et al., 2006).

iv. Temkin adsorption isotherm (Temkin and Pyzhev 1940):

Linearized Temkin adsorption isotherm is given by the equation:

$$\boldsymbol{q_e} = \frac{\boldsymbol{RT}}{\boldsymbol{b_T}} \boldsymbol{ln\, A_T} + \frac{\boldsymbol{RT}}{\boldsymbol{b_T}} \boldsymbol{ln\, C_e} \qquad \textbf{(12)}$$

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 Figure10 (d). The two constants b_T and A_T are calculated from the slope (R_T/b_T) and intercept ($R_T/b_T \cdot \ln A_T$) of the line. The values of A_T, b_T and regression coefficient (R^2) are listed in Table 1. The various constants and regression coefficient R^2 obtained from adsorption isotherms models (Langmuir, Freundlich, DubininKaganer-Redushkevich (DKR) and Temkin) are summarized in Table 1.



(a) (b)

(c) (d)

Fig 10: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for bisorption of zinc (II) by citric acid modified tamarind pod shell (pH: 6.0, biosorbent dose concentration: 5 g/L, contact time: 120 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Table 1: Adsorption isotherm constants for biosorption ofzinc (II) by citric acid modified tamarind pod shell.

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m	β	R^2	K	$1/n$	R^2	β	q_m	E	R^2	A_T	b_T	R^2
38.4615	0.0235	0.9983	0.9044	0.8728	0.9985	-9×10^{-7}	13.6836	0.7453	0.6596	0.5529	342.157	0.8549

L. 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 et al., 1898) (b) the pseudo-second-order equation (McKay et al., 1999) (c) Elovich equation (Chien and Layton et al., 1980) (d) Weber & Morris intra-particle diffusion model (Weber and Morris et al., 1963) are presented below:

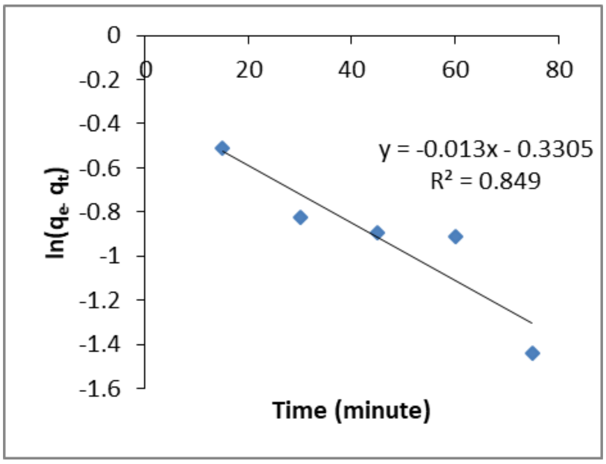
$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

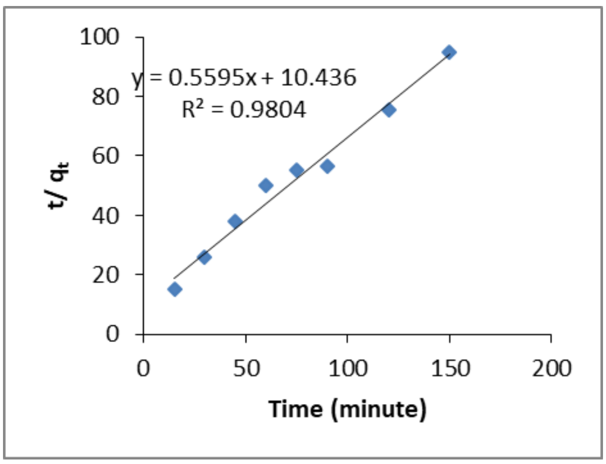
$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (15)$$

$$q_t = k_i t^{0.5} + c \quad (16)$$

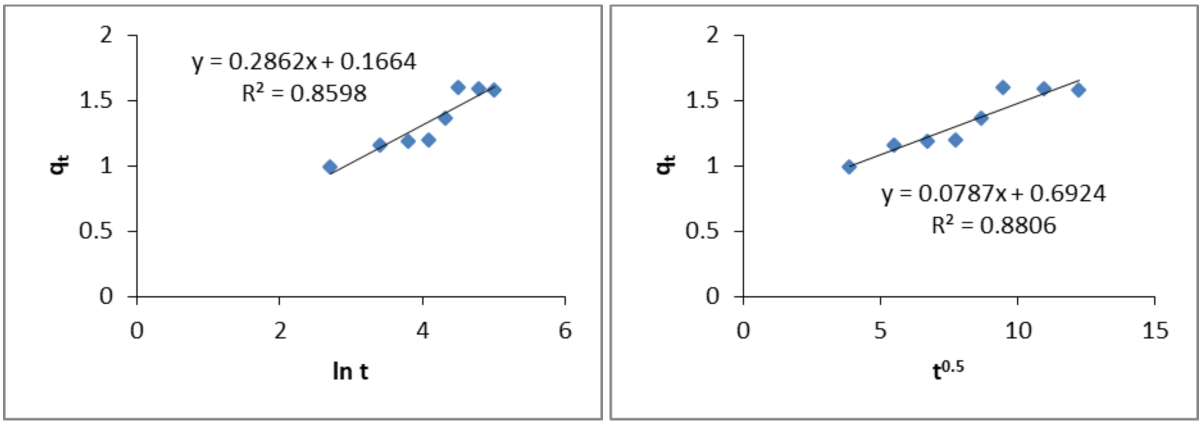
Where q_e (mg g^{-1}) is the solid phase concentration at equilibrium, q_t (mg g^{-1}) is the average solid phase concentration at time t (min), k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of α (mg g^{-1} min^{-1}) and β (g mg^{-1}) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. k_i (mg g^{-1} $min^{-1/2}$) is the intra-particle diffusion rate constant, c is intercept. If the biosorption follows the pseudo-first-order model, 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 adsorption process obeys the pseudo-second order model. If the adsorption process obeys Elovich model, a plot of q_t against *lnt* should be a straight line. Also a plot of qt against $t^{0.5}$ changes lineally the adsorption process obeys the Weber and Morris intra-particle diffusion model. Biosorption of zinc (II) onto biosorbent was monitored at different specific time interval. The zinc (II) uptake was calculated from the data obtained. From the zinc (II) uptake was plotted against time to determine a suitable kinetic model, the adsorption data was fitted into pseudo-first-order model, pseudo-second-order model, Elovich models and the Weber & Morris intra-particle diffusion model. The pseudo-first-order model was plotted for ln (q_e-q_t) against t (Figure 11 (a)). The values of k_1 and q_e values were calculated from the slope (k_1) and intercept (lnq_e) of the plot and shown in Table 2. Kinetic adsorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it (Septhum et al., 2007). The pseudo-second-order model was plotted for t/q_t against t (Figure 11 (b)). 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. The Elovich model was plotted for q_t against *ln t* (Figure 11 (c)). The values of β and α are calculated from the slope (1/ β) and the intercept (ln (α β)/ β) of the plot and values are shown in Table 2. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous [29]. The Weber & Morris intra-particle diffusion model was plotted for q_t against $t^{0.5}$ (Figure 11 (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 pseudo-second-order model showed a strongest correlation value (R^2 = 0.9804) being higher than the correlation coefficient for the pseudo-first-order model, Elovich model and Weber & Morris intra-particle diffusion model. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intra-particle pore diffusion is not only rate-limiting step (Thomas and Thomas et al., 1947). The plot of intra-particle diffusion model 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 biosorbent 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).



(a)



(b)



(c) (d)

Fig 11: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intraparticle diffusion equation, for biosorption of zinc (II) citric acid modified tamarind pod shell (pH: 6.0, biosorbent dose concentration: 5 g/L, zinc (II) concentration: 5mg/L, temperature: 30^{0}C, agitation rate: 120 rpm)

Table 2: Adsorption kinetic data for biosorption of zinc (II) by citric acid modified tamarind pod shell

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intraparticle diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	a	β	R^2	Ki	c	R^2
0.7185	0.013	0.8490	1.7873	0.0299	0.9804	0.5119	3.4940	0.8598	0.0787	0.6924	0.8806

M. Determination of thermodynamic

The effect of temperature on removal of zinc (II) from aqueous solutions in the concentration of zinc (II) 5mg/L and biosorbent dose 5 mg/ml with optimum pH 6.0 was studied. Experiments were carried out at different temperatures from 20^{0}C-40^{0}C. The samples were allowed to attain equilibrium. Sorption slightly increases from. The equilibrium constant (Catena and Bright et al., 1989) at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad (17)$$

$$\Delta G^0 = -RT\ln K_c \quad (18)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (19)$$

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the amount of zinc (II) ions biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0, ΔH^0 and ΔS^0 are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K). The values of ΔH^0 and ΔS^0 were determined from the slope and the intercept from the plot of lnK_c versus 1/T (Figure 12). The values of equilibrium constant (Kc), Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and the 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 intra-particle diffusion. The 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 decreases 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 zinc (II) ions onto citric acid modified tamarind pod shell. The positive values of ΔS^0 shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

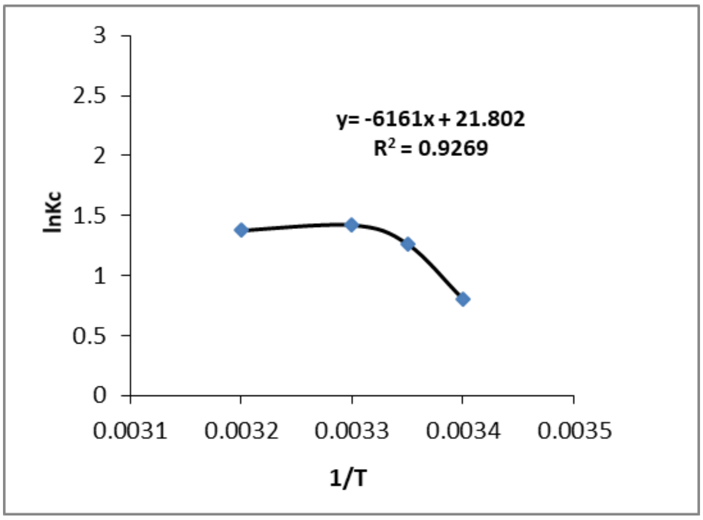


Fig 12: Plot of ln *Kc* against *1/T* for determination of thermodynamic parameters for biosorption of zinc (II) by citric acid modified tamarind pod shell (pH: 6.0, biosorbent dose concentration: 5 g/L, initial zinc (II) concentration: 5 mg/L, agitation rate: 120 rpm contact time: 120 minute).

Table 3: Thermodynamic parameters of biosorption of zinc (II) by citric acid modified tamarind pod shell

Sr. No.	Time (min)	K	Kc = C_{Ae}/C_e	-ΔG^0	ΔH^0	ΔS^0
1	20^{0}C	293	2.2351	1.9590	51.222	181.261
2	25^{0}C	298	3.5330	3.1269		
3	30^{0}C	303	4.1387	3.5779		
4	40^{0}C	313	3.9578	3.5796		

4. Conclusions

The present investigation revealed that citric acid modified tamarind pod shell used as inexpensive, excellent biosorbent for the removal of zinc (II) from aqueous solutions. The optimal parameters such as solution pH, biosorbent dose, initial zinc (II) concentration, and contact time temperature and agitation rate determined in the experiment were effective in determining the efficiency of zinc (II) biosorption onto citric acid modified tamarind pod shell. Biosorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, Temkin isotherm and Dubinin-Kaganer-Redushkevich (DKR) isotherm. The maximum zinc (II) loading capacity (q_e) of citric acid modified tamarind pod shell determined from Langmuir adsorption isotherm was found to be 38.4615 mg g^{-1}. The Pseudo-second-order model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of zinc (II) was spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that citric acid modified tamarind pod shell has considerable biosorption capacity, available in abundant, non-hazardous material can be used as an effective indigenous material for treatment of wastewater stream containing zinc (II). However, further research should attempt to improve the biosorption capacity of biosorbent and apply this method to the removal of metals in large scale.

5. References

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