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Biosorption of bovine serum albumin by *Ulva lactuca* biomass from industrial wastewater: Equilibrium, kinetic and thermodynamic study

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ABSTRACT

Batch biosorption experiments have been carried out for the removal of bovine serum albumin (BSA) from simulated industrial wastewater onto *Ulva lactuca* seaweed. Various vital parameters influencing the biosorption process such as initial concentration of BSA, pH of the solution, adsorbent dosage and temperature have been determined. The biosorption kinetics follows a pseudo-second order kinetic model. Equilibrium isotherm studies demonstrate that the biosorption followed the Freundlich isotherm model, which implies a heterogeneous sorption phenomenon. Various thermodynamic parameters such as changes in enthalpy, free energy and entropy have been calculated. The positive value of ΔH° and the negative value of ΔG° show that the sorption process is endothermic and spontaneous. The positive value of change in entropy ΔS° shows increased randomness at the solid–liquid interface during the biosorption of BSA onto *U. lactuca* seaweed.

1. Introduction

The meat processing industry that manufactures sausages, small goods and other meat-based products produces a large volume of wastewater owing to the continuous rinsing of the meat as it is processed and packaged. A part of this becomes wastewater with a high biological and chemical oxygen demand [1,2]. The remaining part contains only low levels of dissolved organic macromolecules commonly known as slightly contaminated wastewater, which is comprised of proteins, polysaccharides, amino sugars, nucleic acid, humic and fulvic acids, and cell components. Proteins are the major components of all other contaminants in meat processing wastewater [2,3]. A highly efficient primary treatment method to remove such dissolved organic contaminants is needed to reuse and recycle wastewater in the meat industry.

Most of the advanced wastewater treatment plants employ the reverse osmosis (RO) membrane process to remove these low levels of dissolved organic macromolecules. However, these pollutants have the potential to contribute significantly to organic fouling and the cost of treatment is quite expensive [4]. Hence, in general, physio-chemical methods and aerobic processes have been used for the treatment of dilute wastewater from the meat processing industry [2,3]. These strategies aim to reduce the use of critical chemicals and thus their introduction into the environment. Further, they treat existing contamination using more efficient and cost effective methods. The latter case includes both the contaminant and the remediation of contaminated sites, as well as the treatment of wastewater and raw waters for human consumption. Cost effective treatment poses a challenge for the EPA and others in the development of effective risk management strategies. The EPA supports research that addresses new treatment approaches that are more effective in reducing contaminant levels and more cost effective than the currently available techniques.

In recent decades, use of natural materials as biosorbents for the treatment of wastewater containing organic contaminants have been investigated [5]. These natural biosorbents have many advantages such as low cost, abundant availability and biodegradability hence they can be disposed of safely [6]. The present work investigates the application of green seaweed, *Ulva lactuca*, as a biosorbent for the removal of bovine serum albumin (BSA). BSA has been selected to represent proteins in effluent organic matter. Not a great deal of work has been carried out on the removal of BSA using low cost biosorbents, especially seaweeds. The equilibrium, kinetic and thermodynamic studies have also been carried out to investigate the effects of various process parameters.

2. Methods

2.1. Materials

U. lactuca samples were procured from the Central Salt and Marine Chemicals Research Institute, Mandapam Camp, Ramnad

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District, India. The seaweed was rinsed thoroughly with distilled water in order to remove any adhering debris. The seaweed was oven dried at 60 °C for 24 h, then subsequently grounded and sieved to a particle size of 500 μm. The moisture content of the dried seaweed was 4 ± 1% (w/w). BSA was procured from Sigma–Aldrich, Sydney, Australia. BSA concentration was measured using the modified Bradford dye-binding assay [7]. Interference from the components of seaweed was taken into account by using the same quantity of seaweed without BSA as a blank. All other chemicals used were of analytical grade, unless otherwise specified.

2.2. Protonation of U. lactuca

The air-dried seaweed was protonated with 0.1 N sulphuric acid before contacting it with the BSA containing solution [8]. The pretreatment aided in stabilizing the seaweed and retaining the reactive sites intact. This treatment also ensured that any remaining salts such as calcium, magnesium, sodium and potassium were removed from the seaweed surface. The acid treatment was carried out for 6 h to ensure that equilibrium had been reached. The acid treated/protonated seaweed was then washed with double distilled water until a constant conductance was obtained for the filtrate. Finally, the washed materials were air-dried at 60 °C for 24 h, stored at room temperature in an airtight pack and used for further BSA removal experiments.

2.3. Characterization of the U. lactuca

The acidic and ion exchange properties of the *U. lactuca* were determined in order to study the nature and capacity of the biosorbent. The potentiometric titrations of the green seaweed were performed with 1 mM NaCl as background electrolyte. The pH of the seaweed suspension was adjusted to ca. 2.00 with the known amount of 0.1 M HCl. The suspension was then titrated with standard 0.1 M NaOH solution. The pH of the suspension was measured after each addition of NaOH using a HQ-4d digital pH meter (Hach, Germany). After each addition of NaOH, the suspension was allowed to equilibrate until a stable reading was obtained. The number of carboxyl groups per gram of seaweed $[COOH]_{total}$ (mmol g^{-1}) was calculated by an estimation of the position of inflection point (V_{eq}) in the resulting titration curve, using the following equation:

$$[COOH]_{total} = \frac{V_{eq}[NaOH]}{s} \quad (1)$$

The FT-IR spectrum of protonated *U. lactuca* was obtained using the KBr disk technique. The dried seaweed was ground in a mortar along with excess KBr (spectroscopic grade). The disks were pressed in a hydraulic KBr press. The transmission FT-IR spectra were then recorded between 400 and 4000 cm^{-1} using a Shimadzu 8400S FT-IR system.

2.4. Biosorption experiments

Experiments were carried out in order to optimize various vital parameters for the enhanced removal of BSA by *U. lactuca*. The effect of the initial pH of the solution was obtained by agitating 3 g L^{-1} of protonated *U. lactuca* in a series of bottles containing 50 mL of BSA solution of initial concentration 10 mg L^{-1} at different initial solution pH ranging from 3.0, 4.5 and 7.0. The pH of the BSA solution was adjusted using 0.1 M H_2SO_4 and 0.1 M NaOH employing an HQ-4d digital pH meter (Hach, Germany). The effect of the adsorbent dosage on the equilibrium removal capacity was estimated by agitating the BSA solution of initial concentration 10 mg L^{-1} with weighed amounts of protonated seaweed ranging from 3, 5 and 7 g L^{-1}. The effect of the initial concentration of BSA on equilibrium uptake was estimated by contacting 3 g L^{-1} of seaweed with 50 mL of BSA solution of different initial concentration ranging from 5, 10, 30 and 40 mg L^{-1}. The effect of temperature on the removal of BSA was determined by conducting experiments at various initial temperatures (20, 25 and 35 °C) at a constant pH of 4.5. For these experiments, 3 g L^{-1} of seaweed with 10 mg L^{-1} of BSA solutions was employed.

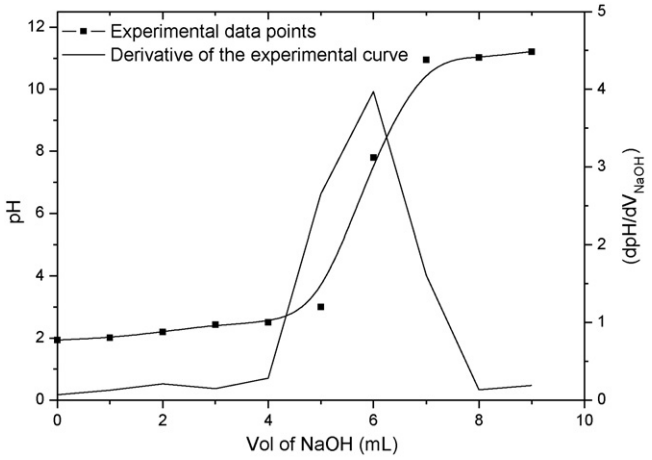

Fig. 1. Acid–base potentiometric titration of the acid-treated *Ulva lactuca* (UL) sample.

Biosorption kinetics and equilibrium experiments were carried out by agitating 50 mL of solution having known initial BSA concentrations, different seaweed dosage and temperature. All experiments were carried out in a Remi rotary mechanical shaker with a constant speed of 150 rpm. Samples pipetted out at different time intervals were analyzed for supernatant BSA concentration using Carry 100-Bio UV–Vis Spectrophotometer (Varian, Australia). The amount of BSA adsorbed onto *U. lactuca* at equilibrium was calculated using the following equation:

$$q_e = \left(\frac{C_0 - C_e}{S}\right) \times V \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of BSA (mg L^{-1}), respectively, q_e is equilibrium BSA concentration on *U. lactuca* (mg g^{-1}), V is the volume of the BSA solution (L) and S is the mass of *U. lactuca* used (g). Biosorption experiments were carried out in triplicate unless otherwise specified.

3. Results and discussion

3.1. Characterization of U. lactuca

Knowledge on chemical composition of the algal cell wall would help to elucidate the BSA binding mechanism of *U. lactuca* seaweed. Several researchers have employed potentiometric titration as a tool to determine the type and number of binding sites available on the adsorbent surface [9]. The potentiometric titration data of *U. lactuca* and the with first derivative plot are presented in Fig. 1. The total organic acidity ($[COOH]_{total}$) has been calculated as 2.07 mmol g^{-1}.

FT-IR offers excellent information on the nature of bonds present on the surface of *U. lactuca* seaweed. The FT-IR spectrum (Fig. 2) of protonated *U. lactuca* in range of 400–4000 cm^{-1} has been taken in order to obtain information on the nature of the cell wall. Several intense characteristics bands in IR spectra can be attributed to functional groups present in protonated *U. lactuca*. FT-IR spectrum of protonated seaweed exhibits broad absorption bands around 3300–3500, indicating the presence of –OH stretching vibrations. Other peaks around 2923.88 (carboxylic acid –OH stretch), 2372.22

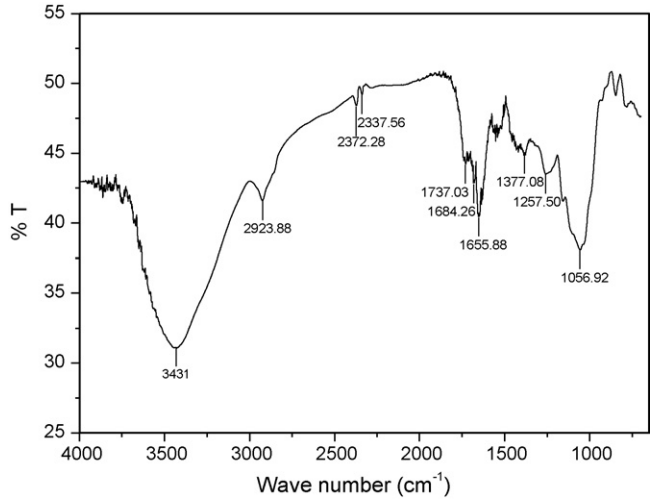

Fig. 2. FT-IR spectrum of protonated *Ulva lactuca* (UL) sample.

(CO–NH), 1655.88 (CO stretch), 1257.50 (C–O and C–N stretch), 1377.08 and 1056.92 cm^{-1} (O–C stretch) have also been observed [10].

3.2. Effect of pH

Biosorption of BSA on protonated *U. lactuca* has been significantly influenced by the pH of experimental solution. Experiments have been carried out by varying the pH of the BSA solution and the results are shown in Fig. 3. It could be observed that BSA biosorption capacity of *U. lactuca* is low at a pH of 3.0 ± 0.1 (40.30%). A maximum biosorption of 72.53% has been obtained for *U. lactuca* at a pH of around 4.3 ± 0.1. With a further increase in pH to about 7.0 ± 0.1, BSA biosorption decreases to about 45.16%. Thus, the optimum pH for removal of BSA has been determined to be 4.3 ± 0.1. The iso-electric points of both *U. lactuca* and BSA need to be taken into consideration in order to determine the removal of BSA by seaweed relative to pH. The reported iso-electric point of *U. lactuca* is around 3.8 ± 0.2 and that of BSA is around 4.7 ± 0.1 [11,12]. The decreased biosorption of BSA at low pH (3.0 ± 0.1) could be attributed to the fact that both BSA and seaweed will be positively charged because the pH is well below the iso-electric point of both the materials. Thus, there would be competition of the binding sites for H^+ ions whereby BSA cannot become easily bound to the sites of seaweed.

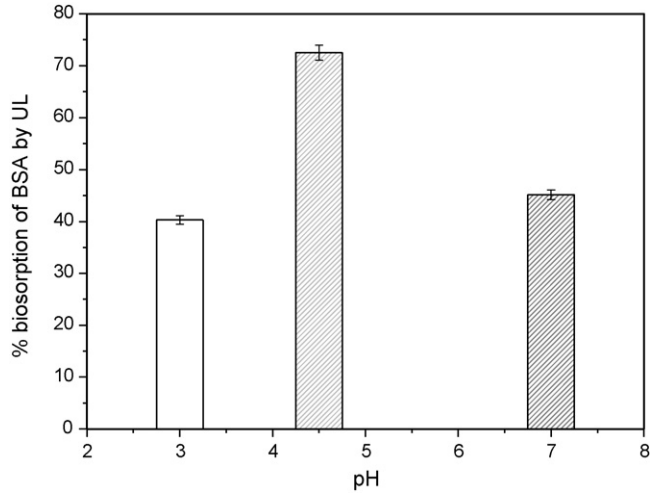

Fig. 3. Effect of pH on BSA biosorption by *Ulva lactuca* (UL) sample.

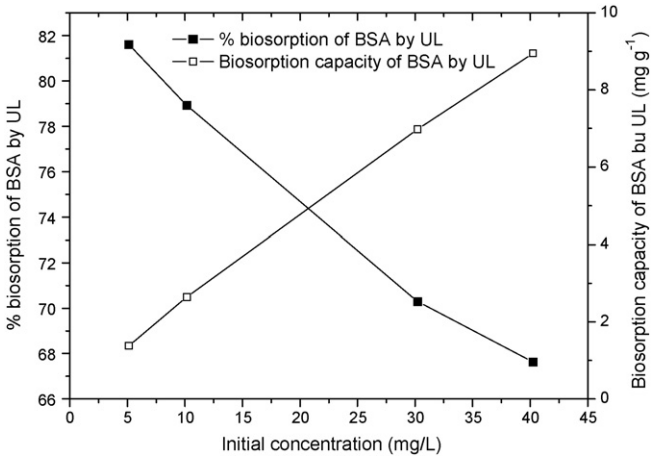

Fig. 4. Effect of initial concentration of BSA on the % biosorption and biosorption capacity of *Ulva lactuca* (UL) sample.

The reason for the increased biosorption of BSA at pH 4.3 ± 0.1 could be attributed to the carboxyl groups in the seaweed, which attain its iso-electric point [13,14], in turn resulting in increased biosorption of BSA. At higher pH (7.0 ± 0.1), both BSA and the seaweed will be negatively charged because the pH is above the iso-electric point of both the materials. Hence, the biosorption of BSA by *U. lactuca* could be qualitatively shown to be an ion exchange process between BSA and the reactive groups present in the seaweed. Thus, for further experiments, the pH range of 4.3 ± 0.2 was chosen.

3.3. Effect of initial BSA concentration

Initial concentration of sorbate in solution provides an important driving force to overcome all resistances between aqueous and solid phases, thus increasing biosorption. In addition, increasing the initial concentration of BSA causes increased collisions between BSA and seaweed, thus enhancing the biosorption process. Fig. 4 shows plots of the percentage biosorption and maximum biosorption capacity of seaweed for BSA at different initial BSA concentrations. From the figure, it could be observed that the BSA biosorption capacity (q_e) of seaweed increased from 1.38 to 8.95 mg g^{-1} as the initial BSA concentration increased from 5 to 40 mg L^{-1}. Thus, the effect of the initial BSA concentration on the biosorption capacity has been found to be of considerable significance.

3.4. Effect of seaweed dosage

Fig. 5 shows a plot of the percentage of BSA removal *versus* time at various seaweed dosages. From the figure, it is observed that removal efficiency increases from 72.88%, 78.34% to 81.98% with increase in seaweed dosage from 3, 5 and 7 g L^{-1}, respectively. This can be attributed to the fact that with increase in seaweed dosage, there is an increase in effective binding sites available for biosorption, which in turn results in the increased removal of BSA. At a higher seaweed dosage, there is a very fast adsorption onto the adsorbent surface that leads to improved biosorption of BSA. In addition, it could be observed from the figure that for a given initial BSA concentration, the rate of biosorption is fast within the first 60 min and thereafter the biosorption rate tends to decrease and reaches an equilibrium. The initial rapid phase of biosorption may be due to the increased number of vacant sites available at the initial stage. As a result, there exist an increased concentration gradient between adsorbate in solution and adsorbate on the adsorbent surface. As time precedes this concentration gradient is reduced due

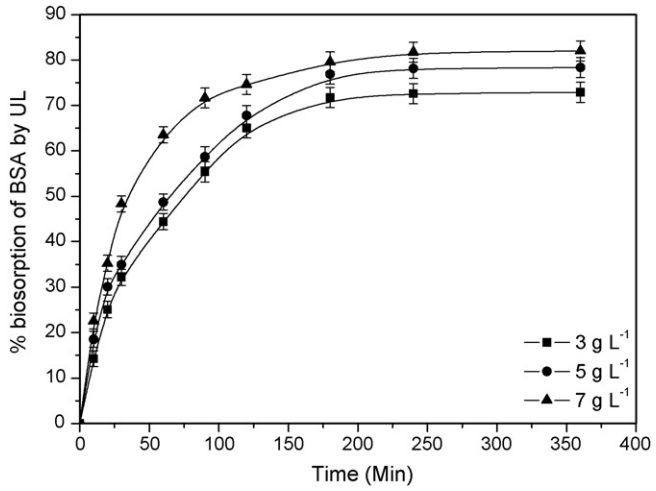

Fig. 5. Effect of adsorbent dosage on the % biosorption of BSA by *Ulva lactuca* (UL) sample.

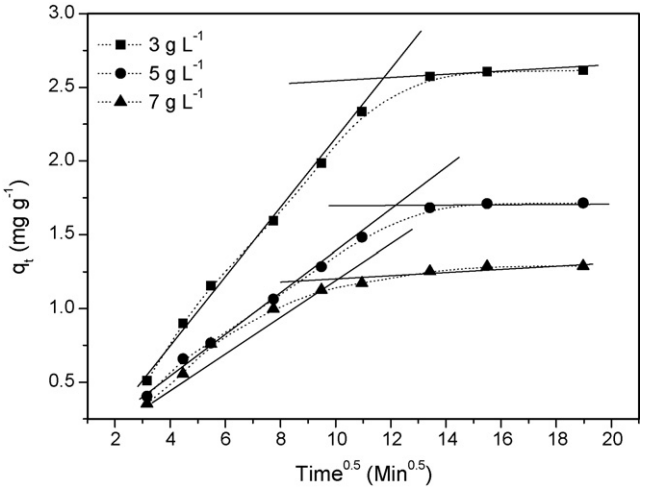

Fig. 7. Intraparticle diffusion analysis of biosorption of BSA by *Ulva lactuca* (UL) sample.

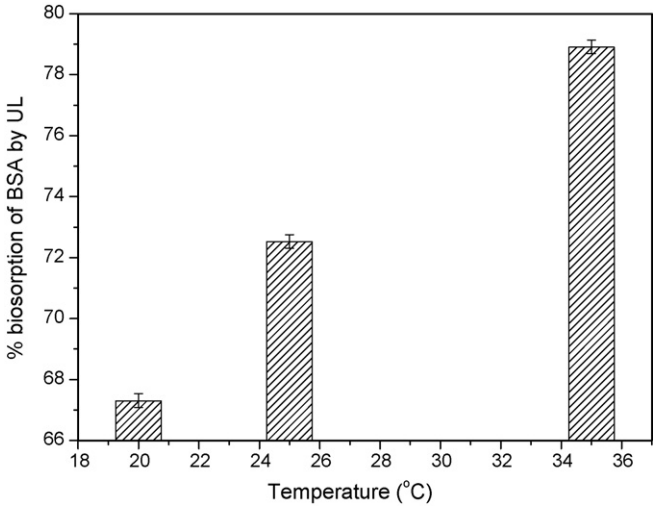

Fig. 6. Effect of temperature on the % biosorption of BSA by *Ulva lactuca* (UL) sample.

to the accumulation of BSA on to vacant sites, leading to a decrease in the sorption rate at later stages.

3.5. Effect of temperature

The effect of temperature on the biosorption capacity of *U. lactuca* has been studied at 20, 25 and 35 °C and the results are shown in Fig. 6. Results show that the percentage of biosorption of BSA increased from 67.31%, 72.53% to 78.91% with an increase in temperature from 20, 25 to 35 °C for an initial concentration of 10 mg L^{-1} of BSA and 3 g L^{-1} of *U. lactuca*. The biosorption of BSA increased with the increasing temperature, suggesting that biosorption between *U. lactuca* and BSA is an endothermic process and the dominant mechanism could be chemisorption.

3.6. Kinetics of the adsorption process

Several kinetic models are available to understand the behavior of biosorbent and also to examine the controlling mechanism of the biosorption process and to test the experimental data. In order to understand the biosorption kinetics, two popularly used kinetic models, viz. pseudo-first order and pseudo-second order kinetic models have been employed [15,16]. The values of q experimentally determined ($q_{e(exp)}$) and calculated ($q_{e(cal)}$). The correlation coefficient (R^2) along with the kinetic rate constants k_1 and k_2 are shown in Table 1. It could be observed from Table 1 that the average R^2 value of pseudo-first order kinetic model (0.986) is lower than that of the pseudo-second order kinetic model (0.997). This clearly indicates that the kinetics of BSA biosorption by *U. lactuca* biomass are better described by pseudo-second order kinetic model. The linearity of the plots (figures not shown) also shows applicability of pseudo-second order kinetic model. The reaction rate constants increase with the increase in the biosorbent dosage. The k_2 values increased from 0.0071 to 0.0279 g mg^{-1} min^{-1} as the seaweed dosage increased. This shows that the rate of biosorption of BSA increased with the increase in the quantity of biosorbent.

The intraparticle diffusion coefficient for biosorption of BSA by *U. lactuca* has been calculated from slope of the plot of the square root of time ($min^{1/2}$) *versus* the amount of BSA biosorbed (mg g^{-1}) (Fig. 7) [17]. From the figure, it is clear that at all biosorbent dosages, the biosorption process follows two phases. It has also been observed that an initial linear portion ended with a smooth curve followed by a second linear portion. The two phases in the intraparticle diffusion plot suggest that the biosorption process proceeds by both surface biosorption and intraparticle diffusion [18]. The initial curved portion of the plot indicates surface biosorption while the second linear portion is due to intraparticle or pore diffusion. Similar results were found for acid dye adsorption on activated palm ash and for Cd adsorption on activated carbon, respectively [19,20].

Table 1
Pseudo-first order and pseudo-second order kinetic parameters for biosorption of BSA by *Ulva lactuca* (UL) sample.

Quantity of biosorbent (g L^{-1})	Pseudo-first order rate constants			Pseudo-second order rate constants		
	k_1 (min^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e(cal)}$ (mg g^{-1})	R^2
3	0.0227	3.234	0.991	0.0071	3.0381	0.995
5	0.0223	2.056	0.979	0.0123	1.9548	0.996
7	0.0201	1.070	0.99	0.0279	1.4028	0.999

Table 2
Freundlich, Langmuir and Temkin isotherm constants for biosorption of BSA by *Ulva lactuca* (UL) sample.

Temp. (°C)	Freundlich constants				Langmuir constants				Tempkin constants			
	k_f	n	R^2	$\Delta G\%$	q_0 (mg g^{-1})	b (L mg^{-1})	R^2	$\Delta G\%$	K_T	f	R^2	$\Delta G\%$
20	1.1	1.306	0.993	7.05	15.873	0.05391	0.957	9.35	2.681	1.107	0.975	13.85
25	1.178	1.325	0.997	5.74	18.0245	0.06281	0.939	10.51	2.914	1.133	0.959	12.92
35	1.477	1.414	0.999	3.65	15.6226	0.09729	0.986	5.00	2.871	1.448	0.973	9.99

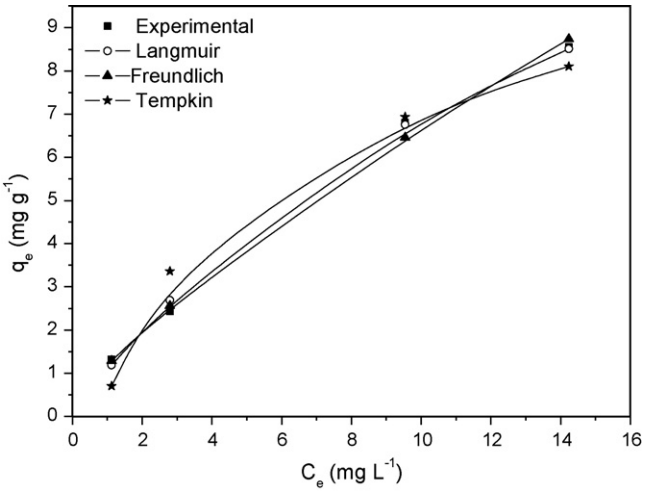

Fig. 8. Comparison of experimental and model fits of Langmuir, Freundlich and Temkin isotherms for the biosorption of BSA by *Ulva lactuca* (UL) sample.

3.7. Equilibrium adsorption studies

Adsorption isotherm equations depict the relation between the amount and concentration of BSA in the solution and the amount of BSA adsorbed onto the *U. lactuca* seaweed when the two phases are in equilibrium, at a given temperature and pressure. In the present work, out of several isotherm equations, three isotherms, namely Freundlich, Langmuir and Temkin adsorption isotherms, have been tested for the validity of the BSA biosorption [21–23].

The Freundlich, Langmuir and Temkin isotherm constants were evaluated at different initial temperatures along with the R^2 values and the results are presented in Table 2. In view of the values of linear regression coefficients in the table, the Freundlich model exhibited a better fit to the adsorption data of BSA than the Langmuir and Temkin isotherm models in the studied concentration range. The predicted Freundlich, Langmuir and Temkin isotherm equations at 25 ± 1 °C for BSA removal onto *U. lactuca* are given in following equations:

$$q_{eF} = 1.178C_e^{0.755} \quad (3)$$

$$q_{eL} = \frac{1.132C_e}{1 + 0.063C_e} \quad (4)$$

$$q_{eT} = 2.914 \ln C_e + 0.3629 \quad (5)$$

Fig. 8 shows the Freundlich, Langmuir, and Temkin isotherm plot for the biosorption of BSA by *U. lactuca* generated using Eqs. (3)–(5). From the figure, it could be observed that the equilibrium data are well represented by Freundlich isotherm equation.

However, both Langmuir and Temkin isotherm models seem to agree well with the experimental data of BSA considering that the average R^2 values are greater than 0.95. Thus, the applicability of Freundlich isotherm has further been substantiated through normalized standard deviation [24,25]. A normalized standard deviation Δq is defined as:

$$\Delta q \ (\%) = 100\sqrt{\frac{\sum_{i=1}^{N}[((q_{exp} - q_{cal})/q_{exp})^{\overleftarrow{2}}]_i}{N-1}} \quad (6)$$

where q_{exp} and q_{cal} are the experimental and calculated q_e values, respectively, and N is the number of data points. The calculated Δq values for Freundlich, Langmuir, and Temkin isotherm at various initial temperatures are shown in Table 2. It could be observed from the table that the Δq values were low for Freundlich isotherm, confirming that the biosorption of BSA by *U. lactuca* followed Freundlich isotherm equation.

The value of the Freundlich constant in particular, "n", which is related to the distribution of sorbate on the sorbent surface, is greater than unity, indicating that BSA is favorably biosorbed under the examined experimental conditions. The value of "n" between 1 and 10 also represents beneficial adsorption [26]. Based on the observed adsorption intensity values ($n > 1$), it can be said that the *U. lactuca* has identical biosorption energy in all sites and BSA interacts only with the active site, but not with other sites. It can be said that as the n value is greater than 1, chemical rather than physical sorption seems to be dominant [26].

3.8. Thermodynamic parameters

The thermodynamic parameters such as changes in standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), have been determined using the following equations [27,28]:

$$k_d = \frac{C_a}{C_e} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

$$\ln K_d = \frac{\Delta S}{R_u} - \frac{\Delta H}{R_u T} \quad (9)$$

where K_d is the distribution coefficient for the adsorption, C_a is the amount of BSA biosorbed onto *U. lactuca* per volume of solution at equilibrium (mg L^{-1}), and C_e is the equilibrium concentration (mg L^{-1}) of the BSA in solution. T is the solution temperature (K) and R_u is the universal gas constant (8.315 J mol^{-1} K^{-1}). ΔH and ΔS are calculated from the slope and intercept of van't Hoff plots of ln K_d *versus* 1/T (Eq. (9)). The results are listed in Table 3. The change in free energy for adsorption of BSA onto *U. lactuca* is −62.29 kJ mol^{-1} at 30 °C, with an initial concentration of 10 mg L^{-1}. Generally, absolute magnitude of change in free energy for physisorption is

Table 3
Thermodynamic parameters for biosorption of BSA by *Ulva lactuca* (UL) sample.

BSA conc.	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1})		
			293 K	298 K	308 K
10	30.247	0.109	62.292	62.839	63.933

between −20 and 0 kJ mol^{-1} and chemisorption has a range of −80 to −400 kJ mol^{-1} [29]. Hence, this process can be considered more related to chemisorption. The negative values of ΔG indicate that the biosorption of BSA onto *U. lactuca* is spontaneous. It can also be noted that the change in free energy decreases with the increase in temperature. The positive values of change in enthalpy (ΔH) and change in entropy (ΔS) shows that the adsorption is endothermic in nature and reflects the increased randomness at the solid/solution interface during the biosorption of BSA onto *U. lactuca*, respectively [30].

4. Conclusion and recommendation

This study proves the efficiency of *U. lactuca* as a potential biosorbent for the removal of BSA from aqueous solutions. However, the disposal of BSA-loaded seaweed poses a solid waste disposal challenge. Thus, solution to the problem disposal of BSA-loaded seaweed is essential. BSA and seaweed, being organic materials, can be efficiently used as a reducing agent in the manufacture of a tanning salt [31] that can be used in the meat processing industry. Moreover, the BSA-loaded seaweed can be utilized for the preparation of biochar, which has been attracting interest due to its potential in carbon sequestration and in improving soil health.

Acknowledgements

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