Research article

# Fabrication of nanofibers using sodium alginate and Poly(Vinyl alcohol) for the removal of $Cd^{2+}$ ions from aqueous solutions: adsorption mechanism, kinetics and thermodynamics

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ABSTRACT

Nowadays, separation of heavy metals from polluted wastewater is one of the most important environmental issues, and various methods have been investigated for treating polluted water and industrial wastewater. Surface adsorption using an inexpensive, biodegradable and environmentally consistent adsorbent can be considered an efficient and cost-effective method. One of these adsorbents is sodium alginate (SA). The purpose of this study was to fabricate composite nanofibers using poly (vinyl alcohol) (PVA) and sodium alginate to remove cadmium metal ion from aqueous solutions. For this purpose, polymer solutions consisting of poly (vinyl alcohol) (10% wt)/sodium alginate (2% wt) with three volume ratios of 0/100, 20/80 and 40/60 were first made, and then nanofibers were produced from the resulting solutions by electro-spinning process. The prepared nanofibers were examined by scanning electron microscopy (SEM) and the synthetic poly (vinyl alcohol)/sodium alginate nanofibers at a ratio of 40/60 were selected as adsorbent. The obtained nanofibers were characterized by Fourier-transform infrared spectroscopy (FTIR). The synthesized adsorbent was used to remove the aqueous solution of cadmium metal; the effect of various parameters such as changes in initial metal ion concentration, pH, temperature, contact time and stirring speed on the adsorption process were investigated, and optimum values of the parameters were obtained. The maximum amount of equilibrium adsorption under optimum experimental conditions was 67.05 mg/gr. The Taguchi experiment design method was used to optimize the three effective factors in the cadmium ion adsorption process. The results of the adsorption process were adapted to different adsorption isotherms such as Langmuir and Freundlich isotherms. The fit of the laboratory data to the Langmuir model was better, and the maximum adsorption capacity through this model was obtained equal to 93.163 mg/g of the adsorbent. Since the performance of an adsorbent depends on the duration of the adsorption process, the kinetics of the adsorption process were investigated by pseudo-first-order equation and pseudo-second-order equation. Moreover, the results indicated that the laboratory data showed a better fit to the pseudo-second-order model. Finally, the thermodynamic perspective was examined, and the process was found to be endothermic and spontaneous. The results showed the optimum values for maximum cadmium uptake.

## 1. Introduction

Over the past few decades, extensive attention has been paid to environmental pollution due to hazardous materials such as heavy metals, which are elements with atomic weights ranging between 63.5 and 200.6, and densities of greater than 5.0 g/cm$^3$ [1]. Heavy metal ions accumulate due to their lack of biodegradability, and their number increases throughout the food chain. From among various metal ions, lead, mercury, cadmium, and chromium (VI) are at the top of the toxicity list [2]. Due to the rapid development of various industries (including mining and smelting, metallurgy, iron and steel industries, electroplating, electrolysis, leather making, production of household electrical appliances, aerospace, and atomic energy), considerable amounts of chromium metal along with the wastes of these industries have directly been released into the environment, jeopardizing natural ecosystems and human general health, especially in developing countries [3]. Therefore, in order to protect the environment, and to reduce the effects of heavy metals on the human body and to decrease the risks

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resulting from them, these metals have to be removed from waste and sewage.

Multiple methods are used for the removal of heavy metal ions, the most common of which are deposition, flocculation, reduction, ion exchange, evaporation, surface adsorption, and membrane processes [4, 5, 6, 7, 8]. Besides their applied advantages, each of these methods has multiple disadvantages, too. One of these disadvantages is the production of high volumes of sludge containing small amounts of heavy metals. Over the past decades, surface adsorption processes have been developed with the aim of removing heavy metal ions [2, 8]. Surface adsorption is a separation process, in which some of the fluid phase components are transferred onto the surface of a solid adsorbent. In surface adsorption, porous solids, whose pores provide a very large surface area, are used. The more the surface area of an adsorbent increases, the more the adsorption capacity increases. The key factor in an adsorption system is the adsorbent. The adsorbents used in this method include various categories of materials such as activated carbon, activated aluminum, microorganisms, fly ash, perlite, zeolites, and natural and synthetic polymers such as chitosan and PVA [9]. From among various adsorbents, nanofibers are greatly suitable for the adsorption of heavy metals due to their high level of porosity, appropriate mechanical properties and small pores [10, 11]. From among the other advantages of nanofibers, besides their large contact surface area per unit mass, we can refer to the possibility of separating these adsorbents from the solution after the completion of the adsorption process, which is impossible for high surface-area powder adsorbents in re-reduction processes that cause secondary pollution to the environment [12].

From among polymers proposed for the preparation of nanofibers, SA, which is a natural copolymer largely found in brown algae, can be pointed out. This polymer is used in biological applications such as tissue engineering, manufacture of drugs, and other industrial applications due to its excellent biocompatibility, biodegradability, and non-toxicity. Another application of SA is manufacture of adsorbents to be used in adsorption processes [13]. Unfortunately, there are some difficulties associated with using sodium alginate as an adsorbent in the preparation of nanofibers due to its hard structure, limited solubility and high viscosity of its solution. One of the solutions to overcome this problem is using a combination of this polymer and those with appropriate rotation of chains and low viscosity such as poly(vinyl alcohol) [14], which is a kind of artificial polymer used to improve physical properties through its combination with other substances with poor physical properties. PVA is highly biocompatible and non-toxic, it is also water-soluble and easily processable [15]. It can be in the form of gel in a variety of solutions, and this capability has resulted in its wide use in medicine, food, health, cosmetic, drug and packaging industries. PVA has high flexibility and toughness, it is also one of the applied polymers used in practical researches due to its high capability of producing films or fibers [16]. It can be used as an adsorbent along with other inorganic and polymeric materials to remove metal or dye pollutants [17, 18], it is appropriate to choose PVA and SA due to the solubility of both polymers in water and creation of a strong polymer-polymer bond that can lead to the production of a stable compound [19]. In addition, by establishing a hydrogen bond, PVA can bond to SA to form SA/PVA nanofibers [20].

In this study, nanocomposite nanofibers were successfully prepared through electrospinning, and they were used to remove cadmium ions from the aqueous solution. The effects of different proportions of SA/PVA on the structure of the forming nanofibers were evaluated through a SEM characterization test. The effects of different parameters including the contact time, the initial concentration of the cadmium solution, the pH of the solution, the temperature, and the speed of the shaker on cadmium adsorption were also investigated. The isotherm model and the type of adsorption kinetics governing the process cadmium adsorption by synthesized nanofibers were also determined. Furthermore, the removal thermodynamics was investigated in this study, and thermodynamic parameters for the determination of the type of removal process were also specified.

The effects of mixing additives with nonofibers on optimal values for the related parameters during adsorption process, the type of nanofibers arrangement and also the resistance of absorbent have been examined. According to literature review and studies, sodium alginate and polyvinyl alcohol synthetic nanofibers have not been used as cadmium adsorbents; and for the first time in the present research, such synthetic nanofibers have been used to remove this heavy metal from aqueous solution. Moreover, the thermodynamics and kinetics of adsorption of this metal by this type of adsorption have been carefully studied. In addition, the factors affecting the adsorption of this heavy metal on synthetic nanofibers have been carefully investigated and analyzed as univariate experiments. According to the results of the adsorption isotherms, the maximum adsorption capacity of this adsorbent is very suitable for cadmium removal, compared to other adsorbents.

## 2. Experiments

### 2.1. Materials

Poly(vinyl alcohol) polymer (n ($C_2H_4O$) (DP = 1700, 99% hydrolyzed)) was purchased from Merck Company, and sodium alginate ($NaAlO_2$), cadmium nitrate tetrahydrate, sodium hydroxide, and hydrochloric acid were purchased from Sigma-Aldrich Company. $Cd^{2+}$ ions were obtained by dissolving cadmium nitrate in bidistilled water, and all materials were used without any purification.

### 2.2. Producing PVA/SA solutions

In order to prepare a 10 wt% poly(vinyl alcohol) solution, first, 10 g of solid poly(vinyl alcohol) along with 90 g of bidistilled water was poured into a 250-ml distillation flask. Next, the distillation flask was connected to a condenser to form a complete set of reflux equipment, and the distillation flask was placed on a heater stirrer. Then, the poly(vinyl alcohol) solution was refluxed at a temperature between 75 °C and 85 °C for 6 h so that a completely clear, uniform solution was obtained. The reason for refluxing the poly(vinyl alcohol) solution is that when the solution is heated, some amount of the available water may evaporate, causing problems to the concentration of the solution [21].

In order to prepare a 2-wt% sodium alginate solution, first, 2 g of solid sodium alginate along with 98 g of bidistilled water was poured into a 250-ml beaker, its top was covered with foil, and it was placed on a heater stirrer. Next, the obtained solution was stirred at room temperature for 2 h so that it could become uniform. Then, the poly(vinyl alcohol) and sodium alginate solutions were mixed together at three weight ratios of 0/100, 20/80, and 40/60 (PVA/SA), each of which was stirred at room temperature for 2 h [22].

### 2.3. Electrospinning of the produced polymer solutions

The nanofibers were fixed using the solutions prepared in Section 2.2 and through the electrospinning process at Nanotarpak Company located in Isfahan Province Science and Technology Park. The electrospinning device was adjusted under the following conditions: a voltage of 18 kV, a tip-to-collector distance (TCD) of 11 cm, and a flow rate of 0.24 ml/min while the collector, in the shape of a horizontal cylinder, spun slowly. Polymer solutions were electrospun at certain ratios using four syringes existing on the nozzle of the device for 1.5 h to obtain suitable nanofibers.

### 2.4. Creation of cross-links on the adsorbent

PVA is a hydrophilic substance easily dissolved in water. That is why cross-links have to be created between its bonds to reduce PVA dissolution in water. In this study, cross-linking was done by applying heat. Therefore, in order to create thermal cross-links, the produced nanofibers, as adsorbents, were kept in the oven at a temperature of 100 °C for

15 h. Then, a piece of nanofiber was weighed and placed in bidistilled water at a temperature of 50 °C for 4 h in order to determine the effect of the cross-links. After drying completely, the weight of the sample was compared with its initial weight. Due to lack of changes in the weight of the sample, thermal crosslinking was considered a suitable method for applying cross-links.

A SEM device (XL30, Philips) was used to examine the structure of the forming nanofibers so that, based on the size and three-dimensional structure of the nanofibers, the most suitable solution ratio could be selected in order to prepare the nanofibers. To this end, first, the surface of the sample was coated with gold to provide a suitable conductivity at its surface. In addition, PVA and SA functional groups were formed in nanofibers, and appropriate interactions between them were determined through Fourier transform infrared (FTIR) spectroscopy (PerkinElmer, Spectrum 65). Then, a piece of the forming nanofibers was placed into a special magazine, and then into the holder of the FTIR device. The wavelength range of the device was selected between 450 and 4000 cm.

## 3. Method of performing surface adsorption experiments

To determine the amount of cadmium cations adsorbed by the adsorbent, a certain volume of the cadmium solution at a specified concentration was added to a certain mass of the adsorbent, and they were then stirred at a constant speed and at a given temperature and time using a shaker equipped with a temperature control. Afterwards, the solid phase, which was in fact the nanofiber that adsorbed the cadmium cations present inside the aqueous solution, was separated by filter paper, and the concentration of cadmium ions inside the transparent solution; that is, the same equilibrium concentration after the adsorption process, was determined using the flame atomic absorption spectrometry (FAAS) method (PerkinElmer, Analyst300).

To this end, solutions with different concentrations were prepared for the studied metal using cadmium nitrate tetrahydrate and bidistilled water. The calibration curve was plotted using these solutions and through reading their concentrations in the flame atomic absorption spectrometer (FAAS).

By measuring the concentration of the sample after the adsorption process, the adsorption rate of the sample was determined through formula 1:

$$q_e = (C_i - C_e)\frac{V}{M} \tag{1}$$

where $q_e$ is the amount of ions adsorbed by the adsorbent at the moment of equilibrium in mg/g of adsorbent, V shows the volume of the solution in liters, M stands for the amount of the adsorbent added to the solution in grams, and $C_i$ and $C_e$ represent the initial concentration and equilibrium concentration of cadmium cations in mg/l, respectively.
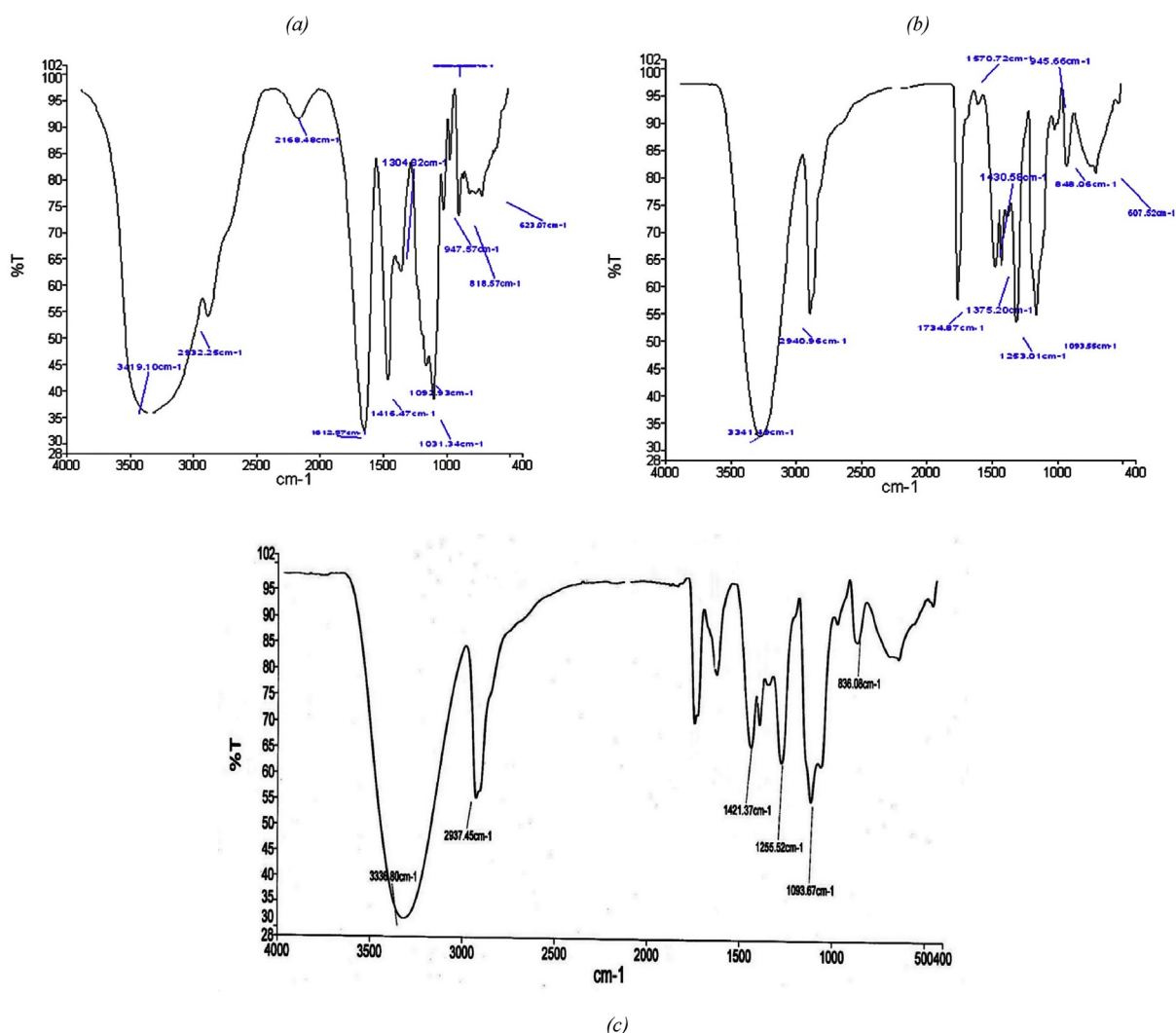


**Figure 1.** a) FTIR of sodium alginate, b) FTIR of poly(vinyl alcohol) and c) FTIR of the PVA/SA (40/60) nanofiber.

In this study, the adsorbent dose and the volume of the cadmium solution were considered constant and equal to 0.002 g and 15 ml, respectively. The pH of the solutions was adjusted by adding 0.1 M hydrochloric acid and 0.1 M sodium hydroxide, and was read using a pH meter (Zagchemie, PTA79).

## 4. Results and discussion

### 4.1. Results obtained from analyzing the fourier-transform infrared spectroscopy (FTIR) of the samples

According to Figure 1a corresponding to the FTIR of sodium alginate, the peak seen at 3419 cm$^{-1}$ is related to hydroxyl groups. It should be noted that the strip, seen in the 3400 cm$^{-1}$ region, belongs to various types of hydrogen bonds in OH groups. The peak seen at 2932 cm$^{-1}$ is attributed to the CH$_2$ group, and the one at 1031 cm$^{-1}$ is related to the structure of stretching C–O–C stretching bonds (saccharides). The peak at 1612 cm$^{-1}$ is indicative of an asymmetric -COO$^-$ stretching bond, (carboxylate), and the peak at 1416 cm$^{-1}$ indicates a symmetric -COO$^-$ stretching bond [23].

In Figure 1b corresponding to the FTIR of poly(vinyl alcohol), the peak seen at 2940 cm$^{-1}$ belongs to the stretching vibration of the CH$_2$ group, the peak seen at 1093 cm$^{-1}$ belongs to the C–O group, and the peak seen at 3341 cm$^{-1}$ belongs to the hydroxyl group (OH) [23].

As for the PVA/SA (40/60) composite adsorbent, as shown in Figure 1c, at peaks seen at 836, 1093, 1255, and 1421 and 2937 cm$^{-1}$, the adsorption rate of the peaks decreased, and some peaks disappeared due to the interaction between SA and PVA.

In addition, the peak seen at 3336 cm$^{-1}$, which belongs to OH groups, has decreased relative to that in pure PVA, which is indicative of the formation of a hydrogen bond between hydroxyl groups in PVA and SA.

Therefore, PVA can modulate the intermolecular interaction of SA, and improve the electrospinning of SA when accompanied by PVA [23].

### 4.2. Examining the structure of the samples through scanning electron microscopy (SEM)

The morphology of the electrospun nanofibers can be affected by the parameters of the electrospinning device such as the electrical voltage and the tip-to-collector distance (TCD), as well as the parameters of the solution such as the concentration of the polymer, the feed mass ratio, and the surface tension. Changes made in the polymer concentration can be very effective in changing the fiber diameter and morphology.

As shown in Figure 2a, the pure PVA nanofiber is non-uniform and heterogeneous, and there is some shrinkage similar to the formation of grains in some areas. As can be seen in Figure 2b, by adding a polymeric solution of sodium alginate with a ratio of PVA/SA = 20/80, the fibers become slightly more uniform and thinner, and the formation of grains is also improved due to the improved concentration of the solution because by adding sodium alginate, the solution becomes slightly thicker, and its electrospinning is improved. As can be seen in Figure 2c, by adding a polymeric solution of sodium alginate with a ratio of PVA/SA = 40/60, the nanofiber becomes much more uniform and thinner than in the case of the solution with a ratio of PVA/SA = 20/80 with no grains. This suggests that the polymeric solution with a ratio of a PVA/SA = 40/60 has a better concentration for producing nanofibers, and greatly improves the electrospinning capability. Since the more uniform and thinner a nanofiber is, the better adsorbent it will be, the nanofiber produced from the polymeric solution with a PVA/SA = 40/60 was selected as an adsorbent. Table 1 provides the description of nanofiber morphology for different types of nanofiber, which were synthesized in this work.
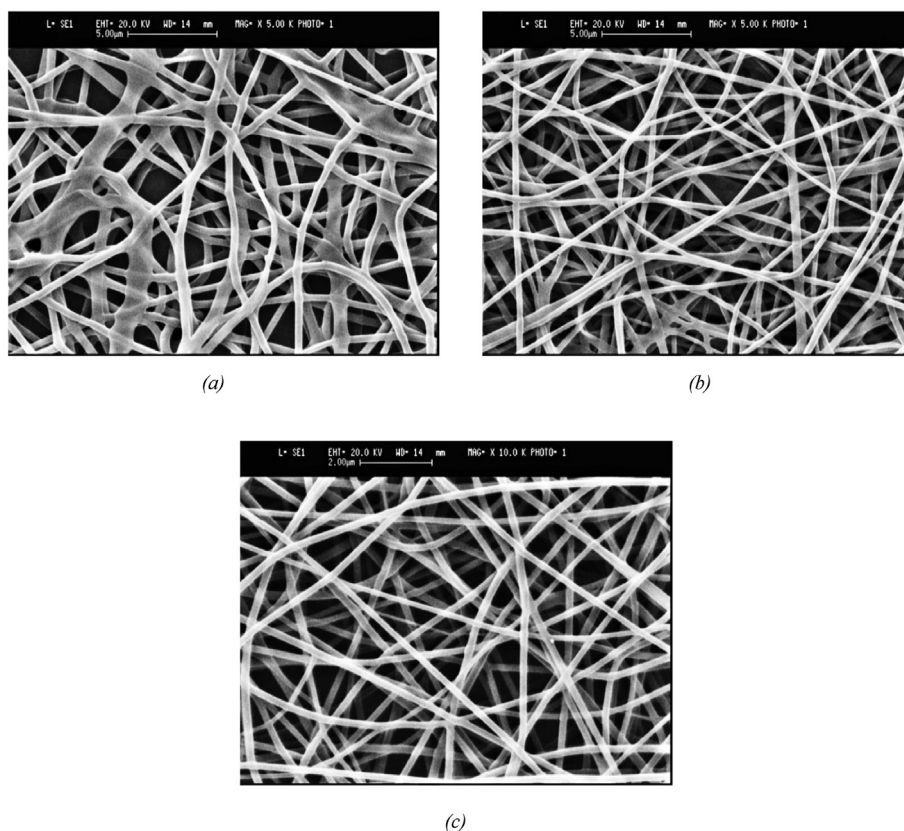
*(a)*

*(b)*

*(c)*

**Figure 2.** a) A SEM image of pure PVA nanofibers, b) A SEM image of nanofibers with a ratio of PVA/SA = 20/80 and c)A SEM image of nanofibers with a ratio of PVA/SA = 40/60.

**Table 1.** The nanofiber morphology for different types of nanofiber.

| Number of image | Type of nanofiber | Nanofiber morphology |
|---|---|---|
| Figure 2a | Pure PVA | non-uniform and heterogeneous and accumulates in some areas |
| Figure 2b | PVA/SA= 80/20 | Slightly uniform and thin with a small amount of grain |
| Figure 2c | PVA/SA= 60/40 | Very uniform and thin and has no grain |

## 4.3. Result of the adsorption test

### 4.3.1. Effect of the contact time

To determine the effect of the contact time and the equilibrium time, 0.002 g of the PVA/SA composite adsorbent was put in contact with 15 mL of cadmium solution with a concentration of 40 ppm and a pH of 5 at different times. As shown in Figure 3, the equilibrium time for the in-vitro removal of cadmium was calculated equal to 90 min, and an equilibrium adsorption rate of 75 mg/g of adsorbent was achieved during the calculated equilibrium time. After 100 min, the adsorption rate slightly decreased, and then it remained almost constant.

The results of the experiments showed that the amount of cadmium ions present in the solution was high at the initial stages of the experiments, thus increasing the number of effective collisions between cadmium ions and adsorption sites existing on the surface. Therefore, cadmium ions are adsorbed faster during the first 40 min (the graph shows a steep slope). As time passes, and cadmium cations are adsorbed by the adsorbent, the amount of metal cations in the solution decreases, the larger part of active sites on the adsorbent surface are saturated with these cations, and the adsorption rate decreases (the slope of the graph decreases). On the other hand, creation of a repulsive force between the cadmium ions adsorbed on the adsorbent and those in the solution reduces the adsorption rate until it is almost constant. In addition, it should be noted that active adsorption sites are in the superficial as well as deep areas of the adsorbent, however, superficial sites are easily exposed to cadmium ions, and have a greater chance of encountering cadmium ions, thus increasing the speed of adsorption, but gradually, as superficial sites are saturated, the adsorption process continues through deep areas, which slows down the adsorption process. Albeit, this does not mean that at the beginning of the adsorption process, the deep areas of the adsorbent do not interfere with the adsorption process [24]. Based on the obtained results, a duration of 100 min was chosen as the equilibrium time.

### 4.3.2. Effect of the initial concentration of the cadmium solution

The experiment for examining the effect of the initial concentration of the cadmium solution on the PVA/SA composite adsorbent was carried out through putting 0.002 g of the adsorbent in contact with 15 ml of solutions with concentrations of 15–120 mg/l (ppm) and a pH of 5. As shown in Figure 4, with the increased initial concentration of cations, the adsorption rate increased. In solutions of higher concentrations, the
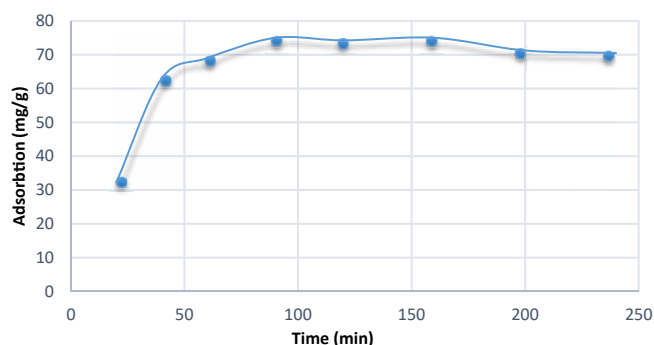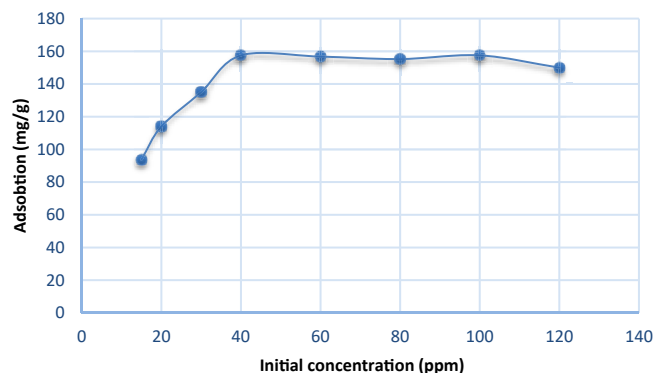


**Figure 4.** Effect of the initial concentration of the cadmium solution on the PVA/SA composite adsorbent.

number of effective collisions with adsorption sites increases due to the increased number of desired cations, which increases the adsorption rate. Furthermore, at higher initial concentrations, the driving force for mass transfer, which is directly related to the concentration of the species in the medium and the mixing rate of the solution will increase, thus increasing the adsorption rate. Therefore, at higher concentrations, the adsorption capacity moves in an upward trend. Due to the occupation of most adsorption sites by the adsorbent at upper parts, this process will continue until all adsorption sites are occupied by cadmium and the adsorption rate becomes constant.

On the other hand, with the initial concentration of cadmium changing from 15 to 40 mg/l, the amount of adsorbed cadmium increased from 93.75 to 157.5 mg/g of adsorbent. The reason for this can be explained as follows: under conditions where the initial concentration of cadmium in the sample increases, the driving force for the adsorption of metal ions to the adsorbent surface increases as well. This is why an increase in the concentration of metal ions will increase the adsorption capacity. From a concentration of 40 ppm upward, mg/g of adsorbent remains constant at a certain level. Therefore, in subsequent experiments, the initial concentration of cadmium cations was chosen equal to 40 ppm.

### 4.3.3. Effect of pH of the solution

In the adsorption process, the pH of the solution has an important and key effect on the adsorption capacity, and can affect the surface charge of the absorbent, the functional groups on active sites, as well as the chemistry of the solution. In order to investigate the effect that pH changes in the cadmium solution have on the adsorption rate, the pH changes were considered from 1 to 7. To this end, samples containing 15 ml of solutions with an initial concentration of 40 ppm and different pHs (1–7) were adjusted by pH meter, and were put in contact with 0.002 g of adsorbent inside the shaker at a speed of 150 rpm and an ambient temperature of 25 °C for 100 min.



**Figure 3.** Equilibrium time for the removal of cadmium.
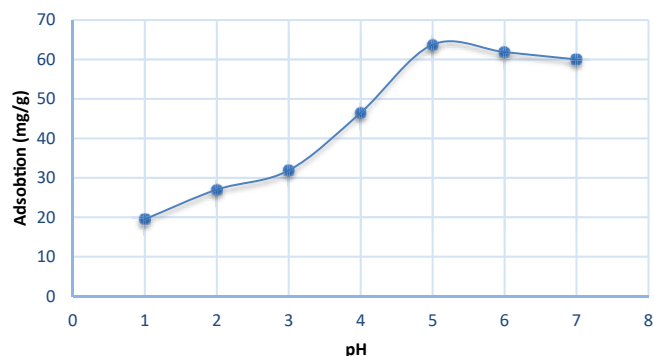


**Figure 5.** Effect of pH on the adsorption of cadmium metal ions.

Figure 5 shows results corresponding to the effect of pH on the adsorption of cadmium metal ions. As can be seen, with pH increasing from 1 to 5, the adsorption of cadmium is increased from 19.5 to 63.7 mg/g of adsorbent, and as the pH changes from 5 to 7, the absorption rate is almost constant with a slight decrease. Therefore, the highest rate of the adsorption of cadmium by the adsorbent occurs at pH = 5. The concentration of hydrogen ions is considered an important parameter that affects the behavior of the metal ions present in the aqueous solution for the adsorption process, which has an effect on the solubility of the existing metal ions and the ionization degree of the adsorbent during the reaction. In other words, pH changes affect the adsorption rate through changing the ionization degree of the adsorbed species because divalent metal ions ($M^{2+}$) can be present in different forms: $M(OH)^{1+}$, $M(OH)_2$, and $M(OH)_3^{1-}$ in aqueous solutions.

The most suitable species for adsorption on the surface of the intended adsorbent is the species $M^{2+}$, which will be the dominant species for each cation at a certain pH. At higher pHs, formation of metal hydroxides coincides with the adsorption process, and becomes effective in the removal of metal species from the solution. At lower pHs, the competition between $H_3O^+$ and $M_2^+$ over occupying active sites reduces the adsorption capacity for metal cations. As can be seen in the graph, as the pH increases, the adsorption capacity increases because the competition between $H_3O^+$ and $Cd^{2+}$ to be adsorbed onto the active sites of the adsorbent surface decreases, and metal ions can be adsorbed onto the adsorbent surface more easily. On the other hand, with an increase in the pH, the negative charge of the surface increases, which in turn increases the electrostatic attraction between cadmium cations and the adsorbent. Given that the pH of deposition at a concentration of 40 ppm is calculated 10 using the solubility product, it does not affect the adsorption process. Therefore, in what follows, the optimum pH for adsorption of cadmium by the PVA/SA composite adsorbent is chosen to be 5.

### 4.3.4. Effect of temperature on the rate of the adsorption of cadmium

In order to investigate the effect of temperature on the process of the adsorption of cadmium by the PVA/SA composite adsorbent, samples containing 15 ml of cadmium solution at a concentration of 40 ppm were put in contact with 0.002 g of the adsorbent inside the shaker within a temperature range of 25–50 °C for 100 min, and were examined. Figure 6 shows the changes in the adsorption rate of cadmium cations with temperature changes, and the effect of temperature on the adsorption process.

As can be seen, with temperature increasing at a certain concentration of cadmium cations, the rate of adsorption of cadmium by the adsorbent increasesbecause as the ambient temperature increases, the mobility of cations and molecules involved in the cadmium adsorption process increases, and as the number of effective collisions between cadmium cations and the existing active sites increases, the cadmium adsorption rate improves as well. According to relevant articles [25], and since it is not economical to raise the temperature for increasing the adsorption rate, it would be better to perform the process at the same temperature of 25 °C.
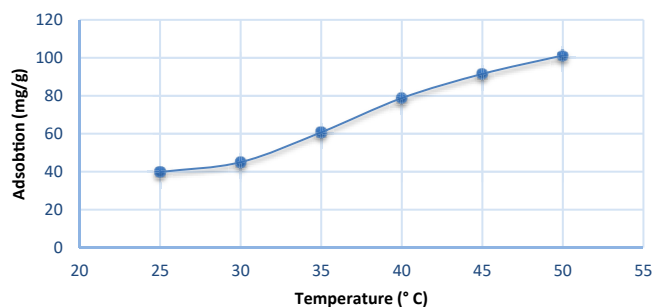
### 4.3.5. Impact of speed of shaker on the adsorption rate of cadmium

In order to investigate the effect of shaker speed on the process of adsorption of cadmium by the PVA/SA composite adsorbent, some samples containing 15 ml of cadmium solution at a concentration of 40 ppm and a pH of 5 were put in contact with 0.002 g of the adsorbent at a temperature of 25 °C within the mixing speed range of 50–250 rpm. The obtained results are presented in Figure 7.

According to the results obtained from these experiments, it can be concluded that during the cadmium adsorption process, the absorption capacity increases with the increased speed of the shaker. The reason is that with the shaker speed increasing, cadmium ions come more in contact with the active surface sites and internal pores of the absorbent, thus increasing the interactions between the cations and the active sites. According to Figure 7, the adsorption capacity increases up to a speed of 150 rpm, and then remains almost constant and does not change much because the active sites of the adsorbent are occupied by cadmium ions. Therefore, the contact between the active sites of the adsorbent and the ions present in the solution improves with the increased speed of the shaker [26]. After determining the optimal values for adsorption, an adsorption experiment was carried out under the same optimal conditions, and the highest adsorption rate was calculated to be 67.05 mg/g.

### 4.3.6. Examination of adsorption isotherms

States of equilibrium related to adsorption are usually presented through an isotherm equation containing parameters that represent the surface properties and tendency of the adsorbent at a constant pH and temperature. The adsorption isotherm expresses the relationship between the amount of the substance adsorbed onto the adsorbent and the concentration of the substance adsorbed into the solution in equilibrium. Different adsorption models have been offered in this regard, the most important of which are Langmuir and Freundlich adsorption isotherms. Langmuir and Freundlich isotherms, the most common and widely used equations for showing information about adsorption equilibrium when examining the adsorption of heavy cations, were used to investigate the process of the adsorption of cadmium cations by the adsorbent [27]. To this end, samples containing 15 mL of cadmium solution at different concentrations along with 0.002 g of the adsorbent were stirred at a temperature of 25 °C for 100 min. Langmuir and Freundlich linear isotherm models, which have so far been used successfully to explain the process of the adsorption of metal ions on different adsorbents, were used to investigate the cadmium adsorption isotherm. Eqs. (2) and (3) represent linear forms of Langmuir and Freundlich isotherms, respectively.

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \tag{2}$$



**Figure 6.** Effect of temperature on the process of the adsorption of cadmium by the PVA/SA composite adsorbent.
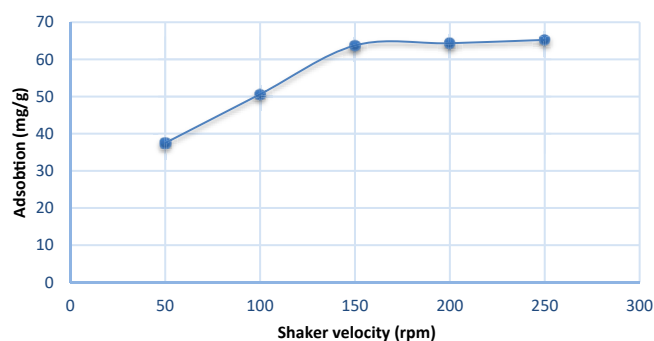


**Figure 7.** Effect of shaker speed on the process of adsorption of cadmium by the PVA/SA composite adsorbent.

where $q_e$ is the concentration of metal ions in equilibrium in the solid phase (mg/g), $C_e$ illustrates the concentration of metal ions in equilibrium in the liquid phase (mg/l), $q_{max}$ depicts the maximum adsorption capacity (mg/g), and $K_L$ refers to the energy related to chemical adsorption (l/mg).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3)$$

$K_f$ and $n$ are the constants of Freundlich adsorption isotherm, which represent the adsorption capacity and adsorption energy, respectively. Therefore, in order to determine the capacity of the adsorption of cadmium on the PVA/SA composite adsorbent, these equilibrium models have been compared with laboratory data. Figures 8 and 9 show the comparison of Freundlich and Langmuir linear models with data obtained in the laboratory. As expected, with the increased equilibrium concentration of cadmium in the samples, the amount of cadmium adsorbed per unit mass of adsorbent increased as well, and its trend can clearly be seen on the Langmuir isotherm graph.

According to Eq. (3), the constants $K_f$ and $1/n$ in the Freundlich model are calculated from the y-intercept and slope of the $Log\ q_e$ versus $Log\ C_e$ graph. In addition, $K_L$ and $q_{max}$ are the constants of the Langmuir isotherm corresponding to free energy and the adsorption capacity of the adsorbent, which are similarly determined from the y-intercept and slope of the $Log\ 1/q_e$ versus $Log\ 1/C_e$ graph. Table 2 provides the constants and correlation coefficients of Langmuir and Freundlich models for the adsorption of cadmium on PVA/SA nanofibers.

Considering the graph corresponding to each model, as well as the value of the correlation coefficient between the model and the experimental data, it is concluded that the Langmuir model with a correlation coefficient equal to 0.9824 has a good fit to the data of this study. The fit of the Langmuir model to the experimental data obtained in this study is indicative of the chemical adsorption and single-layer coating of the absorbent (PVA/SA composite nanofibers) by cadmium ions. In other words, in Langmuir model, it is assumed that adsorption takes place on homogeneous adsorption sites, and each site is only occupied by one pollutant molecule.

All these adsorption sites on the adsorbent surface are of equal energies, and there is neither an interaction between the adsorbed molecules nor a barrier to the adsorption of new molecules by the absorbed molecules. In contrast to the Langmuir model, the Freundlich model is based on the multilayer and heterogeneous adsorption of substances adsorbed onto the adsorbent. The main characteristic of the Langmuir model can be shown in a constant form and without a separation factor through the equilibrium parameter defined as follows (Eq. (4)):

$$R_L = \frac{1}{1 + K_L C_0} \qquad (4)$$

where $K_L$ is the Langmuir isotherm constant (L/mg), and $C_0$ shows the initial concentration of cadmium ions. The equilibrium parameter ($R_L$) determines the type of isotherms. This means that $R_L > 1$ denotes the undesirability of the isotherm, $R_L = 1$ the linearity of the isotherm, $0 < R_L$
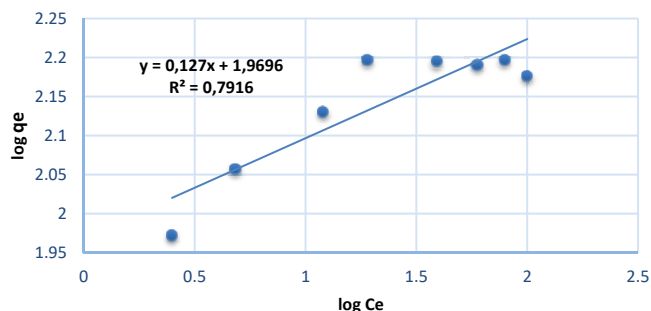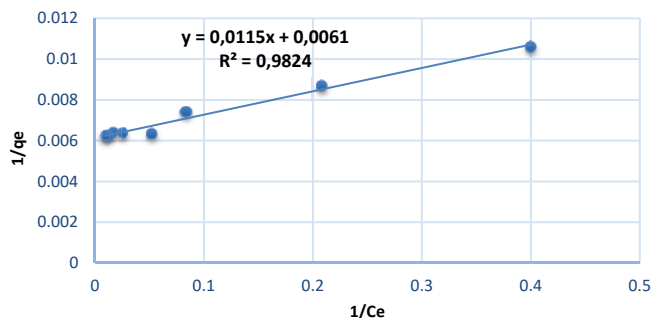


**Figure 9.** Comparison of the Langmuir linear model.

**Table 2.** Constants and correlation coefficients of Langmuir and Freundlich models.

| The Freundlich model | | | The Langmuir model | | |
|---|---|---|---|---|---|
| $K_f$ (mg/g) | $n$ | $R^2$ | $q_{max}$ (mg/g) | $K_L$ | $R^2$ |
| 93.2395 | 7.8740 | 0.7916 | 163.9344 | 0.5304 | 0.9824 |

$< 1$ the desirability of the isotherm, and $R_L = 0$ the reversibility of the isotherm. Therefore, considering the concentration of cadmium in this study, which ranges between 15 and 120 mg/l, the value of the separation factor is calculated and obtained within the range of 0.015–0.111. Therefore, the constant $R_L$ falls in the interval zero to one, which indicates the desirability of the isotherm [27].

According to some researchers, the maximum value for the adsorption capacity of the adsorbent is the most important parameter for the comparison of efficiency between different adsorbents. The maximum amount of cadmium adsorbed per unit mass of adsorbent is obtained equal to 163.9344 mg/g using the Langmuir model. Although due to different laboratory conditions, the adsorption capacity obtained in this study for the adsorption of cadmium on PVA/SA composite polymeric nanofibers (with a wt% ratio of 40/60) is not completely consistent with values obtained for other adsorbents in other studies, in terms of adsorption capacity, PVA/SA composite polymeric nanofibers (with a wt% ratio of 40/60) are considered relatively suitable adsorbents for the removal of cadmium from aqueous solutions.

### 4.4. Results of examining the kinetics of the adsorption reaction

Examining the kinetics of the adsorption process is one of the methods used to analyze empirical data, and justify the mechanisms of the adsorption of a species by an adsorbent under the influence of various processes such as mass transfer, penetration, and chemical reactions. The first-order rate equation, which considers the adsorption process under the control of penetration, and which defines the rate determination stage as the penetration of interchangeable ions into the lattice of the adsorbent, as well as the second-order rate equation, which considers chemical reactions to affect the adsorption process, and which suggests that the adsorption process is of a chemical type, are usually used to examine the kinetics of reactions.

Pseudo-first-order and pseudo-second-order models were used to describe the kinetics of the adsorption of cadmium on PVA/SA composite polymeric nanofibers (with a wt% ratio of 40/60). To this end, according to the study taken into consideration, samples containing 15 mL of cadmium solution at a concentration of 40 ppm along with 0.002 g of the adsorbent were stirred at a temperature of 25 °C during a time interval of 20–240 min Eqs. (3) and (4) describe the pseudo-first-order and pseudo-second-order linear models, respectively. As can be seen in Figures 10 and 11, the pseudo-second-order model is in complete agreement with the data obtained in this study. The coefficients of these two models have been calculated and presented in Table 2. As can clearly be understood
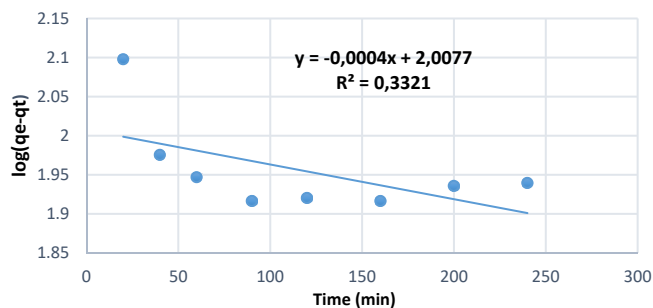


**Figure 8.** Comparison of the Freundlich linear model.
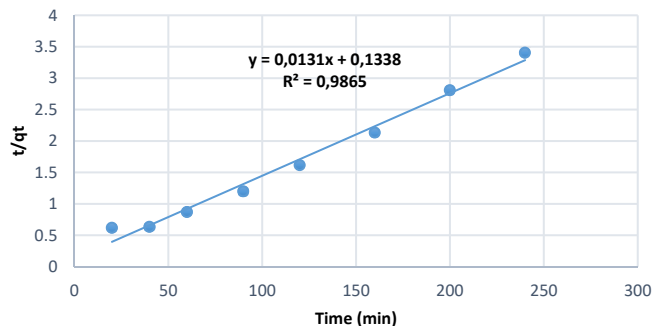
**Figure 10.** First-order rate graph.



**Figure 11.** Second-order rate graph.

from the information provided in Table 3, the correlation coefficient of the pseudo-second-order model is 0.9865, and the laboratory values and those calculated for cadmium adsorbed per unit mass of adsorbent using the pseudo-second-order model are very close together [27]. According to the results obtained from Table 3, the kinetics of the adsorption of cadmium on PVA/SA composite polymeric nanofibers (with a wt% ratio of 40/60) is controlled by a second-order reaction.

The fact that the kinetics of the intended reaction complies with the second-order kinetics proves that the adsorption process having occurred is in fact chemical adsorption, caused by interaction between electrons, which are common between functional groups present at the adsorbent surface and cadmium cations, or which are exchanged between them, and that the adsorption process is a rate limitation stage [28], and other factors such as mass; that is, the speed or duration during which cadmium cations reach the adsorbent surface from the bulk solution, play a less important role in determining the reaction rate [29].

In the experiment carried out, because of stirring the solution using a shaker, the process of transferring cadmium ions from the bulk solution to the adsorbent surface (the penetration process) was done easily. Therefore, the mass transfer process has no effect on the reaction rate.

The information obtained from the second-order rate equation and the correlation coefficient equal to 0.9865 prove that the chemical adsorption is a process which limits the reaction rate. In this model, as the concentration of the absorbed substance increases, the rate of concentration changes versus time increases sharply due to a direct relationship between the rate of concentration changes versus time and the square of the concentration.

### 4.5. Results of examining the thermodynamics of the reaction of the removal of cadmium by the adsorbent

In the process of the removal of ions by the adsorbent, temperature is one of the effective factors, whose effect is examined using thermodynamic parameters. In this section, we deal with examining these parameters.

In order to determine thermodynamic parameters including entropy changes ($\Delta S$), enthalpy changes ($\Delta H$), and the Gibbs free energy changes

**Table 3.** Parameters obtained from the first- and second-order equations.

| The type of the equation | $q_e$ | $K$ | $R^2$ |
|---|---|---|---|
| The first-order rate equation | 101.78 | 0.009 | 0.3321 |
| The second-order rate equation | 76.3358 | 0.001 | 0.9865 |

($\Delta G$), some experiments were carried out on the removal of cadmium cations by the adsorbent made of PVA/SA composite polymeric nanofibers (with a wt% ratio of 40/60). To this end, the experiments were carried out through the application of the adsorbent at temperatures of 25, 30, 35, 40, 45, and 50 °C under optimum conditions for the concentration of cadmium, pH, and contact time. The amount of cadmium removed by the adsorbent was measured; and as expected, the cadmium adsorption rate increased with the increased temperature because as the ambient temperature increases, the mobility of cations and molecules involved in the cadmium removal process increases, thus resulting in the increased number of effective collisions between cadmium cations and active sites existing in the adsorbent, formation of a greater number of complexes, and finally, increased removal of cadmium from the solution by the adsorbent. In what follows, the graph of Ln $K_d$ versus 1/T is plotted and shown in Figure 12. Using Formula 5, the values of enthalpy and entropy were obtained from the slope and y-intercept of the graph, and the Gibbs free energy was calculated for each temperature through Formula 6. Table 4 shows the obtained results.

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

where $\Delta H$ represents standard enthalpy changes, and $\Delta S$ depicts standard entropy changes.

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

The Gibbs free energy is a thermodynamic quantity that shows the spontaneity degree of a reaction. The performance of a process would be thermodynamically possible when the Gibbs free energy changes are negative ($\Delta G < 0$). Considering the information provided in Table 4, it can be seen that the calculated Gibbs free energy is negative. Therefore, the reaction of the removal of cadmium cations by the PVA/SA polymeric nanofibers is a spontaneous reaction.

The negative values of $\Delta G$ suggest that the energy of the bond between cadmium and the adsorbent is stronger than that between cadmium and the aqueous medium. This difference between the potential energies of cadmium cations in aqueous solutions and adsorbents is the cause of the migration and accumulation of cadmium in the adsorbent, and the driving force of the adsorption process. The more negative the value of the $\Delta G$ of a process is, the greater the spontaneity degree of that reaction will be; and the less negative the value of the $\Delta G$ is, the smaller the spontaneity degree of that reaction will be. By comparing $\Delta G$ values at different temperatures in Table 4, it can be seen that $\Delta G$ is more negative at high temperatures, and that as temperature increases, the negativity of $\Delta G$ increases, indicating the effect of temperature, and that as it increases, the spontaneity degree of the reaction increases.

Electrostatic adsorption (ion exchange) is attributed to the attractive force between ions and charged functional groups, and is generally classified as ion exchange, which is considered a stoichiometric process; that is to say, for each ion taken from the solution phase by the exchanger, an equivalent charge of the same sign is substituted in the solution, in a way that each of the phases remains neutral in terms of electrical charge. The heat released in the ion exchange process is usually very small and about 10 kJ/mol (often less than 2 kcal/mol) [24]. Higher values of the Gibbs free energy with a negative sign are indicative of chemical adsorption.

In general, $\Delta G$ for physical adsorption is between zero and -20 kJ/mol, and it is between -80 and -400 kJ/mol [30] for chemical adsorption. During the process of the removal of cadmium by the PVA/SA composite
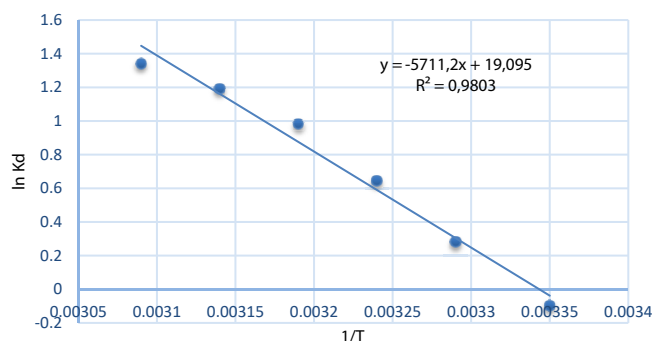
**Figure 12.** *Ln K_d* versus $1/T$ graph.

The graph shows a plot with equation $y = -5711.2x + 19.095$ and $R^2 = 0.9803$.

**Table 4.** Thermodynamic parameters of the removal of cadmium by the adsorbent.

| T (°K) | ΔG(kj/mol) | ΔH (kj/mol) | ΔS (kj/mol.K) |
|---|---|---|---|
| 298.15 | -0.148 | 47.482 | 0.158 |
| 303.15 | -0.643 | | |
| 308.15 | -1.437 | | |
| 313.15 | -2.231 | | |
| 318.15 | -3.025 | | |
| 323.15 | -3.819 | | |

adsorbent, ΔG has remained less than -20, and has not exceeded this range even by increasing the temperature.

## 5. Conclusion

In the present study, we prepared PVA/SA composite nanofibers at certain volume ratios. After determining an appropriate volume ratio equal to 40/60 using a SEM characterization test, we used synthesized nanofibers to remove cadmium ions from aqueous solutions. Parameters affecting adsorption such as contact time, temperature, shaker speed, pH of the solution, and initial concentration of the solution were examined, and their optimal values were obtained equal to 100 min, 150 rpm, 5, and 40 ppm, respectively. The maximum cadmium adsorption rate was obtained equal to 67.05 mg/g under optimal experimental conditions. The equilibrium data were appropriately compared with the Langmuir adsorption isotherm, and the adsorption kinetics data showed that the adsorption process complied with the pseudo-second-order model. It was concluded from the thermodynamic data that the cadmium adsorption process was an endothermic and spontaneous process.

## Declarations

### Author contribution statement

Amin Sadeghizadeh: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Farbod Ebrahimi: Analyzed and interpreted the data; Materials, analysis tools or data; Wrote the paper.

Farnaz Neysan: Analyzed and interpreted the data; Performed the experiments, contributed reagents, materials, analysis tools or data.

Maryam Heydari: Conceived and designed the experiments, analyzed and interpreted the data.

### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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