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# Citric Acid Functionalized *Bougainvillea spectabilis*: a Novel, Sustainable, and Cost-effective Biosorbent for Removal of Heavy Metal ($Pb^{2+}$) from Waste Water

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**Abstract** With increasing concern related to sustainable chemistry, we investigated the biosorption of $Pb^{2+}$ ions from aqueous medium using an environmental friendly and economic biosorbent *Bougainvillea spectabilis* (BS). The BS was modified effectively using citric acid by hydrothermal method. The biosorbent(s) was characterized by scanning electron microscope (SEM), energy dispersion X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and point of zero charge ($pH_{pzc}$). Various process parameters including biosorbent dosage, time of contact, temperature, solution pH, and initial $Pb^{2+}$ ions concentration were studied in batch mode. Kinetic modeling was performed to evaluate the kinetic data and results showed that the studied process followed the pseudo second order (PSO) kinetics. Equilibrium modeling was done using famous equilibrium models, i.e., Langmuir, Freundlich, Dubinin-Kaganer-Radushkevish, and Temkin in non-linear fashion to evaluate equilibrium data by varying initial $Pb^{2+}$ ions concentration from 20 to 180 mg/L. Based on RMSE values, Langmuir model fits best. This paper also discusses thermodynamic parameters (i.e., enthalpy, entropy, and free energy) showing that the process was spontaneous and endothermic in nature. In comparison with BS (*B. spectabilis*), an appreciable increase in uptake capacity of CABS (citric acid modified *B. spectabilis*) was observed in sequestration of $Pb^{2+}$ ions from aqueous medium showing advantage of citric acid modification making it industrially favorable and socially acceptable biosorbent for efficient removal of lead from water.

**Keywords** *Bougainvillea spectabilis* · Lead · Non-linear equilibrium · Thermodynamics · Biosorption kinetics · Citric acid functionalized biosorbent

## 1 Introduction

Heavy metals are a group of metals that have density greater than 5 g/cm$^3$. Many industries like mining,

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fertilizers, ore refineries, electroplating, tanning, batteries, and pesticides are the main cause of heavy metal pollution in water ways. USEPA has developed a chart for the permissible limits of these heavy metals above which these can cause health damage in different ways.

Concern about protection of our environment has gained much attention over the years from a global viewpoint and safe disposal of contaminated waste water is the major environmental issue for the industries to be resolved. Several ways have been adopted to remove this heavy metal pollution from water like precipitation, membrane filtration process, sand filters, ion exchange, reverse osmosis, solvent extraction, etc. (Unuabonah et al. 2007). But some of these methods produce even more toxic solid waste whose disposal becomes a problem. Some are not cost effective or ineffective to treat the metal ions of 100 mg/L concentration or below (Aydın et al. 2008). Hence, need of the day is to find a source, method, or technology that can address all the above problems. To date, in environmental chemistry, use of adsorption process to separate the contaminants has gained esthetic attention and deliberation abroad the nations due to low cost, simplicity of design, ease of operation, and complete removal of pollutants from solutions (Foo and Hameed 2010).

Recent literature showed the importance of low-cost agro-based materials for successful removal of heavy metals from waste water (Salman et al. 2015). Biomass like almond shell and hazelnut shell (Pehlivan et al. 2009), rice husk (Ajmal et al. 2003), wheat straw (Farooq et al. 2011), sawdust (Li et al. 2007), chitosan (Zulkali et al. 2006), mungbean husk (Saeed et al. 2009), sugarcane bagasse (Krishnan and Anirudhan 2003), cocoa shell (Meunier et al. 2003), Sorghum(Jawar) (Salman et al. 2013), and *Gardenia jasminoides* biomass (Rafiq et al. 2015) have been found as effective biosorbents. Literature reveals that sometime use of raw biosorbent causes secondary pollution and showed low metal uptake capacity. Many studies have been carried out and reported in literature to enhance the adsorption capacity of biosorbent using hydrothermal method (Rwiza et al. 2018) and chemical methods such as pre-treatment with organic acids, minerals, oxidizing agents, bases, and other chemicals like KOH, $H_2O_2$, NaCl, $ZnCl_2$, $Na_2CO_3$, epichlorohydrin, and glycerol (Abdolali et al. 2014; Hokkanen et al. 2016).

$Pb^{2+}$ belongs to heavy metal and found to be neurotoxin specially in children and cause mental debilities (Skerfving et al. 2015), dysfunction of kidneys and liver due to its cumulative property (Wan Ngah and Fatinathan 2010). Due to non-biodegradability, it belongs to high ranking persistent environmental toxic chemicals (Man et al. 2013). Sources of lead in the environment include industrial water, food, soil, paint, leaded gasoline, plastic materials, and cosmetic products (Markowitz 2000). Its industrial resources include lead mining, battery recycling industry, and electronic assembly plant effluents (Wan Ngah and Fatinathan 2010). Use of conventional techniques of treating water like flocculation, ultrafiltration, reverse osmosis, sedimentation, and coagulation is not good for lead removal due to high energy consumption (making it expensive) as well as large production of biological and chemical waste leading to metal hydroxides formation (Acheampong et al. 2010; Sud et al. 2008). So, there is need to choose an optimal process and a suitable biosorbent which should be environmental benign as well as cost effective for lead removal.

In the present study, *Bougainvillea spectabilis* has been used as a novel and environment friendly biosorbent. It is an ornamental plant having papery flowers. It is a drought tolerant, requiring a little water for growth and can grow in warm climate areas like in Pakistan with little or no care. Its branches are cut regularly for giving shape and beauty to plant; these branches are the waste material which can be used to clean metal contaminated water. There has been no work reported till now on $Pb^{+2}$ removal from aqueous solution using biomass of *B. spectabilis.*

The main objectives of this study are (i) to explore a new biosorbent and check its efficiency for removal of lead from waste water; (ii) to produce and characterize carboxylic acid functionalized biosorbent that fulfills 4-E strategy, i.e., environmental benign, efficient, easy to prepare, and economical; (iii) elucidate its biosorption process by studying its kinetic, thermodynamics, equilibrium modeling; (iv) to investigate surface morphology of biosorbent by using characterization techniques; and (v) to compare the removal efficiency of raw and modified biosorbent.

## 2 Materials and Methods

### 2.1 Chemicals and Reagents

Analytical grade chemicals and reagents were used in the present study and solutions were made using distilled water. Washing of glassware was done with nitric acid followed by distilled water. Chemicals used include sodium hydroxide, hydrochloric acid, sodium chloride, citric acid, and lead nitrate were bought from Merk/Scharlaw. Stock solution of lead ions (1000 mg/L) was prepared using lead nitrate salt. Standard solutions having different concentrations of lead ions were prepared from stock solution, diluting the calculated aliquots.

## 2.2 Biomass Preparation and Modification

Stalks of *Bougainvillea spectabilis* were collected from local area of Lahore Pakistan, which was then washed and dried in oven at 70 °C followed by grinding in to powder. It was then sieved through 80 mesh size and rinsed with distilled water to remove the dust particles. The biomass was then dried in oven again at 70 °C and stored in a dry box for future use.

The biosorbent was modified with citric acid using hydrothermal approach with slight modification in already reported method (Leyva-Ramos et al. 2012). Briefly, 20 g of BS was added in citric acid (1 M, 200 mL). The mixture was stirred for 2 h at 60 °C after which it was cooled at room temperature for 3 h. Acid was decanted and sorbent was washed with distilled water to remove any excess acid. Sorbent was dried at 80 °C for a day and stored in dry container for further use and labeled as CABS.

## 2.3 Instrumentation

Analysis of $Pb^{2+}$ ions was done using atomic absorption spectrophotometer (AAS) (Perkin Elmer Model-A Analyst 100) at 217 nm. Orbital shaker (VORTEX Model no: OSM-747) was used for adsorption experiments. pH factor and $pH_{pzc}$ were done using digital pH meter (Model: Ino Lab WTW Series). Fourier transform infrared spectrophotometer (Aligent Technologies CARY 630) was used to characterize the biomass in range of 4000 to 600 $cm^{-1}$ determining the surface functionality. A Nova Nano SEM 450 field-emission scanning electron microscope (FE-SEM) was used to determine the surface morphology comparing BS vs CABS and lead loaded BS (Pb-BS) vs lead loaded CABS (Pb-CABS). Energy dispersive X-ray spectroscopy EDX (FE-SEM) was also done for elemental analysis of CABS and Pb-CABS.

## 2.4 Adsorption Experiments

All the experiments were done using 50 mg/L of lead solution using CABS and BS in batch process and effect of different parameters on biosorption such as biosorbent dose, pH, time of contact, temperature, and initial concentration of $Pb^{2+}$ ions were investigated. Effect of change of one parameter was studied keeping all other constant.

### *2.4.1 Experiment of Adsorption Dose*

Fifty milliliters of 50 ppm $Pb^{2+}$ solution was taken in 9 Erlenmeyer flasks of 250 mL and labeled them from no.1 to no.9. Then, 0.1 to 0.9 g of adsorbent concentrations (BS and CABS separately) were placed in flasks from 1 to 9, respectively. Flasks were agitated on orbital shaker at 125 rpm for 30 min at 25 °C and solution was then filtered. The filtrate was then subjected to atomic absorption for study of change in concentration of metal ions. Same procedure was repeated 3 times and concordant reading were taken for further study.

### *2.4.2 Experiment of pH*

Fifty milliliters of 50 ppm solution of $Pb^{2+}$ was taken in 9 Erlenmeyer flasks of 250 mL. pH of metal solutions was adjusted from 1.0 to 9.0 (on the basis of earlier reports) with the help of pH meter using HCl (0.1 M) and NaOH (0.1 M). 0.1 g of adsorbent (BS and CABS separately) was added in each flask and solution was shaken at 125 rpm for 30 min at 25 °C then filtered and filtrate then subjected to study through AAS. Same procedure was repeated 3 times and concordant reading were taken for further study.

### *2.4.3 Experiment of Temperature*

Fifty milliliters of 50 ppm solution of $Pb^{2+}$ was taken in 6 Erlenmeyer flasks of 250 mL. Effect of temperature on biosorption of metal ion was studied at temperature from 10, 20, 30, 40, 50, and 60 °C at 125 rpm for 30 min with 0.1 g of biosorbent (both with BS and CABS separately). Then filtered and subjected to AAS for study of change of metal ion concentration. Concordant value of three repeated experiments was reported.

#### *2.4.4 Experiment of Contact Time and Initial Metal Ion Concentration*

During the biosorption experiment (for both BS and CABS), samples of 50 ppm of $Pb^{2+}$ solution were withdrawn at different time intervals from 5 to 45 min and filtered. Then after filtration, concentration of metal ions in solution was determined by flame atomic absorption spectrophotometer. Effect of initial metal ion concentration was studied by varying the metal ion concentration from 20 to 180 ppm using standard conditions described earlier. Concordant value of three repeated experiments was reported in the study.

Sorption capacity of biosorbent was investigated using the following formula (Eq. 1):

$$q_{e\ (mg/g)} = V \times \frac{(Co - Ce)}{m} \tag{1}$$

Here, $q_{e\ (mg/g)}$ is the uptake capacity of biosorbent, $V$ (mL) is the volume of solution, $C_o$ (mg/L) is the initial metal ion concentration while $C_e$ (mg/L) is the equilibrium concentration of metal ion, and $m$ (mg/g) is the biosorbent dose.

Glassware interference was checked using blank biosorption experiments of lead solution. No interference was observed due to glass ware. All experiments were performed in triplicate and their mean value is reported. Graphs were plotted using Microsoft Excel 2013 program. Root mean square error and regression analysis ($R^2$) was done to check the suitability of kinetic and mathematical models. RMSE value is calculated by the following formula (Eq. 2):

$$\mathrm{RMSE} = \frac{\sqrt{\sum\left(\mathrm{qe}_{(\mathrm{Cal})} - \mathrm{qe}_{(\mathrm{Exp})}\right)^2}}{\mathrm{N}} \tag{2}$$

### 2.5 $pH_{pzc}$ Experiment

Point of zero charge of BS and CABS was determined by taking NaCl solution (0.1 M, 100 ml). Their pH of solutions was adjusted between 2 and 10 using 0.1 M HCl and 0.1 M NaOH. Then 500 mg of BS and CABS was added separately in solutions. The solutions were allowed to attain equilibrium for 48 h with occasional stirring. Final pH of the solutions was measured and a plot between ΔpH (initial pH–final pH) vs initial pH was obtained. The point of intersection of obtained curve with abscissa pointed out the $pH_{pzc}$ of the studied biosorbent.

## 3 Results and Discussion

### 3.1 Characterization of Biosorbent

#### *3.1.1 FTIR Spectroscopy*

FTIR is an important tool for detection of functional groups on biosorbent surface which may be possible binding sites for metal ions attachment. The BS and CABS were subjected to FTIR analysis before and after biosorption of $Pb^{+2}$ ions and results are shown in Fig. 1. FTIR of BS identified the presence of hydroxyl group (3322 $cm^{-1}$), carbonyl group (1617 $cm^{-1}$), carboxyl group (1313 $cm^{-1}$ and 1239 $cm^{-1}$), and ether linkage (1027 $cm^{-1}$) (Socrates 1994). Hence, BS is enriched in oxygen containing functional groups.

Notable changes were observed in the spectrum of CABS when compared with BS. CABS also contain similar functional groups as in BS but are greater in number due to incorporation of citric acid on the surface of BS. The shifting of carbonyl peak to 1719 $cm^{-1}$ and appearance of carboxyl peak at 1157 $cm^{-1}$ affirmed the modification of BS. In addition, the peak of hydroxyl group in CABS becomes more broadened that attributes to the increase in concentration of hydroxyl groups on the surface of CABS. This comparison indicated that CABS can offer more binding sites for $Pb^{2+}$ attachment as compared to BS. FTIR of Pb-BS and Pb-CABS are also shown in Fig. 1. Both the spectra indicated the attachment of $Pb^{2+}$ ions with oxygen containing functionalities. The broadness of hydroxyl peak becomes lessened, disappearance of peak at 1617 $cm^{-1}$ (for BS) and 1719 $cm^{-1}$ (for CABS) and shifting of carboxyl peaks affirmed the attachment of $Pb^{2+}$ ions on BS and CABS.

#### *3.1.2 SEM Analysis*

Surface morphology of biomass was analyzed by scanning electron microscopy in SE mode. Fig. 2 a, b, c, and d is showing the SEM images of BS, CABS, Pb-BS, and Pb-CABS, respectively. Fantastic porous surface was observed in both BS and CABS that offers the appreciable attachment sites for the $Pb^{2+}$ ions. SEM image of Pb-BS and Pb-CABS showed different morphology as

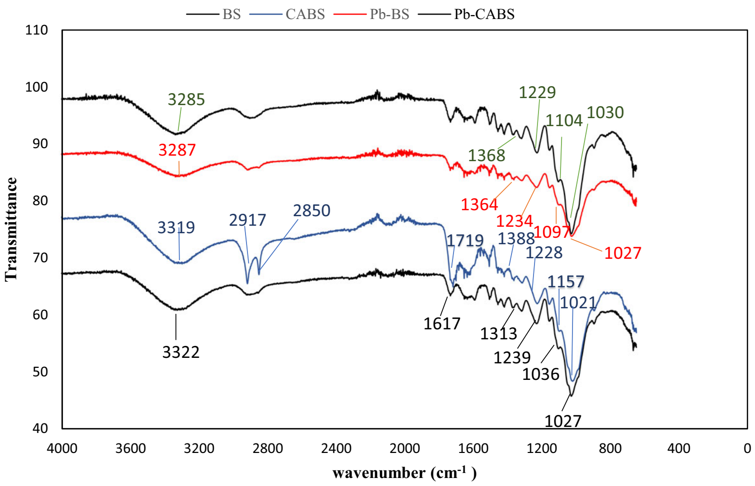


**Fig. 1** FTIR spectra of BS, CABS, Pb-BS, and Pb-CABS

compared to BS and CABS, respectively. This may be attributed to the attachment of $Pb^{2+}$ ions on their surfaces. In addition, the SEM image of Pb-CABS is shinier than Pb-BS due to the greater concentration of $Pb^{2+}$ ions on its surface. This indicated that CABS offered greater binding sites for $Pb^{2+}$ ions attachment (greater metal uptake capacity) and hence can be considered as better biosorbent than BS (Yousaf et al. 2017).

### *3.1.3 EDX Analysis*

As an evidence of $Pb^{2+}$ ion attachment on to the surface of CABS, both CABS and Pb-CABS were subjected to EDX analysis. EDX mapping for CABS and Pb-CABS is shown in Fig. 3 (a, b). A clear signal of presence of $Pb^{2+}$ ions was observed in Pb-CABS. So, EDX analysis provides direct evidence for sorption of lead ions onto CABS.

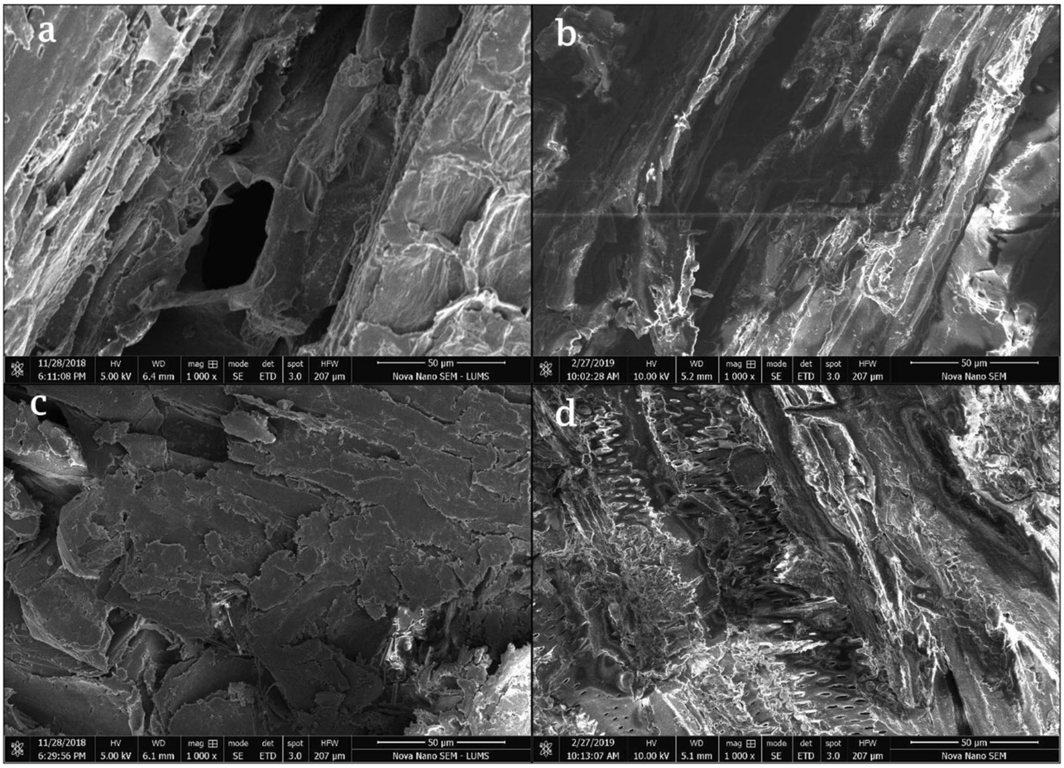


**Fig. 2** SEM images: **a** BS, **b** CABS, **c** Pb-BS, **d** Pb-CABS

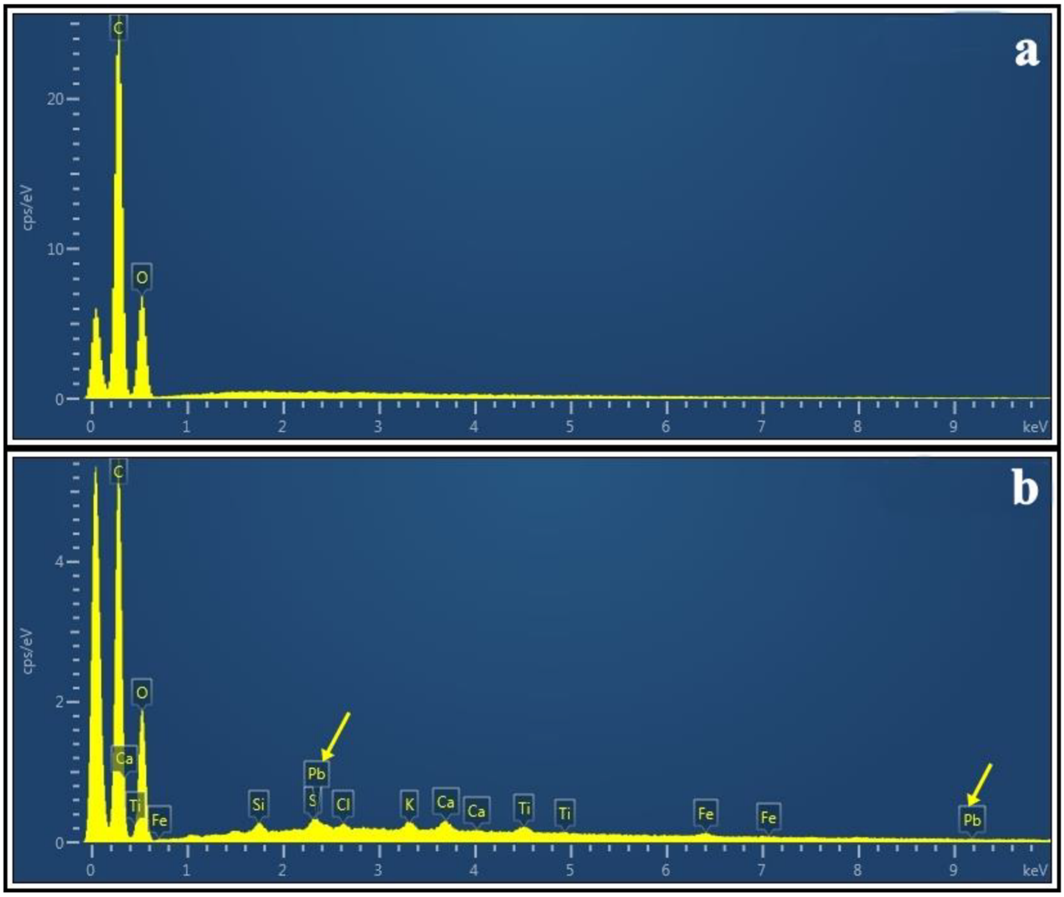


**Fig. 3** EDX images: **a** CABS, **b** Pb-CABS

### *3.1.4 Thermogravimetric Analysis*

Thermogravimetric analysis (TGA) is a technique used to monitor the weight loss of a substance as a function of temperature in controlled environment (Pezoti et al. 2016). To investigate the thermal stability of BS and CABS, TGA was performed. Biosorbent is mainly composed of lignin, cellulose, and hemicellulose. As depicted in Fig. 4, three weight loss steps were observed in both BS and CABS. In the first step from 60 to 270 °C, BS showed approximately 13% weight loss and CABS showed approximately 07% weight loss indicating more thermal stability in this region. This weight loss may be due to loss of free guest water adsorbed on the surface (Yuan et al. 2019).

In the second step from 270 to 370 °C, both biosorbents showed weight loss of almost 55% which can be attributed to degradation of lignin, cellulose, and hemicellulose (Pezoti et al. 2016). In range from 370 to 600 °C, weight of biosorbents decreased slowly. Relatively higher weight loss of CABS than BS is due to degradation of carboxylic acid groups attached on the CABS surface (Wan et al. 2014).

### *3.1.5 Point of Zero Charge ($pH_{pzc}$)*

$pH_{pzc}$ determines the pH value at which substance is found to be neutrally charged in virtue of pH of the medium (de O. Jorgetto et al. 2015). It is the isoelectric point when pH initial of the substance becomes equal to pH final and net surface charge on adsorbent is zero. This parameter is of great importance in determining the optimum conditions for adsorption in term of pH. If pH is greater than $pH_{pzc}$, it shows that adsorbent surface bears negative charge due to deprotonation of functional groups indicating that adsorption of metal cations is feasible and vice versa. Literature shows that decrease in solution pH favors the desorption of metal cations (Hossain et al. 2012). So, pH of the system becomes economical factor in terms of regeneration of

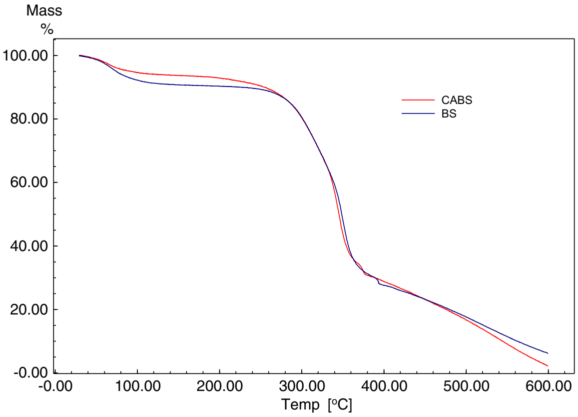


**Fig. 4** Thermogravimetric analysis plot of BS and CABS

biosorbent. As shown in Fig. 5, $pH_{pzc}$ is evaluated to be 5.8 for raw biosorbent (BS) which indicates that adsorbent gains positive charge below pH 5.8 due to protonation of carboxylic and hydroxyl group. Above pH 5.8, surface of adsorbent is negatively charged which will be favorable for adsorption. Also acidic $pH_{pzc}$ suggests dominancy of acidic groups at adsorbent surface (A. O. Jorgetto et al. 2014). The $pH_{pzc}$ value for CABS was found at 4.9 which indicates the incorporation of citric acid onto the biosorbent surface. The decrease in $pH_{pzc}$ value in CABS may attribute to the increment in carboxyl groups onto its surface. Due to this reason, CABS can act as more affective biosorbent as compared to BS for metal cations uptake.

## 3.2 Effect of Adsorbent Dose

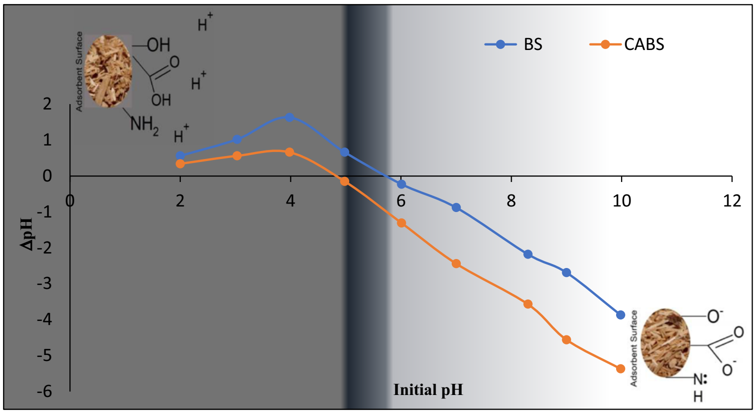
Experiments were conducted to check the effect of biosorbent dose on $Pb^{2+}$ ions removal from aqueous solution using an initial concentration of 50 mg/L of $Pb^{2+}$ while the dose of BS and CABS varied in a range of 0.1–0.9 g/50 mL. The results obtained are shown in a comparative plot (Fig. 6). The plot showed a quick uptake of $Pb^{2+}$ initially followed by the equilibrium and decrease in uptake capacity ($q_e$) with increase in biosorbent dose. BS shows 86.82% removal efficiency of $Pb^{2+}$ at a dose of 0.1 g/50 mL, increasing with the increase in dose rises to maximum of 99.02% at a dose of 0.8 g/50 mL. While using CABS, the removal efficiency has gone up from 90.73% at a dose of 0.1 g/50 mL to a maximum of 99.51% at 0.5 g/50 mL, remaining almost constant at higher dosages. The increase in adsorption with the increase in adsorbent dose is attributed to the availability of adsorption sites for metal adsorption (Fawzy et al. 2016; Manzoor et al. 2013).

Figure 6 also illustrates that under similar condition (say 0.1 g/50 mL), CABS showed high removal efficiency (90.73%) and adsorption capacity (22.63 mg/g) relative to BS, i.e., 86.82% and 21.71 mg/g, respectively. From this discussion, the conclusion can be made that modification of *B. spectabilis* with citric acid increases its functionality which makes it responsible for good efficiency of CABS for $Pb^{2+}$ removal even at low dosages.

## 3.3 Effect of pH on $Pb^{2+}$ Adsorption

pH of the medium has very close relationship while studying the metal ions attachment to biosorbent (Yuan et al. 2019). It not only directs the speciation of metal ions in solution but also controls the charge on biosorbent surface. Different functional groups are present on lignocellulosic surface of BS as confirmed by

**Fig. 5** Plot of point of zero charge of BS and CABS



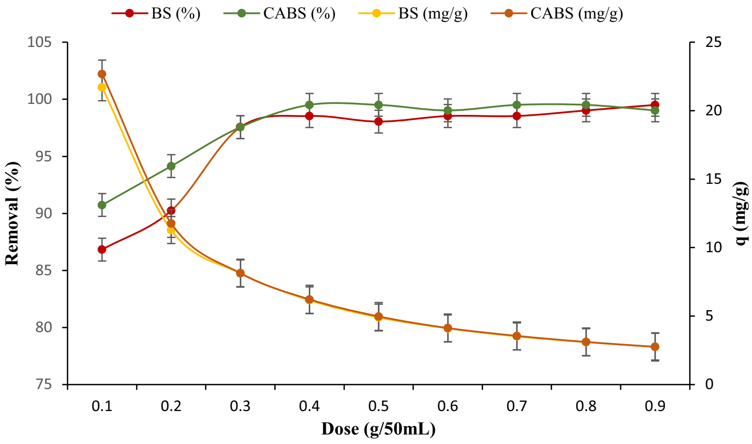


**Fig. 6** Influence of BS and CABS dosage on biosorption of Pb$^{2+}$. Solution concentration (50mg/L); contact time (30mins); agitation speed (125rpm); temperature(25°C); replicates (*n* = 3)

FTIR. These functional groups show different behavior at different pH value. The deciding factor which explains the behavior of functional group on biosorbent surface is its pH$_{pzc}$ value. Lead ions are present in the solution as divalent cation (Pb$^{2+)}$ below pH 6 and start forming precipitates of Pb(OH)$_2$ at higher pH values (Soyol-Erdene et al. 2018

The adsorption of Pb$^{2+}$ ions was investigated over the pH range of 1–9 for both CABS and BS keeping the rest of the factors constant. The comparative pH profile of both BS and CABS is shown in Fig. 7. From graph, it is clear that the adsorption increases with increase in pH up to pH 5–6 then starts decreasing with further increase. In more acidic condition, the surface of adsorbent remains covered with H$_3$O$^+$ ions; this protonation repels the positive metal ions and there is also chance for competitive biosorption of H$^+$ ions with respect to metal cations because of its higher concentration at low pH values. With the increase in pH due to deprotonation, the adsorption sites become available for metal ion attachment (Yousaf et al. 2017) as well as decrease in probability of H$^+$ ions biosorption due to decrease in its concentration. But at high pH value, precipitation of lead hydroxide occurs so biosorption decreases.

pH profile is also helping in finding the beneficial effect of modification of raw BS. Uptake capacity of Pb$^{2+}$ ions was found to be increased significantly using CABS as compared to BS. This increment is due to induction of more functional groups in biomass as a result of citric acid modification.

### 3.4 Kinetic Study (Effect of Contact Time)

To investigate optimum contact time for maximum removal of Pb$^{2+}$ ions, experiments were carried out at different time from 5 to 30 min keeping other parameters constant for both BS and CABS. The kinetic curve for Pb$^{2+}$ uptake by BS and CABS is shown in Fig. 8.

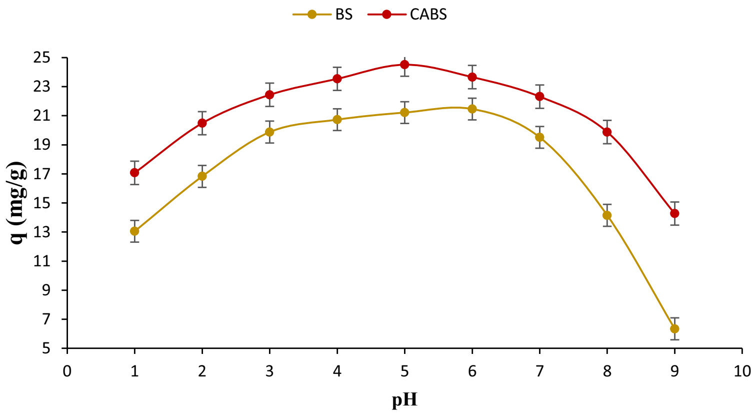


**Fig. 7** Effect of pH on biosorption of Pb$^{2+}$. Solution concentration (50mg/L); adsorbent dosage (0.1g/50mL); contact time (30mins); agitation speed (125rpm); temperature(25°C); replicates (*n* = 3)

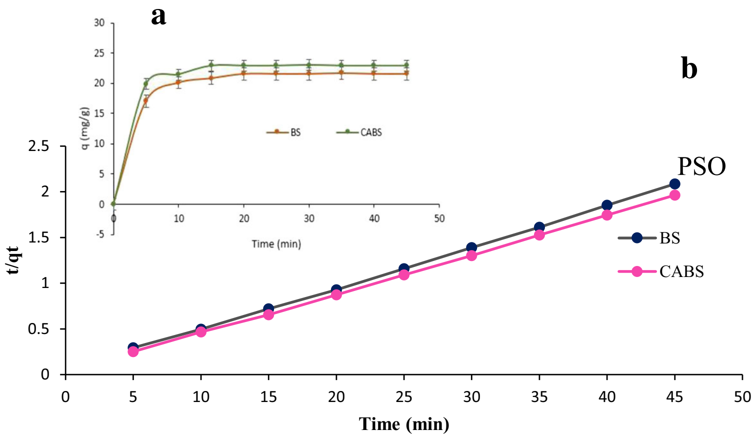


**Fig. 8** **a** PSO kinetic model of BS and CABS. **b** Influence of contact time on biosorption of $Pb^{2+}$. Solution concentration (50 mg/L); adsorbent dosage (0.1 g); agitation speed (125 rpm); temperature (25 °C); replicates ($n = 3$)

Rate of uptake of $Pb^{2+}$ ions decrease with the time eventually attain equilibrium stage. Optimum time to attain equilibrium for $Pb^{2+}$ ions biosorption is found to be 20 min for BS and 10 min for CABS. This shows that modified biosorbent take less time to attain equilibrium making the process more rapid. Equilibrium time is the time when maximum binding sites on biosorbent are available due to concentration gradient initially after which vacant surface sites become less accessible due to potential electrostatic repulsion (Zhang et al. 2018). In addition to active sites, ease in accessibility of metal ions to biosorbent surface also plays important role (Yousaf et al. 2017).

Kinetic data of $Pb^{2+}$ ions biosorption by BS and CABS was also investigated using pseudo first order (PFO) and pseudo second order (PSO) kinetic models. Linear mathematical form of PFO (Eq. 3) and PSO (Eq. 4) are as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1.t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{t}{q_e} \tag{4}$$

Here, $q_\mathrm{e}$ (mg/g) and $q_\mathrm{t}$ (mg/g) are the uptake capacities at equilibrium and $t$ is the contact time, respectively. $K_1$ ($\mathrm{min}^{-1}$) and $K_2$ (mg/g/min) are the rate constant for PFO and PSO reaction, respectively.

The results for kinetic parameters for biosorption of $Pb^{2+}$ in the case of BS and CABS are tabulated in Table 1 and their trend is shown in Fig. 8.

Regression analysis of PFO model shows that $R^2$ value for both BS and CABS is less than 0.98 which shows that the adsorption mechanism does not follow PFO. Moreover, there is large difference between its calculated $q_e$ value and experimental $q_e$ value which reinforces the above statement. The experimental data for kinetics of $Pb^{2+}$ adsorption better fits for PSO model which provides near ideal $R^2$ value for both BS and CABS biosorbent, i.e., 0.999. Moreover, in PSO, there is very small difference (less than 1%) between calculated and experimental $q_e$ value. Therefore, kinetic data was described better by pseudo second order kinetics than pseudo first order kinetic model.

### 3.5 Effect of Initial $Pb^{2+}$ Ions Concentration (Equilibrium Modeling)

Adsorption isotherm is a mathematical model equation which describes the relation between biosorbent and sorbate. These are also used to find out the required amount of biosorbent for a particular sorbate (Hj Ismail et al. 2013).

The equilibrium data for varying initial $Pb^{2+}$ ions concentration (20–180 mg/L) was evaluated by using famous mathematical models including Langmuir, Freundlich, Temkin, and Dubinin-Kaganer-Radushkevish (DKR) models in non-linear fashion. Comparison was done by their RMSE values calculated using Eq. 2 and reported in Table 2. The results in the present study are tabulated in comparison with already reported studies in Table 3.

#### *3.5.1 Langmuir Isotherm*

Langmuir isotherm (Eq. 5) assumes that adsorption occurs on monolayer surface (Athar et al. 2013; Chen et al. 2017).

**Table 1** Kinetic parameters for biosorption of $Pb^{2+}$

| | PFO model | | | $q$ (exp) (mg/g) | PSO model | | |
|---|---|---|---|---|---|---|---|
| | $K_1$ (min$^{-1}$) | $q_e$ (cal)mg/g | $R^2$ | | $K_2$ (mg/g/min) | $q_e$ (cal)mg/g | $R^2$ |
| $Pb^{2+}$ on BS | 0.18 | 10.42 | 0.98 | 21.58 | 0.04 | 22.22 | 0.9995 |
| $Pb^{2+}$ on CABS | 1.52 | 61,821.10 | 0.79 | 22.92 | 0.07 | 23.31 | 0.9997 |

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{5}$$

where $K_L$ (L/mg) is the Langmuir constant, $C_e$ (mg/g) is the equilibrium concentration, $q_e$ is the equilibrium adsorption capacity, and $q_{max}$ is the maximum theoretical adsorption capacity (J. Zhou et al. 2018). It tells that some specific homogenous sites are more active for biosorption (Nadeem et al. 2016) and each active site behaves independently of the neighbor molecule (Yousaf et al. 2017). Monolayer adsorption capacity ($q_{max}$) calculated by Langmuir model for $Pb^{2+}$ in case of BS and CABS is 50.25 mg/g and 67.11 mg/g, respectively. Higher value of $R^2$, i.e., 0.99 for both BS and CABS showed that Langmuir model fits best on adsorption data. RMSE value is 1.20 in case of Langmuir that is minimum as compared to all other models.

**Table 2** Non-linear isothermal parameters for biosorption of $Pb^{2+}$

| Biosorbent | $Pb^{2+}$ on BS | $Pb^{2+}$ on CABS |
|---|---|---|
| Non-linear Langmuir parameters | | |
| $q_{max}$ (mg/g) | 50.25 | 67.11 |
| $R^2$ | 0.99 | 1.00 |
| $K_L$ (L/mg) | 0.31 | 0.34 |
| RMSE | 1.20 | 1.30 |
| Non-linear Freundlich parameters | | |
| $R^2$ | 0.93 | 0.94 |
| $K_F$ | 13.58 | 16.86 |
| $n$ | 2.73 | 2.24 |
| RMSE | 1.93 | 1.74 |
| Non-linear D.K.R parameters | | |
| $q_m$ (mg/g) | 41.60 | 50.49 |
| K (mol$^2$/KJ$^2$) | 3.45E–07 | 2.38E–07 |
| $R^2$ | 0.79 | 0.81 |
| E (KJ/mol) | 1.20 | 1.45 |
| RMSE | 2.94 | 3.36 |
| Non-linear Temkin parameters | | |
| $K_T$ (L*mol/KJ*g) | 9378.18 | 3.17 |
| $B_T$ (KJ/mol) | 1.52 | 14.95 |
| RMSE | 7.91 | 3.70 |

### *3.5.2 Freundlich Isotherm*

Freundlich isotherm (Eq. 6) is most commonly used isotherm for equilibrium study. Freundlich isotherm is an empirical equation describing adsorption on heterogeneous surface escorted by the presence of multifunctional groups and various interactions (L. Zhou et al. 2016).

$$qe = K_F C_e^{1/n} \tag{6}$$

Here, $K_F$ and $n$ are the Freundlich adsorption factor (showing adsorption capacity) and heterogeneity factor (expressing intensity of adsorption), respectively. Relevant parameter results of Freundlich isotherm (listed in Table 2) show that value of $n$ is 2.73 for BS and 2.24 for CABS, indicating that lead ions are feasibly attached with biosorption sites (J. Zhou et al. 2018). Degree of non-linearity between concentration of solution and adsorption is dependent on "n." Unity value of $n$ shows linear adsorption while value of $n$ below unity points towards chemical adsorption and if value of $n$ is greater than unity it indicates physical adsorption. Value of adsorption intensity ($1/n$) is greater for CABS than BS indicating preferential sorption by CABS (Jnr et al. 2004).

### *3.5.3 D.K.R (Dubinin-Kaganer-Radushkevish) Isotherm*

D.K.R model gives information about apparent energy of adsorption and characteristic porosity of adsorbent towards adsorbate. It describes adsorption on uniform pores and distinguishes between physical and chemical adsorption. It does not consider surface of biosorbent as homogenous (Wan Ngah and Fatinathan 2010).

**Table 3** Comparison of pH, adsorption capacity, equilibrium model, and kinetic models of BS and CABS with other modified and unmodified biosorbents for biosorption of $Pb^{2+}$ ions

| Biosorbent | pH | $q_{max}$(mg/g) | Equilibrium model | Kinetic model | References |
|---|---|---|---|---|---|
| BS (UM)[a] | 6 | 50.25 | Langmuir | PSO | Present study |
| *T. resupinatum* | 3 | 10.38 | Langmuir | PSO | (Athar et al. 2013) |
| Newspaper pulp | 6 | 19.1 | Langmuir | PSO | (Pitsari et al. 2013) |
| *Nigella sativa* seeds | – | 2.51 | Langmuir | PSO | (Bingöl et al. 2012) |
| Sorghum | 5 | 6.289 | Langmuir | PSO | (Salman et al. 2014) |
| *Agave sisalana* (sisal fiber) | 7 | 1.34 | Freundlich | – | (Dos Santos et al. 2011) |
| CABS (M)[b] | 5 | 67.11 | Langmuir | PSO | Present study |
| Sodium bicarbonate treated SCB | 5 | 0.95 | Langmuir | PSO and PFO | (Yu et al. 2013) |
| Modified news paper pulp (1 M citric acid) | 6 | 34.60 | Langmuir | PSO | (Pitsari et al. 2013) |
| Thiourea modified Sorghum | 6 | 17.82 | Langmuir | PSO | (Salman et al. 2014) |
| Magnetically modified sugarcane bagasse | 5 | 1.2 | Langmuir | PSO | (Yu et al. 2013) |
| TPP–kaolinite clay | 7 | 126.58 | Freundlich | – | (Unuabonah et al. 2007) |

[a] unmodified

[b] modified

Non-linear D.K.R isotherm expression is as under:

$$q_e = q_m \exp\left(-K\varepsilon^2\right) \qquad (7)$$

Here, $q_e$ is the amount of solute adsorbed per unit adsorbent (mg/g), $q_m$ is the maximum adsorption capacity (mg/g), $K$ is the activity coefficient related to energy of sorption (mol$^2$/KJ$^2$), and $\varepsilon$ is the Polanyi potential (j/mol) which can be calculated from the following equation:

$$\epsilon = RT\ln(1 + 1/C_e) \qquad (8)$$

Value of $E$ that is mean free energy of adsorption per adsorbate molecule when transferred to surface of solid from solution is calculated from equation (Wan Ngah and Fatinathan 2010):

$$E = (2K)^{-0.5} \qquad (9)$$

$E$ value tells about the type of adsorption process. Value of $E$ between 8 and 16 KJ/mol shows adsorption process involve chemical sorption (Laus et al. 2010) and below 8 KJ/mol indicates that adsorption process is physical in nature (Wan Ngah and Fatinathan 2010). DKR parameters are calculated from graph and listed in Table 2. Results show that value of $E$ for lead ions on BS and CABS is 1.20 and 1.45 kJ/mol, respectively, which is lower than the range of 8–16 KJ/mol. Results indicate that adsorption mechanism involved here is physical sorption (J. Zhou et al. 2018).

### 3.5.4 Temkin Isotherm

Temkin model helps in calculating equilibrium binding constant corresponding to maximum binding energy. If binding energy decreases with increase in temperature, it points towards the exothermic process which is favored at high temperature (Aljeboree et al. 2017). This model gives information about interaction between metal ions and material.

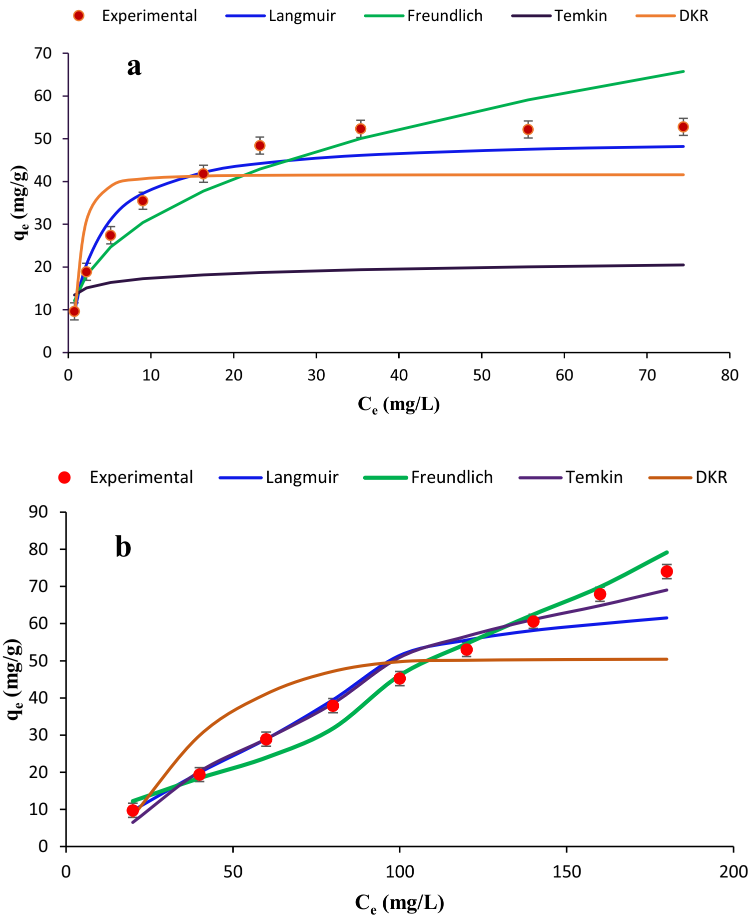
Equation of Temkin is as follows:

$$q_e = B_T \log(K_T C_e) \qquad (10)$$

Here, $B_T$ is the Temkin constant which is related to adsorption heat (KJ/mol) and $K_T$ is the empirical Temkin constant related to maximum binding energy (L/mg). $B_T$ for BS is less than 8 showing weak interaction suggesting process to be physisorption (Theivarasu and Mylsamy 2010) while in case of CABS greater $B_T$ value shows strong attractive force.

A comparitive plot of non-linear modeling of biosorption of $Pb^{2+}$ on BS and CABS is shown in Fig. 9 (a) and (b), respectively. It can be concluded from figure and RMSE value that description of equilibrium data by Langmuir model is superior to other studied models.

**Fig. 9** **a** Non-linear isotherm plot for $Pb^{2+}$ adsorption on BS. **b** Non-linear isotherm plot for $Pb^{2+}$ adsorption on CABS. Initial concentration (20–180 mg/L); adsorbent dosage (0.1 g/50 mL); agitation speed (125 rpm); contact time (30 min); temperature (25 °C); replicates (*n* = 3)



## 3.6 Effect of Temperature: Thermodynamic Study

Temperature plays an important role on biosorption process. So, study of thermodynamics is important to understand the adsorption process (Nazir et al. 2019). Adsorbent metal uptake capacity as a function of temperature is illustrated in Fig. 10 which shows notably increase in $Pb^{2+}$ uptake capacity of biosorbent with increase in temperature up to a certain level suggesting that lead uptake may be an endothermic process (Yuan et al. 2019). This increase in biosorption with temperature may be due to increase in active sites for metal binding or increase in diffusion rate of metal with temperature. Thermodynamic data was obtained by

**Fig. 10** Effect of temperature on $Pb^{2+}$ adsorption. Solution concentration (50 mg/L); adsorbent dosage (0.1 g/50 mL); agitation speed (125 rpm); contact time (30 min); temperature (10–60 °C); replicates (*n* = 3)

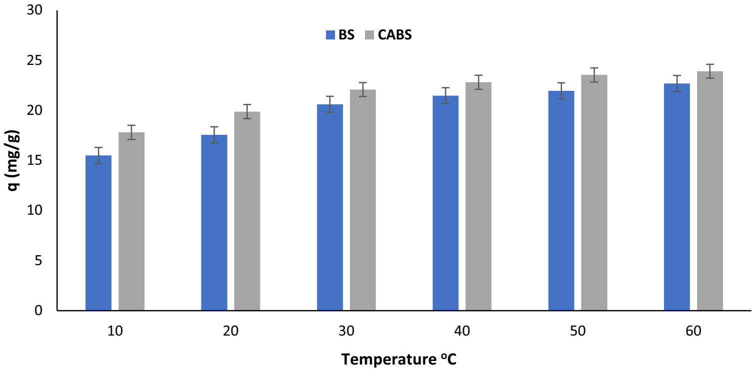


**Table 4** Thermodynamic parameters for biosorption of $Pb^{2+}$ ions

| Adsorbates | ΔG° (KJ/mol) | | | ΔH° (KJ/mol) | ΔS° (KJ/mol) |
|---|---|---|---|---|---|
| | 30° | 40° | 50° | | |
| BS | − 0.40409 | − 2.15055 | − 2.89012 | 1.2933 | 0.0979 |
| CABS | − 1.61579 | − 3.34541 | − 4.28968 | 0.6851 | 0.1242 |

thermodynamic parameters including ΔH° (standard enthalpy), ΔS° (standard entropy), and ΔG° Gibbs free energy using the following formulas and listed in Table 4.

$$\Delta G^\circ = -RTlnK_D \tag{11}$$

$$ln\ K_D = {}^{\Delta S^o}\!/_{R} - {}^{\Delta SH^o}\!/_{RT} \tag{12}$$

$$K_D = {}^{(C_o - C_e)}\!/_{C_e} \tag{13}$$

Here, $T$ is the temperature (K), $R$ is the universal gas constant (8.314 J/mol/K), and $K_D$ is the equilibrium constant calculated from Equation no. 13. ΔH° and ΔS° were calculated from graph.

Positive value of ΔH° confirmed the endothermic nature of process of adsorption supporting the results clinched from Fig. 10. Positive value of ΔS° suggested increase in randomness at solid solution interface enhancing metal ions adsorption stability. Negative value of ΔG° revealed the spontaneous nature of process proving that it is thermodynamically favorable (Wang et al. 2017) (Table 4).

## 3.7 Adsorption Mechanism

The carboxyl functionality of *B. spectabilis* has been increased by incorporation of citric acid onto its surface. This increases the biosorption efficiency and metal uptake capacity of CABS. Plant biomass consists of carbohydrates in the form of lignin, cellulose, and hemicellulose. Large amount of oxygen containing groups (-OH, -CO, $-OCH_3$) which have been determined by FTIR. Many -OH groups are present on surface of biosorbent which can be esterified by carboxylic group (Pezoti et al. 2016). Citric acid contained three carboxylic groups from which one carboxylic group attaches to -OH group of *B. spectabilis* through esterification process and the remaining two become available to bind the metal ions. This increase of oxygen containing functional group will lead to higher electronegativity that will ultimately increase the adsorption capacity of heavy metal cations, i.e., lead ions. It is notable here that these functional groups offer considerable active binding sites for strong interaction with lead ions on surface of biosorbent thus improving the biosorption ability of biosorbent. A schematic diagram showing possible modification and adsorption mechanism is shown in Fig. 11.

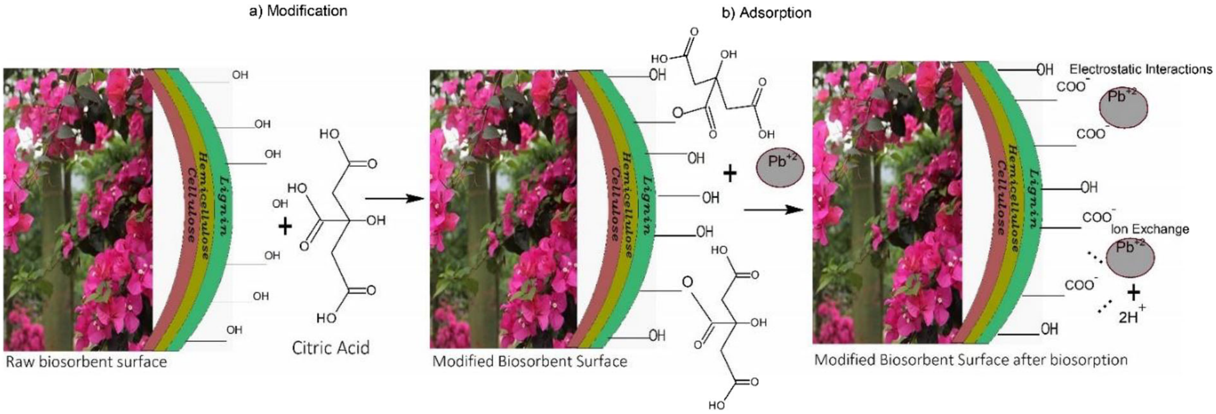


**Fig. 11** Schematic representation of modification process followed by possible biosorption mechanism of lead ions onto CABS

## 4 Conclusions

An environmental benign, low-cost citric acid modified *B. spectabilis* (CABS) was synthesized by simple steps using citric acid. The modification of CABS was confirmed by FTIR, EDX, TGA, and SEM. Comparative biosorption of most toxic heavy metal ions $Pb^{2+}$ on BS and CABS from aqueous solution was the focus of the study.

The main focus of the study was to understand kinetics, nature of binding through different equilibrium models, and rate determining step as well as effect of pH for both BS and CABS. The biosorption of $Pb^{2+}$ ions was shown to be dependent on solution pH with optimum pH value 5 and 6 for BS and CABS, respectively. Using modified biosorbent, the process became more rapid as it need less time to attain equilibrium. Kinetic study showed that adsorption followed pseudo second order model in both BS and CABS. Non-linear approach was used in equilibrium modeling. Langmuir model was found to be the best fit in both cases revealing maximum adsorption capacity 50.25 and 67.11 mg/g for BS and CABS, respectively. From DKR, isotherm value of mean free energy of adsorption shows that mechanism of biosorption is predominantly due to physical process providing feasibility to regenerate the biosorbent via desorption of metal ions. Thermodynamic parameters showed that process was feasible, spontaneous, and endothermic in nature. Increase in adsorption capacity and decrease in time to attain equilibrium shows the effectiveness of modification. It points towards effective use of modified novel biosorbent for treatment of waste water. In short, it is a cheap biowaste with impressive biosorption ability. Its easy availability on industrial scale and reusability makes it an economically favorable and socially acceptable for efficient removal of lead ions from aqueous solution.

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