Mass Transfer, Kinetic, Equilibrium, and Thermodynamic Study on Removal of Divalent Lead from Aqueous Solutions Using Agrowaste Biomaterials, *Musa acuminata, Casuarina equisetifolia* L., and *Sorghum bicolor*

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Abstract—Three distinct agricultural waste materials, viz., casuarina fruit powder (CFP), sorghum stem powder (SSP), and banana stem powder (BSP) were used as low-cost adsorbents for the removal of toxic lead(II) from aqueous solutions. Acid treated adsorbents were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR). The effects of parameters like adsorbent dose, pH, temperature, initial metal ion concentration, and time of adsorption on the removal of Pb(II) were analyzed for each adsorbent individually and the efficiency order was BSP > SSP > CFP. Based on the extent of compatibility to Freundlich/Langmuir/Dubinin—Radushkevich/Temkin adsorption isotherms and different models (pseudo-first and second order, Boyd, Weber's, and Elovich), chemisorption primarily involved in the case of BSP and SSP, whereas simultaneous occurrence of chemisorption and physisorption was proposed in the case of CFP which was correlating with the thermodynamic study results conducted at different temperatures. Based on the observations, it was proposed that three kinetic stages involve in the adsorption process, viz., diffusion of sorbate to sorbent, intra particle diffusion, and then establishment of equilibrium. These adsorbents have a promising role towards the removal of Pb(II) from industrial wastewater to contribute environmental protection.

Keywords: banana bunch-stem powder, casuarinas fruit powder, sorghum stem powder, removal, lead, adsorption

INTRODUCTION

Industry made water pollution becomes a severe problem in the current world as many industrial activities affect the natural flow of waterbodies by introducing harmful heavy metal containing effluents into the water streams [1]. Among all heavy metals, lead is a commonly detectable heavy metal ion in several industrial wastewaters and is considered as a high priority pollutant worldwide in perspective of human and environmental risk. Lead is nonbiodegradable, and its accumulation by the living organisms is associated with toxicity to both flora and fauna even in trace amounts. Lead enters the human systems in many ways such as through breathing air from lead smelting, refining, and manufacturing industries, breathing in fumes while working with leaded glass, ceramics, etc. [2, 3].

Domestic and industrial wastewaters containing lead ions resulting in health hazards are of extreme concern to the public, government, and industries in the current world [4]. The deleterious effects of lead on neurobehavioral development [5] and brain cell function [6] have been investigated. According to the European Union (EU), United States Environmental Protection Agency (USEPA), and WHO, the maximum allowable limit of Pb(II) in drinking water and surface water intended for drinking is 0.010, 0.015, and 0.010 mg L^{-1}, respectively [7]. Hence, easy, effective, economic, and eco-friendly techniques are required for fine tuning of effluent wastewater treatment. The search for an effective low-cost and easily available adsorbent has led to the investigation of different materials applicable to most treatment systems.

The conventional treatment techniques for lead removal from aqueous solutions include chemical precipitation, ion exchange, membrane filtration, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, adsorption, etc. In addition, a number of nonconventional strategies involving the use of nano-

materials [1], biopolymers [3], and hybrid organic–inorganic composite materials [8] have also been reported in the recent past. However, these methods used for the removal of metal ions from aquatic environment are expensive and include incomplete removal, high energy requirements, and production of harmful substances [9]. Hence, among all water treatment methods described, biosorption is a highly preferred technique in terms of initial cost, flexibility of design, ease of operation, insensitivity to toxic pollutants, the availability of different adsorbents and generates high-quality treated effluents [10]. Adsorbent materials from agricultural origin such as rice husk [9], areca nut [11], *Lemnaperpusilla Torr.* aquatic plant [12], etc., are often ideal because of their susceptibility to chemical modification and mono- to multilayer adsorption behavior for better performance. Moreover, the polar functional groups which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups present on the lignin and cellulosic constituents of these agrowastes can have the ability to form complexes with the divalent lead metal ions in aqueous solution [13, 14].

Therefore, the present study is focusing on the use of three chemically modified agricultural waste materials, namely, the casuarinas fruit powder, sorghum stem powder, and banana bunch-stem powder for effective removal of Pb(II) from aqueous solutions. The main objectives of this work are (i) to examine the physicochemical characteristics like specific surface area, surface morphology and structure, and active groups of these adsorbents; (ii) to study the effects of various parameters such as contact time, pH, amount of adsorbent, initial lead ion concentration, and temperature on adsorption in batch in order to optimize the adsorption conditions; (iii) to employ several isotherm models and adsorption kinetics to evaluate the adsorption efficiency of each adsorbent. A comparative analysis throughout the study using these three adsorbents can give better understanding of the adsorption process in terms of efficiency to remove lead metal ion from synthetic aqueous solution.

EXPERIMENTAL

Materials

Raw materials such as casuarinas fruit, sorghum stem, and banana bunch-stem for the preparation of adsorbents are available abundantly in nature. They were cleaned with distilled water, and to reduce the organic leaching and to prevent mould growth during batch sorption the raw materials were washed with 2% formaldehyde solution [15] and completely air dried. The dried material was fine powdered and sieved through standard sieves of particle size from 0.3 to 1.0 mm. Then, the finest powders of casuarinas fruit (CFP) and sorghum stem (SSP) were treated with 1 N H_2SO_4, banana bunch-stem (BSP) was treated with

1 N HNO_3, and they were allowed to soak for 24 h at room temperature. The preliminary studies show that the removal capacity of these treated adsorbents is higher by about 30% compared to those of untreated adsorbents. Hence, treated samples were used throughout the study. The samples were then oven-dried and were cooled back to room temperature and used in the adsorption experiments without any further modification. The biosorbent materials were stored in clean air tight containers. All the chemicals used were of analytical grade.

Instrumentation

The physical-chemical characterization of adsorbents was performed by scanning electron microscopy (SEM) coupled to energy-dispersive X-ray spectroscopy (EDAX) (FEI Quanta FEG 200—high resolution scanning electron microscope) which allows the identification and quantification of the metal ions of the adsorbents. The FTIR spectra of the crude and metal treated adsorbents were performed using Bruker, ALPHA-T to identify the active functional groups responsible for the adsorption.

Preparation of Synthetic Solutions

The standard lead stock solution of 1000 mg L^{-1} concentration certified for atomic absorption spectroscopy was obtained from Loba Chemie laboratory reagents and fine chemicals (India). Working lead solution was prepared in bulk with deionized water and used for the adsorption studies. The initial Pb(II) concentration of the untreated sample was 16 mg L^{-1}. The typical pH of the experiments was about 5, and it was adjusted to the desired value by the addition of few drops of 0.1 M HCl or 0.1 M NaOH.

Batch Adsorption Studies

The experiments were performed in batch process using BSP, CFP, and SSP at room temperature in a 250 mL conical flask containing 50 mL of the reaction mixture. While observing the effect of each parameter, the values of other parameters were kept constant. The removal efficiency of each adsorbent with respect to different parameters like adsorbent dose (5 to 30 g L^{-1}), time (0 to 210 min), pH (2 to 6), temperature (30 to 70°C), and initial lead ion concentration (20 to 200 mg L^{-1}) was determined in individual experiments. In each experiment, the metal ion solution equilibrated with adsorbent was withdrawn and centrifuged, and the final Pb(II) concentration was measured in the liquid phase by atomic adsorption spectroscopy (AAS). The experiment was repeated thrice, and average results have been reported. The relative errors in the experimental results were about 5%.
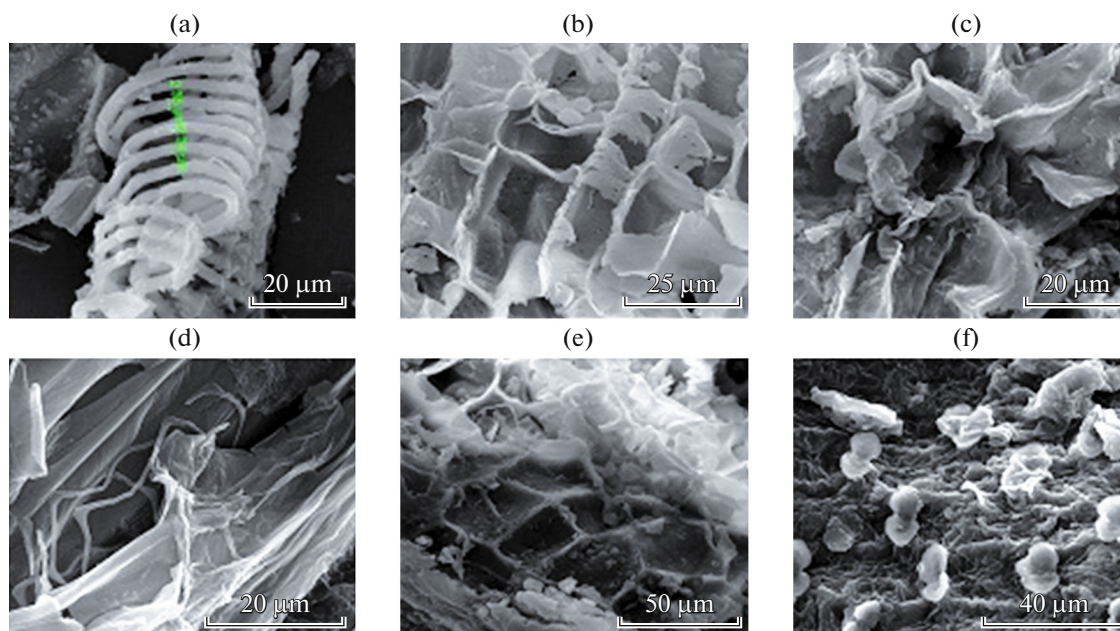
Fig. 1. Scanning electron microscopy images before adsorption using (a) BSP, (b) SSP, and (c) CFP and after adsorption using (d) BSP, (e) SSP, and (f) CFP.

The adsorption capacity and percent Pb(II) removal were determined by the following equations:

$$q_e = \frac{C_o - C_e}{W} V, \qquad (1)$$

$$\text{Percent removal of Pb(II)} = \frac{C_e - C_o}{C_e} \times 100. \qquad (2)$$

Here, C_o is the initial concentration of Pb(II) in the solution, C_e is the final concentration of Pb(II) in the solution after adsorption, q_e (mg g^{-1}) is the adsorption capacity of the adsorbent at equilibrium, V (L) is the volume of the suspension, and W (g) is the mass of the adsorbent.

RESULTS AND DISCUSSION

Characterization of Adsorbent Materials through SEM, EDAX, and FTIR

Samples of the adsorbent materials were coated with a thin layer of gold under vacuum and examined by scanning electron microscope before and after the adsorption of lead to study the surface texture and porosity of the samples for better understanding of the nature of the adsorption process. SEM observations show that CFP and SSP adsorbent materials appear to have rough surface with some pore formation before adsorption as an indication of large surface areas capable of high adsorption, whereas a smooth surface covering of the pores can be observed after adsorption. In the case of SEM surface analysis of BSP, the spiral structures with rough surface before adsorption and a smooth layer covering the spirals after adsorption

explain the likelihood of greater adsorption of lead onto BSP surface (Fig. 1). EDX studies were carried out to determine the chemical composition of adsorbents and were given here in percent weight of elements, before adsorption, BSP: C—62.65, O—34.44, Fe—0.87, Pb—0.00; SSP: C—60.51, O—36.93, Fe—0.73, Pb—0.00; CFP:C—62.70, O—36.23, Fe—0.17, Pb—0.00, after adsorption: BSP: C—52.35, O—41.26, Fe—0.49, Pb—3.08; SSP: C—57.87, O—38.08, Fe—0.25, Pb—1.65; CFP: C—61.44, O—35.05, Fe—0.39, Pb—1.41. In all the adsorbents, the presence of stretching for C—O, C=O, and aliphatic C—H can be confirmed from peaks in the range of 1026—1039 cm^{-1}, 1614—1689 cm^{-1}, and 2917—2920 cm^{-1}, respectively. However, additional peaks in CFP above 3000 cm^{-1} indicate the =C—H stretching and further C=C stretching can be observed from peaks in the range of 1450—1550 cm^{-1}. Broad peaks in the range of 3305—3320 cm^{-1} indicate the presence of carboxylic acid groups in SSP and BSP, whereas dominant sharp peak at 3737 cm^{-1} indicates phenolic groups in CFP (Fig. 2).

EDX and FTIR observations correlate with the compositions of BSP—holocellulose, cellulose, lignin, pectin [16], SSP—cellulose, hemicelluloses, lignin, cutin, silica [17], and CFP — α-pinene, benzaldehyde, 1,8-cineole, furanoid, α-campholenal, 4-terpineol, α-terpineol, α-terpinyl acetate, spathulenol, caryophyllene-oxide, and guaiol [18]. The presence of functional groups like acid, alcohol, and amine is evident from these studies. Protons of phenols/alcohols and carboxylic acid groups in these biosorbents facilitate them for ions getting exchanged during the

(a)

(b)

(c)
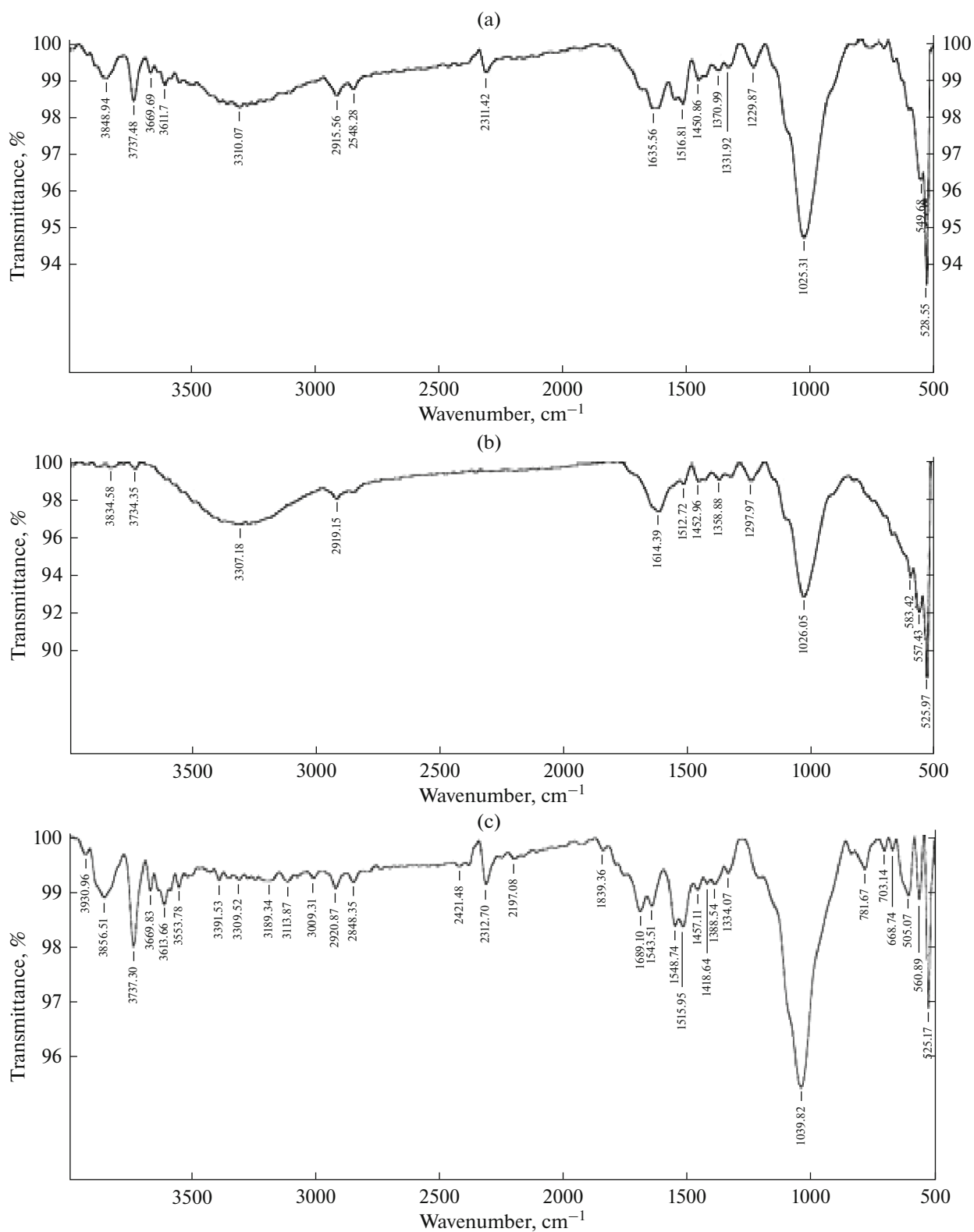
**Fig. 2.** FTIR spectra of three adsorbents (a) BSP, (b) SSP, and (c) CFP before adsorption.

adsorption process. Hydroxyl groups in these biopolymers may function as donors. Hence, the deprotonation of hydroxyl groups can be involved in the coordination with metal ions [19]. Moreover, the presence of a larger number of peaks in CFP compared to SSP can be explained based on the presence of a number of phytochemicals as mentioned above.

Studies on Effect of Agitation Time and Adsorption Kinetics

Changes in Pb(II) concentrations over time were investigated at each 30 min interval in contact time till 210 min, while other parameters were kept constant and are shown in Fig. 3. Saturation of the active points (called the plateau value) was reached in approximately 30, 150, and 180 min using BSP, SSP, and CFP, respectively, which acquaints us that the rapid adsorption of Pb(II) was by BSP. The pattern of Pb(II) removal with time explains the fact that the familiarization between adsorbent and Pb(II) ions which make an attraction with the adsorbent over time increases the adsorption of metal ion onto the adsorbent surface [11, 12, 14]. In terms of the optimum time for removal, the performance of the current biosorbents is comparable with those of the earlier used adsorbents—acorn waste (150 min) [20], modified areca waste (120 min) [11], and fluted pumpkin seed shell (170 min) [21].

From Fig. 3, it is clear that metal sorption follows three step sorption mechanisms in the case of SSP and CFP. During the initial rapid and quantitatively predominant step, a large number of sites are available for the uptake of metal ions on the adsorbents, which permits to overcome all the external mass transfer resistances and occupying the active sites on the biosorbent with higher affinity through bonding with the chelating ligands [11]. During the second slower and quantitatively insignificant step, the diffusion of Pb(II) into the deeper pores creates repulsive forces between the Pb(II) on the solid and the aqueous phases and the existence of different sorption mechanisms might hamper the adsorption process [22], leading to slower adsorption rate. During the final equilibrium phase, the sorption process ceases due to the unavailability of active sites on biosorbents to be occupied by the metal ions or due to repulsive forces between the Pb(II) on the solid and the aqueous phases. In the case of BSP initial rapid step and final equilibrium phases are present.

Kinetic and equilibrium models were employed to analyze the data of the complete adsorption process to better understand the Pb(II) sorption characteristics by the three adsorbents, BSP, SSP, and CFP. Further research on the kinetics of adsorption was carried out by employing pseudo-first order [23] and pseudo-second order kinetic equations [24] to examine the mechanism of Pb(II) adsorption onto these adsorbents, since the literature survey clearly shows that the sorption of Pb(II) from aqueous solutions is either first- or second-order. For example, the removal of Pb(II) by
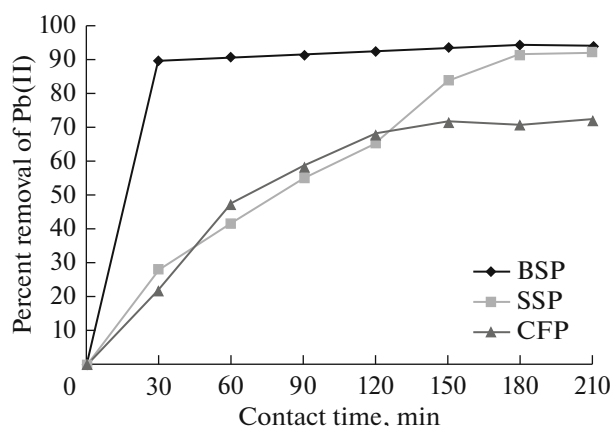
Fig. 3. Effect of agitation time during adsorption at pH 5, 200 rpm, and initial Pb(II) concentration 16 mg L^{-1} using 20 g L^{-1} of BSP, SSP, and CFP.

red mud [25] follows the pseudo-first order biosorption (Eq. (3)), whereas pseudo-second order (Eq. (4)) was found to correlate with the experimental data well by using modified areca waste [11] and fluted pumpkin seed shell activated carbon [21] as adsorbents (adsorption kinetic models are shown in Fig. 4):

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \qquad (4)$$

where q_t and q_e (mg g^{-1}) are the amounts of lead adsorbed on adsorbent material at time t and at equilibrium, respectively, and k_1 and k_2 are the corresponding pseudo-first and pseudo-second order adsorption rate constants.

In the present case, kinetic data are in good agreement with pseudo-second order in terms of the coefficient of determination (R^2) than pseudo-first order using BSP, CFP, and SSP adsorbents. The adsorption kinetic parameters are given in Table 1.

A wide variety of interactions between metal ions and adsorbents like ion exchange, chelation, adsorption by physical forces, entrapment in inter- and intra-fibrillar capillaries and space of the structural polysaccharide network as a result of the concentration gradient and diffusion for effective uptake of Pb(II) in a solution makes biosorption a complex process [11, 21]. The highest adsorption achieved in less time using BSP as an adsorbent material can be explained by the fact that nonconventional adsorbents which contain cellulose and the polar hydroxyl groups on the cellulose could be involved in a chemical reaction and bind heavy metals from solutions [26].

Hence, the simple Elovich equation was also employed for its applicability on the adsorption process (Fig. 3c):
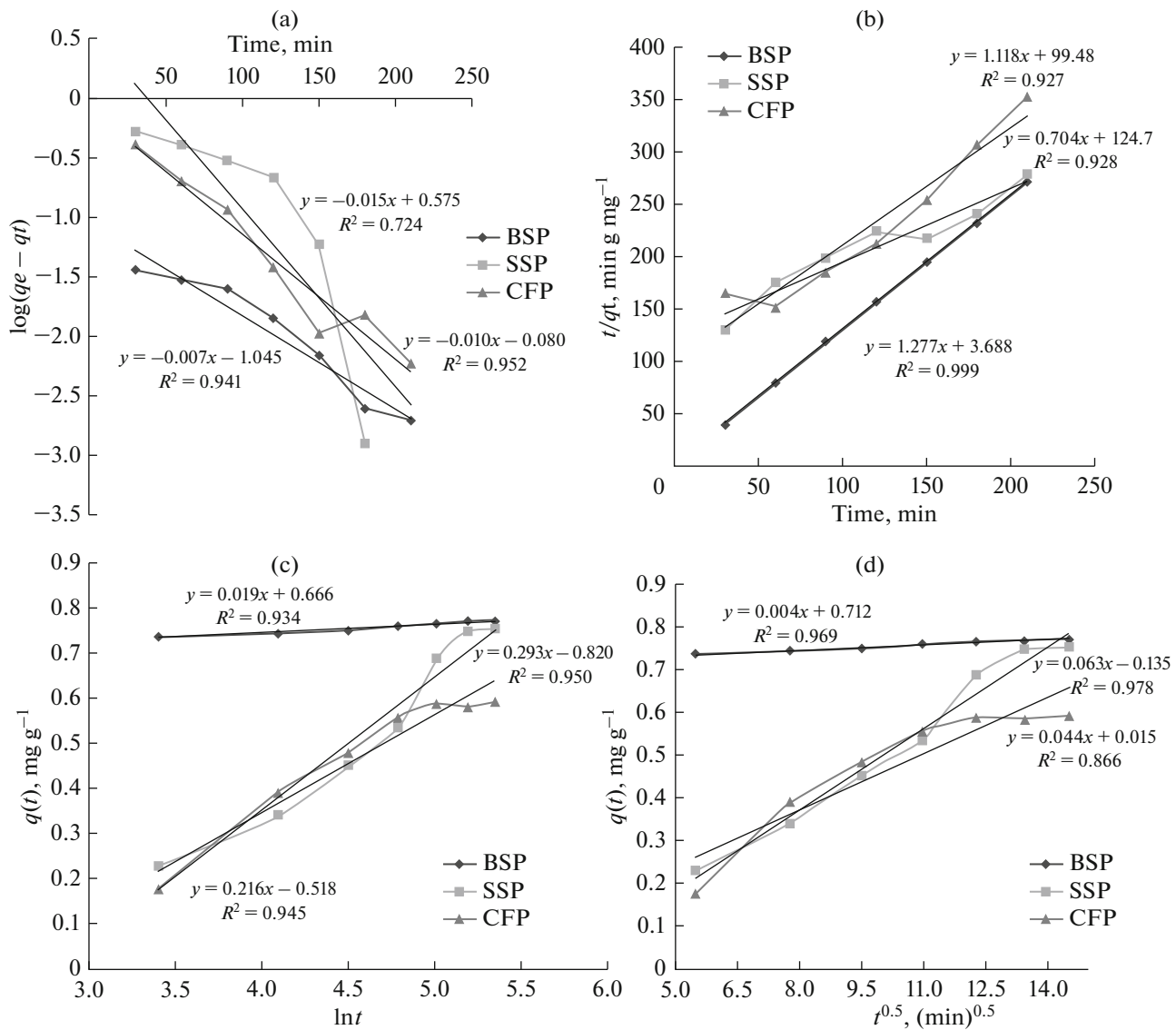
Fig. 4. Adsorption kinetics using (a) pseudo-first order, (b) pseudo-second order, (c) Elovich kinetic model, and (d) Weber's intraparticle diffusion model for 16 mg L^{-1} Pb(II) sorption onto adsorbents at pH 5 and 200 rpm using 20 g L^{-1} of BSP, SSP, and CFP.

$$q_t = \frac{1}{\beta \ln \alpha\beta} + \frac{1}{\beta \ln t}, \qquad (5)$$

where q_t is the amount of Pb(II) sorbed at the time t, α is the initial Pb(II) sorption rate (mg g^{-1} min^{-1}), and β is the desorption constant (g mg^{-1}) during any one experiment.

The interactions between the adsorbate and adsorbent materials follow film diffusion, pore diffusion, and intraparticle transport, among which pore diffusion and intraparticle diffusion are often rate-limiting in a batch reactor, whereas film diffusion is more likely the rate-limiting step for a continuous flow system [27]. Hence, Weber's intraparticle diffusion model was analyzed and showed reasonably good correlation:

$$q_t = K_d t^{1/2} + \theta. \qquad (6)$$

The estimated Elovich and Weber's intraparticle diffusion models and the related statistic parameters are reported in Table 1.

Further, the kinetics data subjected to Boyd kinetics model analysis using the equation

$$B_t = -0.4977 - \ln(1 - F), \qquad (7)$$

where F represents the fraction of the solute adsorbed at any time t (min), revealed the deviation of the metal ions uptake from an aqueous system on the adsorbent, suggesting that the adsorption mechanism was governed by external mass transport where particle diffusion is the rate-limiting step [27]. Nonlinear plots with

Table 1. Lead(II) adsorption kinetic parameters of pseudo-first and pseudo-second order, Elovich, Weber's intraparticle diffusion, and Boyd models using BSP, SSP, and CFP as biosorbents

Model	Pseudo-first-order			Exp. value	Pseudo-second-order			
Adsorbent	q_e, mg g^{-1}	k_1, min^{-1}	R^2	q_e, mg g^{-1}	q_e, mg g^{-1}	k_2, g mg^{-1} min^{-1}	R^2	
BSP	0.352	0.016	0.941	0.758	0.783	0.442	0.999	
SSP	1.188	0.018	0.927	0.536	1.420	0.004	0.928	
CFP	0.923	0.023	0.952	0.483	0.894	0.013	0.927	
Adsorbent	Elovich model			Weber's intraparticle diffusion model			Boyd model	
	α, mg g min^{-1}	$1/\beta$, mg g^{-1}	R^2	k_d, mg g min^{-1}	θ, mg g^{-1}	R^2	R^2	
BSP	3.17×10^{12}	0.019	0.934	0.004	0.712	0.969	0.813	
SSP	0.018	0.293	0.950	0.063	−0.135	0.978	0.767	
CFP	0.02	0.216	0.945	0.044	0.015	0.866	0.895	

low regression coefficients reveal that these adsorbents do not obey the Boyd model.
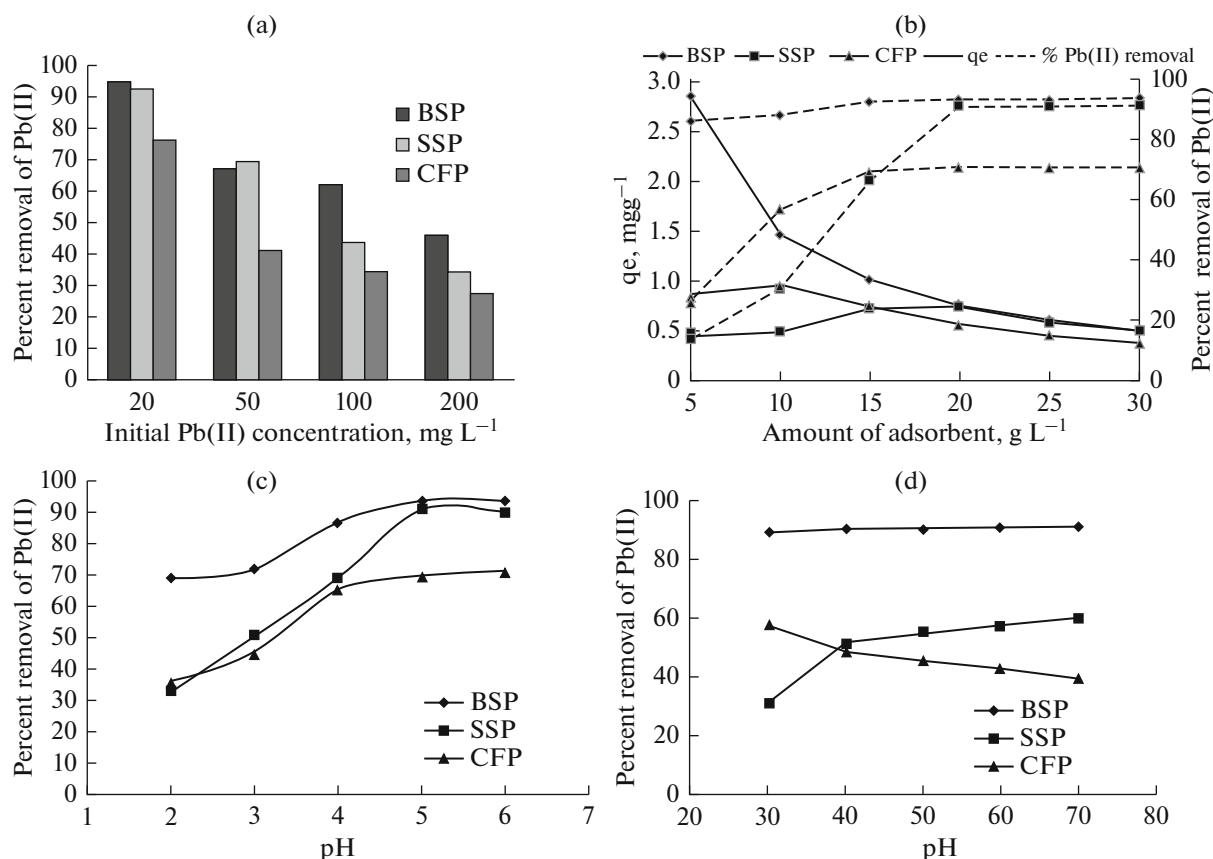
Effect of Concentration of Metal Ion

Adsorbate concentration is the crucial factor during adsorption reaction, since it dictates the mass transfer resistances of the metal between the aqueous and solid phases in an aqueous solution [12, 28]. Incompletion of active adsorption sites of the adsorbent and the aggregation of adsorbent particles at higher concentration are the important factors which contribute to the adsorbate concentration effect. Figure 5a shows the effect of Pb(II) concentration on its removal from the aqueous solution for the adsorbent materials BSP, SSP, and CFP. A continuous decline of percentage removal with an increase in the metal ion concentration was observed. This appears to be due to the competition of metal ions for available binding sites in the biomass and also due to the lack of binding sites for the attachment of Pb(II) ions at higher metal ion concentration levels.

Effect of Adsorbent Dose

In adsorption, the quantity of adsorbent is a considerable factor that affects the adsorption process strongly and it dictates the adsorption efficiency of each adsorbent. It was clear from the experimental results that the adsorption of Pb(II) was increased with an increase in the adsorbent concentration in the reaction mixture due to the availability of a larger number of active sites on the surface of adsorbent [8, 9, 12, 14]. However, unit adsorption was decreased with an increase in adsorbent dosage in all three cases of adsorbents, which may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles and is shown in Fig. 5b.

Effect of pH

As was discussed earlier, the adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cation which in turn mainly depends on the pH of the system, since the organic functional groups on the adsorbent surface may acquire a negative or positive charge depending on the solution pH [9]. Hence, it was thought of important to study the effect of pH on the removal of Pb(II). Patrulea et al. [29] reported that the protonation of the primary amine groups with positive charge in the acidic media affects the adsorption process by electrostatic repulsion of the cationic metal ions present in the medium. According to previously reported findings, the precipitation of Pb(II) ions as lead hydroxides such as $Pb(OH)_2$ occurs at pH values higher than 6 and beyond this point the adsorption efficiency results could be hampered [20]; therefore, the effect of pH on adsorption using BSP, SSP, and CFP was studied in the initial pH range of 2 to 6 in the solution. Literature survey clearly predicts that the Pb(II) uptake capacity of adsorbents increases with an increase in pH in the acidic medium and is predominantly removed in the pH vicinity of 5 [2, 12]. A similar pattern of increasing adsorption percentage with an increase in pH from 2 to 6 was observed in the present case for three adsorbents, and maximum adsorption was observed between pH 5 and 6. The maximum removal of Pb(II) at pH 5 using BSP or SSP and at pH 6 using CFP is due to the ionic attraction attained by the functional groups like carboxylate and −OH groups and is shown in Fig. 5c. As was explained previously, the lower adsorption rate at lower pH values is due to the higher concentration of H$^+$ ions present in the reaction mixture, which compete with the Pb(II) ions for the adsorption sites of biosorbents [30].

Fig. 5. Effect of various parameters on adsorption of Pb(II) from aqueous solutions: (a) initial Pb(II) concentration (303 K, pH 5, 200 rpm, 180 min, and 20 g L^{-1} of BSP, SSP, and CFP), (b) adsorbent dose (303 K, pH 5, 200 rpm, 180 min, and initial Pb(II) concentration 16 mg L^{-1}), (c) pH of the solution (303 K, 200 rpm, 180 min, initial Pb(II) concentration 16 mg L^{-1}, and 20 g L^{-1} of BSP, SSP, and CFP), and (d) temperature of the medium (pH 5, 200 rpm, 180 min, initial Pb(II) concentration 16 mg L^{-1}, and 10 g L^{-1} of BSP, SSP, and CFP).

Effect of Temperature

The alteration of molecular interactions and the solubility of the adsorbate caused by an increase in temperature affect the adsorption process and have significance to say whether the process is endothermic or exothermic, thereby relating to physisorption or chemisorption [8, 31]. The percent adsorption of Pb(II) ions using BSP, CFP, and SSP was investigated by experiments for 16 mg L^{-1} Pb(II) at 303−343 K (Fig. 5d). Thermodynamic parameters (ΔG, ΔH, and ΔS) are given in Table 2.

In general, preferable binding can be expected at higher temperatures for endothermic reactions, since the rise in the kinetic energy of sorbent particles with an increase in temperature due to increased collision frequency between the sorbent and sorbate results in

Table 2. Thermodynamic parameters for the adsorption of Pb(II) onto 10 g L^{-1} of BSP, SSP, and CFP at pH 5, initial Pb(II) concentration 16 mg L^{-1}, and agitation speed 200 rpm

T, K	ΔG, kJ mol^{-1}			ΔH, kJ mol^{-1}		
	BSP	SSP	CFP	BSP	SSP	CFP
303	−5.34	1.32	−0.57	4.52	23.50	−15.05
313	−5.67	0.59	−0.09	ΔS, J mol^{-1} K^{-1}		
323	−6.00	−0.14	0.39			
333	−6.32	−0.87	0.87	BSP	SSP	CFP
343	−6.65	−1.61	1.34	0.03	0.07	−0.05

Table 3. Lead(II) biosorption isotherm parameters, i.e., the Langmuir, Freundlich, D−R, and Temkin models by 20 g L^{-1} of BSP, SSP, and CFP adsorbents at pH 5, 303 K, and agitation speed 250 rpm

Adsorbent, 20 g L^{-1}	Langmuir isotherm			Freundlich isotherm			D−R isotherm			Temkin isotherm		
	K_L, L mg^{-1}	q_m, mg g^{-1}	R^2	K_F, mg g^{-1}	n	R^2	B_D, mol^2 J^{-2}	q_D, mg g^{-1}	R^2	B, J mol^{-1}	A_T, L g^{-1}	R^2
BSP	0.049	5.291	0.931	0.946	3.030	0.936	3×10^{-7}	2.904	0.653	0.722	2.264	0.825
SSP	0.061	3.690	0.937	0.927	3.676	0.971	5×10^{-7}	2.394	0.737	0.501	3.339	0.871
CFP	0.023	3.413	0.866	0.659	2.710	0.902	4×10^{-6}	1.742	0.530	0.548	0.529	0.802

enhanced sorption onto the surface of the sorbent. Moreover, an increase in the temperature of the medium creates the bond rupture of functional groups present on the adsorbent surface and, as a consequence, increases the number of active sorption sites, resulting in enhanced sorption [32]. Thermodynamic results revealed that there is no effect of temperature on the removal of Pb(II) using BSP as an adsorbent. However, in the case of SSP, the removal of Pb(II) ions increased with an increase in temperature and higher removal was observed at 343 K, predicting the process as an endothermic reaction. Hence, this indicates that the enthalpy change ΔH is positive (endothermic) due to an increase in adsorption on successive increase in temperature. Further, negative ΔG values show the thermodynamically feasible and spontaneous nature of the adsorption process and the positive value of ΔS reveals the increased randomness at the solid−solution interface during the adsorption of Pb(II) on the adsorbent material active sites. A similar observation of the maximum adsorption of Pb(II) by modified areca waste was endothermic but spontaneous under studied conditions [11]. However, in the case of CFP, a decrease in the adsorption percentage with an increase in temperature was observed (Fig. 5d). This observation of a decrease in the removal of Pb(II) with an increase in temperature can be explained based on (i) increased escaping tendency of already adsorbed molecules from adsorbent into the bulk solution due to an increase in the total energy of sorbate molecules at higher temperature [31] and (ii) dissolution of sorbing solution, because tannins and other phenol/alcohol compounds are soluble at high temperatures [33]. Though, this seems to corroborate with the well-known fact that sorption capacity is expected to decrease with an increase in solution temperature when the sorption process is exothermic, based on conformation to second order kinetics, the present case using CFP involves both physical and chemical adsorptions. Such simultaneous occurrence of both adsorptions was reported earlier by Ho and McKay [34] and Panday et al. [35].
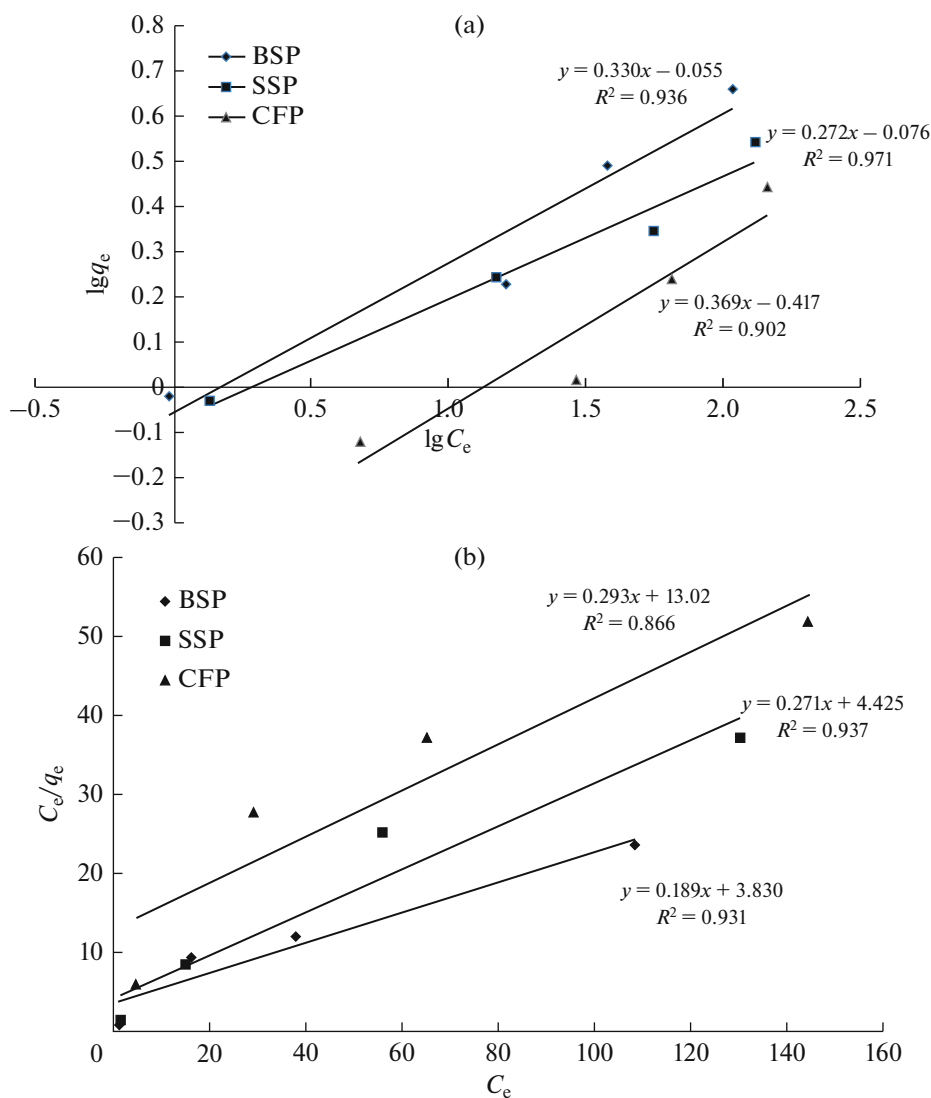
Adsorption Isotherms

Adsorption isotherms are significant in describing the mechanism of adsorption for analyzing the interaction of metal ion on the surface of the adsorbent. Langmuir and Freundlich adsorption isotherm equations were employed in order to evaluate the adsorption efficiency of each adsorbent towards the removal of divalent lead ions from aqueous solutions. From Langmuir/Freundlich adsorption isotherm, the values of characteristic parameters q_m, K_L, n, and K_F were calculated from the slope and intercept of linear dependencies (Fig. 6), and the correlation coefficient R^2 associated to each model is given in Table 3.

The adsorption isotherms were studied by varying the initial concentration of lead ions. Langmuir, Freundlich, D−R, and Temkin models were evaluated for description of metal sorption isotherms (Table 3).

The best fitting order of these models is concluded to be Freundlich > Langmuir > Temkin > D−R. This result showed that the Freundlich isotherm fitted better than the Langmuir isotherm in describing the behavior of Pb(II) adsorption, indicating that the adsorption process involved multimolecular layers of coverage onto the three adsorbents BSP, SSP, and CFP. It is reported in the literature that when a multi-surface adsorption mechanism dominated in an adsorption system, the coexisting metal ions did not compete with Pb(II) ions for the active sites on the adsorbents [36]. Based on this, it could be suggested that the presence of coexisting ions will not affect Pb(II) adsorption by the studied biosorbents.

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as $R_L = 1/[1+K_L C_o]$, where K_L is the Langmuir constant and C_o is the initial concentration of Pb(II). Based on the values of R_L, the Langmuir equation is favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$). Similarly, the value of sorption intensity ($1 < n < 10$) indicates that sorption is Freundlich favorable. As the R_L values in the present case are in the range of 0 to 1 and the n values are less than 10 (Table 3) for the three adsorbents (CFP, SSP, and BSP), Langmuir as well as Freundlich isotherms were favorable for the adsorption process [8]. Hence, both mono- and mul-

Fig. 6. Linear adsorption isotherm plots for (a) the Langmuir model and (b) the Freundlich model on Pb(II) uptake by using 20 g L^{-1} of BSP, SSP, and CFP at pH 5, agitation speed 200 rpm, and 303 K.

tilayer adsorptions occur in the present studies with preference to monolayer adsorption. A similar observation of fitting well the adsorption data with the Langmuir and Freundlich isotherm models was observed in adsorption studies on the removal of divalent lead from the aqueous solution using nanosilver sol-coated activated carbon [37] and tridax procumbens activated carbon [38].

The Temkin isotherm equation explicitly takes into account the adsorbent−adsorbate interactions by ignoring the extremely low and large value of concentrations. It assumes that the heat of adsorption of all the molecules in a layer decreases linearly rather than logarithmic with coverage due to adsorbent−adsorbate interactions. An increase in uptake capacity of BSP, CFP, and SSP with an increase in Pb(II) ion concentration is due to the higher availability of Pb(II)

ions in the solution for the adsorption. Moreover, higher initial Pb(II) concentration increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases, resulting in the higher probability of collision between Pb(II) ions and sorbents. This also results in higher metal uptake [32]. The Dubinin−Radushkevich (D−R) isotherm is an empirical model which is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [39]. In the D−R isotherm ($\ln q_e = \ln q_D - B_D \varepsilon^2$), B_D (sorption energy, mol^2 kJ^{-2}) is a constant related to the mean free energy of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in solution, q_D is the theoretical saturation capacity (mol g^{-1}), and ε is the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J mol^{-1} K^{-1}) is the

Table 4. Comparison of the adsorption capacity (mg g^{-1}) of studied biosorbents for the removal of Pb(II) with other adsorbent materials in the literature

Adsorbent	Adsorbent capacity, mg g^{-1}	Reference
Chitosan biopolymer	2.53	[3]
Rice husk	0.62	[9]
Areca waste	3.37	[11]
Single-walled carbon nanotubes (SWCNTs)	33.55	[22]
Untreated Tabuk clay	30.00	[40]
Khaiber clay	10.00	[40]
Banana bunch-stem powder (BSP)	5.29	This study
Sorghum stem powder (SSP)	3.69	This study
Casuarinas fruit powder (CFP)	3.41	This study

gas constant and T (K) is the absolute temperature. The order of sorption energy values (B_D) for these adsorbents is: BSP < SSP < CFP (Table 3), which explains these metal ion removal capacity as BSP > SSP > CFP.

A comparison of the lead ions uptake capacities of BSP, SSP, and CFP with other biomaterial based sorbents is presented in Table 4. However, a direct comparison may not be possible due to a variety of parameters and conditions employed in each referenced work.

CONCLUSIONS

The maximum adsorption efficiencies of the three adsorbents for Pb(II) removal from aqueous solutions were 94.24, 91.75, and 72.37% using acid functionalized BSP, SSP, and CFP, respectively, and can be correlated with their microporous structures, where rough surface with some cavities for all three adsorbents indicating a high possibility of adsorption. The effects of various experimental parameters such as contact time, initial Pb(II) concentrations, pH, adsorbent dosage, and temperature of the medium on the adsorption process were discussed. It is evident from the kinetic data that chemisorption is the possible adsorption mechanism involved in Pb(II) removal using BSP and SSP as adsorbents, whereas a combination of both physisorption and chemical attachment involved when CFP was used as an adsorbent. Adsorption isotherm studies describe that both mono- and multilayer adsorptions occur in the present studies with preference to multilayer adsorption using BSP, SSP, and CFP as adsorbents. Presented results affirmed the suitability of low-cost adsorbents BSP, SSP, and CFP for lead removal from aqueous environment, and considering the fact that the raw materials of these three adsorbents are abundantly available, the efficient Pb(II) removal from industrial wastewater could be achieved by utilizing these waste materials as adsorbents in large quantities.

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