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Biosorption of Zinc (II) from Aqueous Solution using Tartaric Acid Modified Tamarind (Tamarindus Indica L.) Pod Shell Powder

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Abstract: The ability of tartaric acid modified Tamarind (Tamarindus indica L.) pod shell powder to remove zinc (II) ions from aqueous solution by adsorption was studied. The extent of removal of zinc (II) was found to be dependent on contact time, pH, biosorbent dose, metal concentration and agitation speed. The optimum time, pH, biosorbent dose, metal concentration and agitation speed was found to be pH 6, 5 g, 120 mins, 5 g/L and 120 rpm respectively. The adsorption studies include both equilibrium adsorption isotherms and kinetics. Several isotherm models were investigated and the adsorption isotherm data were best represented by the Freundlich isotherm. The kinetic data were well described by the pseudo- second order kinetic model. The mechanism of adsorption process was determined from the intraparticle diffusion model. The results indicate that tartaric acid modified tamarind (Tamarindus indica L.) pod shell powder could be employed as a lowcost alternative for the removal of zinc (II) from aqueous solution.

Keywords: Adsorption, Tamarind (Tamarindus indica L.) pod shell powder, isotherm, kinetics, Zn (II).

I. INTRODUCTION

Environmental pollution is one of the main problems of the society in the 21st century. The major pollutants include toxic metals, the quantity of which permanently increases in the environment as the result of increased industrial activity. (Sunil Rajoriya *et al.*, 2014). Industrial wastewater contaminated with heavy metals is commonly produced from many kinds of industrial processes. Therefore, if this wastewater is not treated with a suitable process or leaked from storage tanks, it can cause a serious environmental problem in the natural eco-system (Achanai Buasri *et al.*, 2012). Metal pollution is one of the most important environmental problem today. Three kinds of metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am, etc.) Metals can be distinguished from other toxic pollutants, since are non-biodegradable and can accumulate in the living tissues, thus becoming concentrated throughout the food chain (iva melčáková *et al.*, 2010). Removal of toxic heavy metals from industrial wastewater has been practiced for several decades, the conventional physico-chemical removal methods, such as chemical precipitation, electro plating, membrane separation, evaporation or resin ionic exchange, are usually expensive and sometimes, not effective (Kalyani *et al.*, 2009). Biosorption is an innovative technology for removal and separation of heavy metals from aqueous solutions. The search of low cost sorbents for heavy metals is still an aim for the modern science. (Gergana K. Kirova *et al.*, 2015). Incineration of municipal solid waste can introduce about 75% zinc to urban air. Also, municipal wastewater generally contains significant amounts of zinc. The use of municipal and industrial waste in agriculture results in the accumulation of zinc in the surface layers of soil. The degree of toxicity of zinc is not big, but it depends on the ionic form, and changes under the influence of water hardness and pH. The daily average download of zinc by an adult is estimated at about 10-50 mg /day. Fuel and power industries generate 2.4 million tons of As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn annually The metal industry adds 0.39 million tons/yr of the same metals to the environment, while agriculture contributes 1.4 million tons/yr, manufacturing contributes 0.24 million tons/yr and waste disposal adds 0.72 million tons/yr (Pandidurai *et al.*, 2014). The extensive use of Zn cations in a few industrial applications, e.g. for galvanization and electroplating, without proper downstream recovery, has led to contamination of soil and fresh water habitats. Despite this metal being an essential element for activation of some enzymes in human cells, high exposure levels (100–500 mg/day) can be toxic and even carcinogenic. Trace concentration of zinc (II) are important for the physiological function of living tissue and regulate many biochemical process. However, trace amounts of free zinc ions can cause heavy damage to the

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environment and kill organisms. (Israel *et* al., 2012).The threshold limiting value of zinc in drinking water is 5 mg L-1 and in public sewage, inland surface water and marine water it is 15 mg/L (Drinking water specifications, IS-10500, 1991). Ingestion of > 2 g/L causes toxic symptoms like fever, diarrhea, gastrointestinal tract irritation etc in humans. (Venkateswarlu *et al*., 2008). Several conventional method exist for the removal of heavy metal pollutants from waste water include chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption. But the high cost of the materials these method are not generally use. Therefore now a day very innovative and cost effective methods are used for the removal toxic substance from waste water. Bio-sorption of heavy metal from aqueous solution is an efficient technology in industrial waste water treatment. This new technology has been loosely grouped together under the term biosorptions. 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. 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. The most convenient means of determining metal uptake ability is through a batch reaction process. (Thiyakarajan *et al*., 2014). Many studies have been carried out in order to find out effective and low-cost adsorbents. Different adsorbents are used in zinc removal such as chitosan and wheat shell. (Ying Zhang *et al*., 2013). Successful metal biosorption has been reported by a variety of biological materials including papaya wood (Asma et al., 2005), cork biomass (Natalia et al., 2004) and coir (Kathrine and Hans, 2007). Another category of bio-mass that acts as adsorbent is plant leaves. The few cases investigated include palm tree leaves (Fahmi and Abu, 2006) and waste tea leaves (Ahluwalia and Goya, 2005). Sorption studies were carried out with coir pith activated carbon for the removal of Zn (II) (Santhy and Selvapathy, 2004). In the present study modified tamarind pod shell powder to offer this biosorbents as local substitute for existing commercial adsorbent materials.

II.   MATERIAL 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 Biosorbent

The tamarind pod shells (*Tamarindus indica* L.) were collected from local market pune and Gujarat. The collected Tamarind pod shells were washed with several times with distilled water to remove the surface adhered particles, dirt, and other unwanted material & water soluble impurities. Biosorbent was then dried in the sunlight for three days. The dried pieces were ground in a steel mill to get a fine powder and it was sieved to select particles 100 μm in size will be used in all the experiments. The final product was named as tamarind pod shell (*Tamarindus indica* L.) powder. For further use, the dried biosorbent was stored in air tighten plastic bottle to protect it from moisture.

C.   Preparation Of Tartaric Acid Modified Tamarind Pod Shell (Tamarindus Indica L.)

About 25 g grinded tamarind pod shell powder was mixed with 17.5 ml of 1.2 M tartaric acid (TA). The mixture was stirred until homogenous and dried at 80°C in oven for 24 hours was then heated for 90 minutes in 100°C in a water bath. The treated tamarind pod shell powder was subsequently washed with distilled wate and dried for 40 hours in oven at 50°C. The final product was labelled as tartaric acid modified tamarind pod shell (*Tamarindus indica* L.).

D.   Preparation Of Zinc (II) 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.

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).

F. 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-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.

G. 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.

H. 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.

I. 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,

$$\% \, Ad = \frac{(c_i - c_e)}{c_i} \times 100 \qquad (1)$$

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,

$$q_e = \frac{(c_i - c_e)}{w} \times V \qquad (2)$$

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

J. 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 two 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 (equation 3).

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

III. RESULTS AND DISCUSSION

A. Characterization Of Biosorbent By Fourier Transform Infrared (FTIR) Analysis

FTIR offers excellent information on the functional groups present on the surface of the biosorbent and also presents three main advantages as an analytical technique: it is fast, nondestructive and requires only small sample quantities. As seen in the figure biosorbent displays a number of biosorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3413 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 2926 cm-1. The peaks located at 1604 cm-1 is characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biosorbent. The peak at 1512 cm-1 is associated with the stretching in aromatic rings. The peaks observed at 1037 cm-1 are due to C-H and C-O bonds. The –OH, NH, carbonyl and carboxyl groups are important

sorption sites. Biosorbent loaded with zinc (II), the broadening of -OH peak at 3415 cm-1 and carbonyl group peak at 1736 cm^{-1} and 1615 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of zinc (II).
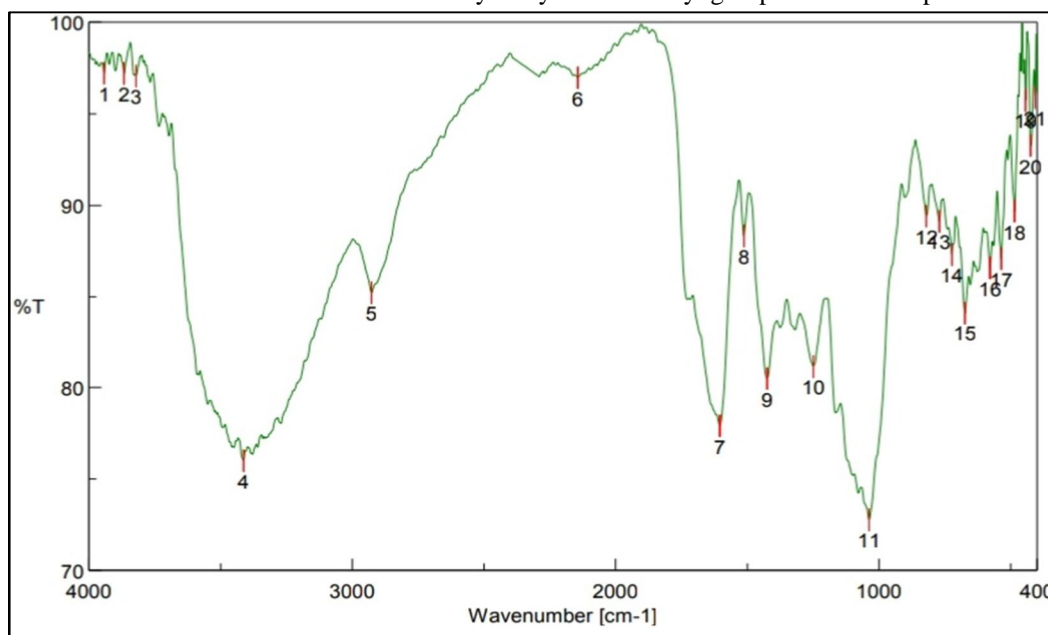
(a)
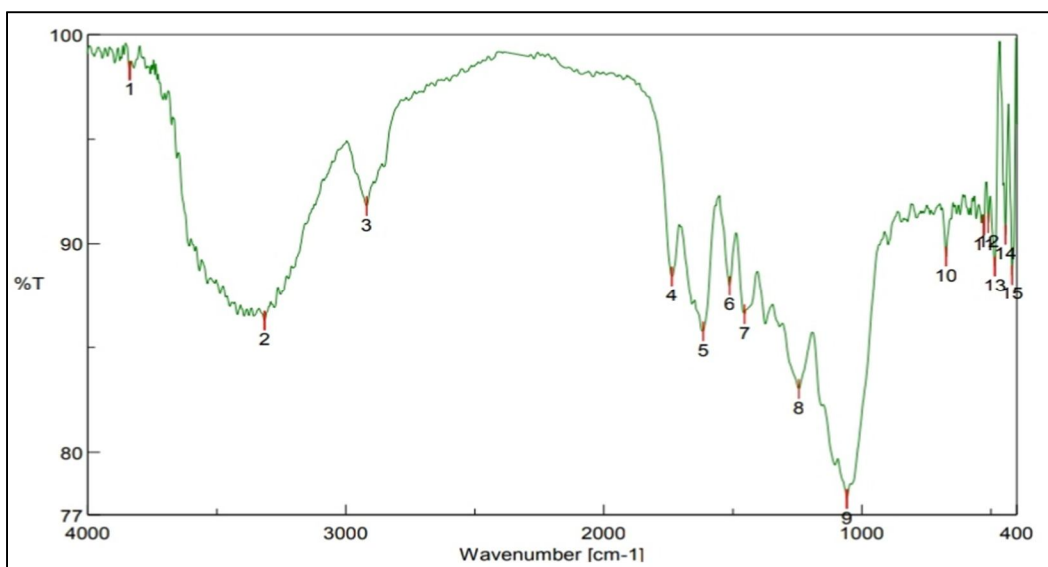
(b)

Figure 1: FTIR spectra (a) Biosorbent tartaric acid modified tamarind pod shell (Tamarindus indica L.) unloaded with zinc (II) (b) Biosorbent tartaric acid modified tamarind pod shell (Tamarindus indica L.) loaded with zinc (II)

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

The surface characteristics, structure and particle size distribution of tartaric acid modified tamarind pod shell before and after biosorption was examined using Scanning Electron Microscope (SEM). Tartaric 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.
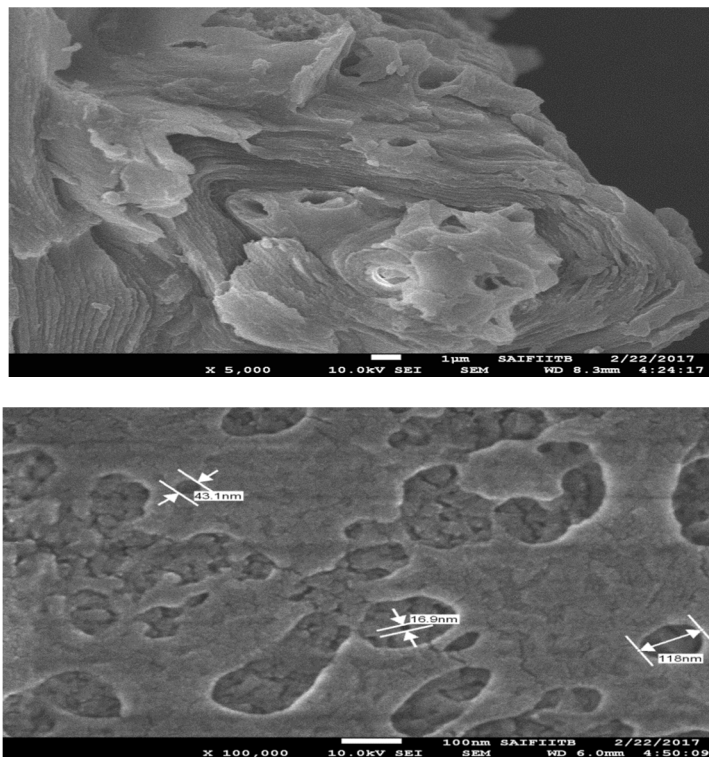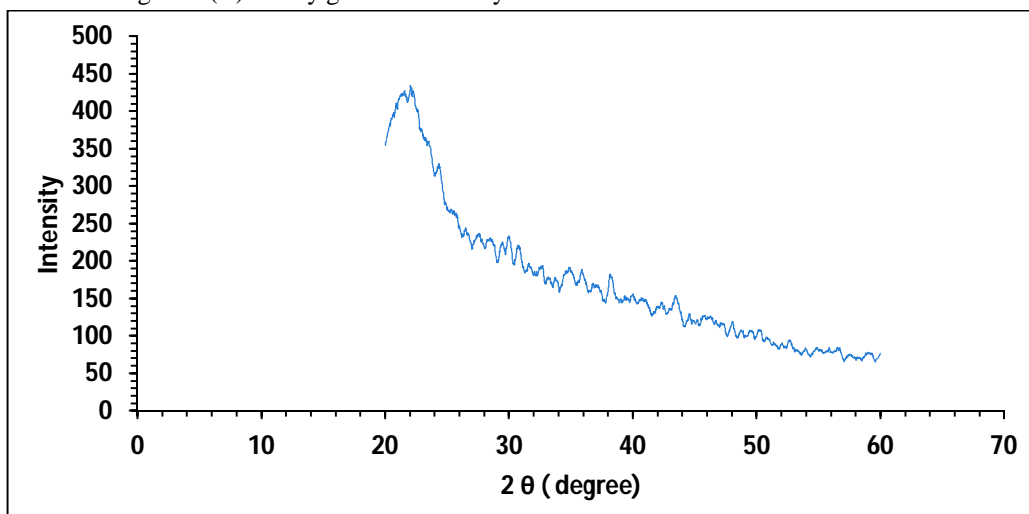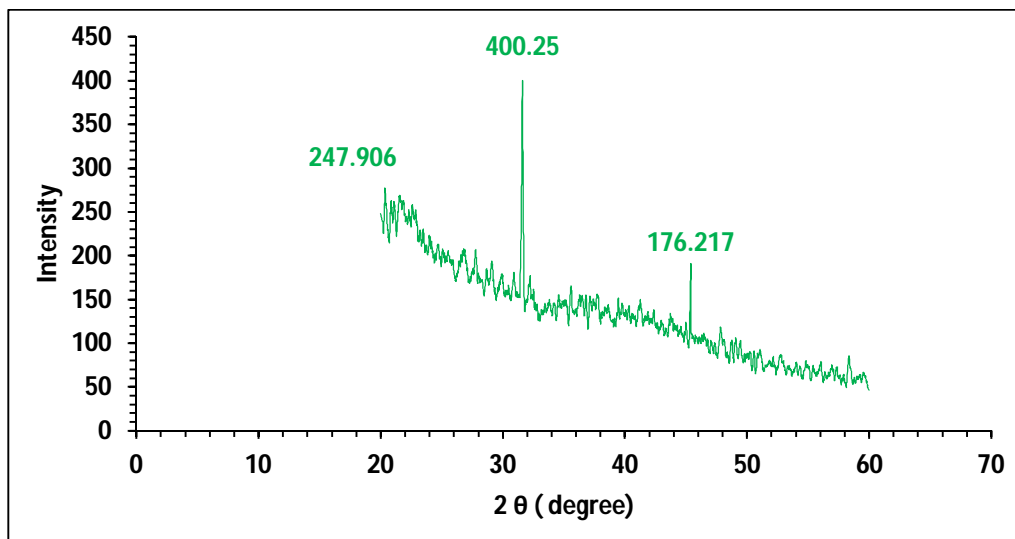
Figure 2:Scanning Electron Microscope (SEM) analysis (a) Biosorbent tartaric acid modified tamarind pod shell unloaded with zinc (II) (b) Biosorbent tartaric acid modified tamarind pod shell loaded with zinc (II)

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 tartaric acid modified tamarind pod shell unloaded with zinc (II) 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 20.34º, 31.6º and 45.38º equivalent to 247.906, 400.25 and 176.217, respectively. In addition, several other low intensity peaks corresponding to other crystalline phases have also been observed. After biosorption of zinc (II), the porosity of the biosorbents decreased. These causes low intensity 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 biosorbents.

(a)

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(c)

Figure 3:X-ray diffraction analysis (XRD) study (a) Biosorbent tartaric acid modified tamarind pod shell unloaded with zinc (II) (b) Biosorbent tartaric acid modified tamarind pod shell loaded with zinc (II)

D. Influence of pH

The pH of the solutions plays a major role in the biosorption process. The charge of metal ions in the solution and the availability of active sites for heavy metals attraction onto the surface of biosobent depend mainly onto pH of the working solution. With the increasing of the pH from 2.0 to 9.0 the metal uptake and removal also increased (Fig. 4). The low removal and uptake at pH 2.0 could be explained with the competition between the protons and the metal cations in solution for the adsorption sites on the biomass surface. When deprotonated carboxyl and hydroxyl groups are negatively charged and can bind positively charged zinc ions. With the increasing of the pH of the solution more functional groups on the cell wall are deprotonated and therefore provide more negatively charged groups for the Zn (II) biosorption. All further experiments were conducted at pH 6.
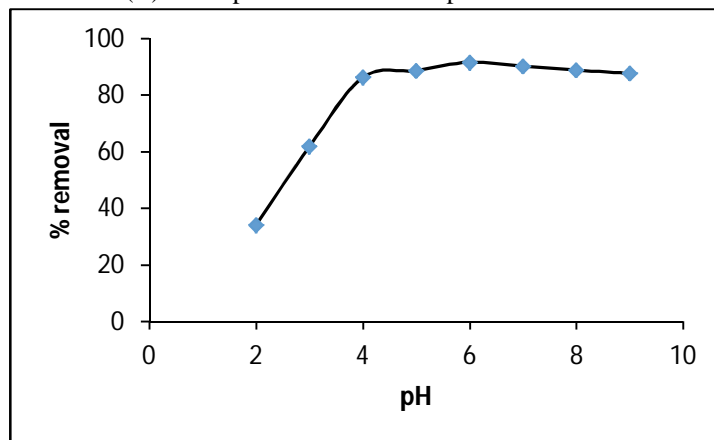

Figure 4: Influence of pH on zinc (II) biosorption by tartaric acid modified tamarind pod shell (Biosorbent dose concentration: 5 g/L, zinc (II) concentration: 5 mg/L, contact time: 120 minutes, temperature: 30^0C, agitation rate: 120 rpm)

E. Influence Of Biomass Concentration

The amount of the biosorbent also influenced the metal uptake and removal of the metal ions. With the increasing of the amount of the biosorbent, the number of the available sites for biosorption also increases, but the metal uptake per gram of biomass decrease. With the increasing of the biomass dosage from 1 to 15.0 g/L the metal uptake decreased from 10 to 15.0 g/L (Fig. 5). When the concentrations of the sorbent are too high it is impossible for metal ions to bind to all available active sites and that leads to low metal uptake. The agglomeration of the biosorbent particles which decreased the contact surface and the active sites could explain the low metal uptake.
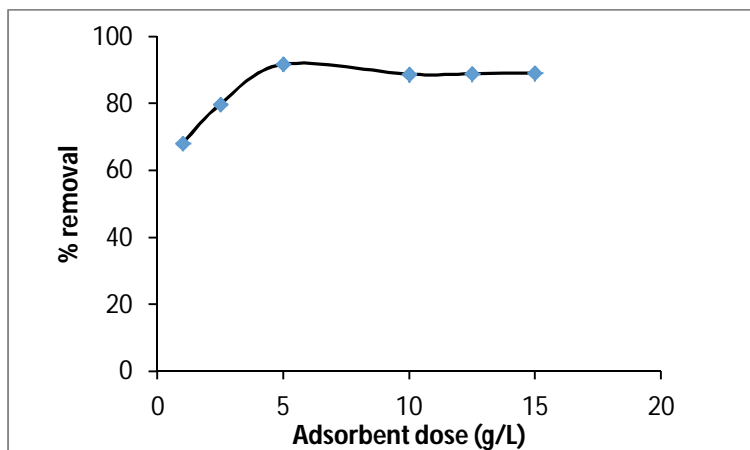
Figure 5: Influence of biosorbent dose concentration on zinc (II) biosorption by tartaric acid modified tamarind pod shell (Tamarindus indica L.) (pH: 6, initial zinc (II) concentration: 5 mg/L, contact time: 120 minutes, agitation rate: 120 rpm, temperature: $30^{o}C$)

F. Influence Of Initial Metal Concentration

To study the influence of the initial concentration on the biosorption performance the initial metal concentrations of the solutions were raised from 5 to 250 mg/L. When the concentration was increased from 100 to 250 mg L^{-1}, the percent removal of chromium (VI) decreased, while adsorption capacities increased with increase in concentration. The decrease in absorption of chromium (VI) at high concentration was due to the saturation of active binding sites. The obtained results are shown in Figure 6.
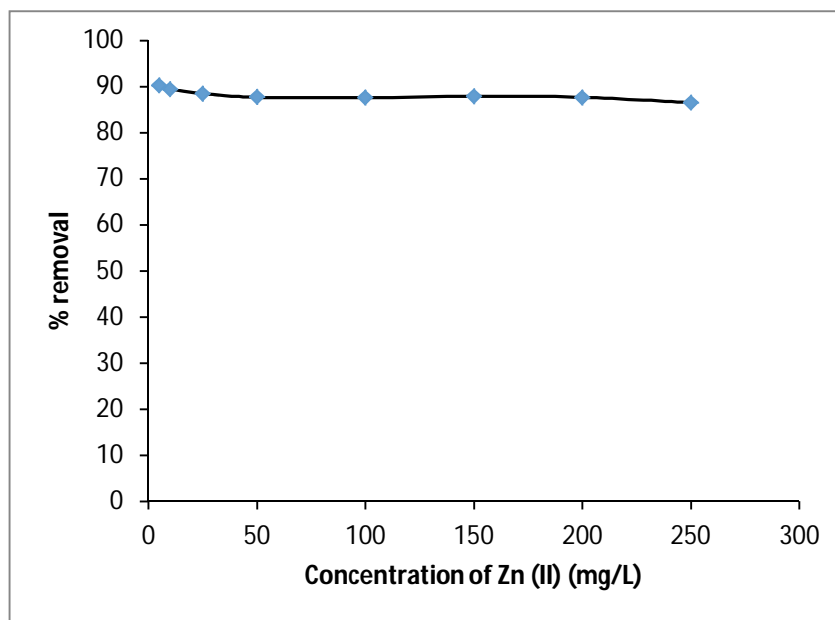

Figure 6: Influence of initial zinc (II) concentration on zinc (II) biosorption by tartaric acid modified tamarind pod shell (Tamarindus indica L.) (pH: 6, biosorbent dose concentration: 5 g/L, contact time: 120 minute, agitation rate: 120 rpm, temperature: $30^{0}C$)

G. Influence Of Stirring Speed

The stirring speed also influenced the biosorption process. Agitation speed takes part in the contact between the metal ions and the biomass and influences the mass transfer in system sorbent-sorbat. Higher metal uptake at 120 rpm and recovery of 91.64%. (selatnia et al., 2004) explained the lower metal uptake at higher agitation speeds with the non-homogeneity of the sorbent-sorbat system as a result of vortex phenomena.
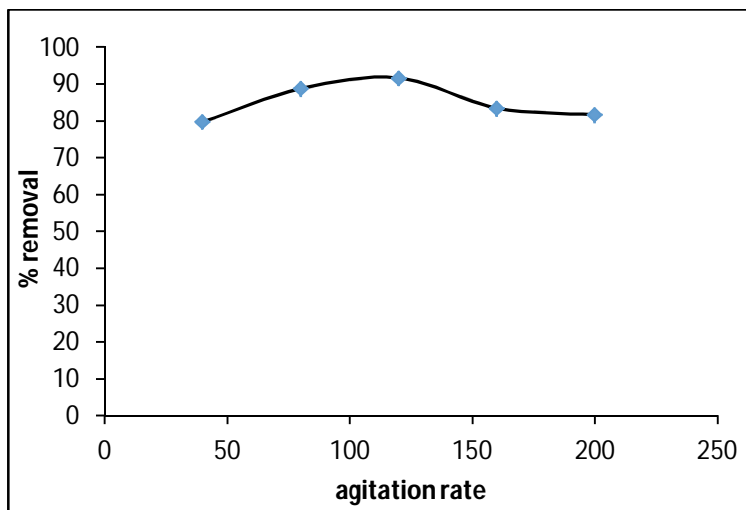
Figure 7: Influence of agitation rate on zinc (II) biosorption by tartaric acid modified tamarind pod shell (*Tamarindus indica* L.) (pH: 6, biosorbent dose concentration: 5 g/L, initial zinc (II) concentration: 5 mg/L , contact time: 120 minute, temperature: 30^0C)

H. Influence Of Contact Time

The data obtained from the biosorption of zinc (II) ions on the tartaric acid modified tamarind pod shell powder showed that a contact time of 120 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed zinc (II) concentrations at the end of 120 min are given as the equilibrium values (5 g/L biosorbent dose; concentration of zinc (II) 5 mg/l), respectively. And the other adsorption experiments were conducted at this contact time of 120 min.

Figure 8: Influence of contact time on zinc (II) biosorption by tartaric acid modified tamarind pod shell (*Tamarindus indica* L.) (pH: 6, biosorbent dose concentration: 5 g/L, initial zinc (II) concentration: 5 mg/L, agitation rate: 120 rpm, temperature: 30^0C)

I. Influence Of Temperature

The Influence of temperature on removal of zinc (II) from aqueous solutions using tartaric acid modified tamarind pod shell was studied at different temperatures from 20^0C-40^0C. The influence of temperature is depicted in Figure 9. Maximum sorption was seen at 30^0C with percentage removal 91.64%.

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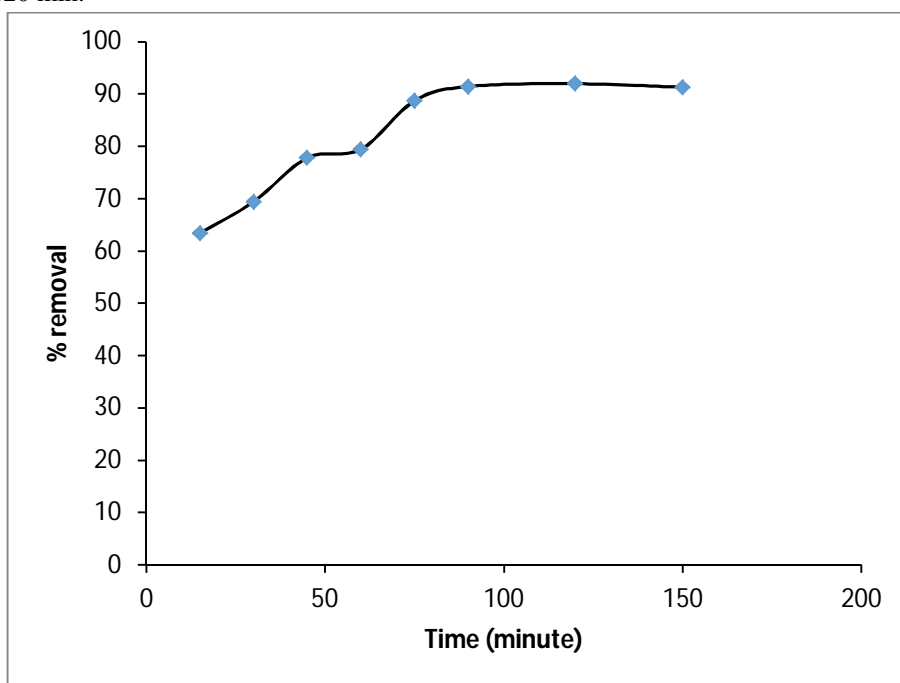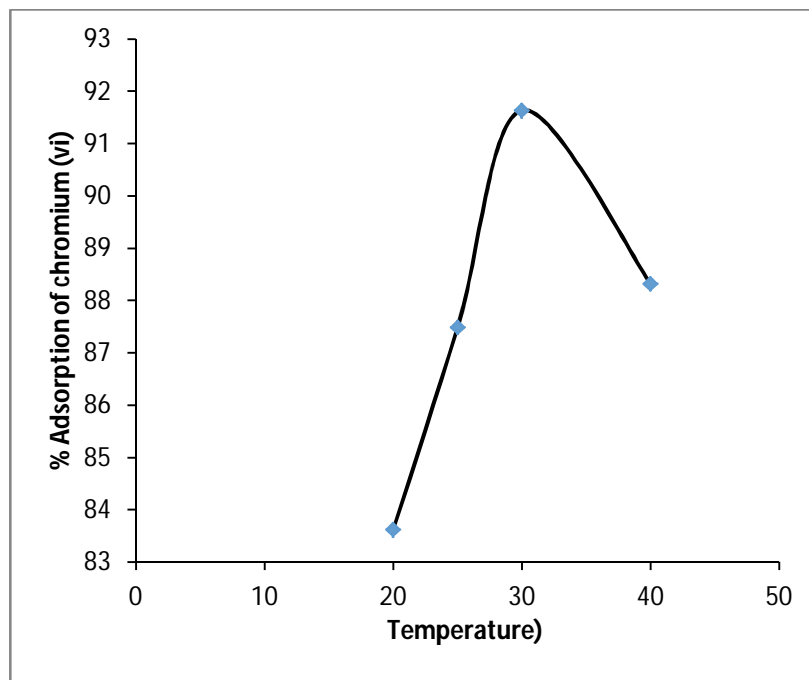Volume 7 Issue I, Jan 2019- Available at www.ijraset.com

Figure 9: Influence of temperature on zinc (II) biosorption by tartaric acid modified tamarind pod shell (Tamarindus indica L.) (pH 6.0, biosorbent dose concentration: 5 g/L, agitation rate: 120 rpm, initial zinc (II) concentration: 5 mg/L, contact time: 120 minutes.)

J. Desorption Study
In application of real wastewater, desorption of heavy metal ions in the biosorbent is important process. Tartaric acid modified tamarind pod shell was the most effective waste biosorbent with desorption efficiency 60.94% (0.1 M hydrochloric acid), 86.73% (0.1 M nitric acid)and 66.77% (0.1 M sulphuric acid). nitric acid has shown highest desorbed capacity of zinc (II) followed by hydrochloric acid and sulphuric acid from tartaric acid modified tamarind pod shell.

K. Adsorption Isotherms
The analysis of the adsorption isotherms data by fitting them into different adsorption 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 adsorption isotherm models: Langmuir, Freundlich, DubininKaganer-Redushkevich (DKR) and Temkin. Adsorption isotherms results for biosorption of zinc (II) by tartaric acid modified tamarind pod shell (*Tamarindus indica* L.) are shown below;

L. Langmuir Adsorption Isotherm (Langmuir, 1918)
The Langmuir equation is applicable for monolayer adsorption onto a surface containing a finite number of identical adsorption sites (Namasivayam *et al.*, 1997). The Langmuir model is described by the following equation:

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

Where q_m is the maximum biosorption capacity of adsorbent (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 adsorprtion capacities and Langmuir constants and is represented as:

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

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 $(1/q_m \cdot b)$ and intercept $(1/q_m)$ of the line. The values of q_m, b and regression coefficient (R^2) are listed in Table 1.
The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent which is calculated using following equation;

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

Where b is the Langmuir constant and C_i is the maximum initial concentration of zinc (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 separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation: 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 0.1030 to 0.8517 for concentration of 5 mg/L to 250 mg/L of zinc (II). They are in the range of 0-1 which indicates favorable biosorption.

Freundlich adsorption isotherm (Freundlich, 1906):

Freundlich equation is represented by;

$$q_e = KC_e^{1/n} \qquad (7)$$

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 sorption data and is represented as:

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

Equilibrium data for the adsorption is plotted as log q vs log Ce, 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 adsorption is chemical process; if n>1, then adsorption 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 1.0763. Since n >1, this indicates that biosorption is a physical process biosorption of zinc (II) ions onto tartaric acid modified tamarind pod shell. The higher value of K (1.7049) indicates the higher adsorption capacity for the tartaric acid modified tamarind pod shell (*Tamarindus indica* L).

M. Dubinin-Kaganer-Radushkevich (Dkr) Adsorption Isotherm (Dubinin And Radushkevich, 1947)

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

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

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

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

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,

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

The E value was found to be 1.1180 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 and Brittenham, 1997). In the present work, E value (1.1180 KJ mol-1) which is less than 8 KJ mol-1, the biosorption of zinc (II) ions onto tartaric acid modified tamarind pod shell (*Tamarindus indica* L.) is of physical in nature (Sawalha et al., 2006).

N. Temkin Adsorption Isotherm (Temkin And Pyzhev, 1940)

Linearized Temkin adsorption isotherm is given by the equation;

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

Where b_T is the Temkin constant related to heat of biosorption (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 10(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). The various constants and regression coefficient R^2 obtained from adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) are summarized in Table 1.

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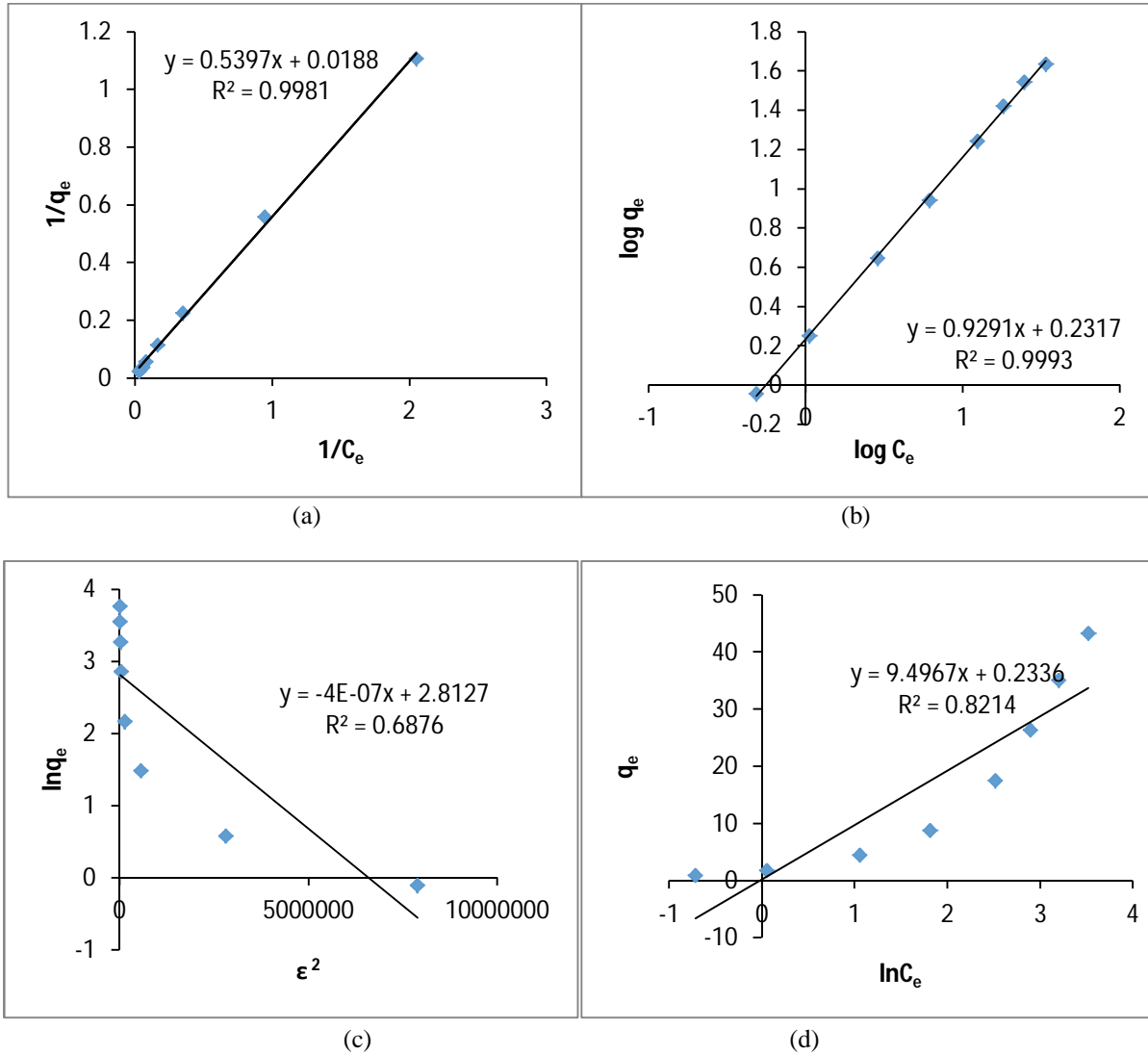*Volume 7 Issue I, Jan 2019- Available at www.ijraset.com*

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

Table 1: Adsorption isotherm constants for biosorption of zinc (II) by tartaric 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
53.191 4	0.034 8	0.998 1	1.704 9	0.929 1	0.999 3	-4×10^{-7}	16.654 8	1.118 0	0.687 6	2.718 2	265.25 0	0.821 4

O. Adsorption Kinetic Models

As aforementioned, a lumped analysis of adsorption rate is sufficient to particle operation from a system design point of view. The commonly employed lump kinetic models, namely (a) pseudo-first-order (b) pseudo-second-order (c) Elovich model (d) Weber & Morris intra-particle diffusion model are presented below;

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

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

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

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

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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. ki (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant, c is intercept.

If the adsorption 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 ln t should be a straight line. Also a plot of q_t against t $^{0.5}$ changes lineally the adsorption process obeys the Weber and Morris intraparticle diffusion model. Kinetic plots depicted in Figure 11 (a) (b) (c) and (d) (Septhum *et al.*, 2007).

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 (ln q_e) of the plot and shown in Table 2. Pseudo-first-order model showered the correlation value (R^2= 0.8405) being lower than the correlation coefficient for the pseudo-second-order model. Kinetic biosorption 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. Pseudo-second-order kinetic model showered the strongest correlation (R^2= 0. 0.9966). This suggests that zinc (II) biosorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical adsorption is the rate limiting step. Zinc (II) reacts chemically with the specific binding sites on the surface of biosorbent. The Elovich model was plotted for qt 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 (Thomas and Thomas, 1997).

The Weber & Morris intra-particle diffusion model was plotted for q_t against t $^{0.5}$ (Figure 11 (d)). The value of ki and c are calculated from the slope (ki) and intercept (c) of the plot and values are shown in Table 2. The Weber and Morris intra-particle diffusion model showed a (R^2= 0. 8883) being lower than the correlation coefficient for the pseudo-second-order 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 (Weber and Morris, 1963).
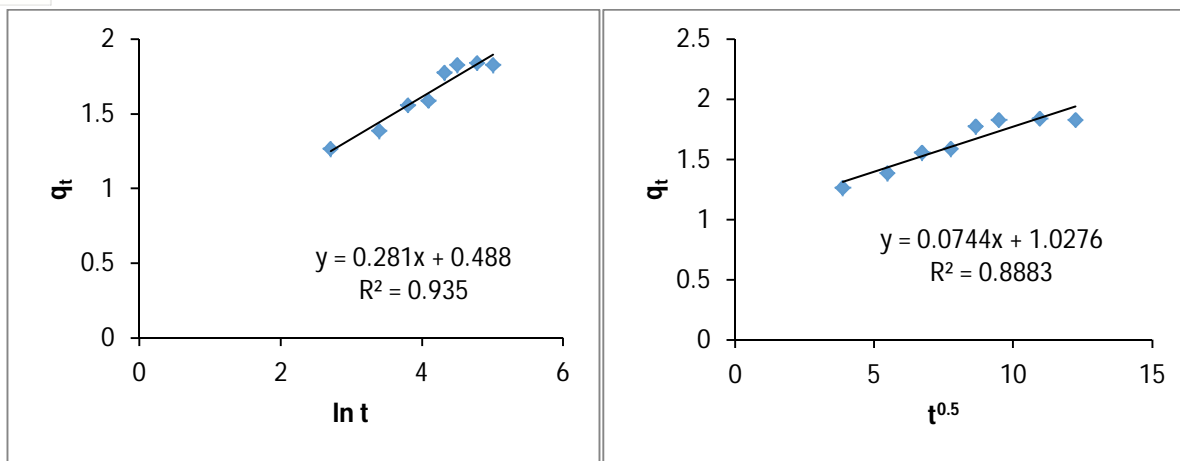
The plot of intra-particle diffusion model showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of biosorbent or the boundary layer diffusion of solute molecules. The second portion 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).
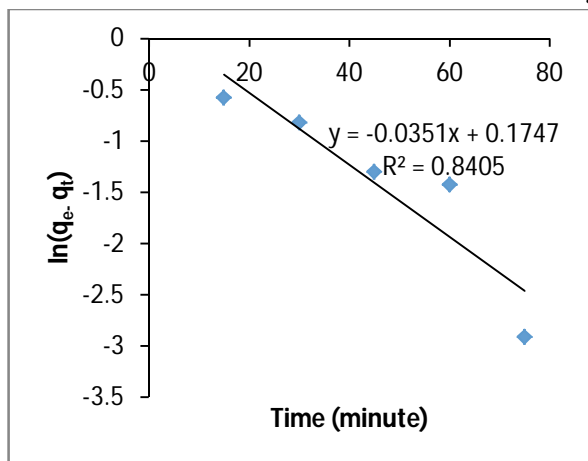
(a)
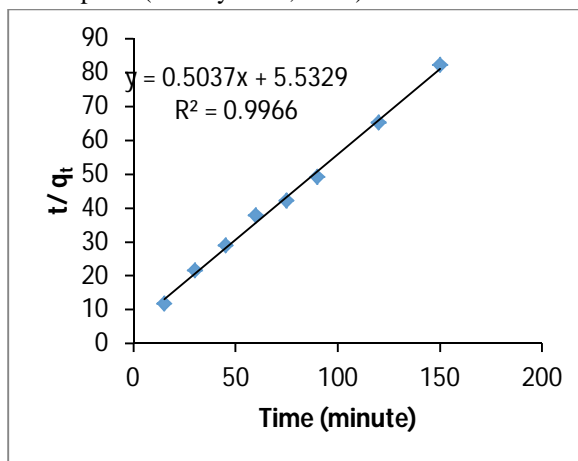
(b)

(c)

(d)

Figure 11: Adsorption kinetic models (a) pseudo-first-order model (b) pseudo-second-order model (c) Elovich model and (d) Weber and Morris intra-particle diffusion model, for biosorption of zinc (II) by tartaric acid modified tamarind pod shell (Tamarindus indica L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, initial zinc (II) concentration: 5 mg/L, temperature: 30^0C, agitation rate : 120 rpm)

Table 2: Adsorption kinetic data for biosorption of zinc (II) by tartaric acid modified tamarind pod shell (*Tamarindus indica* L.)

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	α	β	R^2	Ki	C	R^2
1.1908	0.0351	0.8405	1.9853	0.0458	0.9966	1.5956	3.5587	0.9350	0.0744	1.0276	0.8883

P. Thermodynamic Study

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

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

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

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

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (20)$$

Where *Kc* is the equilibrium constant, *Ce* is the equilibrium concentration in solution (mg/L) and *CAe* is the amount of zinc (II) 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), standard enthalpy (kJ/mol) and standard 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 lnKc versus 1/T (Figure 12). The values of equilibrium constant (Kc), 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 (Kc) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intra-particle diffusion. The value of standard Gibbs free energy change (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) onto tartaric acid modified tamarind pod shell (Tamarindus indica L.). The positive values of ΔS^0 shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

Table 3: Thermodynamic parameters of zinc (II) biosorption by tartaric acid modified tamarind pod shell (Tamarindus indica L.)

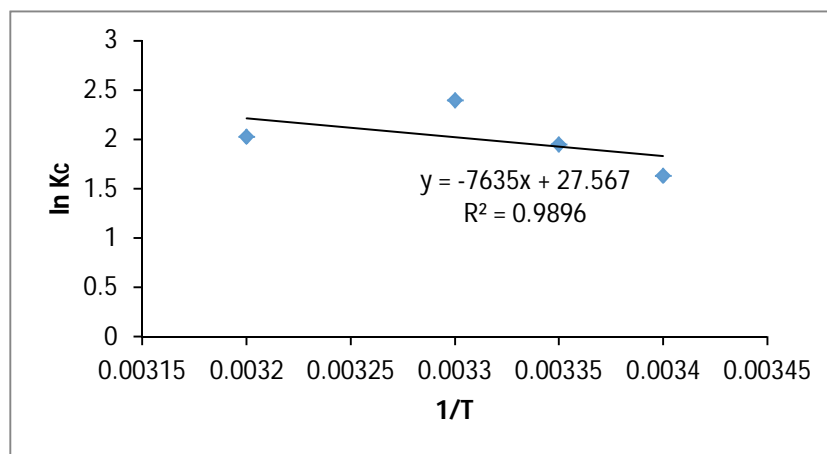| Sr. No.	Temperature (C^0)	Temperature (K)	Kc	$-\Delta G^0$ (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	20^0C	293	5.1087	3.9728		
2	25^0C	298	6.9936	4.8186	63.477	229.192
3	30^0C	303	10.9617	6.0318		
4	40^0C	313	7.5616	5.2644		

Figure 12: Plot of lnKc against 1/T for determination of thermodynamic parameters for zinc (II) biosorption by tartaric acid modified tamarind pod shell (Tamarindus indica L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, zinc (II) concentration: 5 mg/L, contact time: 120 minutes)

IV. CONCLUSIONS

This paper presents an investigation on the biosorption of zinc (II) from aqueous solutions on waste biomass of tartaric acid modified tamarind pod shell powder as a biosorbent. The maximum removal of zinc (II) for tartaric acid modified tamarind pod shell powder after 120 min was 91.97% and 91.64% at optimum pH of 6, respectively. This study shows that the tartaric acid modified tamarind pod shell is an inexpensive and environmentally friendly adsorbent for zinc (II) removal from wastewater.

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