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Biosorption of Alizarin Red dye onto immobilized biomass of *Canna indica:* isotherm, kinetics, and thermodynamic studies

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ABSTRACT

In this study, immobilized *Canna indica* beads were utilized as an effective adsorbent for the removal of alizarin red dye from the aqueous solution. The characterization study for the immobilized *Canna indica* beads was performed using Fourier transform infrared and scanning electron microscopy analysis. In batch adsorption study, different factor influencing parameters such as initial alizarin red dye concentration, solution pH, biosorbent dosage, contact time, and the temperature was studied. It was found that optimum biosorption was at the contact time of 35 min, solution pH at 2.0, biosorbent dosage 3.0 g L^{-1}, and a temperature of 30°C. The experimental results of initial alizarin red dye concentration and contact time data were fitted with different isotherm and kinetic model, respectively. The adsorption process was fitted with Langmuir isotherm model and pseudo-first-order kinetic model. The maximum monolayer adsorption capacity for the newly synthesized biosorbent was found to be 21.69 mg g^{-1}. Thermodynamic investigations reported that negative values, of enthalpy and Gibbs free energy, showing the unconstrained and exothermic nature of adsorption. The results showed immobilized *Canna indica* beads has good adsorption capacity for the removal of alizarin red dye from the synthetic solution.

Keywords: Biosorption; *Canna indica*; Immobilized beads; Alizarin Red; Isotherm; Kinetics

1. Introduction

Rapid urbanization, industrialization, and human anthropogenic activities are the major sources for the environmental pollution throughout the world [1,2]. Synthetic dyes are one of the most important pollutants which have been disposed from different industries such as paint, leather, textile, paper, and rubber, plastic, cosmetic and food industries [3–6]. Synthetic dyes are aromatic water soluble organic colorants and they can cause different harmful effects due to direct discharge into the water streams [7,8]. Among the different dyes, Alizarin Red-S is one of the most toxic dyes which are commonly used as coloring agents in various industries such as textile, paper, cosmetic, and other industries. Alizarin Red-S are highly toxic, water-soluble, and difficult to degrade which causes different health effects to humans such as eye and skin irritation, respiratory system disorders, skin inflammation, systemic injury in blood, airway diseases, emphysema or chronic bronchitis, pneumoconiosis, gastritis, severe headache, and methemoglobinemia [9–14]. Hence, it becomes mandatory that the alizarin red dye contained effluents are subjected to the treatment process before letting them into aqueous environments to reduce the environmental impact.

Different conventional physicochemical techniques have been used for the removal of dyes from various industrial effluents [15–19]. The techniques are chemical precipitation, electrocoagulation, electrochemical treatments

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(electrodialysis, electrochemical precipitation, electrochemical oxidation, and membrane electrolysis), flotation, flocculation, photocatalysis, ion exchange, membrane separation, microfiltration, nanofiltration, ultrafiltration, reverse osmosis, gravimetric method, ozonation, advanced oxidation process, and adsorption [20–28]. However, all the aforementioned strategies are not very effective due to them suffering from various negative aspects such as operational cost, lower efficiency at a lower concentration of dyes and also restricted due to attaining unsatisfactory results which are beyond the permissible limits prescribed by the Environmental Protection Agency [29–32]. Considering all these aspects, many researchers shifted their attention toward adsorption techniques. Biosorption is the most promising technique for the removal of dyes from the industrial effluents due to its unique characteristics such as simple operation, low-cost technique, requires low energy for the removal of dyes, versatility, environment sustainability, no slime formation, and high removal capacity compared with other techniques [33–35].

Different adsorbent materials have been utilized as adsorbents for the removal of dyes from the industrial effluent. The biosorbent material mostly prepared by using the waste material such as agricultural wastes, microorganisms (bacterial and fungal biomass) [36,37]. Generally, waste biomass has been utilized as a biosorbent, furthermore, for the most part, comprises of different important functional groups such as aldehydes, ketones, hydroxyl, alcohol, carboxylic, amine, and ether. This functional group plays an essential role in authoritative the toxic dyes toward the surface of the biosorbents. Though these waste materials in freely suspended state they might cause operational difficulties. To overcome this plagued problem the same material can be used as adsorbent material but not in a freely suspended state, they can be immobilized with different immobilizing agents. By this method, the efficiency of the removal will be increased, and it provides few more advantages such as effective regeneration and reusability of biosorbent material, easier in case of solid–liquid separation process and it causes minimal clogging problem in the continuous flow system [38–40].

In this research, the biosorbent material was prepared using the root tubers of the *Canna indica*. The immobilized *Canna indica* beads were prepared by using sodium alginate and calcium chloride. The characterization of immobilized *Canna indica* root tubers for the adsorption capabilities was done by the following analysis methods Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis. The synthetic dye solution was prepared by using Alizarin red-S in different concentration and the optimum values of each parameter including initial Alizarin red-S concentration, temperature, pH, immobilized biosorbent dosage, and contact time was examined by batch adsorption studies. Equilibrium study of Alizarin red-S dye using immobilized *Canna indica* roots was examined by different adsorption isotherms such as Langmuir, Freundlich, Toth, and Baudu isotherm models. The biosorption rate of the Alizarin red-S dye removal from the aqueous solution was examined by using various kinetic models, pseudo-first-order kinetics, pseudo-second-order kinetics, and Elovich kinetic models and the nature of the adsorption process by using the immobilized *Canna indica* roots was determined by the thermodynamic study via calculating the thermodynamic parameters such as change in standard entropy ($\Delta S°$), enthalpy ($\Delta H°$), and Gibbs free energy ($\Delta G°$).

2. Materials and methods

2.1. Preparation of Alizarin red aqueous solution

Alizarin red is a red-colored anionic dye having the molecular formula of $C_{14}H_8O_4$ and the molecular weight of 240.21 g mol^{-1}. The stock solution of alizarin red (1,000 mg L^{-1}) was prepared by dissolving the required amount of alizarin red dye in the double-distilled water. The required concentrations of working solution from 25 to 150 mg L^{-1} for the batch adsorption study were prepared by dissolving the required amount of stock solution in double-distilled water. The required pH value of the working solutions was adjusted using 0.1 N of HCl and 0.1 M NaOH. All the chemicals required for this study including HCl and NaOH were purchase from HiMedia Laboratories Pvt. Ltd., Mumbai, India.

2.2. Adsorbent preparation

In this study, the immobilized root tuber of *Canna indica* beads used as adsorbent material for the removal of alizarin red from the aqueous solution. For the preparation of immobilized beads, the required *Canna indica* plant saplings were collected from the Kaivalya Garden Center, Anna Nagar, Chennai, Tamilnadu, India. *Canna indica* is the commonly used plant for the treatment of industrial wastewater. The root tubers of the *Canna indica* were separated and dried in the hot air oven at 80°C for 3 h. The dried root tubers were powdered using mortar and pestle and it was stored in the container for future use. The powder was mixed with 2% sodium alginate solution and stirred well for the complete mixing. The immobilized *Canna indica* root tuber beads were prepared with the required 2–3 mm size by slowly injecting the sodium alginate mixture into the 2% (w/v) of calcium chloride solution. The immobilized *Canna indica* root tuber beads were prepared based on the required adsorbent dosage from 0.5% to 4.0%. The mechanical stability of the immobilized *Canna indica* beads were enhanced by curing them in the 2% calcium chloride solution for 4 h. After curing the beads were filtered from the calcium chloride solution using Whatman 42 filter paper, rinsed and washed with double distilled water until the pH of the washing effluent is 7.0. Finally, the prepared beads were used for the characterization and adsorption studies.

2.3. Adsorbent characterization

The characterization study of newly synthesized immobilized *Canna indica* beads was carried out by FTIR and SEM analyses. Then FTIR analysis can be used to identify the presence of different functional groups on the surface of adsorbent material. The surface morphology characteristics of the immobilized beads before and after adsorption were analyzed by SEM analysis.

2.4. Batch adsorption experiment

Batch adsorption experiment was carried out in 250 mL Erlenmeyer flask contains 100 mL of the working solution of alizarin red dye. Batch adsorption experiments were conducted for different adsorption influencing parameters such as temperature, solution pH, initial alizarin red dye concentration, and contact time and biosorbent dosage. For each parameter study, the batch adsorption experiments were carried out by varying the respective parameter and keeping other parameters as constant. The various experimental conditions for the batch adsorption studies are as follows: initial alizarin red dye concentration: 25–150 mg L^{-1}, biosorbent dosage: 0.5–4.0%, solution pH: 2–8, temperature: 30°C–60°C, and contact time: 5–50 min. The prepared immobilized beads were added into the 100 mL of working solution and the mixture was agitated in shaking incubator at 80 rpm. After the mentioned time interval, the supernatant was separated by using Whatman 42 filter paper and the percentage removal of the alizarin red dye from the aqueous solution was calculated by determining the absorbance at the wavelength of 420 nm using a double beam UV-visible spectrophotometer. The percentage removal of alizarin red dye from the aqueous solution was estimated by using the following formula:

$$\%\text{Removal} = \frac{C_0 - C_e}{C_e} \times 100 \tag{1}$$

where C_0 is the initial concentration of alizarin red dye and C_e is the final equilibrium concentration of alizarin red dye.

2.5. Adsorption equilibrium study

The interaction between the alizarin Red dye and the immobilized *Canna indica* beads was studied by adsorption isotherm study. For the adsorption equilibrium study, batch adsorption experiment was carried at 250 mL Erlenmeyer flask contains different initial alizarin red dye concentrations from 25 to 150 mg L^{-1} (25, 50, 75, 100, 125, and 150 mg L^{-1}). To the 250 mL Erlenmeyer flask, 3% of immobilized *Canna indica* beads was added and the flasks were incubated in the shaking incubator for 35 min at 30°C. After the mentioned time interval, the supernatant were separated by using Whatman 42 filter paper and the absorbance of the supernatants was measured at 420 nm using a double beam UV-visible spectrophotometer. The amount of alizarin red dye adsorbed onto the immobilized *Canna indica* beads at equilibrium condition was calculated by using the following equation:

$$q_e = \frac{C_0 - C_e}{m} V \tag{2}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), V is the volume of alizarin red dye solution (L), and m is the mass of adsorbent (g) used for adsorption of alizarin red dye from the aqueous solution.

The two, three, and four-parameter adsorption isotherm models (Langmuir, Freundlich, Toth, and Baudu) are used to explain the interaction between the immobilized *Canna indica* beads and alizarin red dye. By the non-regression analysis, the isotherm parameters values including maximum monolayer adsorption capacity (mg g^{-1}), errors (sum of squared errors (SSE), root mean squared errors (RMSE)) and the correlation coefficient (R^2) values for the different isotherm models were determined with the help of MATLAB R2016a software. The two, three, and four-parameter adsorption isotherm models are as follows:

2.5.1. Langmuir isotherm

The non-linear equation for the Langmuir adsorption isotherm model is given by [41]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_m is the maximum monolayer adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}).

2.5.2. Freundlich isotherm

The two-parameter Freundlich adsorption isotherm equation is given by [42]:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F is the Freundlich constant ((mg g^{-1}) (L mg^{-1})$^{1/n}$) and n is the Freundlich exponent.

2.5.3. Toth isotherm

The three-parameter Toth adsorption isotherm model is described as follows [43]:

$$q_e = \frac{q_{\mathrm{mT}} C_e}{\left(\frac{1}{K_T} + C_e^{\mathrm{mT}}\right)^{\frac{1}{\mathrm{mT}}}} \tag{5}$$

where q_{mT} is the Toth maximum adsorption capacity (mg g^{-1}), K_T is the Toth equilibrium constant, and mT is the Toth model exponent.

2.5.4. Baudu isotherm

The non-linear adsorption isotherm equation for four-parameters Baudu adsorption isotherm model is given as follows [44]:

$$q_e = \frac{q_m b_0 C_e^{(1+x+y)}}{1 + b_0 C_e^{(1+x)}} \tag{6}$$

where b_0 is the equilibrium constant, x and y are the Baudu parameters, and q_m is the maximum adsorption capacity (mg g^{-1}).

2.6. Adsorption kinetics study

Adsorption kinetic study can be used to elucidate the rate mechanism of the adsorption system for the removal of alizarin red dye from the aqueous solution. Adsorption kinetic experiment was carried out in 250 mL Erlenmeyer flask contains 100 mL of 50 mg L^{-1} of initial alizarin red dye concentration, 3% of immobilized *Canna indica* beads were added and then flasks were incubated in the shaking incubator at 30°C for the different time interval from 5 to 50 min (5, 10, 15, 20, 25, 30, 35, 40, 45, and 50 min). After the predetermined time intervals, the flask was withdrawn from the shaker, and mixtures were filtered using Whatman 42 filter paper. Adsorption of alizarin red dye onto the immobilized *Canna indica* beads was determined by calculating the absorbance at 420 nm using double beam UV-visible spectrophotometer. The equation for the determination of the amount of alizarin red dye onto the immobilized *Canna indica* beads at time interims is given as follows:

$$q_t = \frac{\left(C_0 - C_t\right)V}{m} \tag{7}$$

where q_t is the amount of alizarin red dye onto the immobilized *Canna indica* beads at different time intervals (mg g^{-1}) and C_t is the concentration of alizarin red dye at time t (mg L^{-1}). There are three different adsorption kinetic models (pseudo-first-order, pseudo-second-order, and Elovich kinetic models) were used to explain the adsorption rate and adsorption mechanism of the adsorption system. By using these three adsorption kinetic equations the graph was plotted between time (t) and adsorption capacity (q_e) with the help of MATLAB R2016a software. From the graph, the rate constant (k), error values (SSE and RMSE), and the correlation coefficient (R^2) values for all the kinetic models were determined.

2.6.1. Pseudo-first-order kinetic model

The rate equation for pseudo-first-order equation is given as follows [45]:

$$q_t = q_e\left(1 - \exp\left(-k_1 t\right)\right) \tag{8}$$

where k_1 is the pseudo-first-order rate constant (min^{-1}).

2.6.2. Pseudo-second-order kinetic model

Pseudo-second order equation is given by [46]:

$$q_t = \frac{\left(q_e^2 k_2 t\right)}{\left(1 + q_e k_2 t\right)} \tag{9}$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

2.6.3. Elovich kinetic model

Elovich adsorption kinetic equation is described as follows [47]:

$$q_t = \left(1 + \beta_E\right)\ln\left(1 + \alpha_E \beta_E t\right) \tag{10}$$

where β_E is the desorption rate constant (g mg^{-1}) related to the activation energy of adsorption and α_E is the initial adsorption rate (mg g^{-1} min).

2.7. Thermodynamic study

The thermodynamic nature of the adsorption of alizarin red dye onto the immobilized *Canna indica* beads was studied by the thermodynamic study. For the thermodynamic study, the experiment was conducted at different temperatures from 30°C to 60°C in the 250 mL Erlenmeyer flask contains 100 mL of 50 mg L^{-1} of initial alizarin red dye concentration and 3% of immobilized *Canna indica* beads. The different thermodynamic parameters such as Gibbs free energy ($\Delta G°$, kJ mol^{-1}), change in enthalpy ($\Delta H°$, kJ mol^{-1}), and change in entropy ($\Delta S°$, kJ mol^{-1}) are calculated by using the following equations:

$$K_c = \frac{C_{\text{Ae}}}{C_e} \tag{11}$$

$$\Delta G° = -RT\ln K_c \tag{12}$$

$$\text{Log}K_c = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{13}$$

where K_c is the equilibrium constant, C_{Ae} is the amount of alizarin red dye adsorbed onto the immobilized *Canna indica* beads at equilibrium condition (mg L^{-1}), C_e is the concentration of alizarin red dye solution at equilibrium condition (mg L^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The graph was plotted between $1/T$ and LogK_c and the $\Delta S°$ and $\Delta H°$ values are calculated from the graph as slope and intercept.

3. Results and discussion

3.1. Characterization

The characterization study of newly synthesized immobilized *Canna indica* beads was carried out by FTIR and SEM analyses.

3.1.1. FTIR analysis

FTIR study is used to determine the presence of various functional groups on the surface of the immobilized *Canna indica* beads. The FTIR analysis was done within the range of 400 to 4,000 cm^{-1} and the results for before and after the adsorption process are shown in Figs. 1a and b, respectively. From Fig. 1a, there are four different major peaks were observed at different wavenumbers including 3,338; 1,609; 1,415; and 1,030 cm^{-1}. The broad peak at 3,338 cm^{-1} indicates the presence of hydroxyl group frequencies of the hydroxyl group, H-bonded OH stretch. The absorbance peak at 1,609 cm^{-1} corresponds to the secondary amine

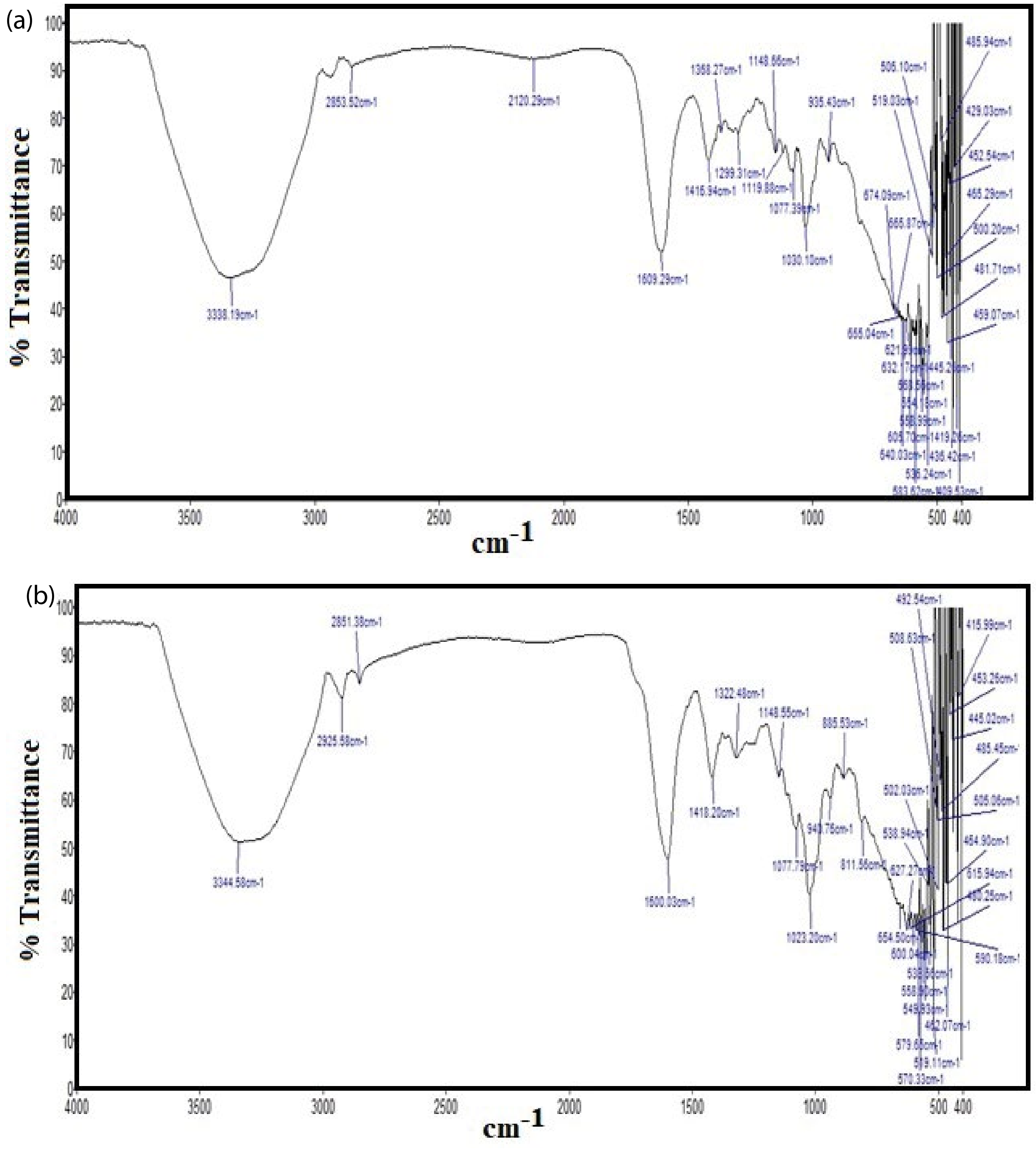

Fig. 1. FTIR image of immobilized *Canna indica* (a) before adsorption and (b) after adsorption.

group (>N–H) of NH bend. The peak in this region is probably due to – OH group and depends on the moisture of the analyzed substance. The narrow peak at 1,415 cm^{-1} specifies the carbonate ion presence and at 1,030 cm^{-1} indicates the primary amine group (N–H) of CN stretch. FTIR spectroscopy results of immobilized *Canna indica* beads before the adsorption process confirmed the presence of necessary functional groups for the removal of alizarin red dye from the aqueous solution. Fig. 1b shows three major peaks at the following wavenumbers: 3,344; 2,925; and 1,023 cm^{-1}. The peaks at 3,344; 2,925; and 1,023 cm^{-1} indicates the presence of hydroxyl group of H-bonded OH stretch, methylene group of C–H asymmetric stretch and organic siloxane or silicone (Si–O–Si), respectively. The functional groups such as hydroxyl and amine group demonstrate the formation of matrix with a cross-linked network. The presence of aliphatic and methylene groups were interacted with alizarin red dye and form the covalent bond and electrostatic interaction between the adsorbent material and alizarin red dye.

3.1.2. SEM analysis

The surface morphology and structure of the adsorbent material (immobilized *Canna indica* beads) were characterized by SEM analysis. Likewise, as the adsorption process is a surface phenomenon, it is for the most part depending on surface characteristics, for example, the quantity of pores present on the surface of the adsorbent material. SEM analysis of the immobilized *Canna indica* beads before and after adsorption process was done at magnification of 6.00 KX (2 μm) and the results are shown in Figs. 2a and b, respectively. SEM results before and after the adsorption process indicate the considerable changes in the immobilized *Canna indica* beads. Fig. 2a shows that present adsorbent material has more number of pores, large cavities, and nonporous solid material with respect to its surface smoothness. It can be seen from Fig. 2b, less number of pores and occupation of the pores by the alizarin red dye in the aqueous solution.

3.2. Batch adsorption experiments

Batch adsorption experiments were conducted to optimize the factor influencing parameters such as solution pH, biosorbent dosage, initial alizarin red dye concentration, contact time, and temperature for the removal of alizarin red dye from aqueous solution onto the immobilized *Canna indica* beads.

3.2.1. Effects of pH

Solution pH is the key factor in the adsorption mechanism. Adsorption of alizarin red dye onto the immobilized *Canna indica* beads was controlled by the factor of solution pH because it determines the alizarin red dye solubility in the aqueous medium. Batch experiment for the determination of optimum pH for the removal of alizarin red dye from the aqueous solution was done at different pH conditions from 2.0 to 8.0 by keeping other parameters including initial alizarin red dye concentration, contact time, biosorbent dosage, and temperature as constant. Effect of solution pH for the removal of alizarin red dye onto the immobilized *Canna indica* beads as shown in Fig. 3. From Fig. 3, it is observed that the percentage removal of alizarin red dye by the immobilized *Canna indica* beads from the aqueous solution was decreased while increasing the solution pH due to alkaline condition of the medium. At the initial pH (pH = 2.0) percentage removal of alizarin red dye from the aqueous solution is high due to anionic nature of the dye and it was attracted by the positively charged ions present on the surface of the adsorbent material. When increasing the solution pH, the surfaces of the immobilized *Canna indica* beads get a negative charge and it does not attract the negatively charged alizarin red dye from the aqueous solution. At higher pH the repulsion takes place between immobilized *Canna indica* beads and alizarin red dye thereby it reduces the adsorption capacity by affecting an electrostatic interaction between immobilized *Canna indica* beads and alizarin red dye. Thus, the removal percentage for alizarin red dye removal from the aqueous solution was decreased while increasing the solution pH.

3.2.2. Effects of adsorbent dosage

Effect of immobilized *Canna indica* beads dosage for the removal of alizarin red dye from the aqueous solution onto immobilized *Canna indica* beads is shown in Fig. 4. The batch adsorption experiment was conducted at a different adsorbent dosage from 0.5% to 4.0% to determine the optimum adsorbent dosage for the removal of alizarin red dye from the aqueous solution. From Fig. 4, it is seen that the percentage removal of alizarin red dye from the aqueous solution was increased while increasing the immobilized *Canna indica* beads dosage. At lower adsorbent dosage the percentage removal of alizarin red dye is lower because at the lower adsorbent dosage availability of active sites on the surface of the immobilized *Canna indica* beads is lower. Percentage removal of alizarin red dye was increased while increasing the adsorbent dosage because the number of active sites was increased for the adsorption of alizarin

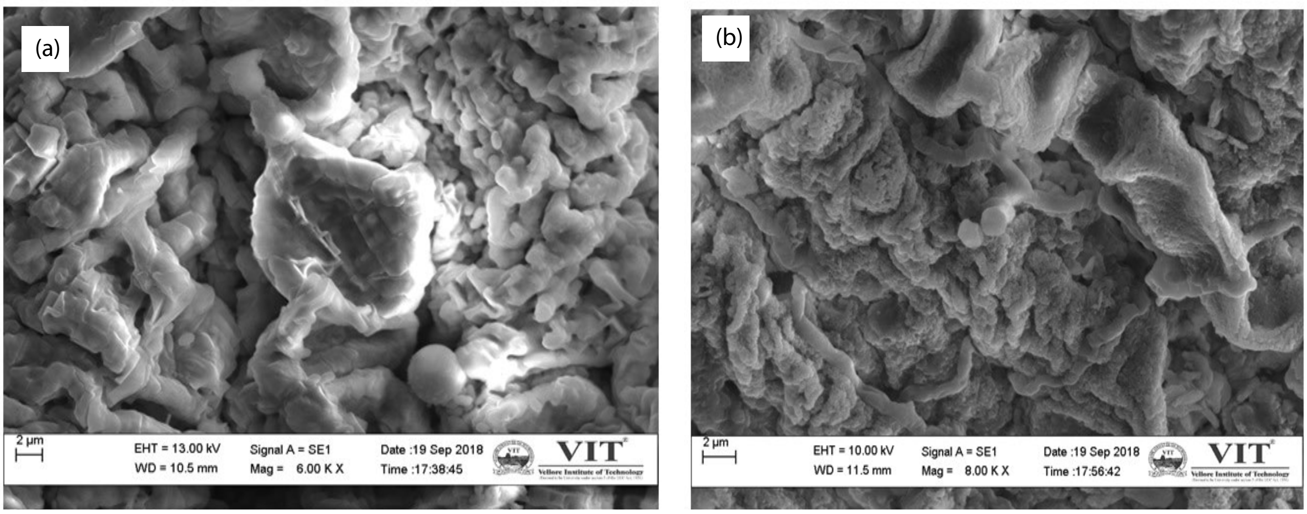

Fig. 2. SEM analysis of immobilized *Canna indica* (a) before adsorption and (b) after adsorption.

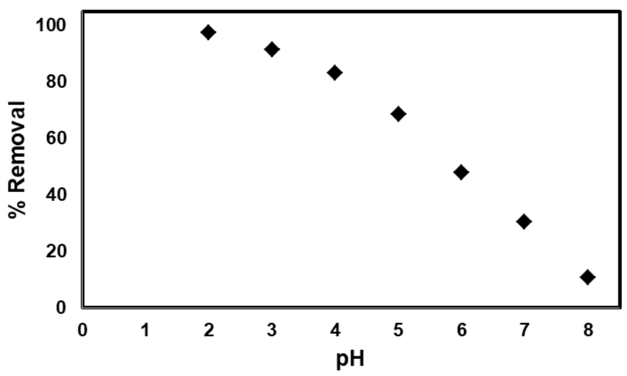

Fig. 3. Effect of pH for the removal of alizarin red dye onto immobilized *Canna indica* beads.

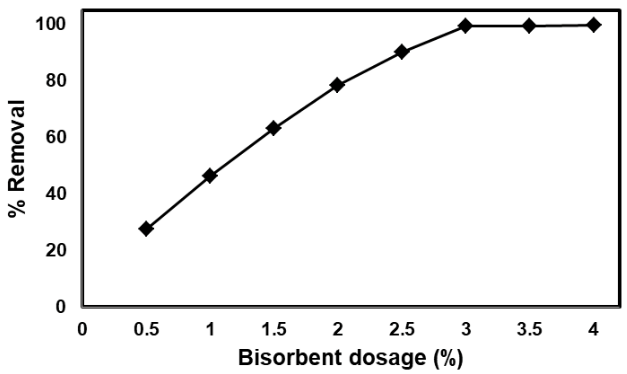

Fig. 4. Effect of biosorbent dosage for the removal of alizarin red dye onto immobilized *Canna indica* beads.

red dye. Further increasing the adsorbent dosage to 3%, result no increase in the removal of alizarin red dye from the aqueous solution and the adsorption process reaches the saturation condition. This occurs due to the unavailability of alizarin red dye in the aqueous solution. Thus the optimum immobilized *Canna indica* beads dosage for the removal of alizarin red dye from the aqueous solution was found to be 3%.

3.2.3. Effects of initial dye concentration

Initial alizarin red dye concentration plays an important role in the adsorption of alizarin red dye onto immobilized *Canna indica* beads. The effect of initial alizarin red dye concentration for the removal of alizarin red dye onto immobilized *Canna indica* beads was determined by conducting the batch adsorption experiment at different alizarin red dye concentration from 25 to 150 mg L^{-1} and the results are shown in Fig. 5. From Fig. 5, it is observed that the percentage removal of alizarin red dye was decreased gradually with increasing the initial alizarin red dye concentration from 25 to 150 mg L^{-1}. It occurred due to the availability of active sites on the surface of the immobilized *Canna indica* beads. At lower concentration, the active sites were available for the prescribed alizarin red dye concentration but in higher concentration because of

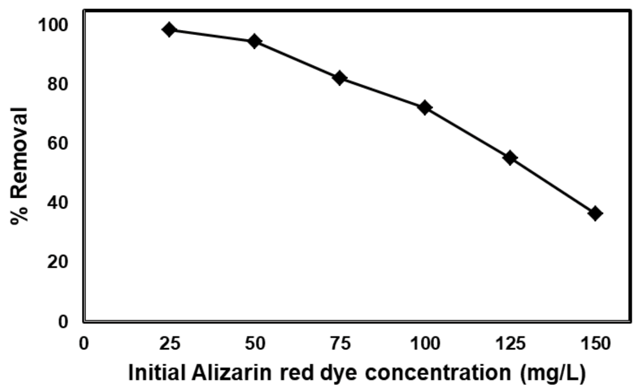

Fig. 5. Effect of initial alizarin red dye concentration for the removal of alizarin red dye onto immobilized *Canna indica* beads.

the unavailability of active sites for the alizarin red dye adsorption or overlying of alizarin red dye onto the immobilized *Canna indica* beads which results in lower removal percentage of alizarin red dye from the aqueous solution. Consequently, the removal percentage of alizarin red dye from the aqueous solution was decreased with increasing the initial alizarin red dye concentration.

3.2.4. Effects of contact time

The batch adsorption experiment for the determination of optimum contact time was carried out in different time intervals from 5 to 50 min by keeping other parameters as constant. The effect of contact time for the removal of alizarin red dye onto immobilized *Canna indica* beads is shown in Fig. 6. It was observed that percentage removal of alizarin red dye from the aqueous solution using immobilized *Canna indica* beads were increased with increasing the contact time from 5 to 35 min. There is no further removal of alizarin red dye from the aqueous solution was observed with increasing the contact time to 40 min. This occurs due to the availability of more active sites at the initial stage and destabilization of driving force, as time progress the adsorption of alizarin red dye onto the available active site increases gradually until achieving the equilibrium condition. Therefore, the maximum contact time for the removal of alizarin red dye from the aqueous solution is found to be 35 min.

3.2.5. Effects of temperature

The effect of temperature on the adsorption of alizarin red dye by immobilized *Canna indica* beads is shown in Fig. 7. The adsorption experiments were carried out by varying the temperatures from 30°C to 60°C and keeping other parameters as constant. From Fig. 7, it is observed that percentage removal of alizarin red dye onto immobilized *Canna indica* beads was decreased with increasing the temperature from 30°C to 60°C. This occurred due to the weakening of attractive force between the alizarin red dye and immobilized *Canna indica* beads and these results indicate that the adsorption process is exothermic in nature.

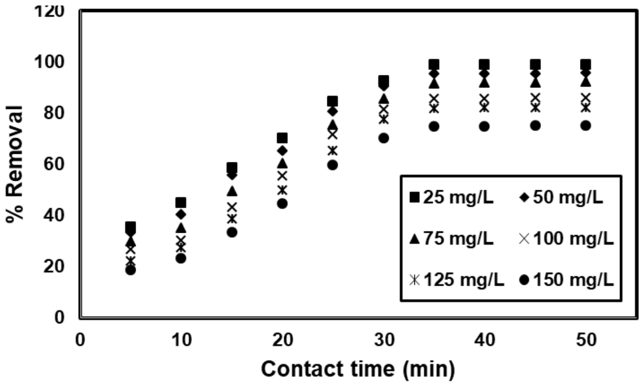

Fig. 6. Effect of contact time for the removal of alizarin red dye onto immobilized *Canna indica* beads.

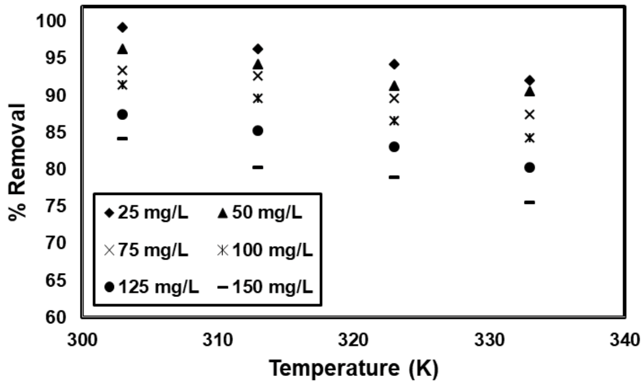

Fig. 7. Effect of temperature for the removal of alizarin red dye onto immobilized *Canna indica* beads.

Therefore, higher percentage removal of alizarin red dye from the aqueous solution using immobilized *Canna indica* beads was observed at 303 K and it could be used as an optimum condition for further studies.

3.3. Adsorption isotherm

The interaction between the alizarin red dye in the liquid medium and the solid surface of immobilized *Canna indica* beads could be explained by the adsorption isotherm analysis. Adsorption isotherm analysis was carried out at equilibrium condition by using four different adsorption isotherm models. In this study two-parameter models; Langmuir and Freundlich adsorption isotherm model, three-parameter models: Toth adsorption isotherm model, and four-parameter model: Baudu adsorption isotherm model was utilized for the determination of maximum adsorption capacity of the immobilized *Canna indica* beads. The non-linear adsorption isotherm study for the adsorption of alizarin red dye onto immobilized *Canna indica* beads are shown in Fig. 8. The adsorption isotherm parameters for different isotherm models and their correlation coefficient (R^2), maximum monolayer adsorption capacity (q_m), and the error values such as SSE and RMSE values have been calculated by using the experimental data with the help of non-linear equation of different isotherm models in MATLAB R2016a software.

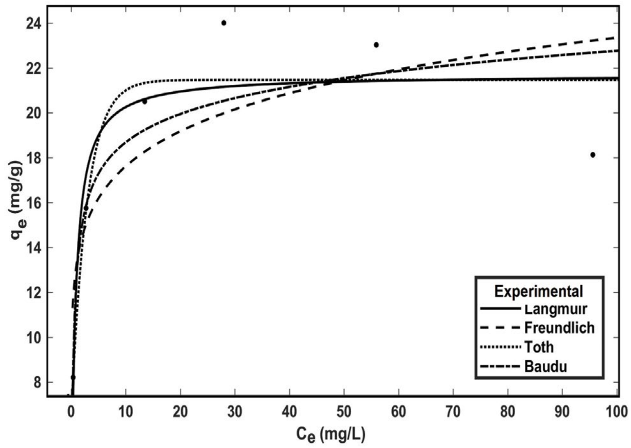

Fig. 8. Isotherm fit for the removal of alizarin red dye onto immobilized *Canna indica* beads.

The adsorption isotherm analysis results are presented in Table 1. From this result, the best fitted adsorption isotherm model for the removal of alizarin red dye onto immobilized *Canna indica* beads was determined based on the correlation coefficient (R^2) values. The calculated correlation coefficient (R^2) and errors (SSE and RMSE) values for four different adsorption isotherm models are as follows: Langmuir isotherm model: R^2 = 0.8507, SSE = 20.09, and RMSE = 2.504, Freundlich isotherm model: R^2 = 0.6316, SSE = 61.19, and RMSE = 3.934, Toth isotherm model: R^2 = 0.8268, SSE = 25.7, and RMSE = 2.627, Baudu isotherm model: R^2 = 0.7837, SSE = 36.35, and RMSE = 4.263. From these results, it was observed that the Langmuir adsorption isotherm model has higher correlation coefficient (R^2) value and lower error values including SSE and RMSE compared with other adsorption isotherm models. Therefore, the results confirmed that the Langmuir adsorption isotherm model is the best-fitted model for the removal of alizarin red dye from the aqueous solution using immobilized *Canna indica* beads and the calculated maximum monolayer adsorption capacity (q_m) value is found to be 21.69. The calculated maximum monolayer adsorption capacity (q_m) value was compared with various adsorbent materials for the removal of alizarin red dye from the aqueous solution are listed in Table 2. This result confirmed that the prepared immobilized *Canna indica* beads have the potential for the removal of alizarin red dye from the aqueous solution. Therefore, the Langmuir adsorption isotherm model is the best-fitted isotherm model for the removal of alizarin red dye by immobilized *Canna indica* beads and it explains this adsorption process as a monolayer and homogeneous in nature.

3.4. Adsorption kinetics

Adsorption kinetic experiment was carried out at different contact time from 5 to 50 min, initial alizarin red dye concentration from 25 to 150 mg L^{-1} and constant temperature (303 K) and constant immobilized *Canna indica* beads dosage (3%) to determine the rate of removal of alizarin red dye from the aqueous solution onto immobilized *Canna indica* beads. Their three different adsorption kinetic

Table 1
Isotherm fit for the biosorption of alizarin red onto immobilized *Canna indica* beads

Adsorption isotherm models	Parameters	Values	R^2	SSE	RMSE
Langmuir	q_m (mg g^{-1})	21.69	0.8507	20.09	2.504
	K_L (L mg^{-1})	1.406			
Freundlich	K_F [(mg g^{-1})(L mg^{-1})$^{(1/n)}$)]	13.29	0.6316	61.19	3.934
	n	8.175			
Toth	q_{mT} (mg g^{-1})	15.02	0.8268	25.7	2.627
	K_T	0.3464			
	m_T	21.47			
Baudu	q_m (mg g^{-1})	12.05	0.7837	36.35	4.263
	x	0.0194			
	y	0.025			
	b_0	1.407			

Table 2
Comparison of maximum monolayer adsorption capacity (q_m) of various adsorbents for the removal of alizarin red dye

S. no	Adsorbent	q_m (mg g^{-1})	Reference
1	*Citrullus lanatus* peels	79.6	[48]
2	Magnetic chitosan	40.12	[49]
3	Activated clay modified by iron oxide	32.70	[50]
4	Immobilized *Canna indica* beads	21.69	Present study
5	Coconut shell activated carbon	19.60	[51]
6	Activated carbon	<20	[52]
7	*Cynodon dactylon*	16.32	[53]
8	Olive stone	16.01	[54]
9	Activated charcoal	8.97	[48]
10	Mustard husk	1.97	[49]

models including pseudo-first-order, pseudo-second-order, and Elovich kinetic models were used to evaluate the rate of removal of alizarin red dye from the aqueous solution. By using MATLAB R2016a software, different parameter values such as rate constant (k), correlation coefficient (R^2), equilibrium adsorption capacity (q_e), and errors including SSE and RMSE were calculated for the different adsorption kinetic models and the values are presented in Table 3. Kinetic results for the removal of alizarin red dye from the aqueous solution onto immobilized *Canna indica* beads are shown in Fig. 9. From Table 3, it is observed that the rate constant values for pseudo-first-order and pseudo-second-order were obtained in the ranges from 0.0581 to 0.034 min^{-1}, 0.0043 to 0.0003 min^{-1}, respectively. The rate constant values were decreased with increasing the initial alizarin red dye concentration and contact time, it occurred due to the competition between the alizarin red dye for the active sites on the surface of immobilized *Canna indica* beads. The experimental equilibrium adsorption capacity (q_e (exp)) value for the removal of alizarin red dye from the aqueous solution using immobilized *Canna indica* beads were compared with the calculated adsorption capacity (q_e) values using MATLAB R2016a software. The best-fitted adsorption kinetic model for the alizarin red dye removal was determined based on the adsorption capacity (q_e) value, correlation coefficient (R^2), and the error (SSE and RMSE) values. From Table 3, the pseudo-first-order kinetic model has the very closely related adsorption capacity (q_e) values with the experimental equilibrium adsorption capacity (q_e (exp)) value than the other two kinetic models. The higher correlation coefficient (R^2) value and lower error values including SSE and RMSE were observed in the pseudo-first-order kinetic model than pseudo-second-order and Elovich kinetic models. From these results, it was observed that the pseudo-first-order kinetic model is the best-fitted model than the pseudo-second-order and Elovich kinetic models for the removal of alizarin red dye from the aqueous solution using immobilized *Canna indica* beads. Pseudo-first- and pseudo-second-order kinetic models were used to explain the physisorption process and Elovich kinetic model is used to explain the chemisorption process. From Table 3, the lower correlation coefficient (R^2) value and higher error (SSE and RMSE) values of Elovich kinetic model than the pseudo-first- and pseudo-second-order kinetic models confirmed that adsorption of alizarin red dye onto immobilized *Canna indica* beads is physisorption in nature.

Table 3
Kinetic fit for the biosorption of alizarin red onto immobilized *Canna indica* beads

C_0 mg L^{-1}	q_e, exp (mg g^{-1})	Pseudo-first-order					Pseudo-second-order				
		q_e (mg g^{-1})	k_1 (min^{-1})	R^2	SSE	RMSE	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	SSE	RMSE
25	8.29	9.01	5.8×10^{-2}	0.97	1.1	0.3707	12.0	4.4×10^{-3}	0.96	1.24	0.39
50	15.98	17.7	5.3×10^{-2}	0.96	5.23	0.8086	24.1	1.1×10^{-3}	0.95	6.00	0.86
75	23.08	26.7	4.6×10^{-2}	0.96	12.7	1.261	37.5	2.2×10^{-4}	0.95	14.6	1.35
100	28.69	34.3	4.3×10^{-2}	0.95	27.1	1.84	49.5	1.8×10^{-4}	0.94	31.4	1.98
125	34.28	43.2	3.7×10^{-2}	0.95	41.6	2.281	64.7	0.9×10^{-4}	0.94	47.7	2.44
150	37.49	49.2	3.4×10^{-2}	0.95	56.9	2.668	75.5	0.7×10^{-4}	0.94	64.4	2.83

Elovich kinetic model

α_E (mg g^{-1} min^{-1})	β_E (g mg^{-1})	R^2	SSE	RMSE
0.4603	0.5073	0.9603	1.476	0.4275
0.0914	2.128	0.9534	6.916	0.9298
0.033	4.194	0.9517	16.6	1.44
0.018	6.135	0.9396	35.39	2.103
0.009	8.911	0.9421	53.11	2.577
0.006	11.01	0.9396	71.17	2.983

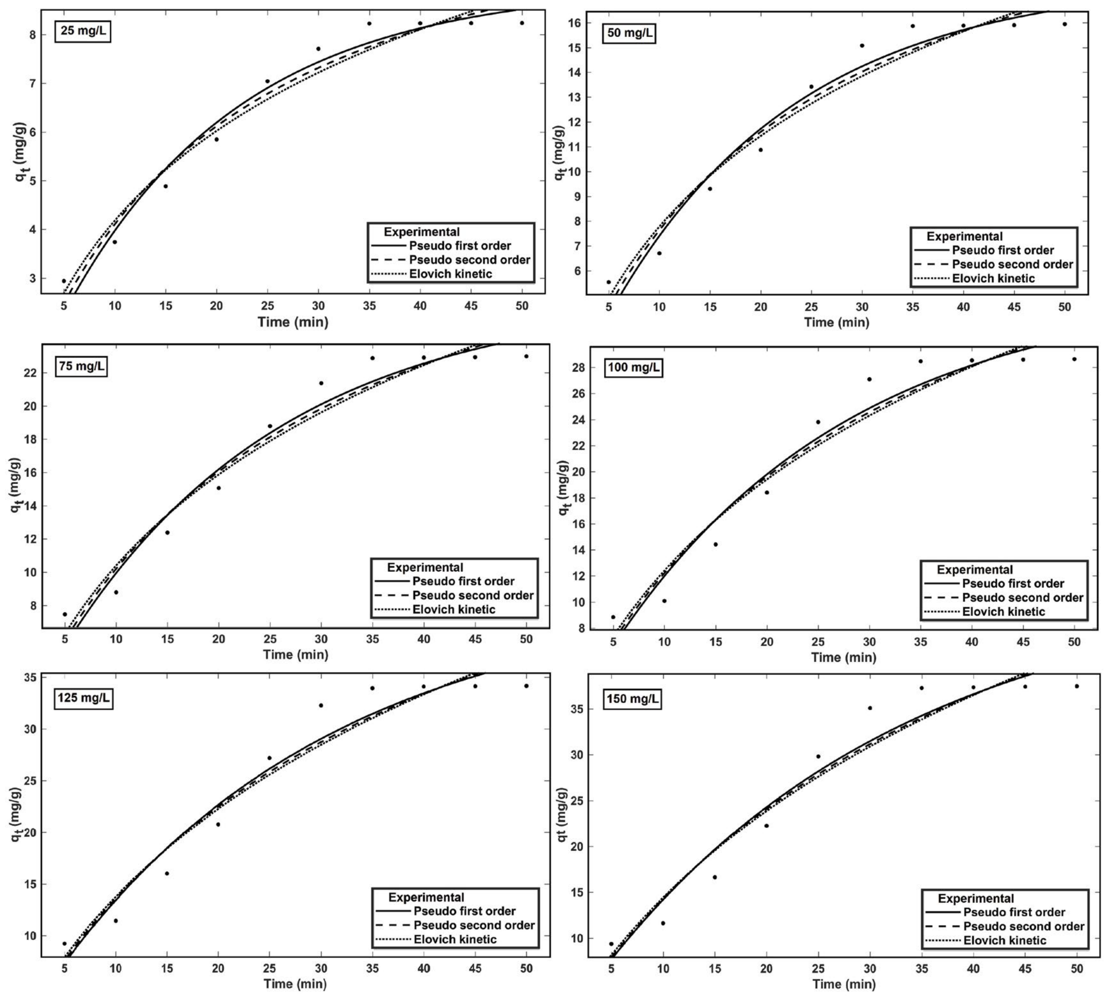

Fig. 9. Kinetic fit for the removal of alizarin red dye onto immobilized *Canna indica* beads.

Table 4
Thermodynamic parameters for the biosorption of alizarin red onto immobilized *Canna indica* beads

Conc of alizarin red dye solution (mg L^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})	ΔG° (kJ mol^{-1})			
			30°C	40°C	50°C	60°C
25	–61.950	–167.64	–11.915	–8.419	–7.449	–6.771
50	–28.701	–68.28	–8.179	–7.218	–6.296	–6.248
75	–20.374	–44.96	–6.617	–6.547	–5.791	–5.365
100	–19.901	–43.93	–5.961	–5.583	–4.994	–4.627
125	–14.972	–33.28	–4.882	–4.539	–4.262	–3.863
150	–14.439	–31.25	–4.200	–3.631	–3.535	–3.105

3.5. Thermodynamic study

Thermodynamic study is used to explain the spontaneity, randomness, feasibility, and nature of the adsorption (exothermic or endothermic) of alizarin red dye onto immobilized *Canna indica* beads by using the thermodynamic parameters including the Gibbs free energy ($\Delta G°$), change in entropy ($\Delta S°$), and change in enthalpy ($\Delta H°$). The thermodynamic results for the removal of alizarin red dye onto immobilized *Canna indica* beads are shown in Fig. 10. The thermodynamic parameters including change in entropy ($\Delta S°$) and change in enthalpy ($\Delta H°$) were calculated by plotting the graph between LogK_c vs. $1/T$. The value of Gibbs free energy ($\Delta G°$) with respect to each temperature and initial alizarin red dye concentration was calculated by using Eqs. (12) and (13). The calculated thermodynamic parameters results are presented in Table 4. From the tabulation report, it was observed that negative value of change in entropy ($\Delta S°$) describes the adsorption of alizarin red dye onto immobilized *Canna indica* beads was enthalpy driven and the negative values for Gibbs free energy ($\Delta G°$) and change in enthalpy ($\Delta H°$) indicates the adsorption of alizarin red dye onto the immobilized *Canna indica* beads from the aqueous solution as feasible, spontaneous, and exothermic nature.

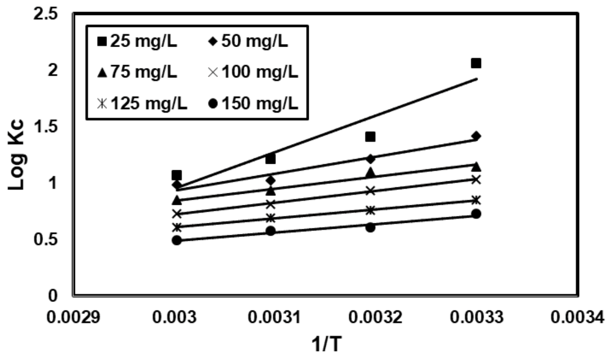

Fig. 10. Thermodynamic study for the removal of alizarin red dye onto immobilized *Canna indica* beads.

4. Conclusion

In this study, the immobilized *Canna indica* beads were prepared by using the root tubers of the *Canna indica* for the removal of alizarin red dye from aqueous solution. FTIR results concluded that the prepared adsorbent material has essential functional groups for the removal of alizarin red dye from the aqueous solution. The structural and surface characteristics of immobilized *Canna indica* beads for effective removal of alizarin red dye from aqueous solution was confirmed by SEM analysis. The batch adsorption experiments were conducted for optimizing the different factors influencing parameters such as initial alizarin red dye concentration, solution pH, immobilized *Canna indica* beads dosage, contact time, temperature. Isotherm studies concluded that the Langmuir adsorption isotherm model is the best-fitted isotherm model for the present adsorption system which explains that the present adsorption system was monolayer and homogeneous in nature. The calculated maximum monolayer adsorption capacity (q_m) was 21.69 mg g^{-1}. Adsorption kinetic results show that the pseudo-first-order kinetic model is the best fitted kinetic model which concluded that the adsorption process is physisorption in nature. Thermodynamic study concluded that adsorption of alizarin red dye onto immobilized *Canna indica* beads was feasible, spontaneous, and exothermic in nature and enthalpy driven. From this experimental study, we presumed that an immobilized *Canna indica* beads have good adsorption capacity for the removal of alizarin red dye from the aqueous solution.

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