



Kausar, A., MacKinnon, G. , Alharthi, A., Hargreaves, J., Bhatti, H. N. and Iqbal, M. (2018) A green approach for the removal of Sr(II) from aqueous media: kinetics, isotherms and thermodynamic studies. *Journal of Molecular Liquids*, 257, pp. 164-172.(doi:[10.1016/j.molliq.2018.02.101](https://doi.org/10.1016/j.molliq.2018.02.101))
This is the author's final accepted version.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/162946/>

Deposited on: 29 May 2018

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk>

A green approach for the Sr(II) removal from aqueous media: Kinetics, isotherms and thermodynamic studies

Abida Kausar^{a,d}, Gillian MacKinnon^b, Abdulrahman Alharthi^c, Justin Hargreaves^c and Haq Nawaz Bhatti^d and Munawar Iqbal^{e,*}

^aDepartment of Chemistry, Government College Women University Faisalabad, Pakistan

^bScottish Universities Environmental Research Centre, East Kilbride, Scotland, UK

^cSchool of Chemistry, University of Glasgow, Glasgow, Scotland, UK

^dDepartment of Chemistry, University of Agriculture, Faisalabad, Pakistan

^eDepartment of Chemistry, University of Lahore, Lahore, Pakistan

Corresponding author e-mail: bosalvee@yahoo.com

Abstract

Adsorption efficiency of native, NaOH-treated and immobilized peanut husk and sugarcane bagasse for Sr(II) removal was studied in batch mode. In view of promising adsorption efficiency of peanut husk versus sugarcane bagasse, the biosorption behaviour of the Sr(II) ions onto peanut husk (native and modified) was studied as a function of pH, biosorbent dose, contact time, initial metal ion concentration and temperature for the maximum removal of Sr(II) ions. Linear and non-linear pseudo-first and second-order kinetic models were applied and value of R^2 and six non-linear regression error functions, namely hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), average relative error (ARE), the sum of the errors squared (ERRSQ/SSE), the sum of the absolute errors (EABS) and Chi-square test (χ^2) were used to predict the most optimum kinetic model. Sorbent-sorbate reaction nature was estimated by fitting equilibrium data by non-linear and transformed linear forms of the Langmuir, Freundlich and Redlich-Peterson isotherms and most optimum isothermal model was optimized by comparing linear and non-linear R^2 value and non-linear regression error functions. HCl proved most successful eluting agent for sorbed Sr(II) ions. Biosorption characteristics and effectiveness of the process was also

confirmed by Fourier transform infra-red spectroscopy (FTIR), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX). In view of promising efficiency of peanut husk as an adsorbent, it could possibly be used for the removal of Sr(II) ions from aqueous medium and is also extendable to other radionuclide.

Keywords: Radionuclide; Biosorption; Strontium; Equilibrium; Kinetic; Non-linear regression

1. Introduction

The radioactive wastes containing long-lived radionuclide have been considered as the most hazardous and dangerous environment pollutants and their treatment have received much attention. Strontium (Sr) has two important isotopes i.e. ^{90}Sr which emits β radiation with a half-life of 28 years and ^{85}Sr which is a γ emitter with a half-life of 64.8 days. Strontium naturally occurs at an average amount of 0.04% and is the 15th abundant element in the earth's crust [1]. The behaviour of strontium (Sr) isotopes in the soil, which may be discharged to the ecosystem as a result of nuclear weapons testing nuclear accidents comes into water, soil and plants, is of great interest. Beyond the four stable isotopes, which are naturally present in soil, ^{90}Sr is also present in the surface soil almost everywhere in the world as a result of fallout from past atmospheric nuclear weapons tests [2, 3].

Currently, various methods have been developed to remove the pollutants (metallic ions, dye etc) radiotoxic ions from aqueous solution, such as chemical precipitation, thermal treatment, membrane, solvent extraction, ion exchange, adsorption and oxidation [4-14]. There is a growing interest in finding cost-effective methods to remove heavy metals from aqueous media. Sorption has been proposed as a promising technique for removing metals from contaminated water, since it has shown potential to achieve good removal at relatively low cost and with low energy demands [15-18]. Sorption is here defined as a collective term for adsorption to the surface and absorption into the structure of a material. Strictly speaking, precipitation is not sorption.

The aim of present study is to evaluate the efficiency of economical sorbent to remove Sr(II) form aqueous solution. In the present work, we have focused on the removal of strontium ion from aqueous solutions using peanut husk, an agricultural waste, as a new adsorbent. In our previous work, we had successfully employed different agrowastes i.e Rice husk and Bagasse for the removal U(VI) and Zr(IV) ion from aqueous solutions [19, 20]. Previously, reports

have been shown that the high concentration of the Sr in Indus river [21], as well as significant Sr concentration in Pakistani diet and need immediate improvements to effectively handle the problem of Sr high concentration resulting in wastewater contamination [22].

2. Materials and Methods

2.1 Reagents and biosorbent preparation

All chemicals used were of analytical grade and purchased from Sigma-Aldrich Chemical Co, USA. A stock solution was prepared by dissolving $\text{Sr}(\text{NO}_3)_2$ in deionized water (Millipore Corp., Milli-Q, 18.2 M Ω cm at 25 °C) and working standards of desired concentration were prepared by diluting the stock solution.

The selected biomass, peanut shell and sugarcane bagasse, were collected from different agricultural industries in Faisalabad, Pakistan. Firstly, biomass was extensively washed with tap water and then three times with deionized water to remove water soluble surface contaminants. After washing, biomass was air dried at ambient temperature, and then ground and sieved (Octagon Siever, OCT-Digital 4527-01) to obtain a homogenous biosorbent material of uniform size (300 μm).

2.2. Initial screening experiment

An initial screening experiment for the removal efficiency of the selected biosorbents for Sr(II) was carried out. 25 mL of a 10 mg Sr(II) L⁻¹ solution at varying pH (pH 3 - 9, pH of each solution adjusted with either dilute NaOH or HCl) was added to 0.1 g of either peanut husk biosorbent (PHB) or sugarcane bagasse biosorbent (SBB) in 50 mL centrifuge tubes (Sarstedt). Method blanks were also taken through the process. The samples were shaken (IKA orbital incubator, 125 rpm at 20°C) for 2 h. After 2 h, the samples were centrifuged (Harrier, 600 rpm), filtered (Whatman No 542 grade filter papers) and the filtrate analysed. To allow the biosorption equilibrium capacity of Sr(II) on selected biosorbents to be determined, the concentration of Sr(II) before and after sorption was determined by Inductively Coupled Plasma - Optical Emission Spectroscopy (Perkin Elmer, Optima 5300 DV) with a Scott style spray chamber and gem tip cross flow nebuliser. Calibration of the instrument was carried out using 0.1, 1.0 and 10 mgL⁻¹ Sr standards prepared for NIST traceable Alfa Aesar Specpure® 1000 mgL⁻¹ standard and instrument performance assessed

by analysing a Certified Reference Standard (ES-H-2 groundwater) with each analytical batch.

The biosorption equilibrium capacity of Sr(II) per unit biomass (mg g^{-1}) dry weight of the biosorbent was calculated using formula shown in Eq. 1.

$$q_e = (C_o - C_e) V/W \quad (1)$$

Where, C_o and C_e are the initial and equilibrium concentrations of Sr(II) in solution, V is volume of solution of desired concentration in litres and W is the amount of biosorbent in g.

2.3. Sr(II) removal

After initial screening, the removal efficiency of native PHB proved most successful in the removal of Sr(II) and was used in further experiments. 1.0 g sub-samples of native PHB were chemically treated by shaking with 100 mL of either 5 % HNO_3 , H_2SO_4 , HCl or 1 % NaOH for 2 h. Each chemically treated sample was then thoroughly washed with deionized water and filtered through (Whatman No 542 grade filter papers). The samples were oven dried at 30°C , ground and sieved as before to obtain a homogenous biosorbent material of uniform size. Immobilization of the native PHB was also carried out using the method of Kausar *et al.*, 2013. Briefly, 2g of native PHB was added to a 40°C prepared sodium-alginate solution and stirred continuously until a homogenous mixture was formed. Uniform beads of Ca-alginate immobilized PHB was then formed by adding the mixture, drop-wise using a burette, into a 1% CaCl_2 (w/v) solution. The beads were kept in the solution of 1% CaCl_2 to allow complete curing, then washed with deionized water and stored at 4°C until required.

2.4. Sorption kinetics and data modelling

To understand the mechanism controlling biosorption, the most commonly used pseudo-first (equation 2) [23] and pseudo-second order (equation 3) [24, 25] kinetic models were used to interpret the experimental data as shown in Eqs. 2-3.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \quad (3)$$

Where q_e and q_t are the amount of metal ions adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, k_1 (min^{-1}) is the pseudo- first-order rate constant and k_2 is the pseudo-second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

After integration, the pseudo-first order (equation 2) and pseudo-second order (equation 3) models can be rearranged to the linear form for data plotting as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (5)$$

Gibbs energy (ΔG°), enthalpy of adsorption (ΔH°) and entropy of adsorption (ΔS°) were determined using the Eqs. 6-7 [26].

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

$$\log \left(\frac{q_e}{C_e} \right) = - \frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (7)$$

Thermodynamic parameters ΔH° and ΔS° were calculated from the linear plot of $\text{Log}(q_e/C_e)$ and $1/T$ from the slope and intercept respectively and ΔG° using equation 6.

2.5. Equilibrium study and data modelling

The classical sorption models of Langmuir (Eq. 8) [27] and Freundlich (Eq. 9) [28] and the hybrid Redlich-Peterson (Eq. 10) [29] were used to characterise the biosorption process and for evaluating the biosorption equilibrium capacity.

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (8)$$

$$q_e = K_F C_e^{1/n} \quad (9)$$

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (10)$$

Where, q_e is the biosorption equilibrium capacity (mg g^{-1}), C_e is the equilibrium concentration of metal ions remaining in solution (mg L^{-1}), q_m is the maximum biosorption

capacity (mg g^{-1}), K_a is adsorption equilibrium constant (L mg), K_F is the binding capacity constant and $1/n$ is a coefficient related to the sorbent:sorbate affinity.

2.6. Error analysis for kinetic and equilibrium models optimisation

To evaluate the best fit model to explain the experimental kinetic and equilibrium data an optimisation procedure involving the ordering of error function was employed [30-33]. Six non-linear error functions were examined using statistical software (R-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) (Boulinguez, *et al.*, 2008), a composite fractional (HYBRD) error function [34], average relative (ARE) error [35], sum of absolute error (EABS) [36], Marquardt and nonlinear chi-square test [37].

2.7. Desorption Study

Desorption studies to regenerate the adsorbent were carried out using eluting agents EDTA, H_2SO_4 , HCl, NaOH and MgSO_4 . To regenerate the adsorbent, firstly Sr(II) was adsorbed under optimised conditions, then the Sr(II) loaded biosorbent was dried in oven at $40\text{ }^\circ\text{C}$ for 24 h and then desorbed in 100 mL of 0.1 M solution of each selected eluting agent. Percent desorption was calculated using relations shown in Eqs. 11-12.

$$\text{Desorption (\%)} = \left[\frac{q_{des}}{q_{ads}} \right] 100 \quad (11)$$

$$q_{des} = C_{des} V/W \quad (12)$$

Where, q_{des} is eluted Sr(II) content (mg g^{-1}) and C_{des} (mg L^{-1}) is Sr(II) concentration in eluent solution of volume V (L) and W is biomass weight (g).

2.8. Characterisation of peanut husk biosorbent (PHB)

Surface area of the native PHB was determined by Brunauer, Emmett and Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, performed on a surface area analyzer (NOVA 2200, Quanta Chrome, USA) using nitrogen as a standard. Surface morphology and surface elemental composition were examined using a JEOL model 2300 Scanning Electron Microscope equipped with an energy dispersive spectrometer (SEM-EDX). X-ray diffraction was used to determine the chemical composition of PHB using a Siemens D5000 X-ray

Diffractionmeter operated at 40 kV and 40mA with CuK_α radiation ($\lambda = 1.54056\text{\AA}$). Assessment of functional groups involved in the biosorption of Sr(II) to PHB was examined by Fourier Transform Infrared Spectrometer (FTIR-8400S, Shimadzu) in the range of 600-4000 cm^{-1} and number of scans were 20-30 and resolution 2 cm^{-1} . Sr (II) loaded and unloaded PHB samples were recorded.

2.9. Statistical analysis

Each experiment was conducted in duplicate to ensure the reproducibility of results. All data represent the mean \pm SD of two independent experiments. The coefficients of equilibrium, kinetic and thermodynamic models were determined using the regression technique.

3. Results and Discussion

3.1. Initial screening of biosorbents and effect of chemical pre-treatment

An initial screening assessment was carried out using the selected agricultural waste biosorbents, peanut husk (PH) and sugarcane bagasse (SB), for Sr(II) removal. The results illustrated that PH had a higher Sr(II) biosorption capacity than SB and therefore was used for further experiments (Fig. 1A). PH was chemically pre-treated using 5 % solutions of HNO_3 , H_2SO_4 and HCl and 1 % NaOH and the removal efficiency of Sr(II) in solution was studied in the pH range 4-9 for all pre-treated peanut husk biosorbent (PHB) forms. An increase in the biosorption capacity of pre-treated 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 [38, 39]. The results showed that acids have no pronounced effect on the removal efficiency of Sr(II) in solution and decrease the biosorption capacity as compared to untreated PH but 1% NaOH had an enhancing effect, significantly increasing the sorption capacity of PH at all pH's tested (Fig. 1B). NaOH -treated PHB was selected for further biosorption optimization studies.

3.2. Sr(II) uptake on PHB

3.2.1. Effect of pH

The effect of pH on Sr (II) sorption onto PHB (0.1 g of native, NaOH-treated and immobilized PHB) was studied in the range of pH 3-9. It is clear from the Sr(II) removal isotherms shown in Figure 2A that acidic conditions did not favor Sr (II) sorption in native PHB but immobilized PHB and NaOH-treated PHB performed relatively well across the entire pH range tested. Maximum uptake was observed at pH 9 for native PHB (1.45 mg g⁻¹) and pH 7 for immobilized PHB (2.35 mg g⁻¹) and NaOH-treated PHB (2.76 mg g⁻¹). At low pH values, competitive sorption of H₃O⁺ ions and Sr²⁺ ions for the same positively charged sites on the sorbents surface lowers the sorption capacity. With the increase of pH values, the sorbents surface became more negative and electrostatic attraction between the Sr²⁺ and sorbent surface is likely to be increased [18]. Similar results have been found by several researchers for Sr²⁺ sorption on different adsorbents [17, 40, 41]. These results are very encouraging when thinking about designing an integrated Sr(II) treatment system for drinking water, as the majority of natural water pH lie between 6.5 and 8, where increased uptake efficiency is observed.

3.2.2. Effect of biosorbent amount

The effect of biosorbent amount on Sr (II) sorption was studied. Results shown in Fig. 2B indicated that maximum biosorption capacity of 2.99 mg g⁻¹, 5.24 mg g⁻¹ and 4.32 mg g⁻¹ was observed with 0.05 g of native, NaOH-treated and immobilized PHB respectively. Further increase in biosorbent weight decreased the biosorption capacity.

3.2.3. Effect of temperature

The temperature of the solution is an important factor during the process of biosorption. It affects the interaction between the biomass and the metal ions, usually by influencing the stability of the metal–sorbent complex, and the ionization of the cell wall moieties [42]. The effect of temperature on biosorption of Sr(II) ions onto native, NaOH-treated and immobilized PHB is shown in Fig. 2C. The effect was small during the initial increase of temperature, becoming more rapid at high temperature. The effect of temperature was more apparent in native PHB compared to the modified PHB's which showed little difference in sorption capacity between 30-50°C. A decrease in the biosorption capacity was observed at high temperature (50-60°C) which may be attributed to deactivation of adsorbent surface at higher temperatures [43].

The thermodynamic parameters results are presented in Table 1. The positive value of ΔH° suggests that the process is endothermic with ΔH° values less than 40 kJ mol^{-1} , suggesting the reaction is physical in nature. The negative values of ΔG° for all three forms of PHB provide evidence of the spontaneity of the reaction with the negative values of entropy change ΔS° suggesting that randomness decreases as the reaction proceeds. The thermodynamic data shows that biosorption of Sr (II) ions onto native, NaOH-treated and immobilized PHB is a favorable process.

3.2.4. Effect of contact time

The effect of contact time on the biosorption of Sr(II) by native, NaOH-treated and immobilized PHB was investigated over the time intervals of 5 to 320 min as shown in Fig. 2D. A maximum biosorption capacity value of 3.81, 4.44 mg g^{-1} and 5.18 was obtained for native, immobilized and NaOH-treated PHB, respectively. During the initial stages of the sorption process, adsorption rate was rapid with $\geq 90\%$ of the added Sr(II) removed from solution within 10 mins for all treatments investigated. After which, uptake rate slowly declined and attained equilibrium at 80 min for native, 160 min for NaOH-treated and 320 min for immobilized PHB. The results of the study revealed that adsorption took place in two phases where the metal ion were physically/chemically taken up onto the surface of the biosorbent before being taken into the inner adsorption sites of the PHB [15, 44]. The first phase, known as a passive surface transport, took place quite rapidly, while the second passive diffusion step transport, took a much longer time to complete [45-48].

3.2.5. Effect of initial Sr(II) concentration and competing ions on the biosorption process

The effect of changing initial metal ion concentration in the range of $10\text{-}100 \text{ mg L}^{-1}$ on Sr(II) removal was studied as it is well known that the initial metal concentration acts as an important driver for the mass transfer of metal ions onto sorbents [15, 49-51]. The effect of initial Sr(II) concentration is shown in Fig. 2E and as expected the PHB and modified PHB exhibited an increase in Sr(II) removal capacity with increasing initial concentration until equilibrium was reached, after which uptake decreased. Sr(II) removal capacity is very high at high concentration for immobilized PHB as compared to native and NaOH-treated PHB with maximum biosorption capacity values of 38.0, 17.6, and 9.4 mg g^{-1} obtained for immobilized, NaOH- treated and native PHB respectively. Gok et al. [52] studied in detail the

biosorption of radio strontium by alginate beads and proved an efficient and inexpensive method of Sr(II) ion removal.

Biosorption of Sr(II) ions was studied in the presence of other cations and anions as industrial wastewater contains many other background electrolytes which may interfere with the biosorption process. Solutions of competing ions were prepared and the influence on the biosorption capacity of PHB studied. The effect of ionic interaction on the sorption process may be represented by the ratio of sorption capacity in the presence of interfering ion (q_{mix}) and without interfering ion (q_0), such that for:

$\frac{q_{mix}}{q_0} > 1$ sorption is promoted in presence of other interfering ions

$\frac{q_{mix}}{q_0} = 1$ sorption is not influenced in presence of other interfering ions

$\frac{q_{mix}}{q_0} < 1$ sorption is suppressed in presence of other interfering ions [53].

The effect of the cations and anions investigated on the biosorption capacity of PHB is reported in Table 2. The presence of other cations and most anions, strongly inhibit the uptake of Sr(II) ions from solution on native and NaOH-treated PHB. However, phosphate have no effect or may even slightly promote the uptake of Sr(II) on NaOH-treated PHB. Although the presence of other cations and anions does inhibit the uptake of Sr(II) from solution onto immobilized PHB, the suppressing effect is less suggesting the immobilized form of PHB may perform better under 'real' conditions. Results revealed that the Sr(II) ions can be removed effectively using peanut husk biomass (immobilized and NaOH pre-treated) to avoid the contamination of natural water resources and under the current scenario of environmental pollution [4, 7, 9, 11-14, 46, 54-73], there is also need to explore and utilize new adsorbents. So far, in comparison to reported studies (Table 3) [1, 74-80], the peanut husk biomass (immobilized and NaOH pre-treated) showed compromising efficiency for the adsorption of Sr(II) ions from aqueous medium.

3.3. Desorption study

Dilute HCl proved to be the most successful desorbing agent for immobilized PHB with EDTA proving most successful for the NaOH-treated PHB. Greater than 95% of the retained Sr(II) was eluted from the modified PHB forms using these desorbing agents. Interestingly, it

was less easy to desorb retained Sr(II) from native PHB with only 40% eluted in the most successful desorbing agent (0.1M HCl) (Fig. 3). This implies the modified forms of PHB may be successfully re-used and/or the retained Sr(II) recovered from solution.

3.4. Biosorption kinetics

Understanding the kinetics of biosorption is important in technology transfer from the laboratory to an industrial scale. Appropriate models can be helpful in understanding the process mechanisms, for analyzing experimental data and predicting outcomes for process optimization of future operational conditions [42, 47, 48]. The rate of the biosorption process depends on the physical and chemical properties of the biosorbent material and the mass transfer mechanism. A number of models have been proposed which evaluate this process and provide estimates of removal rate and the kinetic parameters under selected conditions.

Our results show the biosorption mechanism, over the complete range of the contact time, is best explained by the pseudo-second order kinetic model. Table 4 illustrates that both Linear and non-linear regression analysis R^2 values favor the goodness of fit of the pseudo-second order kinetic model to the experimental kinetic data and the calculated and experimental maximum sorption capacity values are in good agreement with the experimental values of Sr (II) biosorption onto all PHB forms (Fig. 4). In addition, the values of error functions obtained are very small, suggesting good agreement between models and experimental data. For Sr(II) uptake onto native, NaOH-treated and immobilized PHB, the error functions decrease in order pseudo-first order > pseudo-second order again suggesting the better fit of the pseudo-second order kinetic model to the biosorption data (results not shown).

3.5. Equilibrium modelling

The obtained results of Sr(II) uptake on PHB were fitted to three common equilibrium models and evaluated by linear and non-linear regression methods. Table 5 presents the equilibrium modelling results of Sr(II) removal by PHB with the comparative values for the experimental sorption capacity q_e and predicted sorption capacity by Freundlich, Langmuir and Redlich-Peterson isotherms presented in Figure 5. The results show that the Redlich-Peterson model provides the highest R^2 values of 0.99, 0.99 and 0.981 calculated by linear regression and 0.883, 0.897 and 0.967 by non-linear regression for native, NaOH-treated and immobilized PHB respectively. The high values of correlation coefficient suggest that the

Redlich-Peterson isotherm model is comparatively much better at describing the observed results than the Freundlich and Langmuir isotherm models. The trend of error functions confirmed that the equilibrium data of Sr(II) biosorption onto native and NaOH-treated PHB was best fitted to the Redlich-Peterson sorption isotherm with the Langmuir isotherm, whereas the equilibrium data of the immobilized PHB may be better explained by the Langmuir or Freundlich models.

3.6. Characteristics of PHB influencing Sr(II) biosorption

The process of biosorption is complex with many factors affecting this phenomenon. Among these factors, surface morphology and the pore size of adsorbent can have a considerable effect on the process of adsorption. Scanning electronic microscopy (SEM) in conjunction with surface area analysis techniques were used to investigate the surface morphology, texture and porosity of the PHB. The surface morphology of the native PHB is illustrated in Figure 6A and shows the rough and irregular physical features of the PHB structure which contain many pores that may provide a large surface for the Sr(II) ions adsorption. Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis of the PHB support this visual deduction. The results obtained calculate a large surface area and highlight the predominance of meso-pores (IUPAC Classification $20\text{Å} < d < 500\text{Å}$) in PHB which is desirable for the adsorption of metal ions from the aqueous phase (see Fig. 6B). In addition, SEM and Energy Dispersive X-Ray (SEM-EDX) images were used to confirm successful biosorption on native PHB, before and after loading with Sr(II) ions by the appearance of Sr peaks (Fig. 6C).

All plant biomass is composed of cellulose, hemi-cellulose and lignin to varying degrees, with peanut husk being no exception. The XRD pattern confirmed the main crystalline structure of PHB to be cellulose based. The broad peak at $2\theta = 22^\circ$ refers to the cellulose structure and secondary peaks at $2\theta = 16^\circ$ the polysaccharide structure. Thermogravimetric analysis (TGA) was used to investigate the ligno-cellulosic material content of PHB and it was found that >71% weight loss occurred in a major decomposition stage at 200–400°C, which is attributed to the decomposition of cellulose, hemicelluloses and lignin. The predominance of ligno-cellulosic material in PHB provides a rich source of oxygen-containing functional groups (e.g. $-\text{COOH}$, $-\text{OH}$, $-\text{R-OH}$) and it has been suggested that complexation of metals with ionised oxygen-containing functional groups through ion exchange is a major mechanism for metal sorption by biomass. The role of surface

complexation with oxygen-containing functional groups in Sr(II) biosorption on PHB was therefore evaluated by characterising the Sr loaded PHB using FTIR. After Sr(II) sorption, peaks at 3344, 1726 and 1030 cm^{-1} (assigned to O-H, C=O and C-O) weakened or shifted suggesting that the oxygen-containing functional groups are involved in the Sr^{2+} sorption process (Fig. 7).

4. Conclusions

Peanut husk has potential to remove the Sr(II) ions from wastewater even in low concentration. Sorbent amount strongly affected the sorption capacity of Sr(II) onto peanut husk. The pH of the medium affected the sorption capacity and most optimal value was pH 9 for native and 7 NaOH-treated and immobilized peanut husk. Equilibrium was achieved in 80 minutes for Sr sorption onto native and NaOH-treated peanut husk. Native and NaOH-treated kinetic data was fitted to pseudo-second order model. Redlich-Peterson isothermal model had the best correlation to the experimental data of native and NaOH. Maximum biosorption capacity 9.4, 17.6 and 38 mg g^{-1} for native, NaOH-treated and immobilized peanut husk. Thermodynamics showed that removal of Sr(II) was spontaneous and favorable at all studied temperatures. HCl and EDTA proved most successful eluting agents for sorbed Sr(II) ions.

Acknowledgement

The authors are thankful to Higher Education Commission, Pakistan for financial assistance under the project International Research Support Initiative Program (IRSIP).

References

- [1] S. Chegrouche, A. Mellah, M. Barkat, *Desalination* 235 (2009) 306-318.
- [2] W. Guan, J. Pan, H. Ou, X. Wang, X. Zou, W. Hu, C. Li, X. Wu, *Chem. Eng. J.* 167 (2011) 215-222.
- [3] E. Başıçetin, G.I. Atun, *J. Chem. Eng. Data* 55 (2009) 783-788.
- [4] K. Aftab, K. Akhtar, A. Kausar, S. Khaliq, N. Nisar, H. Umbreen, M. Iqbal, *J. Photochem. Photobiol. B: Biol.* 175 (2017) 182-190.
- [5] M.Z. Ahamd, S. Ehtisham-ul-Haque, N. Nisar, K. Qureshi, A. Ghaffar, M. Abbas, J. Nisar, M. Iqbal, *Water Sci. Technol.* 76 (2017) 323-336.
- [6] A. Ashar, M. Iqbal, I.A. Bhatti, M.Z. Ahmad, K. Qureshi, J. Nisar, I.H. Bukhari, *J. Alloy. Comp.* 678 (2016) 126-136.
- [7] I.A. Bhatti, N. Ahmad, N. Iqbal, M. Zahid, M. Iqbal, *J. Environ. Chem. Eng.* 5 (2017) 2740-2751.
- [8] I. Bibi, N. Nazar, M. Iqbal, S. Kamal, H. Nawaz, S. Nouren, Y. Safa, K. Jilani, M. Sultan, S. Ata, F. Rehman, M. Abbas, *Adv. Powder Technol.* 28 (2017) 2035-2043.

- [9] A. Sasmaz, I.M. Dogan, M. Sasmaz, *Water Environ. J.* 30 (2016) 235-242.
- [10] M. Sasmaz, B. Akgül, A. Sasmaz, *Bull. Environ. Contam. Toxicol.* 94 (2015) 598-603.
- [11] M. Sasmaz, B. Akgul, D. Yıldırım, A. Sasmaz, *Int. J. Phytoremediat.* 18 (2016) 1164-1170.
- [12] M. Sasmaz, B. Akgül, D. Yıldırım, A. Sasmaz, *Int. J. Phytoremediat.* 18 (2016) 69-76.
- [13] M. Sasmaz, E. Obek, A. Sasmaz, *Bull. Environ. Contam. Toxicol.* 97 (2016) 832-837.
- [14] M. Sasmaz, E.I.A. Topal, E. Obek, A. Sasmaz, *J. Environ. Manage.* 163 (2015) 246-253.
- [15] R. Nadeem, Q. Manzoor, M. Iqbal, J. Nisar, *J. Ind. Eng. Chem.* 35 (2016) 185-194.
- [16] I. Smičiklas, S. Dimović, I. Plečaš, *Appl. Clay Sci.* 35 (2007) 139-144.
- [17] A. El-Kamash, *J. Hazard. Mater.* 151 (2008) 432-445.
- [18] Y. Chen, J. Wang, *Nucl. Eng. Design* 242 (2012) 445-451.
- [19] A. Kausar, H.N. Bhatti, G. MacKinnon, *Colloid. Surf. B* 111 (2013) 124-133.
- [20] A. Kausar, H.N. Bhatti, G. MacKinnon, *J. Taiwan Instit. Chem. Eng.* 59 (2016) 330-340.
- [21] P. Akhter, N. Baloch, D. Mohammad, S. Orfi, N. Ahmad, *J. Environ. Radioact.* 73 (2004) 247-256.
- [22] K. Pande, M. Sarin, J. Trivedi, S. Krishnaswami, K. Sharma, *Chem. Geol.* 116 (1994) 245-259.
- [23] S. Lagergren, *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (1898) 1-39.
- [24] Y. Ho, G. McKay, *Water Res.* 33 (1999) 578-584.
- [25] Y.-S. Ho, *Water Res.* 40 (2006) 119-125.
- [26] S.A. Khan, M.A. Khan, *Waste Manage.* 15 (1995) 271-282.
- [27] I. Langmuir, *J. Am. Chem. Soc.* 38 (1916) 2221-2295.
- [28] H. Freundlich, *J. Phys. Chem.* 57 (1906) 1100-1107.
- [29] O. Redlich, D.L. Peterson, *J. Phys. Chem.* 63 (1959) 1024-1024.
- [30] K.V. Kumar, S. Sivanesan, *J. Hazard. Mater.* 136 (2006) 721-726.
- [31] K.Y. Foo, B.H. Hameed, *Chem. Eng. J.* 156 (2010) 2-10.
- [32] A. El Hamidi, S. Arsalane, M. Halim, *J. Chem.* 9 (2012) 1532-1542.
- [33] L. Chan, W. Cheung, S. Allen, G. McKay, *J. Chem. Eng.* 20 (2012) 535-542.
- [34] J. Porter, G. McKay, K. Choy, *Chem. Eng. Sci.* 54 (1999) 5863-5885.
- [35] A. Kapoor, R. Yang, *Gas Separat. Purificat.* 3 (1989) 187-192.
- [36] J. Ng, W. Cheung, G. McKay, *Chemosphere* 52 (2003) 1021-1030.
- [37] D.W. Marquardt, *J. Soc. Ind. Appl. Math.* 11 (1963) 431-441.
- [38] Yesi, F.P. Sisnandy, Y.-H. Ju, F.E. Soetaredjo, S. Ismadji, *Adsorpt. Sci. Technol.* 28 (2010) 847-868.
- [39] Y. Safa, H.N. Bhatti, I.A. Bhatti, M. Asgher, *Canadian J. Chem. Eng.* 89 (2011) 1554-1565.
- [40] Q. Li, H. Liu, T. Liu, M. Guo, B. Qing, X. Ye, Z. Wu, *Chem. Eng. J.* 157 (2010) 401-407.
- [41] G. Keçeli, *J. Radioanal. Nucl. Chem.* 268 (2006) 211-219.
- [42] M.A. Tahir, H.N. Bhatti, M. Iqbal, *J. Environ. Chem. Eng.* 4 (2016) 2431-2439.
- [43] Z. Aksu, I.A. Isoglu, *J. Hazard. Mater.* 137 (2006) 418-430.
- [44] S. Aytas, D.A. Turkozu, C. Gok, *Desalination* 280 (2011) 354-362.
- [45] H. Naeem, H.N. Bhatti, S. Sadaf, M. Iqbal, *Appl. Radiat. Isotop.* 123 (2017) 94-101.
- [46] A. Rashid, H.N. Bhatti, M. Iqbal, S. Noreen, *Ecol. Eng.* 91 (2016) 459-471.
- [47] S. Shoukat, H.N. Bhatti, M. Iqbal, S. Noreen, *Micropor. Mesopor. Mater.* 239 (2017) 180-189.
- [48] M. Tahir, M. Iqbal, M. Abbas, M. Tahir, A. Nazir, D.N. Iqbal, Q. Kanwal, F. Hassan, U. Younas, *Acta Ecol. Sinica* 37 (2017) 207-212.
- [49] A. Kanwal, H.N. Bhatti, M. Iqbal, S. Noreen, *Water Environ. Res.* 89 (2017) 301-311.
- [50] A. Kausar, H.N. Bhatti, M. Iqbal, A. Ashraf, *Water Sci. Technol.* 76 (2017) 1035-1043.

- [51] M. Mushtaq, H.N. Bhatti, M. Iqbal, S. Noreen, J. Environ. Manage. 176 (2016) 21-33.
- [52] C. Gok, U. Gerstmann, S. Aytas, J. Radioanal. Nucl. Chem. 295 (2013) 777-788.
- [53] F.V. Pereira, L.V.A. Gurgel, L.F. Gil, J. Hazard. Mater. 176 (2010) 856-863.
- [54] I.A. Bhatti, M.A. Hayat, M. Iqbal, J. Chem. Soc. Pak. 34 (2012) 1012-1022.
- [55] M. Iqbal, Chemosphere 144 (2016) 785-802.
- [56] M. Iqbal, M. Abbas, M. Arshad, T. Hussain, A.U. Khan, N. Masood, M.A. Tahir, S.M. Hussain, T.H. Bokhari, R.A. Khera, Pol. J. Environ. Stud. 24 (2015) 2745-2750.
- [57] A. Babarinde, G.O. Onyiaocha, Chem. Int. 2 (2016) 37-46.
- [58] C. Ukpaka, C. Ukpaka, Chem. Int. 2 (2016) 136-144.
- [59] C.P. Ukpaka, F.U. Igwe, Chem. Int. 3 (2017) 258-267.
- [60] M. Iqbal, Z. Ali, M.A. Qamar, A. Ali, F. Hussain, M. Abbas, J. Nisar, Water Sci. Technol. 76 (2017) 219-235.
- [61] M. Iqbal, I.A. Bhatti, J. Hazard. Mater. 299 (2015) 351-360.
- [62] S. Jafarinejad, Chem. Int. 2 (2016) 242-253.
- [63] S. Jafarinejad, Chem. Int. 3(3) (2017) 241-250.
- [64] C. Ukpaka, S.N.-A. Adaobi, C. Ukpaka, Chem. Int. 3 (2017) 306-317.
- [65] C. Ukpaka, T. Izonowei, Chem. Int. 3 (2017) 46-57.
- [66] A. Sasmaz, O. Sen, G. Kaya, M. Yaman, A. Sagiroglu, Distribution of thallium in soil and plants growing in the Keban mining district of Turkey and determined by ICP-MS, Atom. Spectroscopy 28 (2007) 157.
- [67] A. Sasmaz, M. Yaman, Comm. Soil Sci. Plant Anal. 39 (2008) 2568-2583.
- [68] J. Nisar, M. Sayed, F.U. Khan, H.M. Khan, M. Iqbal, R.A. Khan, M. Anas, J. Environ. Chem. Eng. 4 (2016) 2573-2584.
- [69] A. Babarinde, K. Ogundipe, K.T. Sangosanya, B.D. Akintola, A.-O. Elizabeth Hassan, Chem. Int. 2 (2016) 89-102.
- [70] N.K. Benabdallah, D. Harrache, A. Mir, M. de la Guardia, F.-Z. Benhachem, Chem. Int. 3(2017) 220-231.
- [71] S. Jafarinejad, Chem. Int. 3 (2017) 268-277.
- [72] K. Legroui, E. Khouya, H. Hannache, M. El Hartti, M. Ezzine, R. Naslain, Chem. Int. 3 (2017) 301-310.
- [73] M. Abbas, M. Adil, S. Ehtisham-ul-Haque, B. Munir, M. Yameen, A. Ghaffar, G.A. Shar, M.A. Tahir, M. Iqbal, Sci. Total Environ. (2018) <https://doi.org/10.1016/j.scitotenv.2018.1001.1066>.
- [74] J. Jang, W. Mirana, S.D. Divine, M. Nawaz, A. Shahzad, S.H. Woo, D.S. Lee, Sci. Total Environ. 615 (2018) 698-707.
- [75] S.S. Metwally, I.M. Ahmed, H.E. Rizk, J. Alloy. Comp. 709 (2017) 438-444.
- [76] S.R. Choe, Y. Haldorai, S.-C. Jang, R. Muruganantham, Y.-C. Lee, Y.-K. Han, C. Roh, Y.S. Huh, Environ. Technol. Innovat. 9 (2018) 285-293.
- [77] H.-J. Hong, H.S. Jeong, B.-G. Kim, J. Hong, I.-S. Park, T. Ryu, K.-S. Chung, H. Kim, J. Ryu, Chemosphere 165 (2016) 231-238.
- [78] L. Qiu, J. Feng, Y. Dai, S. Chang, J. Environ. Radioact. 172 (2017) 52-62.
- [79] A. Ahmadpour, M. Zabihi, M. Tahmasbi, T.R. Bastami, J. Hazard. Mater. 182 (2010) 552-556.
- [80] Y. Yin, J. Wang, X. Yang, W. Li, Nucl. Eng. Technol. 49 (2017) 172-177.

1 Table 1. Thermodynamic parameters for Sr (II) biosorption onto PHB as a function of temperature

Temperature (C°)	Native			NaOH-treated			Immobilized		
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
30	-0.00384			-0.01221			-0.00336		
35	-0.00377	8.1898	-0.015	-0.01219	13.48	-0.0042	-0.00327	8.41	-0.017
40	-0.00369			-0.01217			-0.00319		
50	-0.00355			-0.01215			-0.00310		
60	-0.00341			-0.01213			-0.00300		

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

3

4 Table 2. Comparison of the effect of different interfering cations and anions on Sr(II) biosorption onto peanut husk

5

Cations	$\frac{q_{mix}}{q_0}$ Native			$\frac{q_{mix}}{q_0}$ NaOH-Treated			$\frac{q_{mix}}{q_0}$ Immobilized		
	5 mg L ⁻¹	10 mg L ⁻¹	15 mg L ⁻¹	5 mg L ⁻¹	10 mg L ⁻¹	15 mg L ⁻¹	5 mg L ⁻¹	10 mg L ⁻¹	15 mg L ⁻¹
Co ²⁺	0.016	0.016	0.016	0.018	0.018	0.018	0.85	0.68	0.53
Cu ²⁺	0.016	0.016	0.016	0.035	0.006	0.006	0.84	0.72	0.56
Ni ²⁺	0.016	0.016	0.016	0.090	0.040	0.040	0.85	0.85	0.45
Cd ²⁺	0.020	0.010	0.010	0.050	0.003	0.003	0.88	0.75	0.61
Zn ²⁺	0.016	0.016	0.016	0.030	0.008	0.020	0.87	0.75	0.60
Mn ²⁺	0.016	0.016	0.016	0.080	0.007	0.050	0.86	0.73	0.75
Pb ²⁺	0.016	0.016	0.016	0.050	0.050	0.050	0.87	0.72	0.56
Anions (0.1M)	$\frac{q_{mix}}{q_0}$ Native			$\frac{q_{mix}}{q_0}$ NaOH-Treated			$\frac{q_{mix}}{q_0}$ Immobilized		
Cl ⁻¹	0.199			0.372			0.704		
CH ₃ COO ⁻¹	0.172			0.362			0.707		
SO ₄ ³	0.051			0.209			0.552		
I ⁻¹	0.064			0.304			0.866		
PO ₄ ³⁻	0.126			1.03			0.727		

6

7

8 Table 3. Comparison of Sr(II) on to different adsorbents and peanut husk biomass (present study)

Adsorbents	Sorption capacity	References
Rice straw-based biochar (RSBC)	175.95 mg g ⁻¹	Jang et al. [74]
Hydroxyapatite-cobalt(II) ferrocyanide, HAFC	13.44 mg g ⁻¹	Metwally et al. [75]
Polymer hydrogel composed of alginate/humic acid/Fe-aminoclay.	45.65 mg g ⁻¹	Choe et al. [76]
Alginate/Fe ₃ O ₄ composite	400.0 mg g ⁻¹	Hong et al. [77]
<i>Saccharomyces cerevisiae</i> (<i>S. cerevisiae</i>)	150 mg g ⁻¹	Qiu et al. [78]
Almond green hull	116.3 mg g ⁻¹	Ahmadpour et al. [79]
<i>S. cerevisiae</i>	81.96 mg g ⁻¹	Yin et al. [80]
Activated carbon	5.07×10 ⁻⁴ molg ⁻¹	Chegrouche et al. [1]
Peanut husk	9.4 mg g ⁻¹	Present Study
Native	17.6 mg g ⁻¹	
NaOH-treated	38.0 mg g ⁻¹	
Immobilized PH		

9

10

11 Table 4. Comparison of parameters of kinetic models for Sr(II) biosorption onto PHB by linear and non-linear regression methods.

Parameters	Pseudo-first order					
	Linear regression method			Non-linear regression method		
	Native	NaOH-treated	Immobilized	Native	NaOH-treated	Immobilized
$K_1(\text{L min}^{-1})$	0.0123	0.0241	0.0161	0.420	0.596	0.190
q_e calculated (mg g^{-1})	2.63	0.153	1.466	3.72	5.16	4.30
q_e experimental (mg g^{-1})	3.80	5.18	4.44	3.80	5.18	4.44
R^2	0.629	0.515	0.883	0.715	0.854	0.918
	Pseudo-second order					
	Linear regression method			Non-linear regression method		
	Native	NaOH-treated	Immobilized	Native	NaOH treated	Immobilized
$K_2(\text{g mg}^{-1} \text{min}^{-1})$	0.319	0.894	0.0840	0.328	0.665	0.0730
q_e calculated (mg g^{-1})	3.80	5.19	4.47	3.80	5.20	4.52
q_e experimental (mg g^{-1})	3.80	5.18	4.44	3.80	5.18	4.44
R^2	1.00	1.00	0.999	0.971	0.957	0.880

12

13

14

15 Table 5. Equilibrium models parameters for Sr(II) sorption onto peanut husk by linear and non-linear regression methods.

Parameters	Freundlich Isotherm					
	Linear regression method			Non-linear regression method		
	Native	NaOH-treated	Immobilized	Native	NaOH-treated	Immobilized
$K_F(\text{mg g}^{-1})(\text{L mg}^{-1})^n$	3.01	8.75	10.3	3.85	8.94	7.11
n	3.34	6.53	2.47	0.207	0.147	0.594
R^2	0.990	0.957	0.892	0.807	0.896	0.961
Langmuir isotherm						
	Linear regression method			Non-linear regression method		
	Native	NaOH-treated	Immobilized	Native	NaOH-treated	Immobilized
	$q_m(\text{mg g}^{-1})$	8.89	16.5	49.8	9.38	15.3
$K_a(\text{L mg}^{-1})$	0.429	0.522	0.142	0.242	1.16	0.770
R_L	0.0320	0.0270	0.0700	0.0120	0.0120	0.0140
R^2	0.973	0.966	0.819	0.882	0.714	0.782
Redlich-Peterson isotherm						
	Linear regression method			Non-linear regression method		
	Native	NaOH-treated	Immobilized	Native	NaOH-treated	Immobilized
	A (L g^{-1})	2.69	2840	28.0	2.52	2497
B ($\text{dm}^3 \text{mg}^{-1}$) ^g	0.286	272	3.09	0.296	273	0.0210
g	1.00	0.860	0.413	0.976	0.860	1.38
R^2	0.990	0.999	0.981	0.883	0.897	0.967

16
17

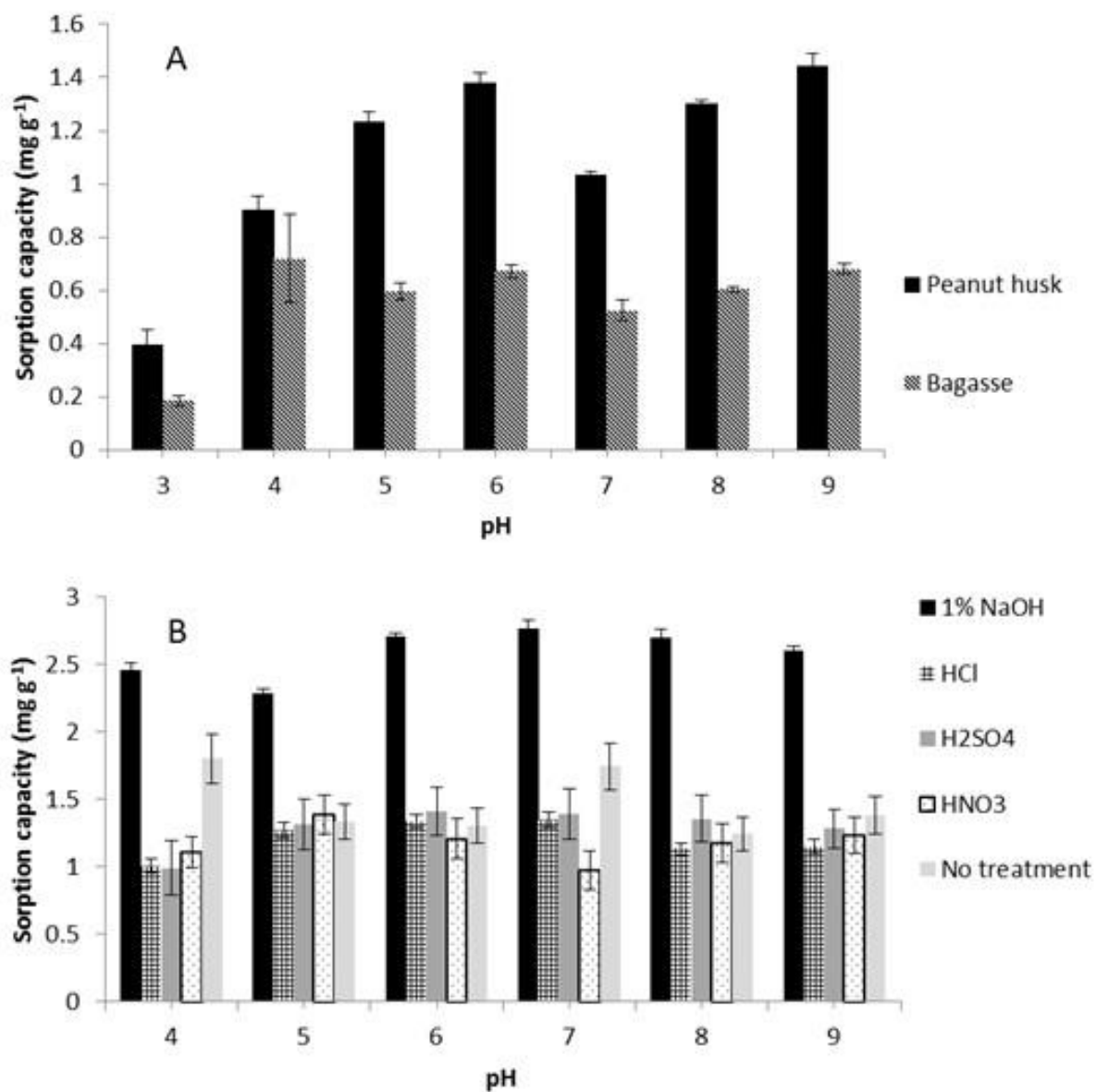


Figure 1: A) Screening of biosorbents for Sr(II) removal and B) Effect of pretreatment of peanut husk on biosorption of Sr(II).

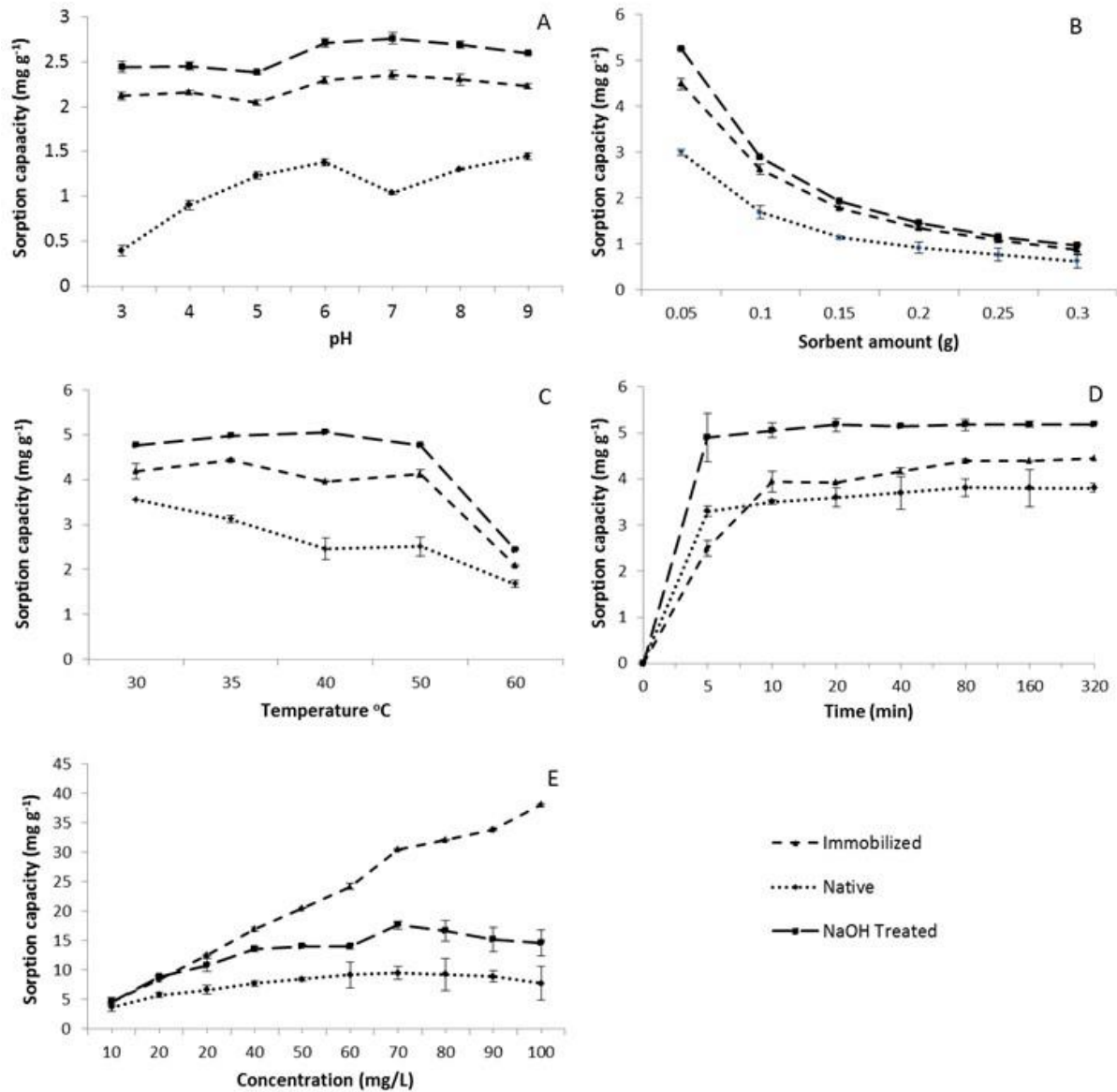


Figure 2: Effect of A) initial pH, B) sorbent amount, C) temperature, D) time and E) initial metal ion concentration on Sr(II) biosorption onto PHB.

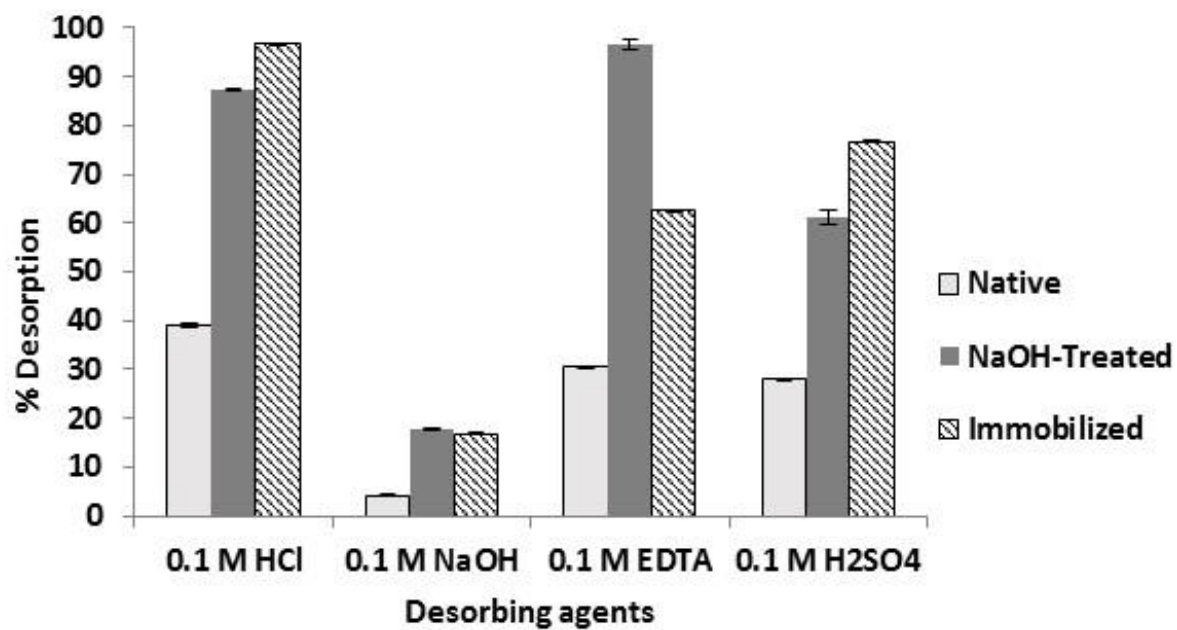


Figure 3: Comparison of different desorbing agents on Sr(II) biosorption onto PHB.

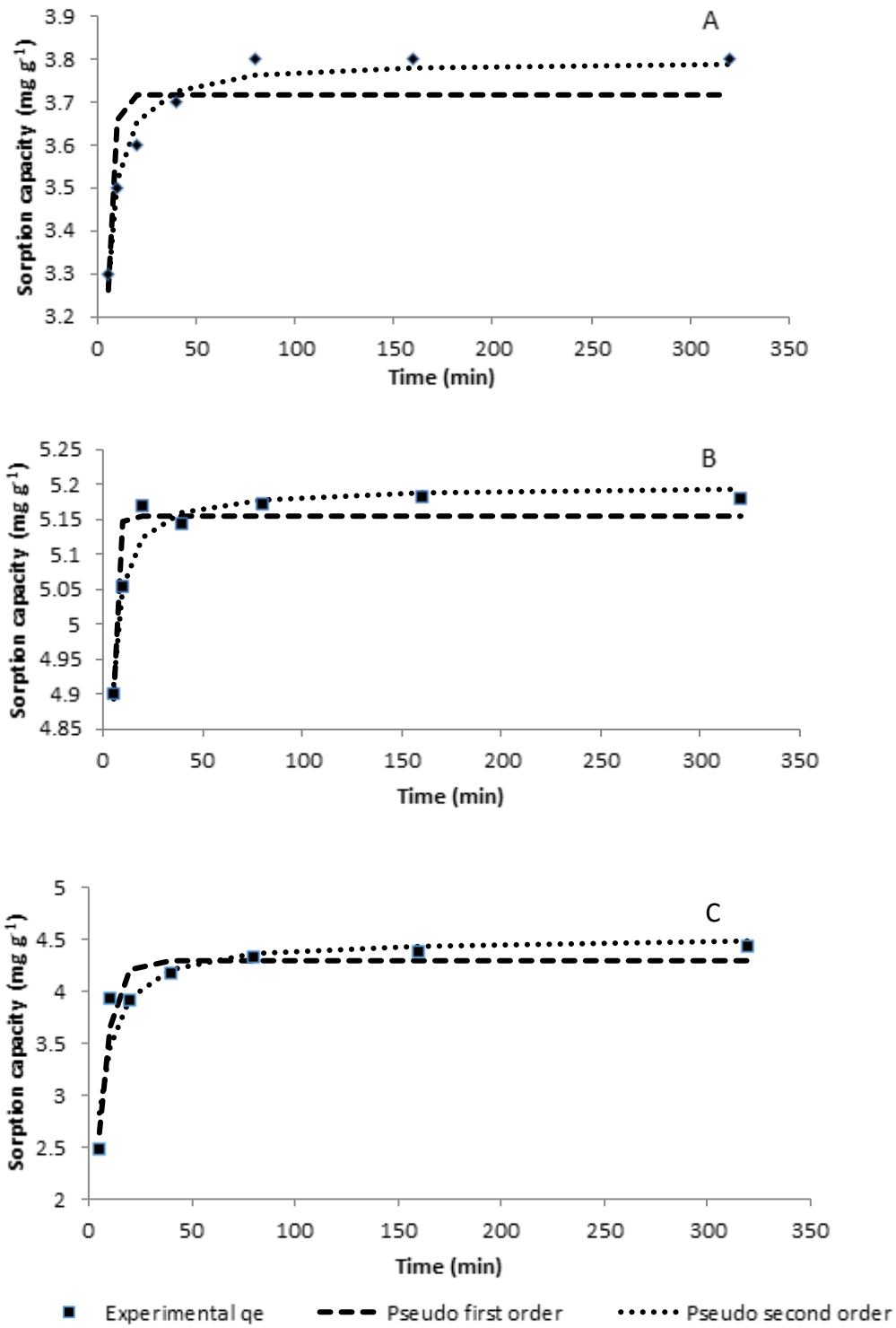


Figure 4 Comparison of kinetic models for Sr(II) biosorption onto PHB A) Native, B) NaOH-treated and C) Immobilized.

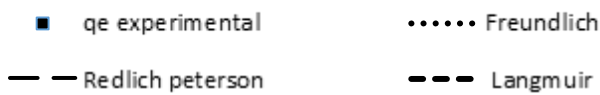
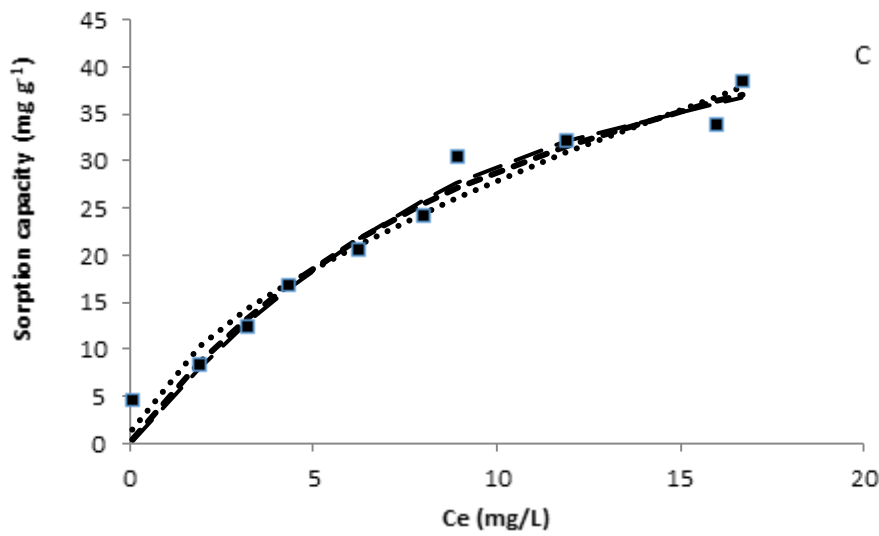
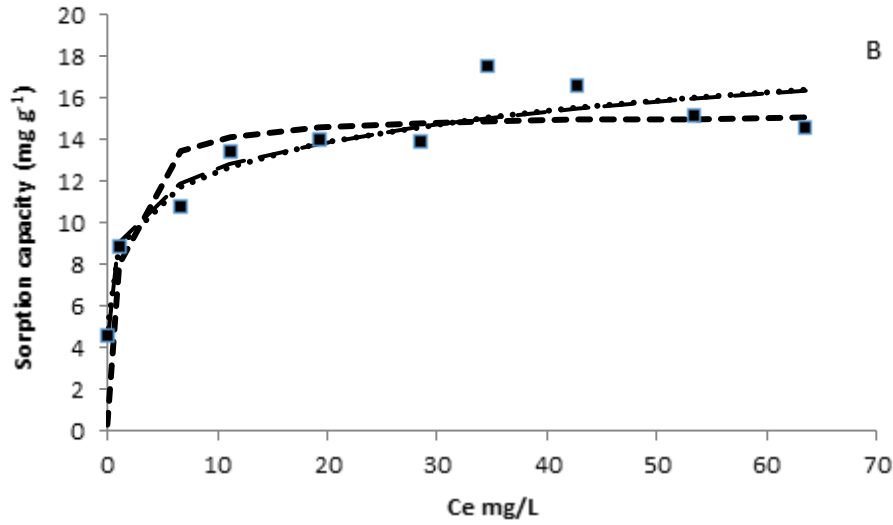
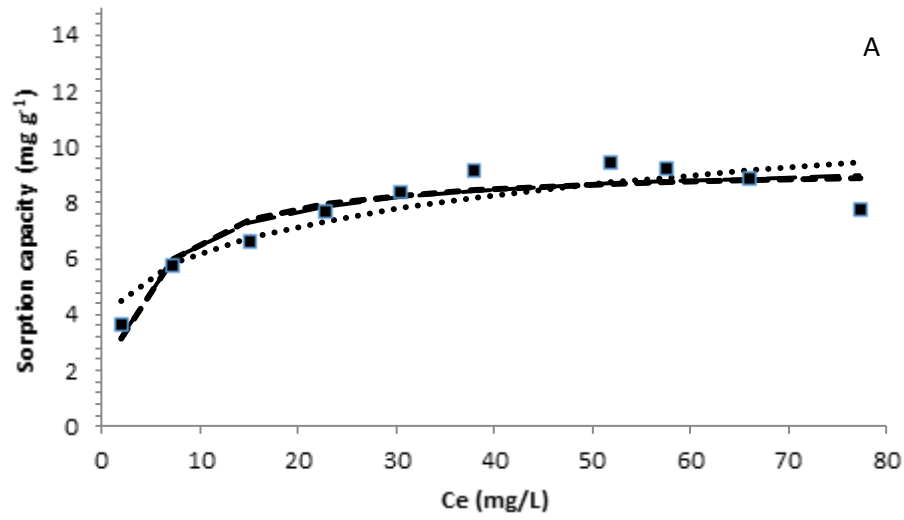


Figure 5. Comparison of equilibrium models for Sr(II) biosorption onto PHB A) Native B) NaOH-treated and C) Immobilized.

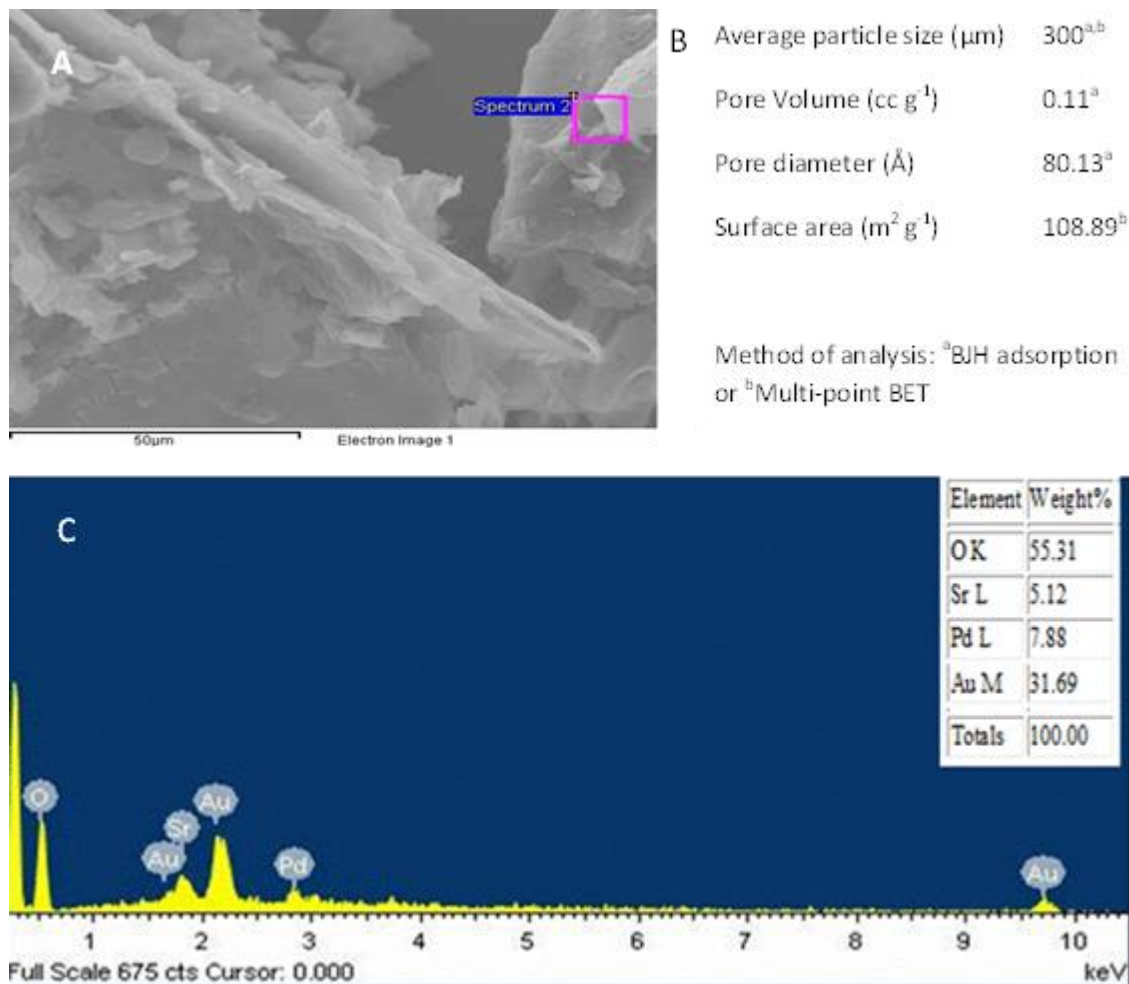


Figure 6A) SEM and C) EDX spectra of Sr(II) loaded PHB and B) Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) pore size and volume analysis of native PHB.

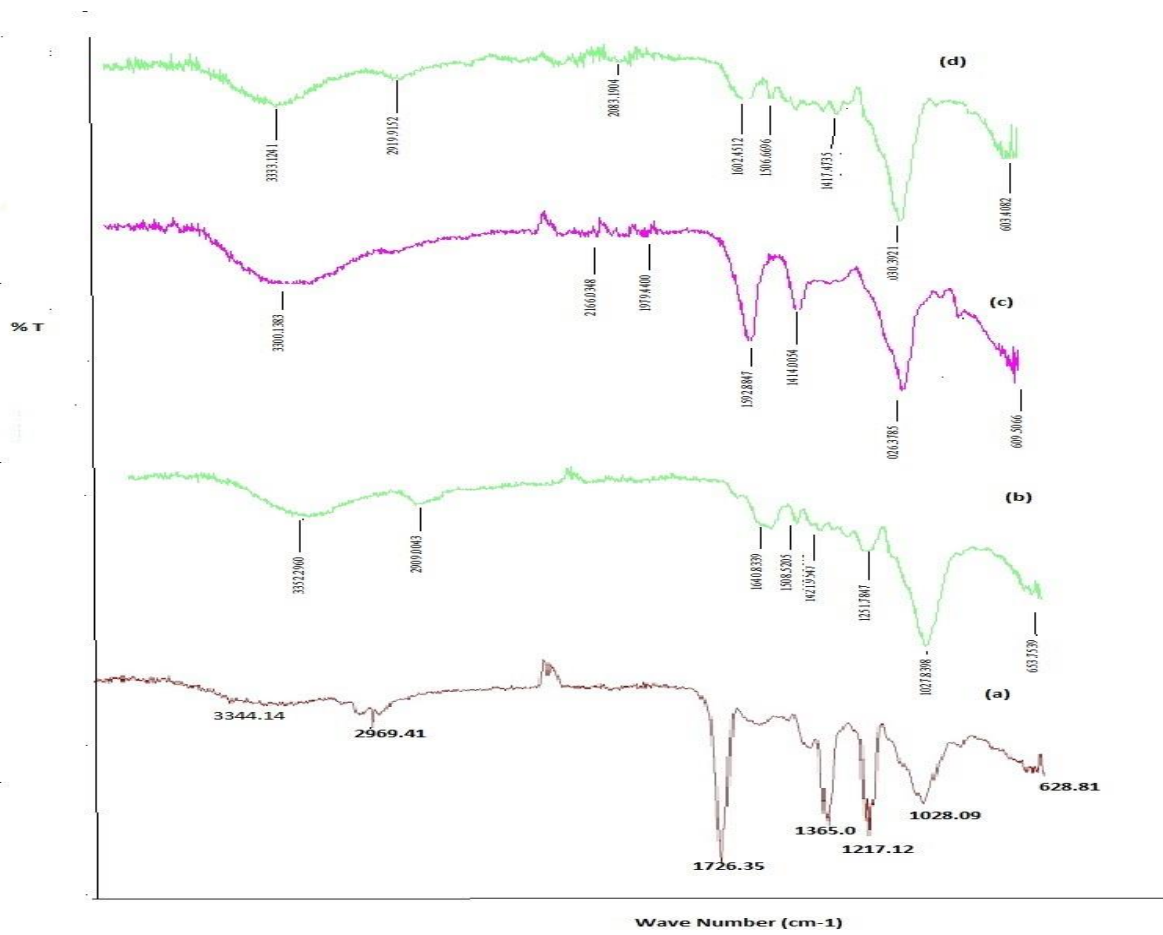


Figure 7. FT-IR spectra of (a) Native PHB and (b) Native PHB loaded with Sr(II) with assigned functional groups.