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Utilization of *Sapindus saponaria* (soap nut) bark powder for the removal of Cu(II) ions from aqueous environment

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ABSTRACT

Sapindus saponaria bark powder (SSBP), an agro-waste material was investigated as a biosorbent for the removal and recovery of Cu(II) from aqueous solution. This biosorbent was characterized by infrared spectroscopy, X-ray diffraction, scanning electron microscopy and elemental analysis. The influence of various parameters such as effect of initial pH, contact time, metal ion concentration and sorbent dose on the removal of Cu(II) was investigated using batch process. Langmuir, Freundlich and Dubinin–Radushkevich isotherm models were applied to describe the adsorption isotherms. The Langmuir model fitted the equilibrium data better than the other isotherm models. The maximum adsorption capacity of Cu(II) was calculated from the Langmuir isotherm and found to be 37.09 mg g^{-1} at pH 5.0. The kinetic studies revealed that the biosorption of Cu(II) onto SSBP followed the pseudo-second-order rate model. Evaluated thermodynamic parameters, ΔG°, ΔH° and ΔS°, showed that the biosorption of Cu(II) onto SSBP was an endothermic process. Desorption studies were carried out with dilute hydrochloric acid for quantitative recovery of the metal ions as well as to regenerate the adsorbent.

Keywords: Biosorption; *Sapindus saponaria* bark; Isotherms; Kinetics; Thermodynamics; Copper

1. Introduction

There is a need to reconsider our water consumption patterns and the way we exploit our water resources in view of rapidly increasing population and depleting water resources. In addition, water pollution by heavy metals has been prime concern for many years. Heavy metals are not biodegradable, and their presence in various streams and lakes leads to bioaccumulation in living organisms causing health problems in animals, plants and human beings. Copper is one of the most common metal pollutants in wastewater discharged from industrial activities such as mining, plating baths, fertilizer, paints and pigments industry besides drainage discharge [1]. Copper is stated as one of the toxic metals, the health hazards associated with Cu(II) include kidney damage, severe headache, hair loss, hypoglycaemia, increased heart rate, nausea, widespread capillary damage and central nervous system irritation followed by depression [2]. The World Health Organization

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recommendation for maximum allowed concentration of Cu(II) in drinking water is 1.5 mg L^{-1} [3]. Therefore, it is essential to develop methods and materials for the removal of Cu(II) ions from water for maintaining water quality and protection of human health.

Different treatment technologies based on solvent extraction, chemical precipitation, ion exchange, coagulation, adsorption, chemical oxidation/reduction and biosorption methods are available for the removal of metal ions from aqueous solutions [4]. The disadvantage of these methods is the production of large amount of sludge. Among these methods, biosorption has potential to be an alternative to conventional processes for the removal of metals with the advantages of using less chemicals, nearly a passive process, and operation and maintenance costs are low. Of late, there has been an increase in the usage of agriculture/plant/algae waste as biosorbent including sugar beet pulp [5], tea leaves powder [6], sour orange residue [7], tea waste [8], pomegranate peel [9], sunflower leaves [10], wheat straw [11], date palm seeds [12], *Cinnamomum camphora* leaves powder [13], cashew nut shells [14], walnut, hazelnut and almond shells [15] and *Spirogyra* species [16], for the removal of metal ions from aqueous solutions. Most of the above-mentioned agricultural materials contain polysaccharides and lignin which are associated with the functional groups like carboxyl, hydroxyl and amino groups. These groups are responsible for metal ion sorption [17]. The abundance of a large amount of surface functional groups makes various agricultural wastes as alternatives to expensive synthetic adsorbents [18]. As SSBP is simple to prepare, has high biosorption capacity and availability in plenty, *it* was investigated for the possibility of Cu(II) ion removal.

Sapindus saponaria is a deciduous tree, belongs to the family of *Lychee* and grows in the warm temperature to tropical regions of the world. The species is widely grown in upper reaches of the Indo-Gangetic plains, Shivaliks and sub-Himalayan tracts of India. The trunk is straight and cylindrical, nearly 4–5 m (13–16 ft) in height and its bark is abundantly available in India with no commercial value. Since it contains many functional groups, we have studied this agricultural waste material as a biosorbent for the removal of Cu(II) from wastewater.

The main objectives of this study include preparing the biosorbent from the agriculture waste, SSBP, characterizing the biosorbent using Fourier transform infrared spectroscopy, scanning electron microscopy and X-ray powder diffraction techniques, optimizing the experimental conditions such as effect of pH, sorbent dose, contact time and initial metal ion concentration for Cu(II) removal, determining the kinetic and isotherm equilibrium parameters of Cu(II) sorption onto SSBP. Biosorption capacity of the SSBP was compared with other biosorbents in the application of water treatment studies.

2. Material and methods

2.1. Preparation of adsorbent

S. saponaria bark was collected from the village of Doruvupadu in SPSR, Nellore District in the state of Andhra Pradesh (India). Bark samples were air dried and grounded in a steel ball mill to make fine powder and washed with double deionized water to remove surface impurities (Fig. 1). The washed powder was further washed and boiled in double distilled water repeatedly till the colour is removed completely, then dried at 70˚C for 24 h and stored in a desiccator to prevent the moisture.

2.2. Chemicals and equipment

All chemicals used in this study were of analytical reagent grade. Deionized double-distilled water (DDW) was used throughout the experimental studies. Stock copper solution (1 mg mL^{-1}) was prepared by dissolving $CuSO_4{\cdot}5H_2O$ in distilled water. Working standards were prepared by progressive dilution of stock copper solution using DDW water. Analytical reagent grade HCl, NaOH and buffer solutions (Merck) were used to adjust the solution pH. An Elico (LI-129) pH meter was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0 and 9.2. FT-IR spectrometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA) was used for the IR spectral studies (4,000–400 cm^{-1}) of biosorbent. Vario EL, Elementar, Germany was used for elemental analysis of the SSBP. The copper concentration in the samples was determined by atomic absorption spectrophotometer (AAS, Shimadzu AA-6300) with copper hollow cathode lamp. Samples for X-ray diffraction measurements were prepared by grounding the adsorbent with small amount of methanol in an agate mortar. The mixture was smear mounted onto the zero-background quartz window specimen holder and allowed to air dry. Wide angle X-ray diffraction patterns of samples were recorded on an X-ray diffraction (XRD 6000, Shimadzu), using Kα radiation (=1.5406 Å) at 40 kV and 30 mA.

2.3. Batch biosorption studies

Metal sorption capacity of SSBP was determined in batch experiments using known amount of the sample with 50 mL of aqueous Cu(II) solutions in a series of 250-mL stoppered flasks. The solution pH was adjusted to the desired value by adding HCl or NaOH. The sealed bottles were shaken at 30℃ using a mechanical shaker for prescribed time to attain the equilibrium. The suspensions were filtered off and the concentrations of metal ions were determined by AAS. Experiments were carried out by varying the solution pH (2–8), adsorbent dose (100–800 mg), initial concentration of Cu(II) solution (20–180 mg L^{-1}) and contact time (10–90 min). The amount of metal ions sorbed (Q_e), was computed by the following equation:

$$Q_e = \frac{v}{m}(C_0 - C_e) \tag{1}$$

where C_0 and C_e are the initial and equilibrium Cu(II) concentrations, respectively, whereas "*v*" and "*m*" are the solution volume and mass of the biosorbent, respectively. Blank test was performed in the same experimental conditions without biosorbent (Fig. 1).

3. Results and discussion

3.1. Characterization of the biosorbent (SSBP)

The biosorbent (SSBP) was characterized through the FT-IR, SEM and XRD analyses. The physicochemical characteristics like moisture content, bulk density, ash content and the percentage of carbon, hydrogen and nitrogen of the SSBP are presented in Table 1.

Table 1
Physicochemical characteristics of SSBP

Characteristics	Values
Bulk density (g/cm^3)	0.53 ± 0.05
Moisture content (%)	3.55 ± 0.14
Ash content (%)	10.1 ± 0.45
Electrical conductivity (μs/cm)	42.5 ± 1.16
Carbon (%)	40.98 ± 1.72
Hydrogen (%)	5.276 ± 0.56
Nitrogen (%)	0.79 ± 0.03
Oxygen[a] (%)	52.95 ± 2.18

[a] Estimated by difference.

3.1.1. FT-IR Analysis

The FT-IR spectra of pure (Fig. 2(a)) and Cu(II)-loaded SSBP (Fig. 2(b)), in the range of 4,000–500 cm^{-1}, were recorded to confirm the presence of functional groups that are usually responsible for the Cu(II) biosorption. A strong peak at 1,030 cm^{-1} indicated the presence of C–O stretching of alcohols and carboxylic acids [19]. The bands appearing at 1,362 and 1,507 cm^{-1} are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups and carboxylate moieties, respectively [20]. The peaks at 2,848, 2,916 and 1,645 $cm^{-1}$are due to the C–H stretching frequency and C=O stretching mode of primary and secondary amides [21]. The strong band at 1,030 cm^{-1} confirms the lignin structure of the adsorbent. The broad bands appeared at 1,600–1,500 cm^{-1} due to the presence of C=O in quinine structure. The IR spectral studies revealed that the adsorbent contains carboxyl and carbonyl functional groups, which are mainly responsible for the sorption of Cu(II) through the chemical bonding.

3.1.2. X-ray diffraction (XRD)

X-ray diffraction spectra of SSBP are shown in Fig. 3. The X-ray diffraction spectrum of SSBP biosorbent indicates amorphous regions and peaks at 16°,

Fig. 1. Pictures of (a) soap nut bark and (b) soap nut bark powder.

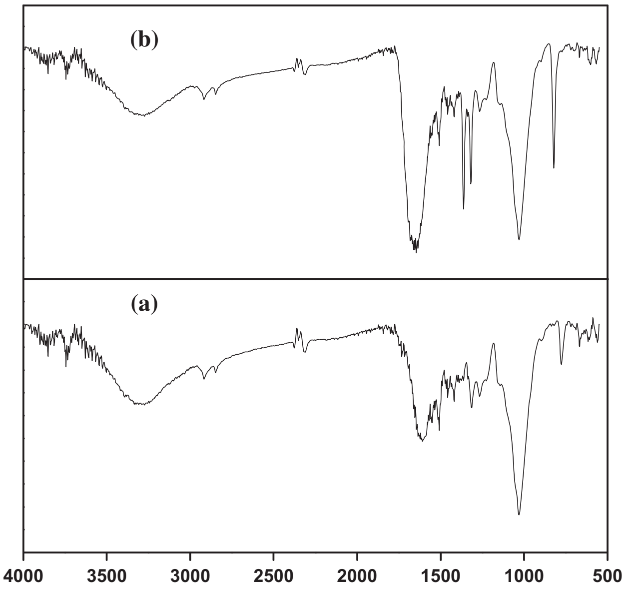

Fig. 2. FTIR spectra of (a) SSBP and (b) Cu(II)-loaded SSBP.

21˚, 29˚ and 36˚. The spectrum did not show any crystalline peaks supporting that the adsorbent is amorphous. The presence of amorphous regions, which is favourable for the biosorption of Cu(II) onto SSBP.

3.1.3. Scanning electron microscopy

Scanning electron microscopy is immensely a useful tool to examine the morphological features of the biosorbent. The scanning electron micrographs of pure and Cu(II)-loaded SSBP are shown in Fig. 4(a) and (b), respectively. It clearly showed the presence of porosities on the SSBP surface, which indicated that SSBP is an effective adsorbent for Cu(II) biosorption. However, as seen in Fig. 4(b), the surface of SSBP changed significantly after sorption of Cu(II).

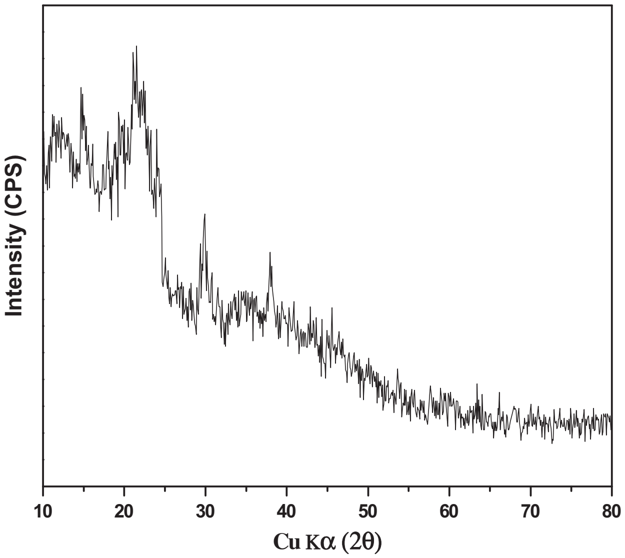

Fig. 3. Powder XRD of SSBP.

3.2. Effect of pH

The pH of the solution is the most important factor that influences the biosorption process; it controls the sorption of metal on the solid–water interfaces [22]. It is known that metal species [M(II)] are present in water as M^{2+}, M(OH)$^{+}$, M(OH)$_2^0$, M(OH)$_2$(s), etc. and species composition varies with pH. It was observed that the uptake of metal ions was significantly affected by the pH of the solution. The effect of pH on the removal of Cu(II) by SSBP was carried out at different pH values (2.0–8.0) by keeping all other parameters as constant, and the results are shown in Fig. 5. It is clear that maximum sorption was observed around pH 3–5. Our results are in agreement with the reported values in the literature [23–25]. For further studies, optimum pH for Cu(II) removal was fixed as 5.0. At initial Cu(II) concentration of 50 mg L^{-1}, Cu(II) removal efficiency was 28.51% at a solution pH of 2.0, but % removal increased sharply when solution pH increases from 3.0 to 5.0. The effect of pH can be explained by considering the surface charge on the adsorbent material [20]. The point of zero charge (pzc) of the SSBP was experimentally determined as 4.1. When the pH is less than pzc, the surface of the adsorbent is positively charged, hence the sorption Cu(II) is low due to the competition between the higher concentration of H^{+} ions with positively charged metal ions. When the pH is greater than pzc, the surface of the adsorbent is negatively charged, enhancing the electrostatic attraction between the positively charged Cu(II) ions and the negatively charged adsorbent (SSBP) surface, resulting in increase in the sorption of Cu(II) ions onto SSBP. However, at higher pH values ($\text{pH} > 5$), biosorption has decreased due to the formation of metal hydroxide precipitates.

3.3. Effect of adsorbent dose

The uptake of Cu(II) from solution was affected by quantity of biomass. The dependence of metal ion sorption on the dose was studied by varying the amount of adsorbent from 100 to 1,000 mg by keeping all other parameters such as pH (5.0), initial metal ion concentration (50 mg L^{-1}) constant, and the results are

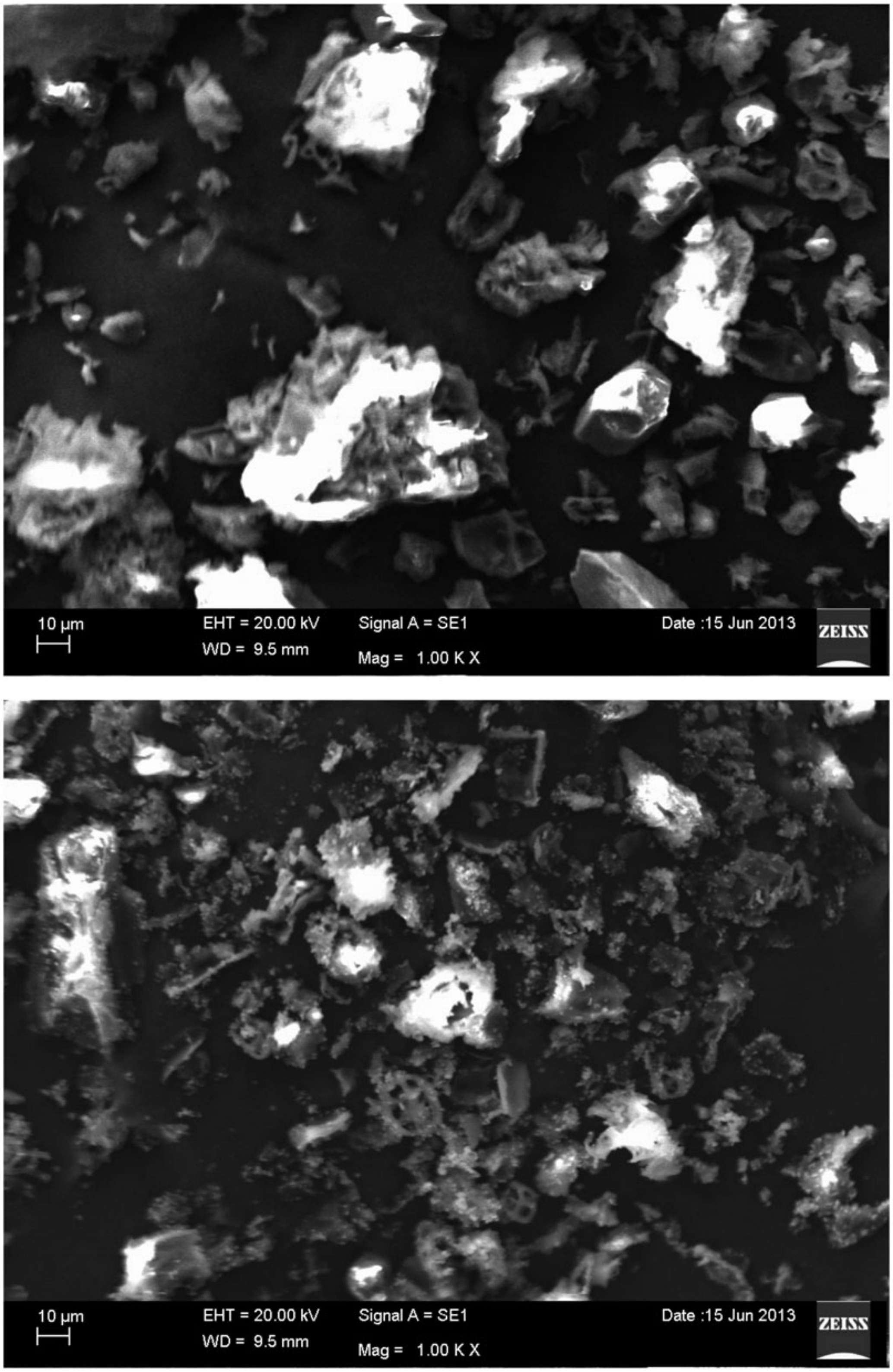

Fig. 4. SEM images of (a) SSBP and (b) Cu(II)-loaded SSBP.

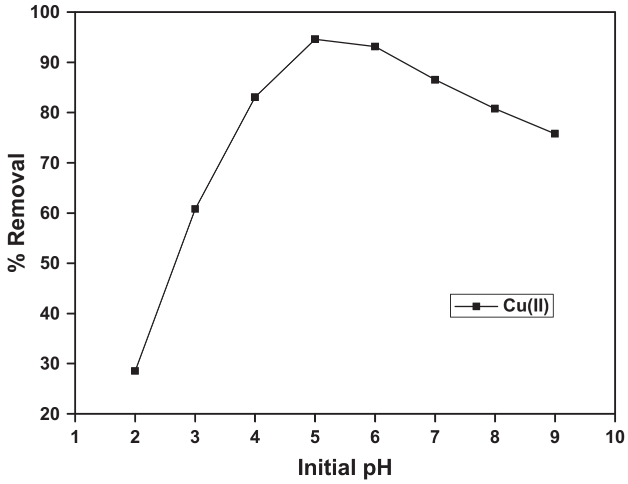

Fig. 5. Effect of initial pH on the removal of Cu(II) on SSBP.

presented in Fig. 6. The results indicate that the sorption of metal ions increased with increasing the dose of adsorbent initially due to the greater availability of exchangeable sites [26]. Maximum removal of Cu(II) was observed with an adsorbent dose of 300 mg, after increasing the dose of adsorbent sorption of metal ions increased slowly and reached a constant value due to saturation of sorption sites. Hence, the dose of adsorbent of 300 mg was used for further batch studies of biosorption.

3.4. Effect of contact time on the removal of copper

Fig. 7 shows the effect of contact time on the removal of copper. Experimental studies were carried out for different time intervals (5–90 min) with different initial concentrations (10, 25, 50 mg L^{-1}) at pH 5.0. The results indicated that more than 60% of Cu(II) was adsorbed within 20 min, and equilibrium adsorption was attained in 60 min. After the contact period of 60 min, there was no further increase and became almost constant. Therefore, optimum time was fixed as 60 min for further studies.

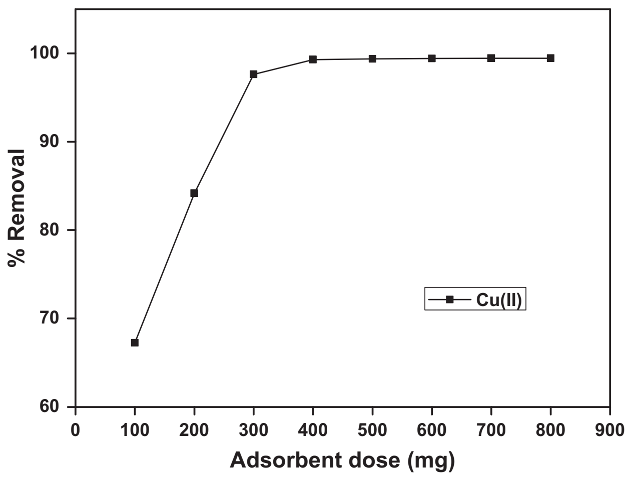

Fig. 6. Effect of adsorbent dose on the removal of Cu(II) on SSBP.

3.5. Kinetic studies

Kinetic studies were performed in order to examine the biosorption of Cu(II) onto SSBP and to identify the potential rate-controlling step. Various kinetic models have been used to analyse the kinetic data obtained from batch studies. Data were analysed using three kinetic models; Lagergren's pseudo-first-order, McKay and Ho's pseudo-second-order and intraparticle diffusion models.

The linear form of the pseudo-first-order equation was proposed by Lagergren [27] and it is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{2}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the adsorption amounts at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the rate constant in the pseudo-first-order adsorption process. The constants were determined experimentally by plotting $\log(q_e - q_t)$ vs. t, and are presented in Table 2. The correlation coefficient values

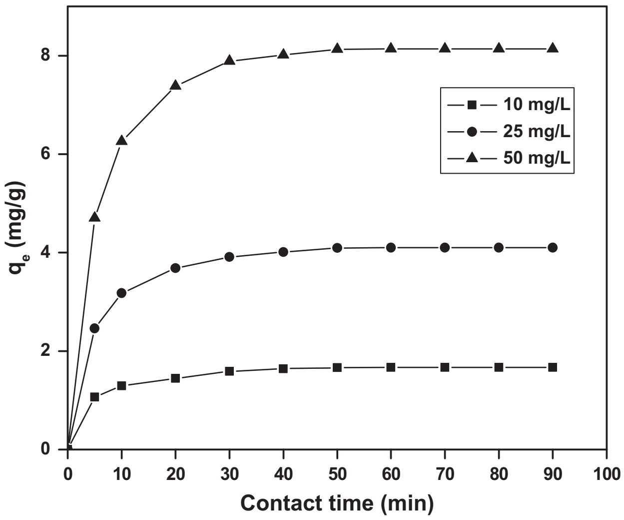

Fig. 7. Effect of contact time on the removal of Cu(II) on SSBP.

Table 2
Kinetic parameters for the biosorption of Cu(II) onto SSBP at different metal ion concentrations

Cu(II) conc. (mg L^{-1})	Experimental value $q_{e,exp}$ (mg g^{-1})	Pseudo-first-order			Pseudo-second-order			Weber and Morris		
		$q_{e,cal}$ (mg g^{-1})	k_1 (×10^{-2}) (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 (×10^{-2}) (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_{id} (mg^{-1} g min$^{-0.5}$)	R^2
10	1.666	1.193	9.93	0.9889	1.730	8.78	0.9998	1.210	0.075	0.896
25	4.100	3.732	11.48	0.9537	4.276	7.55	0.9998	3.243	0.194	0.871
50	8.135	9.199	13.4	0.9546	8.487	3.87	0.9997	7.355	0.396	0.851

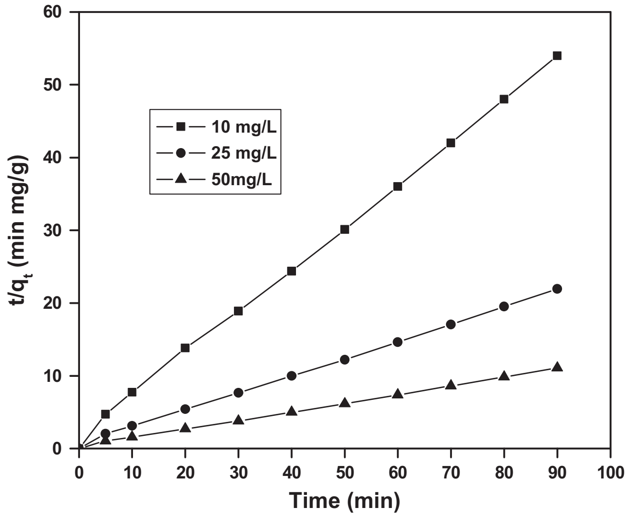

Fig. 8. Pseudo-second-order kinetic model for Cu(II) onto SSBP.

are less than 0.96, which is an indicative of a poor correlation and also $q_{e,cal}$ determined from the model is not in a good agreement with the experimental values of $q_{e,exp}$. Therefore, the pseudo-first-order model is not suitable for modelling the biosorption of Cu(II) onto the SSBP.

The pseudo-second-order equation [28], based on adsorption capacity at equilibrium, can be expressed by:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 (g/mg min^{-1}) is the rate constant of the second-order equation. k_2 and q_e were obtained from intercept and slope of the plot of t/q_t vs. t as shown in Fig. 8. The pseudo-second-order rate constants, k_2 and q_e, are presented in Table 2. The values of correlation coefficients are nearly equal to 1 (0.9998, 0.9998, 0.9997) and the theoretical $q_{e,cal}$ values are closer to the experimental $q_{e,exp}$ values. Therefore, the sorption kinetics of Cu(II) follows more favourably by second-order kinetics model rather than pseudo-first-order kinetic model.

The intraparticle diffusion model is based on the theory proposed by Weber and Morris [29], which is given by Eq. (4):

$$q_t = k_{id} t^{0.5} + c \quad (4)$$

where k_{id} (mg g^{-1} min$^{-1/2}$) is the rate constant of intraparticle diffusion. q_t (mg g^{-1}) is the amount of

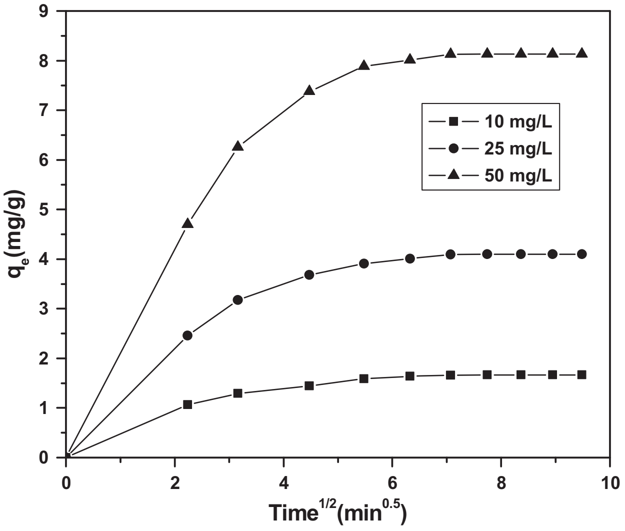

Fig. 9. Intraparticle diffusion kinetics for adsorption of Cu(II) onto SSBP.

Cu(II) sorbed at time t and c (mg g^{-1}) is the intercept. Intraparticle diffusion rate constant k_{id} and the value of "c" can be obtained from the plot of q_t vs. the square root of time as shown in Fig. 9, and the values are presented in Table 2. The values of correlation coefficients are not satisfactory and the line/curve does not pass through the origin, which indicates the intraparticle diffusion is not the only rate-limiting step in determining the kinetics of the process.

In view of these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cu(II) onto SSBP.

3.6. Adsorption isotherm models

The sorption isotherm models were used to describe the interaction of metal ions with the biomass. The experimental data were analysed using Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherm models.

The Langmuir isotherm model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface [30], which is represented by:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{5}$$

The linear form of the equation can be written as:

$$C_e/q_e = C_e/Q_m + 1/Q_m b \tag{6}$$

where c_e and q_e are the equilibrium concentrations of copper in the adsorbed and liquid phases in mmol g^{-1} and mmol g^{-1}, respectively. K_L is the Langmuir biosorption constant (L mg^{-1}) relating to the free energy of biosorption. Q_m and b are the Langmuir constants, Q_m is the maximum metal adsorption capacity (mmol g^{-1}) and b is the sorption equilibrium constant (L mg^{-1}). These were calculated from the intercept and slope of the plot c_e vs. q_e, and listed in Table 3. The maximum biosorption capacity was increased from 30.65 to 37.09 mg g^{-1} with an increase in the temperature from 293 to 313 K due to the enhancement of the collisions between the biosorbent and sorbate species (Fig. 10). The correlation coefficients R^2 and χ^2 values at three different temperatures are listed in Table 4. R^2 values, at three different temperatures, are closer to 1 indicating the Langmuir isotherm model is more suitable to explain the biosorption data of Cu(II) onto SSBP.

The essential features of the Langmuir biosorption isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined in Eq. (7):

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{7}$$

where K_L is the Langmuir constant (L mg^{-1}) and C_0 is the initial adsorbate concentration (mg L^{-1}). The values of R_L, if are in the range of 0–1 at all initial Cu(II) concentrations, confirm the favourable uptake of copper.

Table 3
Isotherm parameters for Cu(II) onto SSBP at different temperatures

	Langmuir		Freundlich		Dubinin–Radushkevich	
Temp. (K)	$Q_{\max}$ (mg g^{-1})	b (L mg^{-1})	K_F (mg g^{-1})	n	Q (mg g^{-1})	K
293	30.65 ± 1.23	0.1 ± 0.01	4.86 ± 0.32	2.1 ± 0.10	20.99 ± 1.56	0.015 ± 0.005
303	33.18 ± 0.94	0.15 ± 0.02	6.40 ± 0.93	2.1 ± 0.25	23.03 ± 1.79	0.009 ± 0.003
313	37.09 ± 0.84	0.24 ± 0.01	8.48 ± 0.79	2.0 ± 0.19	25.54 ± 1.53	0.004 ± 0.0008

Table 4
Chi-square and correlation coefficient of isotherms at different temperatures

	Langmuir		Freundlich		Dubinin–Radushkevich	
Temp. (K)	R^2	χ^2	R^2	χ^2	R^2	χ^2
293	0.991	0.511	0.990	0.577	0.849	9.317
303	0.995	0.289	0.985	1.052	0.854	10.457
313	0.997	0.189	0.958	3.408	0.923	6.330

Freundlich isotherm model describes the adsorption on an energetically heterogeneous surface of adsorbed molecules [31], which is represented by:

$$q_e = k_F C_e^{1/n} \tag{8}$$

where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed and liquid phases in mg g^{-1} and mg L^{-1}, respectively. k_F and n are the Freundlich constants characteristic of the system, indicating the adsorption capacity and adsorption intensity, and these values are presented in Table 3. It is clear that the Freundlich model could not fit all the experimental data well, as R^2 values are not closer to unity.

The Dubinin–Radushkevich (D–R) model, which does not assume a homogeneous surface or a constant sorption potential as the Langmuir model, was also used to test the experimental data to determine physical or chemical type of sorption. The D–R isotherm [32] is described by Eqs. (9) and (10):

$$q_e = Q_m \exp\left(-K\left[RT \ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \tag{9}$$

$$q_e = Q_m \exp(-K\varepsilon^2) \tag{10}$$

where Q_m is the maximum amount of the metal ion that could be sorbed onto unit weight of sorbent (mg g^{-1}), ε is the Polanyi potential which is equal to RT ln(1 + $1/C_e$), where R and T are the universal gas constant (kJ mol^{-1} K^{-1}) and the absolute temperature (K), respectively. The K in Eqs. (9) and (10) is related to the mean free energy of sorption per mole of the sorbate, when it is transferred to the surface of the solid from infinity in the solution and this energy can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2K}} \tag{11}$$

The correlation coefficients (R^2) and χ^2 values of all three adsorption models are summarized in Table 4. R^2 values obtained from the Langmuir isotherm model are closer to 1 than compared to Freundlich and Dubinin–Radushkevich adsorption isotherms models. The order of χ^2 values obtained from three isotherm models is as follows: Langmuir < Freundlich < Dubinin-Redushkevich. Lower χ^2 values from Langmuir isotherm model exhibit a better fit to the equilibrium data than Freundlich and Dubinin–Radushkevich adsorption isotherms. Therefore, the biosorption process of Cu(II) by SSBP can be interpreted as a monolayer adsorption.

3.7. Thermodynamic analysis

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated and used to decide whether the biosorption was a spontaneous process or not. These parameters are calculated from Eqs. (12)–(14):

$$\Delta G^\circ = -RT \ln K_L \tag{12}$$

where R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature (K) and K_L is the Langmuir constant. The values of ΔH° and ΔS° were computed from the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{14}$$

The changes in enthalpy (ΔH°) and entropy (ΔS°) were estimated from the slope and intercept of the plot of ln K_L vs. $1/T$ (figure not shown). The values of ΔG°, ΔH° and ΔS° for the biosorption of Cu(II) onto SSBP are given in Table 5. The Gibbs free energy (ΔG°) values were negative and increased with increasing the temperature from 293 to 313 K, which

Table 5
Thermodynamic parameters of Cu(II) biosorption onto SSBP at different temperatures

Temp. (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
293	−2.72	40.5	0.147
303	−4.04		
313	−5.68		

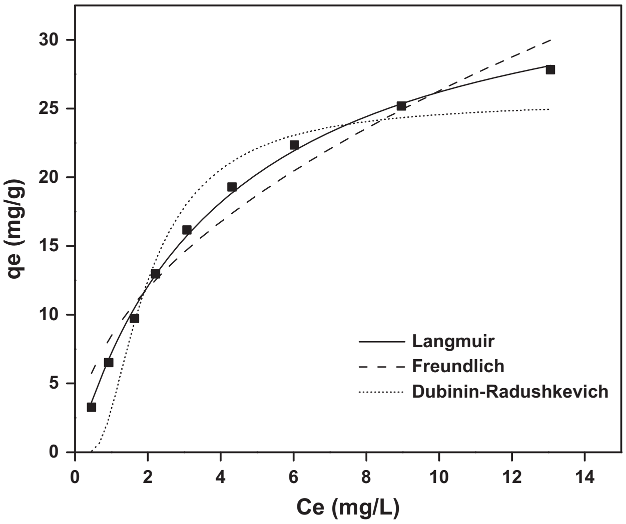

Fig. 10. Biosorption isotherms of Cu(II) onto SSBP.

indicated the spontaneous nature of the biosorption which is thermodynamically favourable under the experimental conditions. Positive value of ΔH° suggests that biosorption of Cu(II) onto SSBP is endothermic. The positive value of ΔS° indicated increased randomness at the biosorbent/solution interface during the biosorption of Cu(II) onto SSBP (Fig. 10).

3.8. Comparison of SSBP with other biosorbents

The biosorption capacities of various biosorbents for the removal of Cu(II) as reported in literature are presented in Table 6. These results indicate that SSBP is a better biosorbent for the removal of Cu(II) compared to other biosorbents. Therefore, it could be concluded that the SSBP biomass has a good potential for the removal of Cu(II) from aqueous solutions.

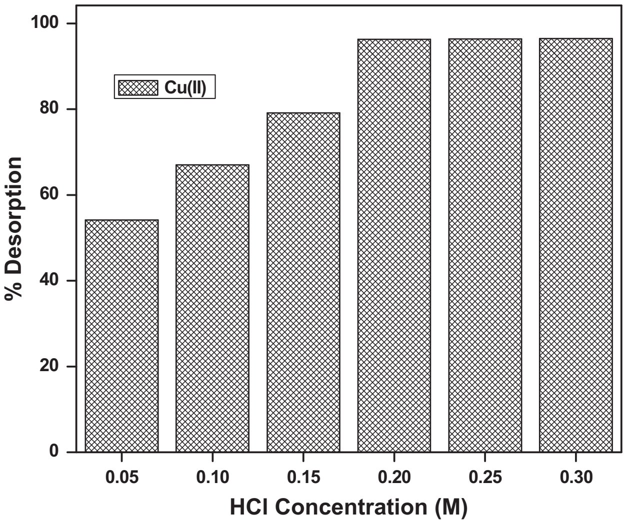

Fig. 11. Desorption of Cu(II) ions from SSBP.

4. Desorption studies

Desorption studies are important in order to regenerate the adsorbent and recover the metal ions. A few cursory experiments were conducted to desorb the metal ions from the loaded biomass with different concentrations (0.05–0.30 M) of hydrochloric acid. HCl was chosen on the premise that the maximum adsorption was observed at pH 5 and, hence, lower pH should help desorption. The results are shown in Fig. 11. The results showed that desorption of metal ions increased with the increase in HCl concentration from 0.05 to 0.2 M, and then become almost stable. Desorption of Cu(II) by HCl can be attributed to the disruption of coordination with copper ions. Hence, recovery of metal ions and reusability of adsorbent is feasible with the application of SSBP of treatment of industrial effluents.

Table 6
Comparison of maximum adsorption capacities (Q_{max}) of Cu(II) with various biosorbents

Biosorbent	Q_{max} (mg g^{-1})	Refs.
Wheat straw	5.0	[33]
Coconut shell	19.88	[34]
Carrot residues	32.74	[35]
Peanut shell	25.4	[36]
Pinus silvestris biomass	28.83	[37]
Citric acid modified barley straw	31.71	[38]
Banana peel	8.24	[39]
Sugar beet pulp	28.5	[5]
SSBP	37.09	This study

5. Conclusion

The ability of *S. saponaria* to adsorb Cu(II) were studied by batch experiments. FT-IR spectra showed that the functional groups included carbonyl and carboxyl groups involved in the Cu(II) sorption process. SEM analysis shows that SSBP has a porous structure. The experimental parameters like pH of the solution, biomass dosage, contact time, initial metal ion concentration and temperature influenced the biosorption efficiency of Cu(II) onto SSBP. Adsorption equilibrium was better described by the Langmuir isotherm model than other isotherm models. Maximum adsorption capacity of SSBP on removal of Cu(II) was found to be 37.09 mg g^{-1} at 313 K. The sorption kinetics of Cu(II) could be explained by pseudo-second-order kinetic model with best correlation coefficient. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of Cu(II) onto SSBP was spontaneous and endothermic. The investigations showed that *S. saponaria* bark is an effective and economical biosorbent for the removal of Cu(II) from aqueous solutions.

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