



Kausar, A., Bhatti, H. N., and MacKinnon, G. (2016) Re-use of agricultural wastes for the removal and recovery of Zr(IV) from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers*, 59, pp. 330-340. (doi: [10.1016/j.jtice.2015.08.016](https://doi.org/10.1016/j.jtice.2015.08.016))

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Deposited on: 3 May 2016

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**Re-use of agricultural wastes for the removal and recovery of Zr(IV) from aqueous solutions**

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## **Abstract**

This study assesses the feasibility of Zr(IV) removal and recovery from aqueous solutions by novel biosorbents prepared from selected agricultural wastes. Sugarcane bagasse was selected for further investigation after showing increased biosorption capacity during the initial screening experiment. The biosorption efficiency of native (untreated), SDS-treated and immobilised bagasse for Zr(IV) removal was studied and optimization of the experimental conditions carried out including pH, biosorbent weight, contact time, initial metal ion concentration and temperature to maximise adsorption. Sorbent-sorbate reaction behaviour was estimated by fitting equilibrium data by non-linear and transformed linear forms of the Langmuir, Freundlich and Redlich-Peterson isotherms as well as pseudo-first and second-order kinetic models. The best fitting isothermal or kinetic model was optimized by comparing linear and non-linear  $R^2$  value and non-linear regression error functions.  $H_2SO_4$  proved to be the most effective desorbing agent in recovery of the sorbed Zr(IV) ions from all forms of bagasse. Biosorbent characterisation and effectiveness of the process was confirmed by Fourier transform infra-red spectroscopy (FT-IR), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX). The data illustrate that native (untreated), SDS-treated and immobilised bagasse have great potential to remove and recover Zr from wastewater.

**Key words:** Biosorption; Environmental Preservation; Equilibrium; Kinetic; Modelling; Waste-water

## **1. Introduction**

During the last decades, the unique physical and chemical properties of Zirconium (Zr) have increased its industrial use, leading to an increased annual production from mines where it is sourced. This has led to higher releases to the environment from several anthropogenic sources including nuclear power production, ceramic dusts, heavy metal mining, improper waste dumping, incidental release e.g. leakage, corrosion and from atmospheric fallout. Zr is widely used in many chemical industry processes and in nuclear reactors owing to its useful properties like hardness, corrosion-resistance and permeability to neutrons. Like other persistent heavy metals that pollute the terrestrial and aquatic environments, Zr is of increasing environmental concern.

Among the various methods available for water treatment, adsorption has received much attention since it not only reduces environmental contamination but also allows for water recycling and chemical recovery, which increases the feasibility of the process. Biosorption of heavy metals can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. The biosorption of metals to the biomass surface occurs mainly as a result of both physical binding involving London–Vander Waals forces and electrostatic attraction, or by chemical binding such as ionic or covalent bonding between the adsorbent and the adsorbate. Unlike monofunctional ion exchange resins, biosorbents can contain many functional sites such as carboxyl, amino, phosphate, sulfate, phenol, carbonyl, amide and hydroxyl moieties for adsorption [1]. This technology is gaining the interest of many researchers, with native (untreated) and chemically and physically modified adsorbents being considered as cheap and environmentally friendly materials for removal of pollutants from aqueous solutions [1-8]. Using agricultural waste products, such as fruit peels, shells, straw, and coconut coir, as adsorbents is a low-cost and simple approach for removing heavy metals from wastewater. In the last two decades, a variety of agricultural waste products have been

explored as low cost and readily available adsorbents either in their natural form or following a physical or chemical modification [2, 9].

Sugarcane bagasse is a residue from the sugarcane crushing process and although it can be used as a fuel in the sugarcane industry, vast quantities are produced worldwide and end up as an industrial waste produced by the sugar industry. It is composed mainly of lignin (20-25%), polyoses (25-30%) and cellulose (40-50%), with a small amount of other extractive components and ash [10-11]. The sugar industry in Pakistan is one of the oldest and largest industries in India and the production of sugarcane bagasse causes significant disposal problems. The objective of the present study was to evaluate bagasse, along with other agricultural waste products, as economical biosorbents for the removal of Zr(IV) from aqueous solution. The most successful biosorbent was then further modified to enhance biosorption uptake capacity and the kinetic, equilibrium and thermodynamic reactions of the sorption process detailed, in order to assess the potential for technology transfer from laboratory to industrial scale.

## **2. Material & Methods**

### **2.1. Chemicals**

All chemicals used were of analytical grade and purchased from Sigma-Aldrich Chemical Co, USA. A 1000 mg L<sup>-1</sup> Zr(IV) stock solution was prepared by dissolving zirconyl oxychloride (ZrOCl<sub>2</sub>.8H<sub>2</sub>O) salt (Fisons, Loughborough, England) in with double distilled deionized water (DDW) (pH 7, conductance 4 μS cm<sup>-1</sup>) and working standards of desired concentration were prepared by diluting the stock solution.

### **2.2. Collection and preparation of biosorbents**

Selected agricultural wastes (rice husk, cotton sticks, peanut shell, sugarcane bagasse, rice bran and wheat bran) were collected from agricultural fields and industries of Faisalabad, Pakistan. Selected biowastes were extensively washed with tap water and then three times with DDW to remove water soluble surface contaminants. After washing, biowastes were air dried at ambient temperature then cut, finely ground (blender) and sieved (Octagon Siever, OCT-Digital 4527-01) to obtain a homogeneous material of uniform size (300  $\mu\text{m}$ ). The prepared biosorbent material was stored in air tight jars until further use.

### **2.3. Initial screening of biosorbent**

Screening was carried out by adding 0.1 g of each biosorbent in 250 mL Erlenmeyer flasks containing 50 mL of 50 mg L<sup>-1</sup> Zr(IV) solution of pH 3.5. Solutions were shaken for 2 h at 125 rpm and then filtered (Whatman No 42 filter paper). The Zr(IV) concentration of the filtrate was then analysed by the spectrophotometric method described in Section 2.7.

### **2.4. Physical and chemical pre-treatments of selected biosorbent**

Sugarcane bagasse (bagasse) proved to be the most successful biosorbent tested for Zr(IV) adsorption during the initial screening experiment therefore, it was selected for further chemical and physical pre-treatment. 1.0 g sub-samples of bagasse biosorbent were chemically treated by shaking with 100 mL of either 5 % Hydrochloric acid (HCl), Nitric acid (HNO<sub>3</sub>), Ethylene diamine tetra acetic acid (EDTA), Sodium hydroxide (NaOH), Sodium dodecyl sulphate (SDS), Cetyl trimethylammonium bromide (CTAB), Ammonium hydroxide (NH<sub>4</sub>OH), Polyethyleneimine (PEI), Calcium chloride (CaCl<sub>2</sub>), glutaraldehyde and Triton solutions for 2 h. Each sample was then extensively washed with DDW and filtered (Whatman No 42 filter paper). Sub-samples of bagasse biosorbent were also physically modified by autoclaving (1.0 g of biosorbent/100 mL of water for 15 min) and boiling (1.0 g

of biosorbent /100 mL of water for 10 min). Finally, all chemically and physically treated bagasse samples were oven dried at 30 °C, ground with a mortar and pestle and kept in air tight jars until further use.

## **2.5. Immobilisation of bagasse**

Immobilisation of the bagasse biosorbent was carried out using the method of Kausar *et al*, 2013 [5]. Briefly, 1.0 g of sodium–alginate was dissolved in 100 mL of water by heating on a hotplate until boiling. The solution was allowed to cool to approximately 40 °C then 2 g of bagasse biosorbent was added and stirred until a homogeneous mixture was formed. The mixture was then added drop-wise, using a burette, into a solution of 1% CaCl<sub>2</sub> (w/v), forming uniform beads of bagasse immobilised Ca-alginate. The beads were kept in the 1 % CaCl<sub>2</sub> (w/v) for at least one hour to allow complete curing, then washed with DDW and stored at 4 °C in DDW until further use.

## **2.6. Batch biosorption studies**

Batch biosorption experiments using native (untreated), chemically-treated, physically-treated and immobilised bagasse were carried out in 250 mL Erlenmeyer flasks containing 50 mL of known concentrations of Zr(IV) solution and amount of biosorbent with a constant shaking speed of 125 rpm for a defined time period. To optimise the conditions for maximum Zr(IV) removal, different sorption affecting parameters were investigated including pH (the pH of each solution was adjusted with 1M HCl providing a range from 1-4), biosorbent amount (0.05-0.3 g), initial metal ion concentration (25-200 mgL<sup>-1</sup>), shaking time (5-740 min) and temperature (30–60 °C). After shaking, the solution was filtered and the Zr(IV) concentration determined . The biosorption equilibrium of zirconium per unit biomass (mg of Zr g<sup>-1</sup>) dry weight of the bagasse was calculated using formula

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

Where  $C_0$  and  $C_e$  are the initial and final concentrations of Zr(IV) in solution ( $\text{mg L}^{-1}$ ),  $V$  is volume of Zr(IV) solution of desired concentration in litres and  $W$  is the dry weight of bagasse added (g).

## 2.7. Analytical determination of Zr

Zirconium concentrations were measured by the spectrophotometric assay of Aktar *et al*, 2008 [3] based on the reaction of zirconium with xylenol orange. Briefly, a solution of xylenol orange (0.05%) was prepared by dissolving the dry powder in 0.6 N HCl. This reagent was added in the ratio of 2 mL xylenol orange reagent to 23 mL sample solution (2:23, v/v) to provide a final volume of 25 mL. The solutions were mixed and allowed to stand for approximately 10 min after which the absorbance was measured at 535 nm (CECIL CE-7200 spectrophotometer) against the reagent blank. A standard calibration curve was prepared by adding xylenol orange reagent to standard solutions of 0, 5, 10, 20, 30, 40 and 50  $\mu\text{g}$  of Zr(IV)/mL of final volume in a similar procedure as the sample. The concentration of Zr(IV) present in unknown samples was calculated from this standard curve.

## 2.8. Equilibrium and sorption kinetics

Adsorption isotherms were used to characterize the biosorption process and for evaluating biosorption capacity. To understand the mechanism controlling biosorption, the most commonly used pseudo-first and pseudo-second order kinetic models were used to interpret the experimental data. Error analysis was used to explain the experimental equilibrium and kinetic data with linear and non-linear regression analysis of equilibrium and kinetic models performed using Microsoft Excel 2007 and the statistical software R (Version 2.15.1) respectively.



## 2.9. Thermodynamic study

The thermodynamic parameters for the adsorption process, namely Gibbs energy ( $\Delta G^\circ$ ), enthalpy of adsorption ( $\Delta H^\circ$ ) and entropy of adsorption ( $\Delta S^\circ$ ) were determined by carrying out the adsorption experiments at different temperatures and using the following equations [12].

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (2)$$

$$\text{Log} (q_e/C_e) = -\Delta H^\circ/2.303RT + \Delta S^\circ/2.303R \quad (3)$$

Thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were computed from the linear plot of  $\text{Log} (q_e/C_e)$  and  $1/T$  from slope and intercept respectively using Microsoft Excel 2007 and  $\Delta G^\circ$  from equation 2.

## 2.10. Desorption Studies

Desorption studies to regenerate the biosorbent were conducted using EDTA,  $\text{H}_2\text{SO}_4$ , HCl, NaOH and Magnesium sulphate ( $\text{MgSO}_4$ ), to compare their ability to elute adsorbed Zr(IV) ions. To regenerate the biosorbent, Zr(IV) was adsorbed under optimized conditions and the metal loaded residue dried in an oven at  $40^\circ\text{C}$  for 24 h. The loaded biosorbent was then desorbed in 100 mL of 0.1 M solution of each selected eluting agent, by shaking for one hour at a speed of 125 rpm. The percentage of Zr(IV) desorbed was calculated by the following:

$$\% \text{ Desorption} = \left[ \frac{q_{\text{des}}}{q_{\text{ads}}} \right] * 100 \quad (4)$$

and

$$q_{\text{des}} = C_{\text{des}} V/W \quad (5)$$

where  $q_{\text{des}}$  is the eluted metal content ( $\text{mg g}^{-1}$ ) and  $C_{\text{des}}$  ( $\text{mg L}^{-1}$ ) is the metal concentration in the eluent solution of volume,  $V$  (L) and biomass weight,  $W$  (g).

## 2.11. Biosorbent characterization

### 2.11.1. Determination of surface composition

The surface microtopography and composition of the bagasse was examined using a JEOL model 2300 Scanning Electron Microscope equipped with Energy Dispersive X-Ray (SEM-EDX) before and after loading with Zr(IV). Surface elemental composition of the biosorbent was examined by EDX. Analyses were conducted on each sample under optimized conditions using Pt coating to avoid charge indulgence during SEM scanning in an Ar atmosphere at current of 6 mA.

### 2.11.2. Determination of functional groups

Fourier Transform Infra-Red (FT-IR) spectroscopy (IR Perkin Elmer 1600 spectrometer) of unloaded and Zr loaded, native (untreated) bagasse was carried out to identify the chemical functional groups responsible for sorption of the metal ions. KBr disks of biosorbent material were prepared and FTIR data were observed and recorded over 400-4000  $\text{cm}^{-1}$  (software Bio-Rad Merlin).

## 2.12. Statistical analysis

Each experiment was conducted in duplicate to ensure the reproducibility of results. All data represent the mean  $\pm$  standard deviation of two independent experiments. The value of coefficient of determination ( $R^2$ ) of equilibrium, kinetic and thermodynamic models were determined using either linear regression (Microsoft Excel 2010) or non-linear regression (R statistical software, Version 2.15.1) using the following formula:

$$R^2 = \frac{(q_{e,exp} - q_{e,calc})^2}{\Sigma (q_{e,exp} - q_{e,calc})^2 + (q_{e,exp} - q_{e,calc})^2} \quad (6)$$

The subscripts “exp” and “calc” show the experimental and values calculated from the model [13].

### **3. Results and Discussion**

#### **3.1. Screening of biosorbents**

An initial screening experiment was performed to determine the biosorbent showing the best potential for Zr(IV) uptake. The biosorption capacity for native (untreated) forms of bagasse, wheat bran, cotton sticks, rice bran, rice husk and peanut husk were 10.48, 8.83, 7.64, 7.83, 6.35 and 7.46 mg g<sup>-1</sup> respectively. Due to its higher uptake capacity, bagasse was selected for further studies.

#### **3.2. Effect of pre-treatments**

The biosorption capacity (q) values of native (untreated) bagasse biosorbent and physically and chemically treated bagasse were in the following order: SDS; 13.5, native (untreated); 11.9, NaOH; 10.9, CTAB; 10.7, glutaraldehyde; 9.11, autoclave; 9.50, boiling 8.56, HNO<sub>3</sub>; 7.94, Triton; 6.62, EDTA; 6.31, H<sub>2</sub>SO<sub>4</sub>; 6.19, HCl; 5.33, PEI; 4.85, NH<sub>4</sub>OH; 4.08, MgSO<sub>4</sub>.7H<sub>2</sub>O; 2.67, NaNO<sub>3</sub>; 1.84, and CaCl<sub>2</sub>; 0.817 mg g<sup>-1</sup> respectively. An increase in the biosorption capacity of modified biosorbents can be attributed to increased exposure of active metal binding sites caused by chemical modifications of the cell wall components or removal of surface impurities. For example, pre-treatment may cause increase in biosorption capacity by removing lipids and proteins that mask binding sites or by removing some mineral matter which will increase access to metal binding sites. Surfactant pre-treatment introduces lyophobic and lyophilic groups capable of adsorbing at the biosorbent surface: solution interface. The adsorptions of heavy metals onto biomass from aqueous solution have been shown to be enhanced in the presence of surfactants due to reduced surface tension and increased wetting power [14]. From all the modified treatments, SDS-treated bagasse

showed maximum removal of Zr (IV) ions and was selected for further biosorption optimization studies.

### **3.3. Effect of pH, biosorbent weight, shaking time, initial metal ion concentration and temperature on Zr(IV) biosorption**

The effect of pH on Zr(IV) biosorption onto native (untreated), SDS-treated and immobilised bagasse was studied in the pH range of 1-4 due to  $Zr(OH)_4$  precipitation at higher pH values [15]. It is clear from Fig.1(a) that extremely acidic conditions did not favour Zr(IV) sorption with an increase in biosorption capacity with increasing pH being observed at pH 3.5 for native ( $14.1 \text{ mg g}^{-1}$ ) and immobilised ( $10.7 \text{ mg g}^{-1}$ ) and pH 3 for SDS-treated bagasse ( $14.9 \text{ mg g}^{-1}$ ) biomass. Other researchers have also noted maximum biosorption of Zr within this pH range on different biosorbents [3, 16].

Removal efficiency and biosorption capacity are highly dependent upon sorbent weight due to the fact that the number of available binding functional groups on an adsorbent surface is a function of the adsorbent amount. The effect of weight of biosorbent used was studied in the range of 0.05-0.3 g with results, illustrated in Fig. 1(b), indicating that a maximum biosorption capacity of  $31.0 \text{ mg g}^{-1}$ ,  $35.9 \text{ mg g}^{-1}$  and  $21.9 \text{ mg g}^{-1}$  was observed for native (untreated), SDS-treated and immobilised bagasse respectively using 0.05 g of biosorbent. Further increase in biosorbent dose decreased the biosorption capacity which could be explained by aggregation of biomass and a subsequent decrease in the available effective exposed area for biosorption of metal ions [17, 18].

The effect of shaking time on the biosorption of Zr(IV) ions by native (untreated), SDS-treated and immobilised bagasse was investigated over the time intervals of 5 to 740 min as

shown in Fig. 1(c). A maximum biosorption capacity of 35.2, 45.2 and 31.3 mg g<sup>-1</sup> was obtained for native (untreated), SDS-treated and immobilised bagasse respectively. During the initial stages of the biosorption process, the adsorption rate was rapid, after which, the uptake rate slowly declined and tended to attain equilibrium at 160 min for native (untreated) and SDS-treated and 320 min for immobilised bagasse. The results indicate that adsorption took place in two phases which suggest the metal ions may have been physically/chemically taken up onto the surface of the biosorbent (rapid, passive surface transport) before being taken up into the inner adsorption sites (slower, passive diffusive transport) of bagasse cell walls [19 - 22].

The effect of changing initial metal ion concentration on Zr removal was studied in the range of 25-200 mg L<sup>-1</sup> by keeping the other parameters constant. The results shown in Fig. 1(d) illustrate the very high metal uptake capacity at high concentration and mirror the trend reported for other biomaterials [2, 23]. A maximum biosorption capacity of 107, 111, 71.5 mg g<sup>-1</sup> was obtained for native (untreated), SDS-treated and immobilised bagasse at initial concentrations of 150, 200 and 125 mg L<sup>-1</sup> respectively.

The effect of temperature on biosorption of Zr(IV) ions onto native (untreated), SDS-treated and immobilised bagasse is shown in Fig. 1(e). The effect of higher temperatures on the biosorption process was detrimental and the effect was more pronounced in native (untreated) bagasse as compared to SDS-treated and immobilised forms of bagasse. The maximum biosorption capacity was obtained at 30°C.

### **3.4. Equilibrium and kinetic models of adsorption**

### 3.4.1 Equilibrium modeling

The design and operation of sorption processes require equilibrium sorption data for use in mass transfer models which can then be used to predict the performance of the sorption contact processes under a range of operating conditions. In order to examine the biosorption process, the relationship between the variation of solid phase concentration or the amount of solute adsorbed per unit mass of solid ( $q_e$ ), to the variation of equilibrium solution phase concentration ( $C_e$ ) was investigated. The most widely used two parameter sorption isotherms i.e. Freundlich, Langmuir and three parameter equation i.e. Redlich-Peterson were used to determine the Zr(IV) metal ion biosorption mechanism employing both linear and non-linear regression methods. Table 1 compares the values of adsorption capacities ( $K_F$ ,  $q_m$ ,  $A$ ) obtained from Freundlich, Langmuir and Redlich-Peterson adsorption isotherms using linear and non-linear regression methods. Fig 2 a-c compares the adsorption capacities obtained by the various adsorption isotherms with that of experimental values for Zr(IV) biosorption by native (untreated), SDS-treated and immobilised forms of bagasse.

#### 3.4.1.1 Freundlich isotherm

The Freundlich equation [24] is an empirical equation employed to describe heterogeneous systems, in which it is characterised by the heterogeneity factor  $1/n$ . The empirical equation can be written as:

$$q_e = K_F C_e^{1/n} \quad (7)$$

and a linear form of the Freundlich equation can be obtained by taking logarithms of Eq 7

$$[33]: \log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad (8)$$

The Freundlich constants of  $K_F$  and  $1/n$  are calculated from the intercept and slope respectively in the linear regression method.

In the case of Zr(IV) removal (see Table 1), the value of  $R^2$  and agreement between calculated and experimental values does not favor closeness of fit of the data to the Freundlich model. The values of  $n$  calculated for all bagasse forms indicate a good moderate adsorption process.

### 3.4.1.2 Langmuir isotherm

The Langmuir equation [25] is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent and has found successful application in many real sorption processes of monolayer adsorption. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer (as  $C_e \rightarrow \infty$ ) capacity can be represented by the expression:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (9)$$

with a linear expression of the Langmuir equation being:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \quad (10)$$

Therefore, a plot of  $C_e/q_e$  versus  $C_e$  gives a straight line which allows calculation of the Langmuir constants  $q_m$  and  $K_a$ . Where  $q_e$  is the amount of metal ions sorbed on the biomass ( $\text{mg g}^{-1}$ ) at equilibrium,  $C_e$  is the equilibrium concentration of metal ions ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum biosorption capacity describing a complete monolayer adsorption ( $\text{mg g}^{-1}$ ) and  $K_a$  is adsorption equilibrium constant ( $\text{L mg}^{-1}$ ) that is related to the free energy of biosorption.

The values of Langmuir sorption isotherm parameters calculated for the Zr(IV) sorption process by linear and non-linear methods are given in Table 1. A useful parameter for estimating the nature of the sorption process is given by the  $R_L$  value, where  $R_L > 1$

suggest the nature of the biosorption mechanism is unfavourable,  $RL = 1$ ; linear in nature,  $0 < RL < 1$ ; a favourable process and  $RL = 0$  suggesting an irreversible process [26]. The values of  $R_L$  obtained in the present study are in the range of 0-1 (see Table 1), indicating that the biosorption process is favourable for Zr removal from wastewater using bagasse. The  $R^2$  values of the linear regression method shows the good fit of the Langmuir adsorption isotherm to the sorption equilibrium data of Zr(IV) for native (untreated) and modified forms of bagasse. The maximum sorption capacity values calculated by Langmuir for native (untreated), SDS-treated and immobilised forms of bagasse are not close to the experimental values (see Fig. 2a-c).

### 3.4.1.3 Redlich-Peterson isotherm

Redlich-Peterson [27] incorporated three parameters into an empirical isotherm combining elements from both the Langmuir and Freundlich equations and the assumption that the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption.

$$q_e = \frac{AC_e}{1+BC_e^g} \quad (11)$$

The non-linear form can be converted into the linear form by taking natural logarithms:

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B) \quad (12)$$

This equation reduces to a linear isotherm at low surface coverage, and to the Langmuir isotherm when  $g = 1$ . The exponent,  $g$  lies between 0 and 1. Thus, when  $g=1$ , the Redlich-Peterson equation becomes the Langmuir equation, and, when  $g = 0$ , the equation represents Henry's law. Redlich-Peterson constant  $B$  and  $g$  can be calculated from the linear plot of  $\ln\left(A\frac{C_e}{q_e} - 1\right)$  vs  $\ln(C_e)$  and the value of Redlich-Peterson constant  $A$  can be calculated by maximizing  $R^2$  using trial and error method in Microsoft Excel solver adds in function [28].



The results in Table 1 show that  $R^2$  values of 0.843, 0.914, 0.858 calculated by linear regression and 0.992, 0.895 and 0.972 by non-linear regression are obtained for the Redlich-Peterson isotherm for native (untreated), SDS-treated and immobilised bagasse respectively. The high values of each correlation coefficient suggest that the Redlich-Peterson isotherm is much better than the Freundlich isotherm and comparable with the Langmuir isotherm for explaining the biosorption process of Zr(IV) on bagasse biosorbent. This is further supported by the good agreement between the closeness of experimental and calculated maximum sorption capacity values (see Fig. 2a-c).

### 3.4.2 Biosorption kinetics

A well planned kinetic study can play an important role in the technology transfer of biosorption results from laboratory to industrial scale. Appropriate models can be helpful in understanding the reaction process, for analyzing experimental data and for prediction purposes which allows process optimization of future operational conditions [29]. The rate of biosorption depends on the physical and chemical properties of the biosorbent material and the mechanism of mass transfer [13]. A number of models have been proposed in order to estimate the removal rate and the kinetic parameters to evaluate the mechanism of the process.

#### 3.4.2.1 Pseudo-first order kinetic model

The pseudo-first order kinetic model [30] based on solid capacity, expresses the mechanism of removal as sorption preceded by diffusion through a boundary. It considers that the process of sorption is partially first ordered depending on the concentration of free sites and that the change in metal ions concentration with respect to time is proportional to the power one. The non-linear and linear forms of the model are given below.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (13)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (14)$$

Where  $q_e$  and  $q_t$  are the amount of metal ions adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min) respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo- first-order rate constant. Values of  $k_1$  are calculated from the plots of  $\log(q_e - q_t)$  versus  $t$ .

### 3.4.2.2 Pseudo-second order kinetic model

Pseudo-second order kinetic model [31, 32] is based on the assumption that biosorption follows a second rate kinetic mechanism where the rate of occupation of sorption sites is proportional to the square of the number of unoccupied sites. Linear and non-linear forms of pseudo- second order expressions used in this study are presented below.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (15)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (16)$$

Where  $q_e$  and  $q_t$  in pseudo-second order equations are the amount of metal ions adsorbed on adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively, and  $k_2$  is the pseudo-second order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ). Based on the experimental data of  $q_t$  and  $t$ , the equilibrium sorption capacity ( $q_e$ ) and the pseudo-second-order rate constant ( $k_2$ ) can be determined from the slope and intercept of a plot of  $t/q_t$  versus  $t$ .

Table 2, which illustrates the values of  $R^2$  calculated by linear and non-linear methods for Zr, show that the pseudo-first order kinetic model does not show a good fit with the kinetic sorption data of native (untreated), SDS-treated and immobilised forms of bagasse used. Similarly the calculated and experimental maximum sorption capacity values are not in good agreement with the experimental values as shown in Table 2, supporting the conclusion that the first order kinetic model is not fitted well for entire data range of contact time. The biosorption mechanism is however, explained by the pseudo-second order kinetic model.

The linear regression analysis shows the good fit of the pseudo-second order kinetic model to the experimental kinetic data of Zr (IV) biosorption onto native (untreated) and SDS-modified forms of bagasse biosorbent. The comparison between experimental and predicted sorption capacity by pseudo-first and second-order model values is shown in Fig. 3, with the superior fit of the pseudo-second order model to the experimental data apparent for the native (untreated) and SDS-treated bagasse.

### **3.4.3 Error analysis for equilibrium and kinetic model optimization**

An optimization procedure was performed which involved ordering of the error functions investigated to evaluate the best fit isotherm to explain the experimental equilibrium and kinetic data [33 – 36]. In this study, six non-linear error functions were examined using R statistical software (Version 2.15.1), by minimizing the respective error function across the time and concentration range studied. The error functions employed were the sum of the squares of the errors (SSE) [13], a composite fractional error function (HYBRD) [37], an Average relative error (ARE) [38], the Sum of absolute error (EABS) [39], the Marquardt [40] error function and a Nonlinear chi-square test [13]. The general procedure to find an adequate model by means of the error functions is to calculate the error function for all isotherms and make a comparison between values obtained by different error functions for each isotherm. Overall, optimum parameters are difficult to identify directly, hence, ordering results to make a comparison between values of error functions can lead to meaningful results.

#### **3.4.3.1 Error analysis for optimization of equilibrium isotherms**

The results evaluating the best isotherm to explain the experimental equilibrium data are presented in Table 3. The order of the error functions for the native (untreated), SDS-treated and immobilised bagasse is in the following order:

SSE	Freundlich>Langmuir>R-P
EABS	Freundlich>Langmuir>R-P
ARE	Freundlich> Langmuir >R-P
HYBRID	Freundlich> Langmuir> R-P
MPSD	Freundlich> Langmuir >R-P
$\chi^2$	Freundlich> Langmuir> R-P

The trend of error functions for the sorption isotherms concluded that the equilibrium data of Zr(IV) biosorption onto native (untreated), SDS-treated and immobilised bagasse is best fitted to Redlich-Peterson sorption isotherm.

### 3.4.3.2 Error analysis for optimization of kinetic model

The results evaluating the pseudo-first and pseudo-second order kinetic equation optimization for the biosorption process of Zr(IV) ions onto bagasse are presented in Table 3. The error functions can be ordered for native (untreated), SDS-treated and immobilised bagasse as follows:

SSE	pseudo-first order>pseudo-second order
EABS	pseudo-first order>pseudo-second order
ARE	pseudo-first order>pseudo-second order
HYBRID	pseudo-first order>pseudo-second order
MPSD	pseudo-first order>pseudo-second order
$\chi^2$	pseudo-first order>pseudo-second order

It is concluded that the second-order kinetic model is best fitted for the Zr(IV) sorption onto native (untreated), SDS-treated and immobilised bagasse. This was also found for Zr biosorption by *C. versicolor* biomass [2] and for removal of Zr from aqueous solution by modified clinoptilolite [41].

### 3.12. Thermodynamics studies

Thermodynamic parameters at varying temperatures for native (untreated), SDS-treated and immobilised bagasse are presented in Table 4. The positive value of  $\Delta H^\circ$  suggests that the process is endothermic with  $\Delta H^\circ$  values greater than  $40 \text{ kJ mol}^{-1}$ , suggesting the reaction might be chemical in nature. The negative values of  $\Delta G^\circ$  for all three forms of bagasse provide evidence of the spontaneity of the reaction at low temperature with the negative values of entropy change ( $\Delta S^\circ$ ) suggesting that randomness decreases as the reaction proceeds. All the thermodynamic evidence suggests that biosorption of Zr(IV) ions onto native (untreated), SDS-treated and immobilised bagasse is a favorable process.

### 3.13. Desorption studies

The selected desorbing agents efficiency for the desorption of Zr(IV) ions decrease in the following order for native (untreated), SDS-treated and immobilised bagasse respectively:

$\text{H}_2\text{SO}_4 > \text{HCl} > \text{EDTA} > \text{MgSO}_4 > \text{NaOH}$  (Native)

$\text{H}_2\text{SO}_4 > \text{HCl} > \text{MgSO}_4 > \text{NaOH} > \text{EDTA}$  (SDS-treated)

$\text{H}_2\text{SO}_4 > \text{HCl} > \text{EDTA} > \text{MgSO}_4 > \text{NaOH}$  (immobilised bagasse)

The superior desorption efficiency of  $\text{H}_2\text{SO}_4$  for bagasse biosorbents is in accordance with previous findings by Bhatti and Amin, 2013 [2] and Hanif et al., 2013 [23] for Zr(IV) on other biosorbent materials.

### 3.14. Biosorbent characterization

Scanning electron microscope and Energy dispersive X-Rays (SEM-EDX) images, used to study surface morphology and composition of native bagasse, before and after loading with Zr(IV) ions confirmed the presence of the adsorbed Zr ions on loaded bagasse. The FTIR

spectra of native (untreated) and Zr loaded native (untreated) bagasse were plotted to determine the vibration frequency changes in the functional groups as a means of understanding which functional groups were involved in Zr adsorption. Fig. 4 compares the shift in wavelength of the main peaks of functional groups in native (untreated) bagasse with Zr loaded, native (untreated) bagasse. Despite the complex nature of the bagasse biosorbent, evidence that several functional groups appear to be playing a role in the adsorption process could be found. The loss of the absorption band at  $1730\text{ cm}^{-1}$  between the native (untreated) bagasse and the loaded bagasse, suggest involvement of ester and carboxyl acid groups [42]. The strong C–O band confirming the presence of lignin structures in sugarcane bagasse assigned to  $1055.06\text{ cm}^{-1}$  [43] in the native (untreated) bagasse shifts position and intensity to about  $1051.2\text{ cm}^{-1}$  suggesting  $-\text{OCH}_3$  group involvement. The intense and broad bands at around  $3329\text{ cm}^{-1}$  and  $2910\text{ cm}^{-1}$ , assigned to OH group and C–H stretching respectively [44], alter significantly between the native (untreated) and Zr loaded, native (untreated) samples.

#### **4. Conclusion**

Pollution of fresh water sources from heavy metal containing wastewater is still one of the most important environmental problems for many countries worldwide. The impact of heavy metal contamination released into the water environment can be severely detrimental, both to the aquatic environment and human health and can lead to clean drinking sources becoming unusable. In this era of changing climate, water security is of paramount importance and should be protected as a valuable resource. This study aimed to exploit the potential of selected indigenous agro-wastes as biosorbents for the treatment of Zr-containing synthetic aqueous solutions. Screening results showed that bagasse has the highest potential to treat Zr(IV) containing wastewater prior to release into a water body among selected agro-wastes

and pre-treatment with SDS enhanced the removal efficiency of the bagasse. The pH of the aqueous medium strongly affected the removal of Zr(IV) and maximum uptake capacity was observed at pH 3.5 for native (untreated) and immobilised bagasse and pH 3 for SDS-treated bagasse. Equilibrium was achieved in 160 min for native (untreated) and SDS-treated bagasse and 320 min for immobilised bagasse and thermodynamic studies showed that removal of Zr was spontaneous at low temperature. Maximum biosorption capacity values of 107.4, 111.4, 71.5 mg/g were obtained for native (untreated), SDS-treated and immobilised bagasse respectively with H<sub>2</sub>SO<sub>4</sub> proving to be the most successful eluting agent for recovery of the Zr. The Redlich-Peterson model provided the best correlation to the experimental data of native, SDS-treated and immobilised bagasse for Zr(IV) removal and the kinetic data was well fitted to the pseudo-second order model. This information will enable the biosorption process to be successfully modelled, allowing transfer of this methodology from the laboratory to a larger scale batch trial. From results of the present research we can conclude that effluent wastewater containing these metal ions have the potential to be treated in an efficient and economical way in developing and agricultural countries like Pakistan, using this method. Further work is needed however, to trial this method using 'real' effluent wastewater and on a larger scale.

## **5. Acknowledgement**

The authors acknowledge the research grant provided by the Higher Education Commission, Pakistan under the Indigenous 5000 PhD fellowship programme.

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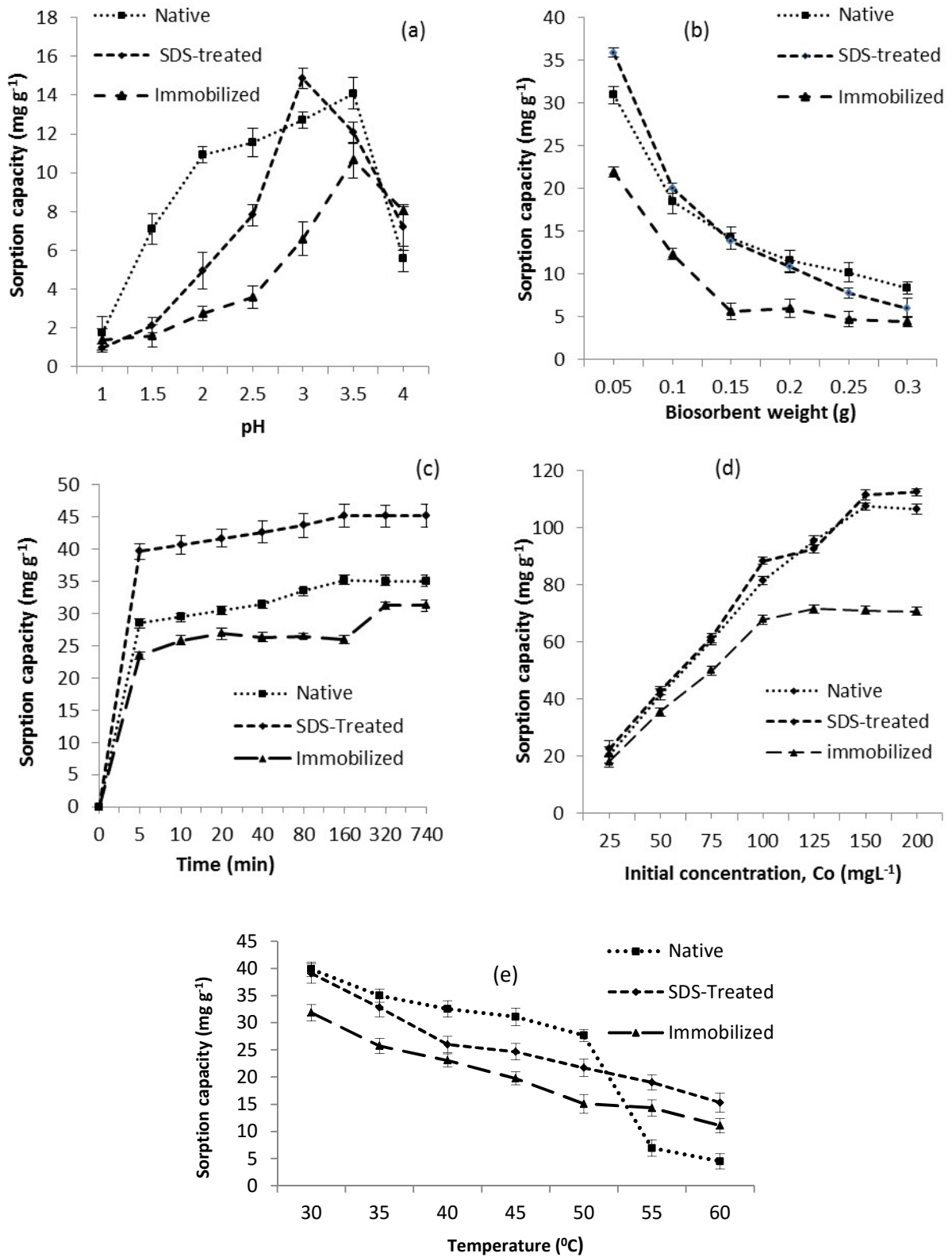
## Figure Legends.

**Fig. 1(a) Effect of pH on Zr(IV) biosorption onto bagasse biosorbents.** Biosorbent weight used 0.1 g/50 mL,  $C_0 = 50 \text{ mg/L}$ , reaction time 2 h,  $T = 30^\circ\text{C}$  and pH (1-4). **(b) Effect of biosorbent weight used on biosorption of Zr(IV) onto bagasse.** Biosorbent weight used 0.05-0.3 g/50mL,  $C_0 = 50 \text{ mgL}^{-1}$ , reaction time 2 h,  $T = 30^\circ\text{C}$ , pH=3.5 (native (untreated) and immobilized) and pH 3 (SDS-treated). **(c) Effect of shaking time on biosorption of Zr(IV) onto bagasse.** Biosorbent weight used 0.05g/50mL,  $C_0 = 50 \text{ mgL}^{-1}$ , reaction time 5-740 min,  $T = 30^\circ\text{C}$  and pH 3.5 (native (untreated) and immobilized, pH 3 (SDS-treated). **(d) Effect of initial metal ion concentration on biosorption of Zr(IV) onto bagasse.** Biosorbent weight used 0.05g,  $C_0 = 25\text{-}200 \text{ mgL}^{-1}$ , shaking time 160 min (native (untreated), SDS-treated), 320 min (immobilized),  $T = 30^\circ\text{C}$  and pH 3.5 (native (untreated) and immobilized) and pH 3 (SDS-treated). **(e) Effect of temperature on Zr(IV) biosorption onto bagasse.** Biosorbent weight used 0.05g/50mL,  $C_0 = 50 \text{ mgL}^{-1}$ , shaking time 160 min (native (untreated) and SDS-treated) and 320 min (immobilized),  $T = 30^\circ\text{C}$  and pH 3.5 (native (untreated) and immobilized) and pH 3 (SDS-treated).

**Fig. 2. Comparison of equilibrium isotherms for Zr(IV) sorption onto bagasse biosorbents,** (a) native (untreated), (b) SDS-treated and (c) immobilized.

**Fig. 3. Comparison of kinetic models for Zr(IV) biosorption onto bagasse biosorbents,** (a) native (untreated), (b) SDS-treated and (c) immobilized.

**Fig. 4. FTIR spectra of bagasse biosorbents and possible functional groups involved in Zr(IV) biosorption,** (a) native (untreated) bagasse, (b) Zr(IV) loaded native bagasse.



**Fig. 1(a) – (e).**

**(a)**

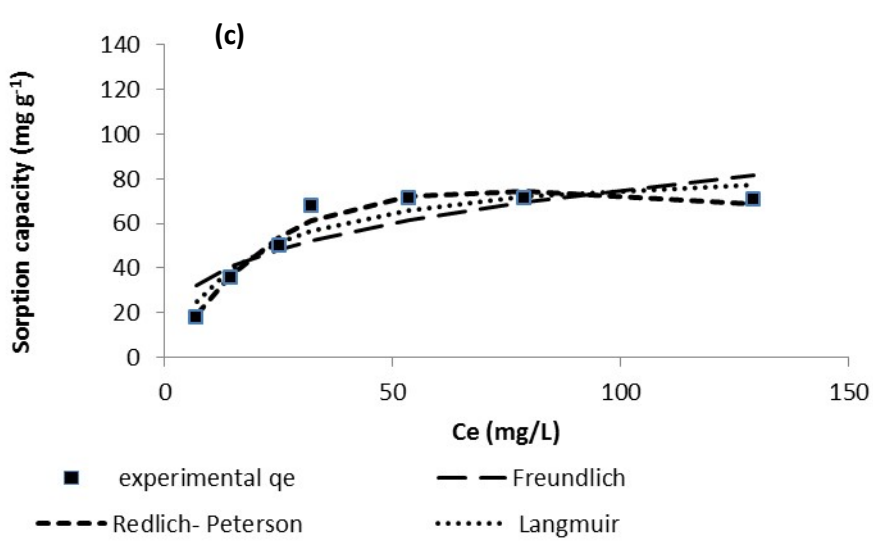
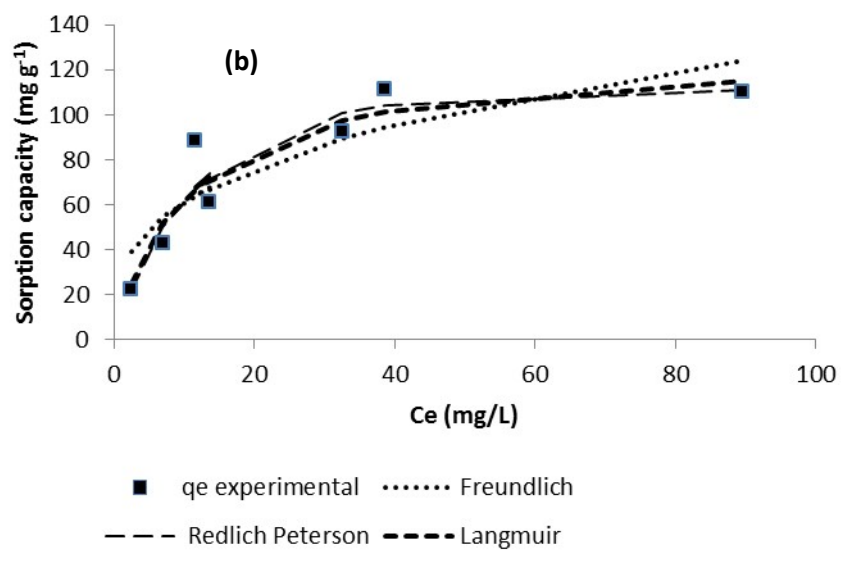
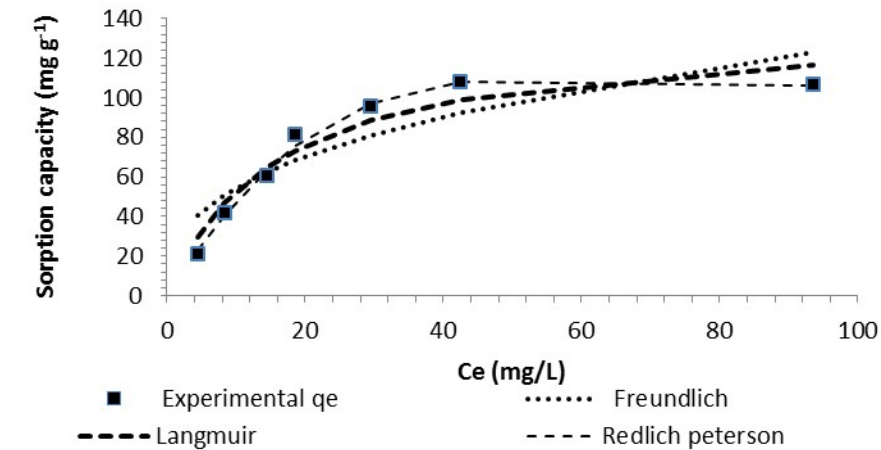


Fig. 2 (a) – (c).

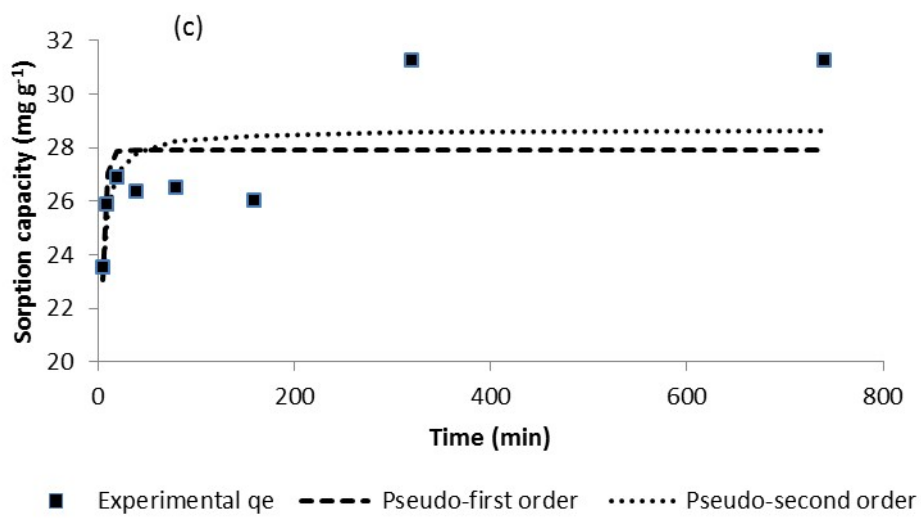
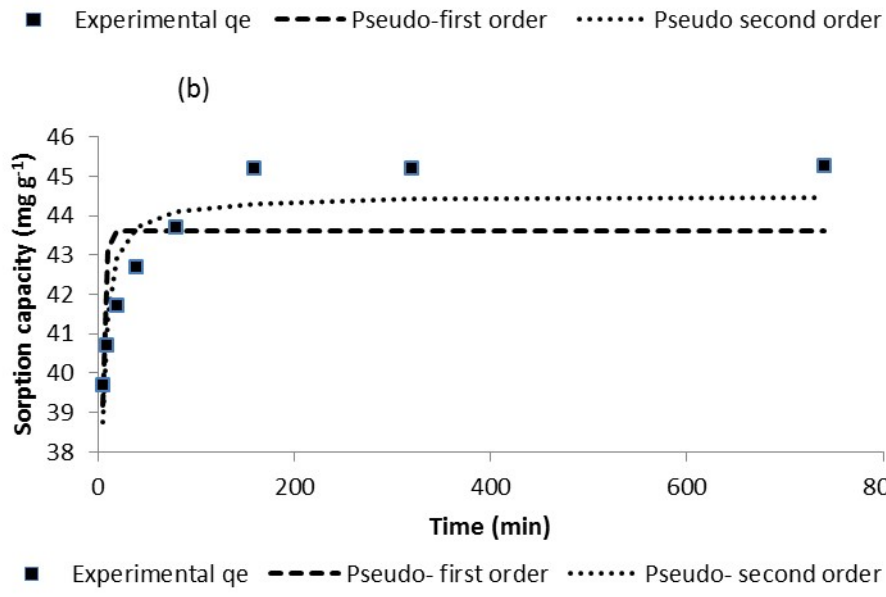
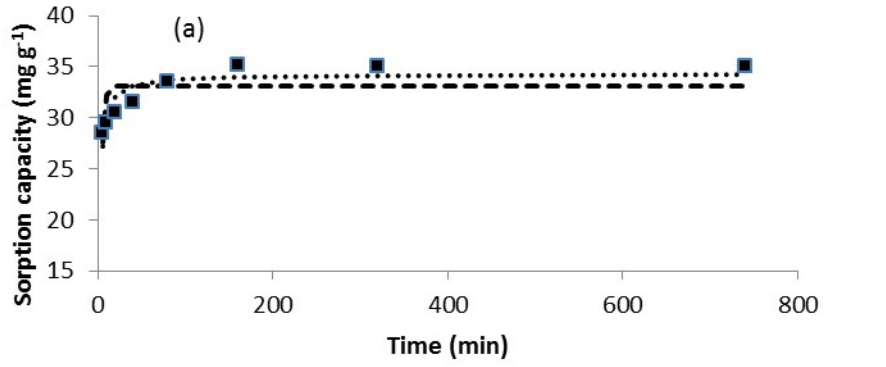
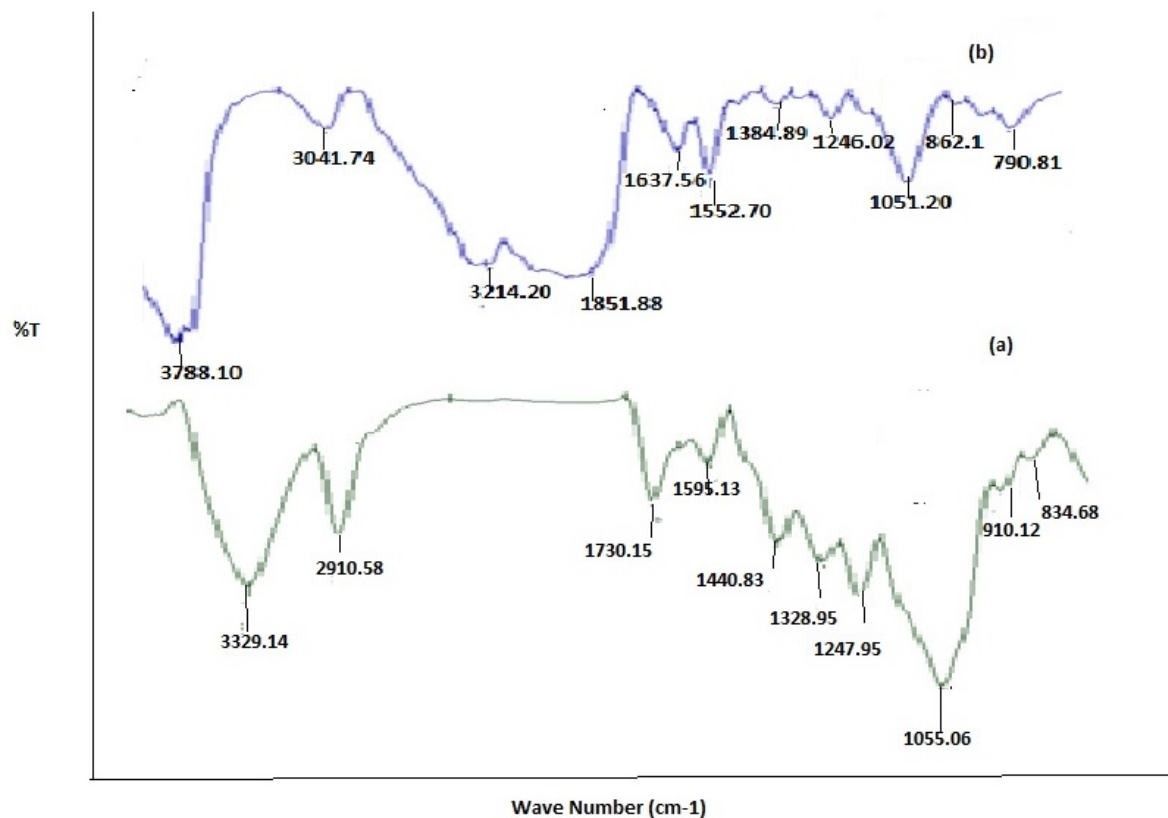


Fig. 3 (a) – (c).





Possible function groups	(a) Native (untreated) bagasse (cm <sup>-1</sup> )	(b) Zr (IV) loaded, native (untreated) bagasse (cm <sup>-1</sup> )
O-H functional groups (carboxylic acids, phenols and alcohols)	3329.14	3214.20
C-H (stretching of alkanes)	2910.58	-
C=O (Carboxylic acid)	1730.15	-
C-H stretching (aldehydes)	1595.13	1552.70
C-N (amines)	1055.06	1051.20
C-H stretching	834.68, 910.12	862.10

Fig. 4.

**Table 1.** Equilibrium model parameters for Zr(IV) biosorption onto bagasse biosorbents by linear and non-linear regression methods.

Equilibrium model	Freundlich Isotherm					
	Linear regression method			Non-linear regression method		
	Native (untreated)	SDS-treated	Immobilised	Native (untreated)	SDS-treated	Immobilised
$K_F(\text{mg g}^{-1})(\text{L mg}^{-1})^n$	12.4	18.9	9.73	23.5	29.3	17.4
$n$	1.82	2.21	2.41	0.364	0.321	0.318
$R^2$	0.841	0.839	0.807	0.794	0.785	0.746
Isothermal model	Langmuir isotherm					
	Linear regression method			Non-linear regression method		
	Native (untreated)	SDS-treated	Immobilised	Native (untreated)	SDS-treated	Immobilised
$q_m(\text{mg g}^{-1})$	129	125	82.6	137	128	88.2
$b(\text{L mg}^{-1})$	0.0640	0.970	0.0629	0.0622	0.0971	0.0560
$R^2$	0.967	0.983	0.976	0.937	0.888	0.902
Isothermal model	Redlich-Peterson isotherm					
	Linear regression method			Non-linear regression method		
	Native (untreated)	SDS-treated	Immobilised	Native (untreated)	SDS-treated	Immobilised
$A(\text{L g}^{-1})$	6.10	10.8	12.2	5.29	9.86	2.90
$B(\text{dm}^3 \text{mg}^{-1})^g$	0.0454	0.0762	0.839	0.00324	0.0409	0.00260
$g$	0.914	1.000	0.604	1.55	1.14	1.53
$R^2$	0.843	0.914	0.858	0.992	0.895	0.972

**Table 2.** Comparison of parameters of kinetic models for Zr(IV) biosorption onto bagasse biosorbents by linear and non-linear regression methods.

Kinetic model	Pseudo-first order kinetic model					
	Linear regression method			Non-linear regression method		
	Native (untreated)	SDS-treated	Immobilised	Native (untreated)	SDS-treated	Immobilised
$K_1(\text{min}^{-1})$	$5.07 \times 10^{-3}$	$6.64 \times 10^{-3}$	$2.30 \times 10^{-3}$	0.354	0.457	0.350
$q_e$ calculated( $\text{mg g}^{-1}$ )	35.2	45.2	31.3	33.2	43.6	27.9
$q_e$ experimental( $\text{mg g}^{-1}$ )	3.58	2.49	5.50	35.2	45.3	31.3
$R^2$	0.673	0.694	0.747	0.426	0.445	0.353

Kinetic model	Pseudo-second order kinetic model					
	Linear regression method			Non-linear regression method		
	Native (untreated)	SDS-treated	Immobilised	Native (untreated)	SDS-treated	Immobilised
$K_2(\text{mg g}^{-1} \text{min}^{-1})$	0.0123	0.0139	$3.45 \times 10^{-3}$	0.0225	0.0303	0.0291
$q_e$ calculated ( $\text{mg g}^{-1}$ )	35.2	45.2	31.5	34.2	44.5	28.7
$q_e$ experimental( $\text{mg g}^{-1}$ )	35.2	45.5	31.3	35.2	45.3	31.3
$R^2$	1	1	0.998	0.783	0.816	0.880

**Table 3.** Optimisation of equilibrium isotherms and kinetic models for Zr(IV) biosorption onto bagasse biosorbents by error functions.

Error Function	Native (untreated)			SDS-treated			Immobilised		
	Freundlich isotherm	Langmiur isotherm	Redlich-Peterson isotherm	Freundlich isotherm	Langmiur isotherm	Redlich-Peterson isotherm	Freundlich isotherm	Langmiur isotherm	Redlich-Peterson isotherm
SSE	1397	426	54.9	1513	787	737	691	268	76.6
EABS	91.5	53	14.9	92.2	63.3	56.3	58.4	36.7	18.4
ARE	26.6	14.4	4.19	24.2	13.3	11.1	21.5	12.5	5.06
HYBRID	626	166	24.2	543	209	240	376	120	31.9
MPSD	47.3	22.9	7.81	38.8	17.8	18.3	38.8	20	7.81
Chi-Sq/x <sup>2</sup>	21.8	6.91	0.95	14.7	5.61	1.32	23.8	11.2	10.3

Error Function	Native (untreated)		SDS-treated		Immobilised	
	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order	Pseudo-first order	Pseudo-second order
SSE	29.4	11.1	18.5	6.12	33.00	25.6
EABS	14.1	8.69	10.7	6.77	14.2	11.8
ARE	5.51	3.42	3.11	1.98	6.27	5.24
HYBRID	15.4	5.88	7.23	2.39	18.7	14.9
MPSD	6.96	4.33	4.12	2.37	8.00	7.22
Chi-Sq/x <sup>2</sup>	0.897	0.349	0.434	0.142	1.12	0.889

**Table 4.** Thermodynamic parameters for Zr(IV) biosorption onto bagasse biosorbents as a function of temperature.

Temp. (°C)	Native (untreated)			SDS-treated			Immobilised		
	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$
30	-0.00422			-0.0026			-0.00114		
35	-0.00264			-0.00179			-0.00036		
40	-0.00107	99.9	-0.317	-0.00094			0.00043		
45	0.00051			-9.99E05	53.6	-0.168	0.00121	48.6	-0.157
50	0.00209			0.00074			0.00200		
55	0.00367			0.00159			0.00278		
60	0.00525			0.00242			0.00356		

\* $\Delta G^\circ = \text{kJ mol}^{-1}$ ;  $\Delta H^\circ = \text{kJ mol}^{-1}$ ;  $\Delta S^\circ = \text{J mol}^{-1} \text{K}^{-1}$