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Optimization of the Ba^{+2} uptake in the formation process of hydrogels using central composite design: Kinetics and thermodynamic studies of malachite green removal by Ba-alginate particles

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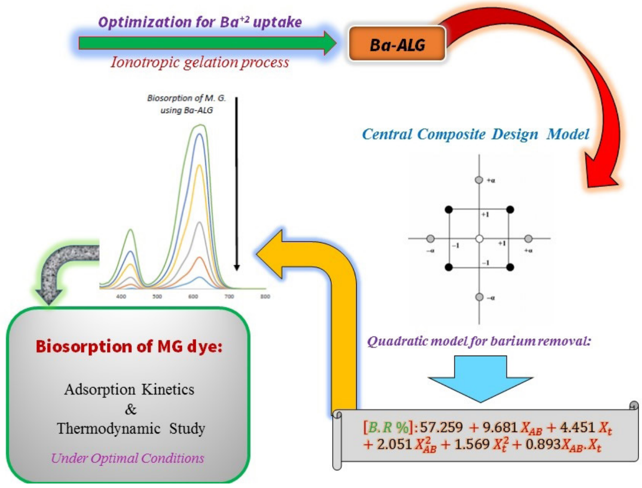
HIGHLIGHTS

- The optimal conditions for the barium uptake in the ionotropic gelation process were successfully evaluated using RSM based on the CCD model.
- The biosorption rate of MG dye using Ba-ALG was followed by the pseudo-second-order kinetics model.
- The thermodynamic study confirmed that the adsorption process was spontaneous by endothermic behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

Biocompatible materials, as efficient sorbent, are used for the removal of dyes and heavy metals ions from water and industrial wastewater. In this work, the optimal conditions for the maximum barium uptake in the formation process of Ba-alginate beads (Ba-ALG) were determined using the central composite design (CCD). The operational factors were evaluated for polymer/barium ratios of 1:3, 1:2, 1:1, 2:1, and 3:1 and residence times of 20, 30, 75, 120, and 180 minutes. The optimal ratio of sodium alginate to barium concentration for cations uptake was obtained at 3:1. Ba-ALG could not form a spherical and stable structure at higher polymer/cross-linker ratios. Validation tests illustrated the high accuracy of the selected model to determine the optimal experimental conditions in the barium uptake process. The maximum barium uptake is 88.61%, which was achieved at X_{AB}=1.5 (optimal ratio of polymer to Ba^{+2}) and X_t=1.5 (180 min). The ability of Ba-ALG to adsorb dye was also evaluated. Kinetics, equilibrium, and thermodynamic studies for adsorption of malachite green (MG) by Ba-ALG were statistically described. The adsorption results match the pseudo-second-order kinetics, suggesting that there was MG dye uptake to the adsorbent in monolayers due to its chemical affinity. The thermodynamic parameters were also determined by the Gibbs free energy function, confirming that the adsorption process was spontaneous and accompanied by an endothermic reaction.

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1. Introduction

Heavy metal ions found in industrial wastewater are one of the most serious environmental problems [1,2]. The heavy metals (such as lead, copper, chromium, cadmium, nickel, iron, zinc, arsenic, manganese, mercury, and barium) are non-biodegradable, toxic, and carcinogenic and tend to accumulate in living organisms. These pollutants are present in the wastewater of oil refineries, petrochemical companies, and some other industrial units, such as steel, electronics manufacturing, power generation, textile, and battery construction [3-5]. Barium is a common heavy metal, and high levels of its compounds in the air (such as barium sulfate and barium carbonate) causing respiratory problems. This metal ion has a high solubility in an aqueous solution, so its presence in water directly affects human health. In some cases, a low concentration of barium in water can lead to respiratory problems, high blood pressure, heart rate changes, heartburn, muscle weakness, changes in nerve reactions, and heart damage; at higher amounts, it will lead to paralysis and even death [6]. Dyes present in drinking water can be harmful for human consumption, and most are stable to degradation [7].

There are various methods for the removal of dyes and heavy metals from wastewater, such as chemical precipitation, ion-exchange, a membrane filter, and adsorption. Each of these methods has advantages and disadvantages based on simplicity, flexibility, process efficiency, and cost, as well as technical and maintenance problems; unfortunately, most of these methods also have shortcomings due to high cost or incomplete removal of heavy metals and the production of toxic sludge. Adsorption, a simple process for the removal of dyes and heavy metals from wastewater, is one of the most effective and low-cost methods [8,9]. Hydrogels as renewable, non-toxic, cheap, and biodegradable adsorbents, are three-dimensional polymer networks with a high capacity to absorb water or bio-fluids. Hydrogels are available in both natural and synthetic forms, depending on the source of preparation. Two important groups of natural polymers for the preparation of hydrogels include proteins (such as collagen and gelatin) and polysaccharides (such as starch, chitosan, alginate, and agarose) [10]. Sodium alginate is a linear copolymer obtained from brown algae. This polysaccharide has received a great deal of attention due to its biodegradability, bioavailability, hydrophilic properties, easy extraction procedure, and pH sensitivity [11-14].

One of the most salient properties of alginate, which highlights the importance of this natural polymer for industrial and biotechnological applications, is the ability to produce a variety of sequential 1,4-linkage with other materials and form the electrostatic bonds between its chains and divalent cations, such as barium via α-L-guluronic and β-Dmannuronic acid residues. This polysaccharide shows the unique ability to selectively adsorb divalent ions of alkaline earth metals and also has extensive applications in medicine, pharmaceuticals, biotechnology, the food industry, etc. [15]. Alginate has been studied as a biosorbent mainly after the ionotropic gelation [16]. But this work focuses on the optimal conditions for barium uptake during the formation process of Ba-ALG. The adsorption of MG dye using Ba-ALG has also been studied. Kinetics and thermodynamic descriptions for adsorption of MG, as an organic and cationic dye, by Ba-ALG were investigated.

2. Materials and methods

2.1. Materials

Sodium alginate of medium viscosity (3500 cps, 2% w/v aqueous solution at a room temperature of about 25°C) and barium chloride were purchased from Sigma-Aldrich (USA). MG powder was purchased from Merck (Germany). Double distilled water was used throughout the study. HCl and NaOH were obtained from Shimi Azma Ltd., (Iran).

2.2. Apparatus

Metal measuring was carried out using a flame-type atomic absorption spectrometer (SavantAA AAS, GBC, Australia). Spectra recording was performed using a T80$^+$ UV-Vis Spectrophotometer (PG Instruments Ltd., England). The centrifuging was performed with a Hermle Z205-A (Benchmark Hermle, USA).

2.3. Preparation of Ba-Alginate particles; barium removal measurement

$BaCl_2$ salt and the sodium alginate powder were separately dissolved in deionized water under a magnetic stirrer (400 rpm at 25 °C) for 1 hour to prepare the final solutions of 1500 ppm Ba^{+2} (as synthetic wastewater) and 2% (w/v) sodium alginate, respectively. According to the desired experimental conditions, variables amounts of sodium alginate (2.5 to 22.5 mL) was dripped through a burette with a nozzle's tip diameter of 1.2 mm into a beaker containing 100 mL of barium chloride solution at an adjusted flow rate of 120 $mL.min^{-1}$ and uniform distance between the burette and cross-linker media.

Spherical and mono-sized Ba-ALG were prepared using ionotropic gelation via interactions between the carboxylic groups of alginate and divalent barium ions. The precipitated hydrogels were collected after certain contact times (20 to 180 min). The gelation media containing the remaining cations was centrifuged at 6000 rpm for 4 min to separate any possible solids from the solutions. Barium removal was determined indirectly as follows. The removal of barium from the aqueous solution was calculated by determining the difference between the initial total amounts of $BaCl_2$ in a beaker and the remained-heavy metal ions in the supernatant at the end of the ionotropic gelation process. The barium content remaining in the solution was measured with a flame-type atomic absorption spectrometer. Adjustment of pH was made by adding 0.1 M HCl or 0.1 M NaOH. As in a previous dye removal study, the pH value of the solutions in this study was controlled at 10 [16].

2.4. Design of experiments (DOEs) and optimization of barium removal

In the present study, the DOEs were performed by Minitab-18 software. The central composite design model (CCD) was used to determine the number and conditions of the required tests, and the response surface methodology (RSM) to analyze the optimal conditions for barium removal from aqueous solutions using sodium alginate via ionotropic gelation. Effects of the main operational parameters, such as the concentration ratio of sodium alginate to barium (AB) and the residence time of hydrogels in barium solution (*t*), were studied. The parameters and levels range of (-1 to +1) with α=1.5 was determined based on the CCD model given in Table 1, where α is the distance from the axial point to the central point. Before the selecting levels, pre-tests were performed to remove out of effective ranges. In other words, in the pre-tests, the barium removal changes for a residence time of more than 180 min and an AB of more than 3:1 are not significant. According to the above description, the levels presented in Table 1 were used for the evaluation of the variables based on the CCD model.

Table 1. The parameters and levels range

Factors	Symbols	Range of Levels				
		-α	-1	0	+1	α
Alginate to barium ratio	AB	1:3	1:2	1:1	2:1	3:1
Residence time (min)	*t*	20	30	75	120	180

The operational factors were evaluated for an AB of 1:3, 1:2, 1:1, 2:1, and 3:1 and residence times of 20, 30, 75, 120, and 180 min. Using CCD, 13 experiments were done in 4 factorial points and 4 axial points at five central points to determine the errors. The experimental design and results of the tests are summarized in Table 2. Analysis of variance (ANOVA) is a reliable method to analyze and define the degree of certainty in the experimental data [17,18]. Hence, statistical ANOVA analysis was carried out on the model. The response variable was fitted with a full quadratic model in order to relate the barium removal to this variable. The mathematical model used is given in Eq. (1).

$$B.R. = \gamma_0 + \gamma_1 X_1 + \gamma_2 X_2 + \gamma_3 X_1^2 + \gamma_4 X_2^2 + \gamma_5 X_1 X_2 \qquad (1)$$

where *B.R.* is barium removal %, X_1 and X_2 are the uncoded independent variables, γ_0 is the offset term, γ_1

Table 2. DOEs for two independent factors and their responses.

Run No.	Manipulated variables		Response
	X_{AB}	X_t	B.R%
1	1.0	-1.0	64.80
2	1.0	1.0	75.00
3	0.0	0.0	57.60
4	0.0	0.0	57.20
5	0.0	0.0	56.50
6	-1.0	1.0	54.70
7	-1.0	-1.0	48.07
8	0.0	0.0	57.40
9	0.0	0.0	57.70
10	0.0	-1.5	54.00
11	-1.5	0.0	47.00
12	1.5	0.0	77.17
13	0.0	1.5	68.00

and γ_2 are the linear coefficients, γ_3 and γ_4 are the quadratic coefficients, and γ_5 is the interaction coefficient between X_1 and X_2. The mathematical experimental model was considered via ANOVA, resulting in a significance level of 5%. ANOVA was also used to determine the significance of the second-order models. The statistical significance of the second-order models was determined by the F-value. The calculated F-value is defined as the mean squares regression (including linear, square, and interaction) and the mean-square residual as shown in Eq. (2).

$$F-value = \frac{MS_{regression}}{MS_{residual}} \tag{2}$$

In which, mean squares regression and mean square residual can be calculated using Eqs. (3) and (4), respectively [17].

$$MS_{regression} = \frac{SS_{regression}}{DF_{regression}} \tag{3}$$

$$MS_{residual} = \frac{SS_{residual}}{DF_{residual}} \tag{4}$$

2.5. Bach adsorption studies

The ability of Ba-ALG in the adsorption of cationic dyes was studied. Thirty prepared beads containing 21 mg alginate were added to 50 mL of MG solution (15-100 mg.L^{-1}). The mixture was stirred for 100 minutes. The particles containing MG were collected from the mixture, and the solution was centrifuged to determine the residual concentrations of MG in the supernatant using a UV–Vis spectrophotometer at λ_{max}= 618 nm. The kinetics of the MG absorption in batch systems was studied at room temperature. The adsorption of the adsorbate (MG) per unit gram of adsorbent (Ba-ALG), q_e, was obtained from the following equations.

$$q_t = (C_0 - C_t) \times \frac{V}{M} \tag{5}$$

$$q_e = (C_0 - C_e) \times \frac{V}{M} \tag{6}$$

$$MG\ removal\ efficiency\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{7}$$

where C_0 (mg.L^{-1}) and C_e (mg.L^{-1}) are the initial and final concentration of *MG*, respectively. q_e (mg.g^{-1}) is the MG sorption capacity. C_t (mg.L^{-1}) and q_t (mg.g^{-1}) are the concentration and sorption capacity of MG at time t (min), respectively. M (g) is the mass of MG and V (L) is the volume of the initial solution.

3. Result and discussions

3.1. Response and analysis of variance

A quadratic model for barium removal was obtained by the least square of error method, which is presented as follows.

$$B.R. = 57.259 + 9.681X_{AB} + 4.451X_t + 2.051X_{AB}^2 + 1.569X_t^2 + 0.893X_{AB}\,X_t \tag{8}$$

Comparison of the measured and predicted values of barium removal from the wastewater showed that R^2 and R_{adj}^2 in the barium removal model were 0.9969 and 0.9948, respectively. Standard deviation analysis for the quadratic model of barium removal is reported in Table 3, indicating the total degree of freedom is 12. Furthermore, regression and residual error degrees of freedom are 5 and 7, respectively.

A comparison between F-values presented in Table 3 shows that the greater the F-value calculated for the model, the higher the significance level. The p-values less than 0.05 indicate that the model terms are significant; so, the linear, square, and 2-way interaction independent variables are the significant regression terms.

As shown in the *Pareto* graphic analysis of the investigated factors (Fig. 1), parameters A, B, AA, BB, and AB (or X_{AB}, X_t, X_{AB}^2, X_t^2 and $X_{AB}X_t$) have crossed the hypothetical point limit, and they confirm the significance of these parameters. These results also confirm the obtained data from the regression equation.

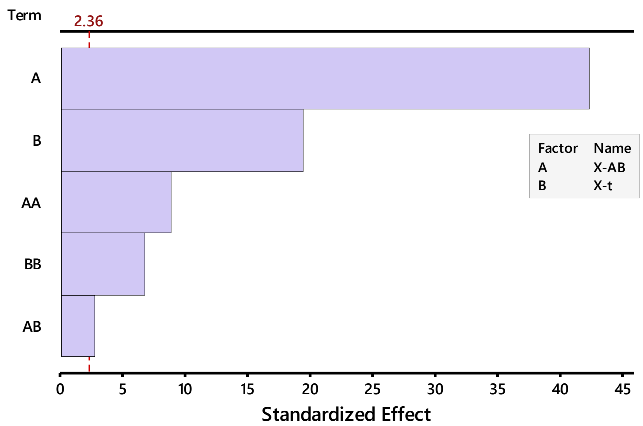


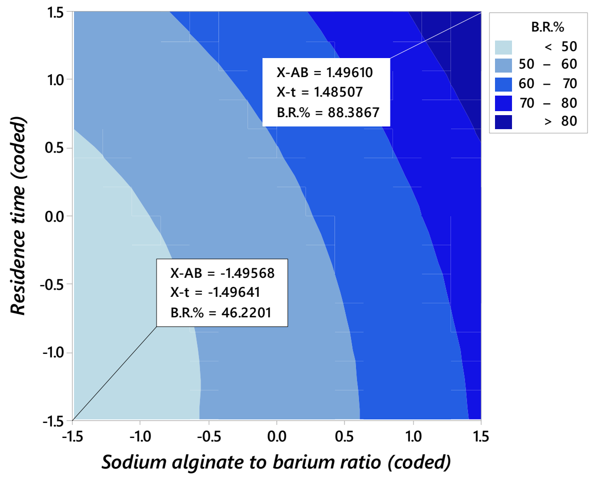
Fig. 1. Pareto graphic analysis for the standardized effect of the investigated factors.

Table 3. Standard deviation analysis for the quadratic model of barium uptake.

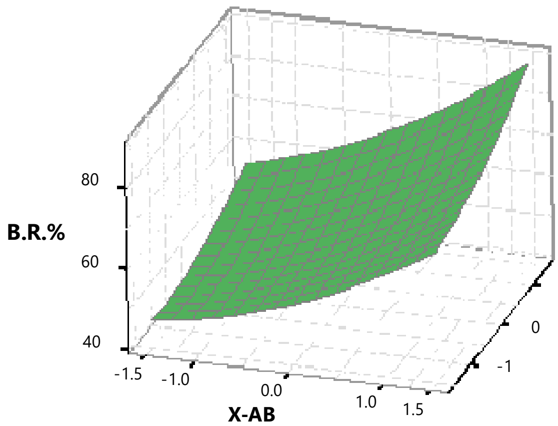
Sources	DF	SS	MS	F-Value	p-Value	Degree of significance
Regression	5	1015.24	203.047	456.88	< 0.001	Highly significant
X_{AB}	1	796.57	796.567	1792.36	< 0.001	Highly significant
X_t	1	168.37	168.366	378.84	< 0.001	Highly significant
X_{AB}^2	1	34.86	34.859	78.44	< 0.001	Highly significant
X_t^2	1	20.40	20.396	45.89	< 0.001	Highly significant
$X_{AB}X_t$	1	3.19	3.186	7.17	0.032	significant
Residual error	7	3.11	0.444	-	-	-
Lack-of-fit	3	2.20	0.734	3.23	0.143	No significant
Pure error	4	0.91	0.227	-	-	-
Total	12	1018.35	-	-	-	-

The empirical model plots for barium removal are drawn in a contour plot, response surface diagram, and interaction plot using Minitab tools (Figs. 2 and 3). Contour and response surface diagrams of barium removal are plotted in Fig. 2. As can be seen in Fig. 2, the barium removal percent was higher at high levels of operational factors. According to the interaction plot shown in Fig. 3, and in line with results obtained in the contour plot and response surface diagram (Figs. 2 and 3), barium removal increased as $X_{AB}X_t$ increased. However, this incremental slope was more evident at different ratios of the polymer-to-metal (X_{AB}). Model numerical optimization was carried out to predict the optimal conditions to achieve the maximum amount of barium removal from the aqueous solution. Based on the results presented in Fig. 4, the maximum barium removal is 88.61%, which was achieved at X_{AB} = 1.5 and X_t= 1.5.

As illustrated in CCD results (Table 3), *lack-of-fit* was not significant, thereby confirming the validity of the model [19]. Moreover, based on the practical validation test at optimal conditions, the metal removal was measured to be 86.4%, and this slight difference between the amount predicted by the model (88.61%) and the value obtained in practical terms indicates the accuracy and validity of the proposed model.



(a)



(b)

Fig. 2. Effect of sodium alginate to barium ratio (*AB*) and residence times on barium removal (*B.R.*) in percentages: (a) contour plot and (b) response surface.

3.2. Adsorption kinetics study

Profiles of the adsorbed quantity of MG versus contact time are normally assessed to investigate the rate of removal using pseudo-first-order and pseudo-second-order kinetic models. The linearized forms of these models are expressed as Eqs. (9) and (10), respectively.

$$ln(q_e-q_t) = ln\ q_e - k_1.t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where q_e (mg.g^{-1}) and q_t (mg.g^{-1}) are the amounts of the

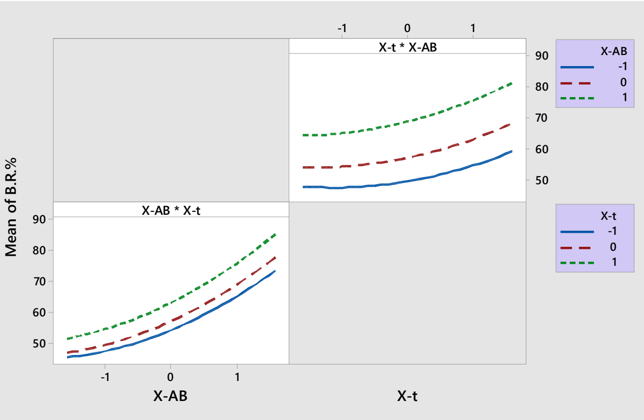


Fig. 3. Interaction plot for barium removal.

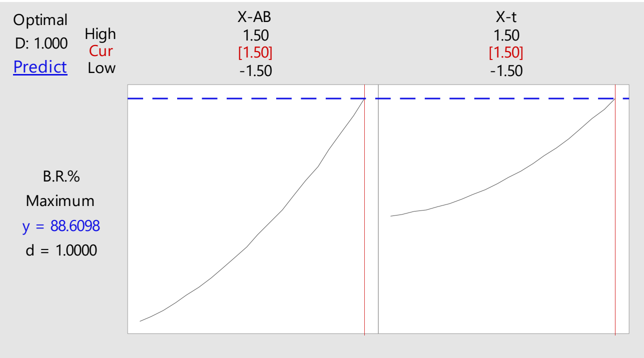


Fig. 4. Optimization plot for barium removal.

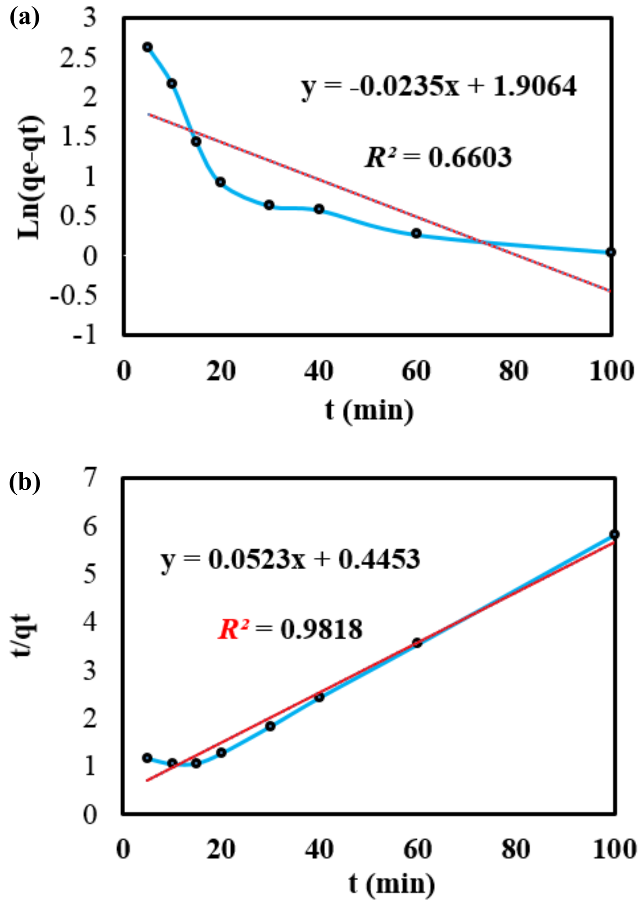


Fig. 5. (a) The pseudo-first order kinetics plot and (b) the pseudo-second order kinetics plot.

studied dye adsorbed on Ba-ALG at equilibrium and at any time *t* (min), respectively, and k_2 ($g.mg^{-1}.min^{-1}$), k_1 (min^{-1}) are rate constant of adsorption for pseudo-second-order and pseudo-first-order adsorption kinetics, respectively. The kinetics plots of the pseudo-second-order and pseudo-first-order for MG are shown in Fig 5. It was observed that the value for pseudo-second-order kinetic was greater than the pseudo-first-order kinetic, which suggests that the rate-controlling step in the removal is the chemical interaction between functional groups of Ba-ALG and MG in the solution (Table 4).

3.3. Thermodynamic study

The biosorption of MG on Ba-ALG was investigated at different temperatures ranging from 298 to 318 K to highlight the involved thermodynamic behavior and whether it is a chemisorption or physisorption process. The thermodynamic parameters, such as change in Gibbs free energy (ΔG^0), standard entropy change (ΔS^0), and standard enthalpy change (ΔH^0), have been calculated from Eqs. (11) and (12).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{11}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

where T (K) and R ($8.314\ J.K^{-1}.mol^{-1}$) are the investigated temperature and the ideal gas constant. The equilibrium constant (K_c) was expressed as $K_c = q_e/C_e$ [20]. The values ΔH^0 and ΔS^0 were obtained from the slopes and intercepts of the plot $\ln K_c$ versus $1/T$ (Fig. 6), and all thermodynamic parameters are shown in Table 5.

Table 4. Kinetic parameters for MG.

Kinetic models	**Pseudo-first-order**			**Pseudo-second-order**		
	q_e ($mg.g^{-1}$)	k_1 (min^{-1})	R^2	q_e ($mg.g^{-1}$)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
	6.729	0.023	0.660	19.120	0.006	0.982

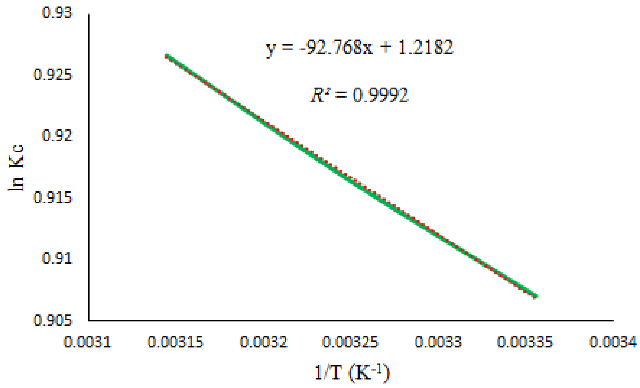


Fig. 6. Activation energy estimation; determination of enthalpy and entropy for MG biosorption.

Table 5. Thermodynamic parameters for the biosorption of MG on Ba-ALG.

ΔG^0 (kJ.mol^{-1})			ΔH^0 (J.mol^{-1})	ΔS^0 (J.mol^{-1}.K^{-1})
298 K	308 K	318 K		
-2.247	-2.348	-2.449	+771.27	+10.128

4. Conclusions

In this study, the optimal conditions for barium uptake in the ionotropic gelation process were determined using RSM based on the CCD model. Regression equation, *Pareto* graphical analysis, contour plot, 3D response surface, and related data show that all experimental parameters had a significant effect on the barium uptake in the process of bead preparation. The optimal ratio of polymer to cross-linker concentration was obtained at 3:1. However, at values higher than the determined ratio, Ba-ALG cannot form a spherical and stable structure. Results have shown the acceptable accuracy of the statistical model to predict the optimal conditions for barium uptake. The MG biosorption rate via Ba-ALG was followed by the pseudo-second-order kinetics model. The thermodynamic study revealed that the adsorption process was endothermic and spontaneous.

Acknowledgments

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