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Analysis of lithium separation by modified zeolite using fuzzy logic: equilibrium, kinetics and thermodynamic

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ABSTRACT

Modified natural zeolite with crown ethers such as 12crown4, 15crown5, 6crown18 and benzo-15crown5 have been characterized using Fourier transform infra-red, scanning electron microscope and Brunauer–Emmett–Teller instruments. Concentration of 0.01 mg/L of complexing agent and modification time of 240 h were obtained as optimum parameters. Effective parameters such as pH, adsorbent dose, contact time, type and concentration of crown ethers, ion strength, and initial concentration of lithium ion and temperature of complex formation were also investigated and optimized in this adsorption process. Under the optimized experimental conditions pH equal to 7, one gram of adsorbent in 2 mL solution of 0.01 mg/L and temperature of 40°C, the most lithium adsorption (87%) was acquired. The effect of interference ions on the adsorption process was also considered. The results showed that Freundlich model is one of the best descriptive models for this process. The adsorption kinetics of lithium on modified zeolite follows the pseudo second-order model. Thermodynamic parameters were calculated and shown that adsorption process is an endothermic and spontaneous process. Statistical analysis of experimental results was done by fuzzy logic tool of MATLAB software and three-dimensional diagrams of different parameters effect on the adsorption percentage were also presented.

Keywords: Lithium; Natural zeolite; Clinoptilolite; Crown ether; Benzo15 Crown5; Adsorption

1. Introduction

In recent years, the importance of lithium industry has been the center of attention because of its application in lithium ion batteries and increasing in the production of fuel for fusion reactor, tritium. Nowadays, it is used as sources of energy in transportation vehicles and as a device to store energy in smart houses and networks. Moreover, lithium and some of its compounds are so useful in glass and ceramic industries as well as in lubricating, hydrometallurgy, nuclear energy, aerospacing and chemical/ pharmacy industry and so on [1,2]. Because of lithium presence in sea water, it can be regarded as a huge source of lithium in earth which is 66% of the whole lithium in the world. The extraction of lithium from sea water leads to the inexpensive production of that. Therefore, there should be an affordable way for lithium recovery from sea salty water [3]. There are not extensive compatible methods used in the separation of lithium from solutions, but there have been done a lot of researches and actions to extract lithium as metal or salt such as precipitation process [4], evaporation and precipitation [2], liquid-liquid extraction [5], adsorption [6], ion-exchange [7], biological recycling of lithium via microorganisms [8] and membrane process [9]. Adsorption process is one of those methods in which lithium recovery using lithium adsorbents has extensively been analyzed [6,10]. Adsorption method for separation of lithium from different environments has also been applied using organic materials as well as mineral materials [11]. Different types of activated carbon [12,13], hydrogen and sodium amberlite

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ion exchange resins [14] were used to separate lithium and then two types of synthetic zeolite with the same aim by other research groups were used as well [7]. In the research molecular sieves areas, spinel-type manganese oxides [15,16], aluminum oxides [2,5] and titanium oxides [17] were analyzed in order to be used in the process of lithium separation from seawater.

In order to modify zeolites, crown ether family was used such as benzo15crown5 which have high selectivity towards lithium ions [18]. These compounds were directed by electrostatic effects of dipole ion between cation and electron donor atoms with negative charge lead on polyether rings [19]. The aim of this research is to investigate on lithium adsorption process from aqueous solutions by modified zeolite. Different parameters such as type and concentration of ligand, time of modification and ion strength for zeolite modification were optimized and analysis of Fourier transform infra-red (FT-IR), scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET) were done on each. To determine the concentration of lithium in the sample, inductively coupled plasma-optically emission spectroscopy (ICP-OES) was used. Some parameters such as pH, adsorbent dose, temperature, time and initial concentration optimized and effect of interferers in seawater were all considered in advance for adsorption process.

Fuzzy logic was used to analyze the experimental results. It is a suitable application to predict process performance with current data and to generalize the data to unavailable ones. Fuzzy control system is used in some chemical processes rarely but there are some documents proving the fact that fuzzy logic is also used to predict the separation process [20]. In this work, predictions of adsorption percentage was achieved through using inference fuzzy logic of MATLAB software (7.12.0 version), perfect. Three-dimensional diagrams present the effects of different parameters on the adsorption percentage too.

The ultimate aim in this work is an investigation on evaluation of results to equilibrium, kinetics and thermodynamic of raw and modified zeolites using fuzzy logic in lithium separation.

2. Experimental

2.1. Chemical materials

All used materials in this research: Lithium chloride salt (LiCl), 12crown4 ($C_5H_{16}O_4$), 15crown5 ($C_{10}H_{20}O_5$), 6crown18 ($C_{12}H_{24}O_6$), benzo15crown5 ($C_{14}H_{20}O_5$), Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) from Merck company of Germany were bought. Zeolite of natural clinoptilolite was prepared from an area located in the north-west of Iran, named Mianeh. In order to prepare solutions from all above-mentioned materials, distilled water was used. To evaluate interference ions effects on the capacity of lithium adsorption, metal salts such as KIO_3, NaCl, $Mg(OH)_2$, $CaCl_2.H_2O$ and $Sr(NO_3)_2$ were used as sources of interference ions.

2.2. Equipment

In order to determine the concentration of metal ions in solutions especially lithium ion at wavelength of 670.784 nm, before and after adsorption, ICP-OES, model 7300DV made in USA was used. For comparing the main features of samples such as topography and morphology, SEM of model Zeiss evo 18 made in Germany was used and also for studying all effects of interference from surface and size of zeolite particles before and after modification, BET apparatus of model Covanto crom made by Nova 2000 was applied. Another device, Bruker Vector 22 FT-IR was also applied to recognize spectrum and fundamental groups on natural and modified zeolite. Heidolph shaker, model Vibermax 100 made of Germany, was used to mix zeolite with modifier solutions. Measuring of pH was done by sartorius basic meter PB-11 mechatronics. To weight the salts and zeolites, digital balance with 0.0001 g sensitivity, model BA 1105 made of sartorius mechatronics was used. Magnetic mixer, Wise Stir model MSH-20A was used to join adsorbent and solution.

2.3. Method

2.3.1. Preparation and modification of zeolite

Natural clinoptilolite zeolite which is used in this research has been prepared from the north-west zone of Iran named Mianeh and mesh size was about 200 µ*m*. To use this zeolite, first, the particles smaller than 100 µ*m* were separated by ion sieves, then, in order to remove the aqueous soluble impurities, the obtained powder was contacted in temperature of 343°K for 3 d. After purification and washing, purified material was contacted in 2 liters of sodium hydroxide solution (0.1 mg/L) for 2 weeks. For zeolite modification, 50 mL of ligand solution of 0.01 mg/L of crown ethers was poured in 100 mL polyethylene container. Also, 5 g of natural clinoptilolite zeolite was added into it. Then, the containers were put in the shakers at 200 rpm in the room temperature. After the end of contact time, the modified zeolite was separated from the solution by using a filter paper and was dried in the room temperature for 24 h.

2.3.2. Experiments of adsorption

In order to do each adsorption experiment, 20 mL of aqueous solution containing lithium ion with determined concentration was prepared and adsorbent was added. The container was put on the magnetic stirrer and after a while, the adsorbent was separated from the solution by filter paper. All experiments were performed by natural zeolite as well as the modified one and comparisons were also done. Before each set of experiment, sampling was done from the prepared solution with the aim of determining the initial concentration. All obtained samples were poured in 10 mL containers. At the end of adsorption experiments and after separation by filter paper, sampling was done once more from the purified liquid. Measurement of concentration, either initial or final, was done through ICP-OES instrument. Having the initial and final concentrations, adsorption capacity and percentage were determined by Eqns. (1) and (2), respectively:

$$q = \frac{V\left(C_i - C_f\right)}{m} \tag{1}$$

$$Ad\% = \frac{q \times {}^{m}\!/\!_{V}}{C_i} \times 100 = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

In both equations, V stands for solution volume (liter), C_i and C_f stand for concentration of adsorbate in the aqueous solution at the beginning and at the end of the process (mg/L), respectively, m stands for adsorbent dose which is measured in gram and q for adsorption capacity (mg/g).

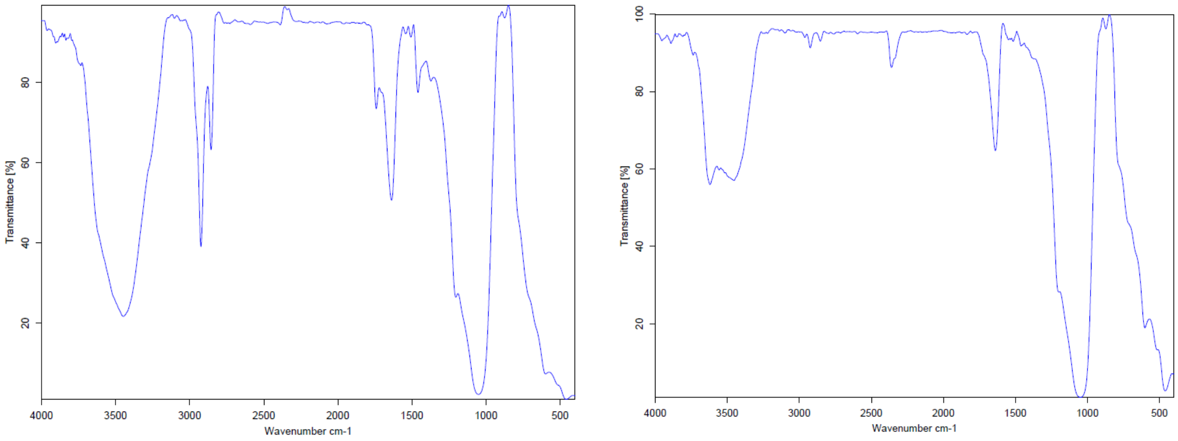
3. Results and discussion

3.1. Characterizing the adsorbent

In order to investigate on the effects of modification process in structural characteristics of zeolite, FT-IR, SEM and BET analysis were done before and after modification of zeolites. The FT-IR spectroscopy, SEM and BET are used to a large extent to characterize the zeolite materials and to follow adsorption reactions. Through FT-IR analysis, functional groups change in adsorbent surface was shown. Analysis of spectrum was done in the range of wavenumber of 400–4000 cm^{-1}. Fig. 1 show FT-IR spectrum of zeolite before and after modification by crown ethers, respectively. It shows the finger print area, the water bonding peaks, functional groups of OH^{-}, silica oxide, and aluminum oxide of natural and modified zeolites. The change in these characteristics can be clearly inferred from the comparison of figures.

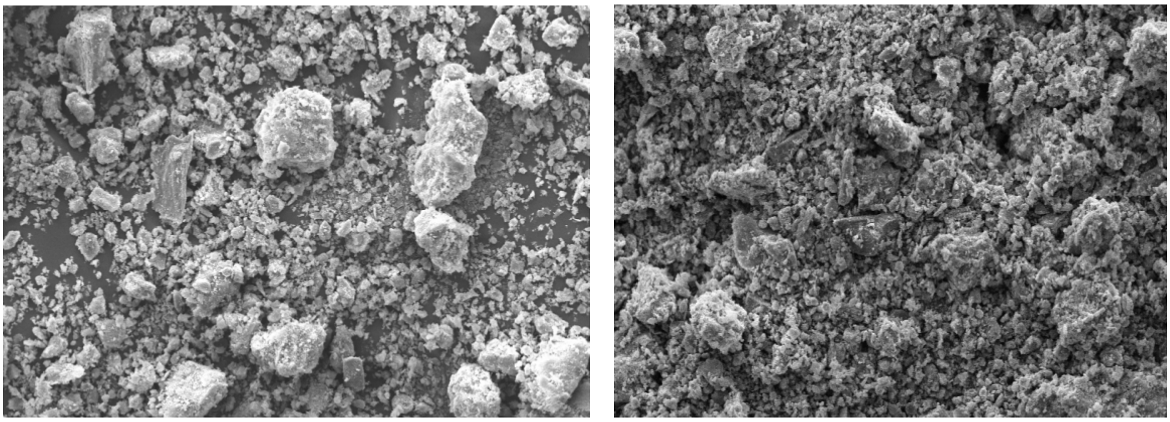
The natural clinoptilolite zeolite morphology changes before and after modification was evaluated by SEM. The results show that Si to Al ratio was changed from 4.28 to 3.31 after modification process. Fig. 2a shows that natural zeolite surface is heterogeneous and has low porosity. Zeolite particles smaller than 100 µ*m* are recognizable separately or as bulky masses. Fig. 2b is regarded as a confirmation on modification of natural zeolite by crown ethers.

BET was also used in determining the surface area, pores diameter and volume of natural and modified zeolites. The results are presented in Table 1. The above-mentioned average diameter had increasing while the pore volume and surface area were increased. On the other hand, through placing functional groups in pores, pores volume



(a) (b)

Fig. 1. FT-IR spectrum of natural (a) and modified (b) zeolites.



(a) (b)

Fig. 2. SEM image of natural (a) and modified (b) zeolites.

Table 1
Specifications of natural and modified zeolites using BET analysis

Types of adsorbent	Natural zeolite	Modified zeolite
Pore diameter (nm)	7.991	9.441
Pore volume (cm^3/g)	0.07	0.06
Surface area (m^2/g)	37.37	26.78

and their surface area amount were decreased and some of the adsorption sites were gone unreachable.

3.2. Modification of zeolite

The considered parameters for modification of clinoptilolite zeolite were mixing time, type and concentration of crown ethers as well as ion strength. 240 h for modification time, 0.01 mg/L, concentration of benzo15crown5 ligand solution was the best condition for modification of clinoptilolite zeolite.

In order to investigate on the effects of ligand type, four crown ether with concentration of 0.1 mg/L and 50 mL, 5 g of natural zeolite were modified in the shaker for 240 h. Fig. 3 shows the effect of ligand type on the lithium ion adsorption percentage in which benzo15crown5 and 15crown5 ligands had better efficiencies. 15crown5 ligand was used in this work to make a complex with lithium ion. These ligands are widely used in the lithium adsorption for most of the adsorbents [21].

In order to observe the effect of benzo15crown5 ligand concentration, different amounts of 0, 0.01, 0.05, 0.08 and 0.1 mg/L have been tested. Concentration of zero of benzo15crown15 ligand (mg/L) means that natural zeolite has been applied. The results shown in Fig. 4 reveal that there is not any relationship between ligand concentration and the adsorption percentage. In a way that with increasing in ligand concentration, the holes in the surface of zeolite are being saturated and they prevent the adsorption of lithium [22]. Therefore, use of ligands with low concentration is much more affordable.

The ion strength was investigated for extraction of cations with natural zeolite. Therefore, the calcium chloride was used that is soluble in water and the simplest form of the Ca^{2+} ion with the highest power. Modified zeolite (0.1 g) with 10 mL solution of 2 mg/L calcium chloride was contacted for 24 h in a shaker. After drying, the adsorption experiment with 20 mL aqueous solution of 0.1 mg/L lithium in 40°C temperature and pH: 7 were also done. The results show that the ion power had a negative effect on the lithium adsorption and 10.10% of lithium adsorption was obtained.

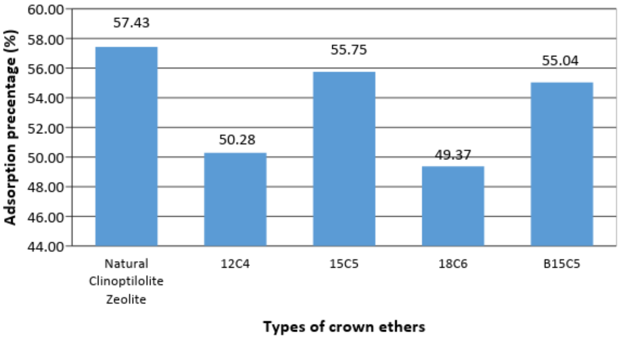


Fig. 3. Effect of crown ethers on adsorption percentage (crown ether concentration: 0.1 mg/L, adsorbent dose: 0.1 g, sample volume: 20 mL, temperature: 40°C, pH: 7, time: 5 min, initial concentration of lithium: 1 mg/L).

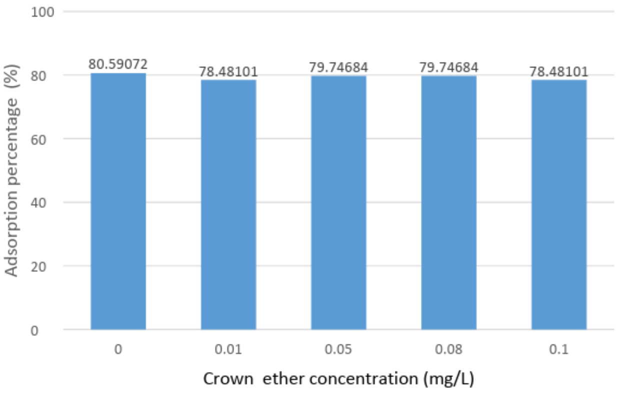


Fig. 4. Effect of crown ether concentration on adsorption percentage (adsorbent dose: 0.1 g, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH: 7, time: 5 min, initial concentration of lithium: 0.1 mg/L).

3.3. Effective factors on the lithium adsorption

3.2.1. pH effect

pH of aqueous solution has a significant effect on metal ion adsorption due to its influence on the sites, surface bonding and charges of adsorbent. This effect was investigated on lithium adsorption by natural and modified zeolites in the range of pH from 4 to 9 shown in Fig. 5. In solutions with low pH (pH < 4), the adsorption amount is small because of the increasing of the positive charge on the zeolite surface and followed that electrostatic repulsion between lithium ion and functional groups increased [23]. In solutions with more pH (4 < pH < 7), negative charge on zeolite surface will be changed and with increasing of pH (7 < pH < 8), electrostatic repulsion is decreasing. Decreasing in the density values of positive charge leads to more adsorption of lithium ion. Increasing of pH also leads to sediment and rally of metal on the zeolite surface that goes to the increasing of adsorption mechanism [24]. The highest percentage of adsorption for lithium ion was carried out in pH$_{pzc}$ of natural and modified zeolites.

3.2.2. The effect of adsorbent dose

The amount of adsorbent is considered as another significant parameter on the adsorption process because of force gradient increase of lithium adsorption. Fig. 6 shows the effect of adsorbent dose (0.02–1 g) in 20 mL aqueous solution on the lithium adsorption by means of natural and modified zeolite. As can be inferred from Fig. 6, the per-

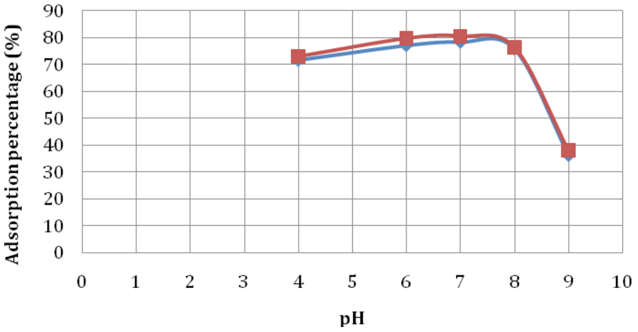


Fig. 5. pH effect on the lithium adsorption percentage by natural (red) and modified (blue) zeolites (adsorbent dose: 0.1 g, crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, time: 5 min, initial concentration of lithium 0.1 mg/L).

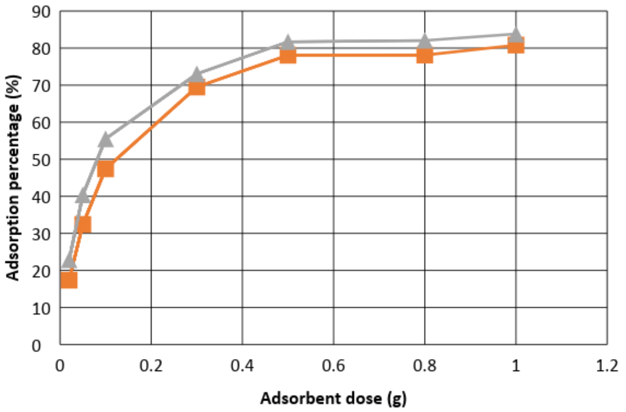


Fig. 6. Effect of adsorbent dose on the lithium adsorption percentage by natural (red) and modified (blue) zeolites (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, time: 5 min, initial concentration of lithium: 0.1 mg/L).

centage of lithium ion adsorption is increased by increasing the amount of adsorbent. The reason for this increase is the ability to reach more adsorption centers with more adsorbents. At the constant initial concentration of metal ion, more adsorbent amount leads to the increasing of lithium ion adsorption percentage with having more active adsorbents [25].

3.2.3. The effect of interference ions

Customary ions in drinking and industrial water like sodium, potassium, calcium and magnesium are regarded as interferences in adsorption process. These ions have negative effects on the zeolite selective adsorption especially in the high concentrations. In this research, the effects of these ions on the capacity of lithium adsorption by natural and modified zeolites in the optimized conditions (adsorbent dose: 1 g, pH: 7, crown ether type: B15C5, temperature of 40°C and contact time of 5 min) that was achieved in aforementioned parts was investigated. Also, the percentage of each ion in the solution was fitted similar to the caspian seawater amounts. The results showed a decrease in the lithium adsorption percentage from 87% to 9.5%. Therefore, the capacity of adsorbent mass in the presence of interference ions effects on the coefficient of metal ion activities limiting the transformation of lithium to adsorbent surface. In the other hand, some of the active sites occupied by interference ions and obviously, it decrease the capacity of lithium adsorption by the zeolites.

3.2.4. The effect of contact time/adsorption kinetics

In order to reach an equilibrium time for more extraction and to know the kinetics of adsorption process, lithium ion adsorption on modified zeolite was investigated as a function of contact time in the interval of 5–120 min in the same amount of adsorbent and equal concentrations of lithium ion. Fig. 7 shows that lithium ion adsorption percentage on zeolite at initial times are so quick and across this stage the changes in the percentage is decreasing and it will be constant during 60 min. At first, since the majority of adsorption centers are empty, metal ions are being adsorbed to the zeolite immediately; but through passing some seconds, adsorption centers are being occupied. Therefore, ions diffusion to the solution among the adsorbed ions and their connection to the empty centers are getting more complexity [26,27].

In order to evaluate the lithium ion adsorption mechanism on the zeolite, on the base initial studies, two kinetics models pseudo-second order [Eq. (3)] and interparticle diffusion model [Eq. (4)] were used to analyze experimental data [25].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{3}$$

$$q_t = k_{id} t^{1/2} + C \tag{4}$$

In these equations, q_e and q_t show the amount of adsorbed material in equilibrium time and given time to the model, respectively. k'_2 is also measured according to g/(mg·min) and is a rate constant in pseudo-second order model. In Eq. (4), parameter of K_{id} is constant of interparticle diffusion model according to mg/(g·min$^{0.5}$) and C is constant related to the thickness of bounding layer [28]. Kinetics constants were calculated by the linear fitting of two models (Figs. 8 and 9), the results are presented in Table 2.

The results presented in Table 2 approve that pseudo-second order kinetics model (R^2: 0.9991) is a better model to describe this process. This model also shows that lithium ion adsorption on modified zeolite is controlled by adsorption which is included in valence forces or exchanged electrons between adsorbent and adsorbed material. According to this model, the adsorption process is highly dependent on the amount of lithium ion in the solution and available adsorption centers, as it proportionated by squared number of empty centers. On the other hand, quick adsorption on modified zeolite reveals that these chemical reactions such as ion exchange and complexation are regarded as the rate limiting step of this process [24]. Considering obtained R^2 amount for interparticle diffusion model presented in Table 2, it can be inferred that the penetration in the inner holes of zeolite could not have any significant effect on the lithium adsorption on modified zeolite.

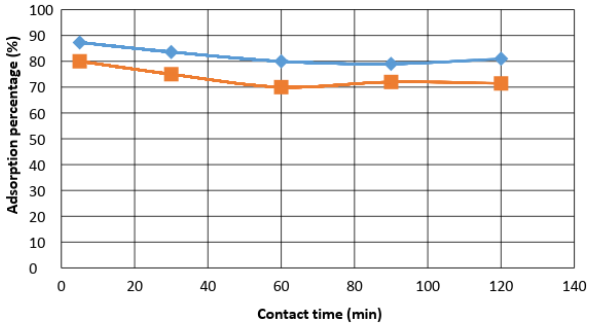


Fig. 7. Effect of contact time on the lithium adsorption percentage by natural (red) and modified (blue) zeolites (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, adsorbent dose: 1 g, initial concentration of lithium: 0.1 mg/L).

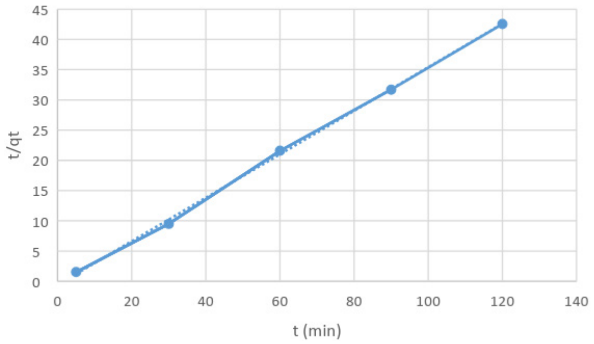


Fig. 8. Pseudo-second order kinetics model for the lithium adsorption on natural and modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, adsorbent dose: 1 g, initial concentration of lithium 0.1 mg/L).

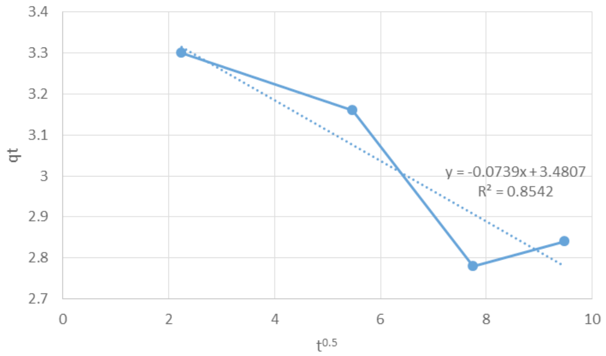


Fig. 9. Interparticle diffusion kinetics model for the lithium adsorption on natural and modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, adsorbent dose: 1 g, initial concentration of lithium: 0.1 mg/L).

Table 2
Adsorption kinetics parameters of pseudo-second order and interparticle diffusion models

Types of model	k'	$q_{e,}$ (mg/g)	R^2
Pseudo-second order	0.22 (g/mg·min)	2.78	0.9991
Interparticle diffusion	0.07 (mg/g·min$^{0.5}$)	3.48	0.8542

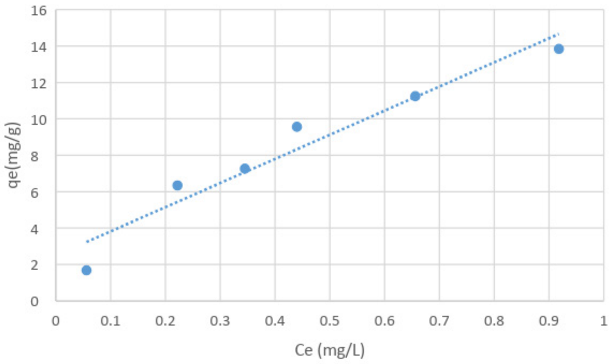


Fig. 10. Effect of lithium ion initial concentration on the lithium adsorption on natural and modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, adsorbent dose: 1 g, time: 5 min).

3.2.5. The effect of initial concentration/ adsorption isotherm

Adsorption equilibrium isotherm is used to describe the interaction between solute particles and adsorbent and it is also very important in designing the adsorption system. Fig. 10 shows lithium ion adsorption capacity in the different initial lithium ion concentrations from 0.1 to 1.6 mg/L. It is clear that the lithium adsorption on the zeolite is dependent on its initial concentration. Lithium ion adsorption capacity is increasing with the ion concentration. And this fact could also be related to the increasing of gradient force which is increased by lithium ion concentration as well [25].

To describe the equilibrium between the adsorbed lithium ions on modified zeolite, two common adsorption isotherms Langmuir [Eq. (5)] and Freundlich [Eq. (6)] were used.

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_L.q_m} \qquad (5)$$

In Eq. (5), q_m (mg/g) and k_L (L/mg) are constant in Langmuir that are related to the highest amount of single layer and adsorption energy, respectively. q_e (mg/g) and C_e (mg/L) show the equilibrium adsorption and concentration of adsorbed part, respectively.

$$\text{Ln}\,(q_e) = \text{Ln}\,(K_F) + \text{n Ln}\,(C_e) \qquad (6)$$

In Eq. (6), k_F is Freundlich constant based on $\left[\frac{\text{mg}}{\text{g}} \times \left(\frac{\text{L}}{\text{mg}}\right)^n\right]$ that is related to the adsorption capacity and n is dimensionless constant that is related to the

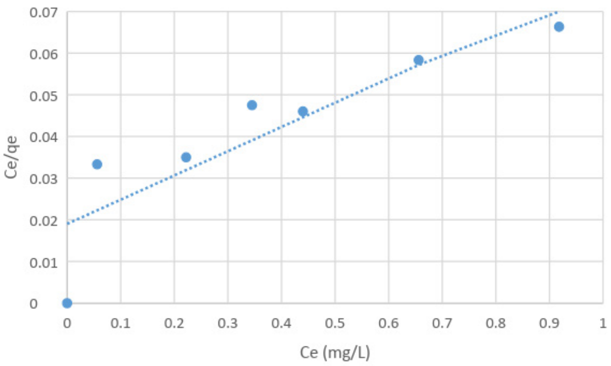


Fig. 11. Langmuir isotherm for lithium adsorption on the modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, adsorbent dose: 1 g, time: 5 min).

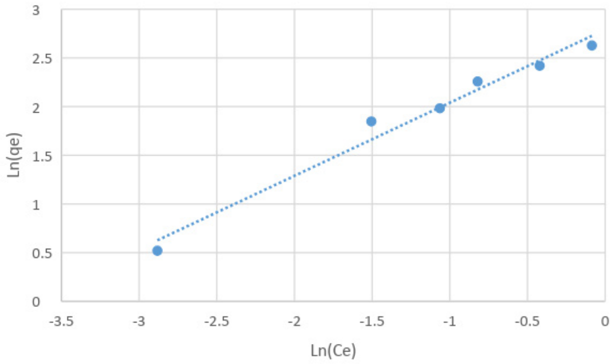


Fig. 12. Langmuir isotherm for the lithium adsorption on modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, temperature: 40°C, pH_{pzc}: 7, adsorbent dose: 1 g, contact time: 5 min).

Table 3
The amount of Langmuir and Freundlich isotherm parameters

Types of isotherm	K	q_m (mg/g)	R_L	*n*	R^2
Langmuir	0.032 (mg/g)	52.63	0.95	…..	0.7828
Freundlich	16.29 ($mg^{1-n}\cdot L^{n}/g$)	…..	…..	0.75	0.9767

strength of bonding. The amount of *n* is between 0 and 1; the closer value of it to 1 shows more adsorption force between the adsorbent and adsorbate [29]. Isotherm constants and correlation coefficients (R^2) are the results of linear fittings (Figs. 11 and 12) for two models of Langmuir and Freundlich which are presented in Table 3.

Regarding the obtained R^2 values for two models, it is clear that Freundlich model has the best fit matching with the experimental data of lithium ion adsorption on modified zeolite. This model confirms that the adsorption takes place on heterogeneous surfaces and the adsorbent surface has some adsorption parts with different capacities that are filled first by their strength order.

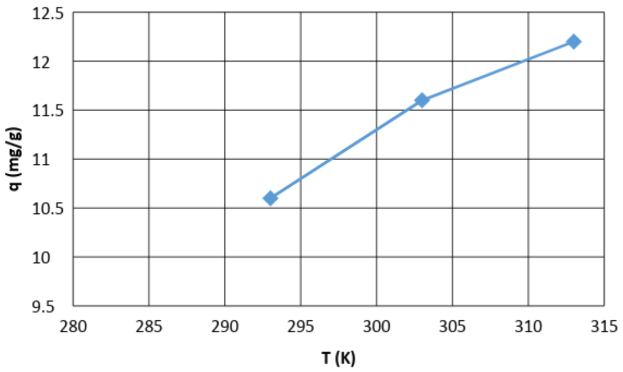


Fig. 13. The effect of temperature on the lithium adsorption on modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, pH_{pzc}: 7, adsorbent dose: 1 g, time: 5 min).

3.2.6. The effect of temperature/ adsorption thermodynamic

The effect of temperature on the lithium ion adsorption on modified zeolite was investigated (Fig. 13). By increasing the temperature, the adsorption percentage will also be increased that shows the nature of process is endothermic. Experimental data were used to estimate thermodynamic parameters.

Thermodynamic parameters were also used to compute Gibbs free energy ($\Delta G°$), enthalpy changes ($\Delta H°$) and Entropy changes ($\Delta S°$) by following formula:

$$\Delta G° = -RT\ln(K_d) \tag{7}$$

$$K_d = \frac{C_0 - C_e}{C_e}\cdot\frac{V}{m} \tag{8}$$

$$Ln\left(K_d\right) = \frac{\Delta S°}{R} - \frac{\Delta H°}{R}\cdot\frac{1}{T} \tag{9}$$

In Eqs. (7)–(9), k_d stands for distribution coefficient, C_e and C_0 respectively show initial and equilibrium concentration of metal ion in solution based on mg/L, *T* is based on kelvin, R is generally constant (8.314 $J\cdot mol^{-1} K^{-1}$), *V* is solution volume based on mL and *m* stands for mass in gram. In order to compute thermodynamic parameters $\Delta H°$ and $\Delta S°$, Van'tHof diagram [Eq. (9)] was drawn $\ln(k_d)$ is based on 1/T (Fig. 14) then after linear fitting slope and y-intercept were also obtained.

In order to obtain the k_d and ΔG^0, Eqs. (7) and (8) were used, respectively. The related results are presented in Table 6. Considering positive sign of $\Delta H°$, it can be inferred that the adsorption of lithium on modified zeolite is an endothermic process. The positive nature of $\Delta S°$ reveals that this system has increasing irregularities that can be result of H^+ production in the ion exchange reaction between lithium ion and zeolite. The negative amount of $\Delta G°$ shows that binding energy of adsorbent-lithium is more powerful than solvent-lithium. Therefore, this difference between potential energy of system components can be regarded as distribution gradient force of lithium ions in the system and spontaneous adsorption of lithium on modified zeolite [30]. As shown in Table 4, increase in temperature has very low effect on $\Delta G°$.

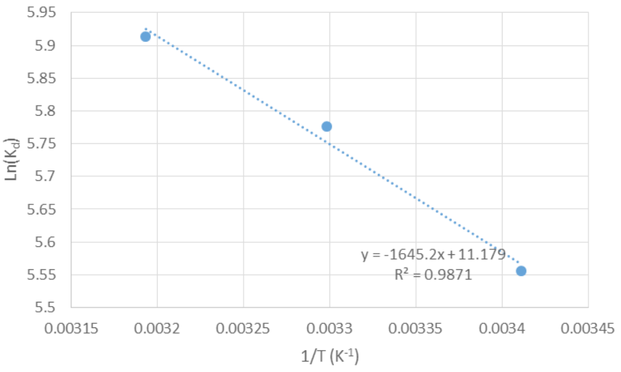


Fig. 14. VantHof diagram of lithium adsorption on the modified clinoptilolite zeolite (crown ether concentration: 0.1 mg/L, crown ether type: B15C5, sample volume: 20 mL, pH_{pzc}: 7, adsorbent dose:1 g, time:5 min).

Table 4
The amount of thermodynamic parameters of the lithium adsorption on modified zeolite

(kJ/mol) ΔG°			ΔS (J/mol·K)	ΔH° (kJ/mol)
T: 313 K	T: 303 K	T: 293 K		
–15.394	–14.556	–13.539	86.76	11.83

3.3. Statistical analysis of experimental results by fuzzy logic

There are different fuzzy deduction approaches such as Mamdani, Sugeno and Tisocomoto applied extensively. Their differences are in output collection process and fuzzification approach. The most current approach is Mamdani fuzzy deduction method. This method was introduced by Ibrahim Mamdani in 1975 to control a steam engine [31]. This system was so applicable because it was very intuitive. It was also very popular because it had succeeded in controlling automatically, analytical decision making and data categorization in the computer systems [19]. In this research, an advanced smart model based on Mamdani fuzzification system in prediction of the lithium adsorption on modified zeolite was used. In fuzzification process, 5 different parameters consisting of pH, contact time, adsorbent mass, initial concentration and temperature were defined at 3 levels, high, medium and low. According to this, (3^5) 243 rules for fuzzy system training were considered. After development of an efficient model based on fuzzy logic (FL), the model can also be used in predicting the adsorption percentage of different inputs in training data area [32]. In Table 5, experimental data derived from experiments with the predicted amounts that had been done by MATLAB (version 7.12.0) were presented.

A good compatibility between results of FL and experimental data shows that FL prediction is able to do modeling for lithium ion adsorption from aqueous solution. Figs. 15–19 show a confirmation on the compatibility of FL and experimental results.

Figs. 20–25 show the predicted amount of adsorption percentage based on operational parameters in the three-dimensional diagrams according to FL.

Table 5
The comparison between experimental data derived from experiments and predicted adsorption percentage by FL

pH	Time (min)	Adsorbent dose (g)	C_0 (mg/L)	Temp. (°C)	%R (exp.)	%R (fuzzy)
7	5	0.1	1	40	46	50
7	5	0.1	0.7	40	51	52
7	5	0.1	0.5	40	58	55
7	5	0.1	0.1	40	60	58
4	5	1	0.1	40	71	75
6	5	1	0.1	40	77	85
7	5	1	0.1	40	78	80
8	5	1	0.1	40	75	74
7	5	0.1	0.1	40	55	75
7	5	0.5	0.1	40	81	83
7	5	0.8	0.1	40	82	84
7	5	1	0.1	40	83	85
7	5	1	0.1	20	56	55
7	5	1	0.1	30	61	70
7	5	1	0.1	40	64	75
7	5	1	0.1	50	67	73
7	5	1	0.1	40	87	85
7	30	1	0.1	40	83	84
7	60	1	0.1	40	73	55
7	90	1	0.1	40	75	55

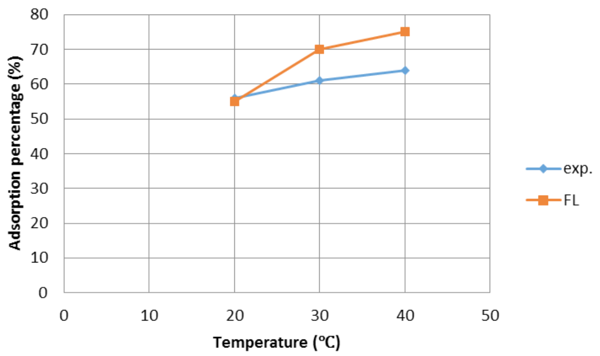


Fig. 15. The comparison between experimental data and FL prediction for the effect of temperature.

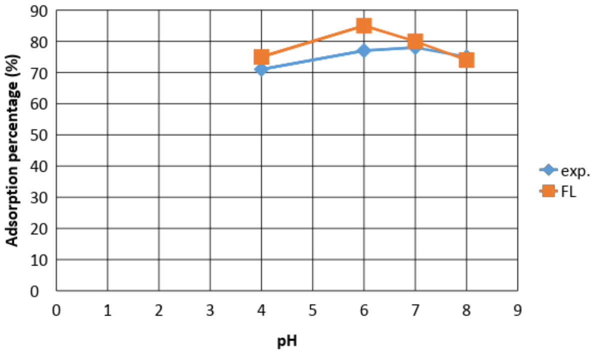


Fig. 16. The comparison between experimental data and FL for the effect of pH.

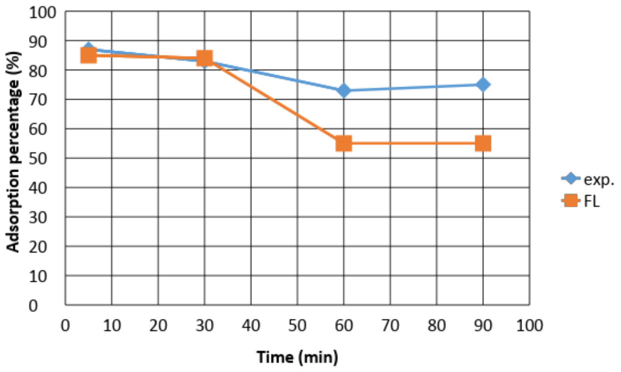


Fig. 17. The comparison between experimental data and FL for the effect of time.

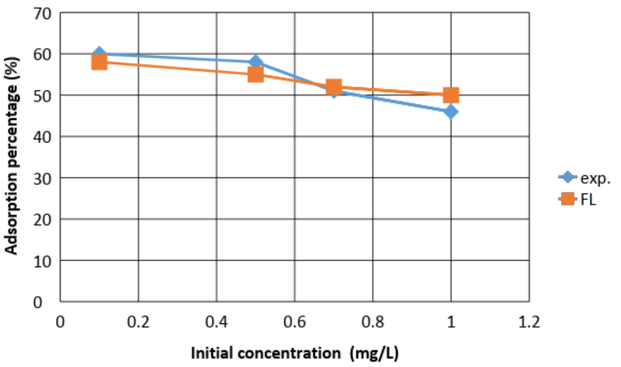


Fig. 18. The comparison between experimental data and FL for the effect of initial concentration.

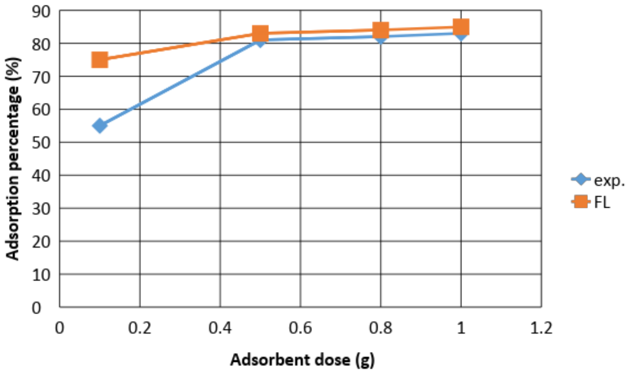


Fig. 19. The comparison between experimental data and FL for the effect of adsorbent dose.

4. Conclusion

Natural zeolite was modified by crown ethers and lithium ion adsorption from aqueous solution was studied. Parameters such as modification time, type and concentration of crown ethers, ion strength, concentration of lithium ion and temperature of complex formation were optimized and then were characterized by FT-IR, SEM and BET. Effects of pH, adsorbent dose and contact time on the adsorption percentage were investigated. Equilibrium, thermodynamic and kinetics studies were also done. Modification time of 240 h, crown ether of benzo15crown5 and 0.01 mg/L concentration were obtained as optimum parameters. The highest percentage of adsorption for lithium ion was in the condition, pH_{pzc}: 7, one gram of adsorbent in 20 mL solution with concentration of 0.1

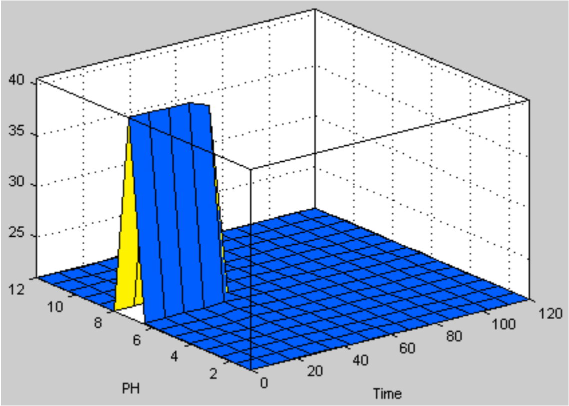


Fig. 20. The effects of pH and time on the adsorption percentage.

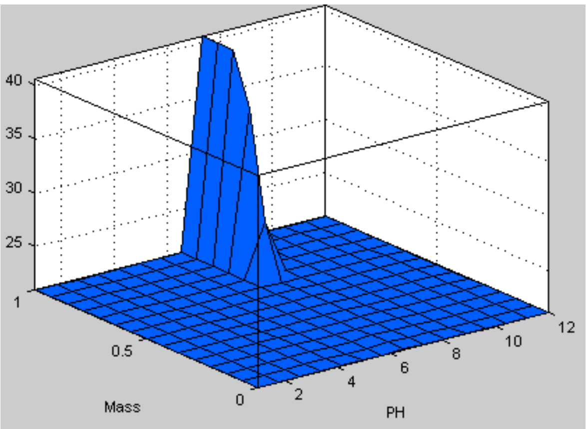


Fig. 21. The effects of pH and adsorbent dose on the adsorption percentage.

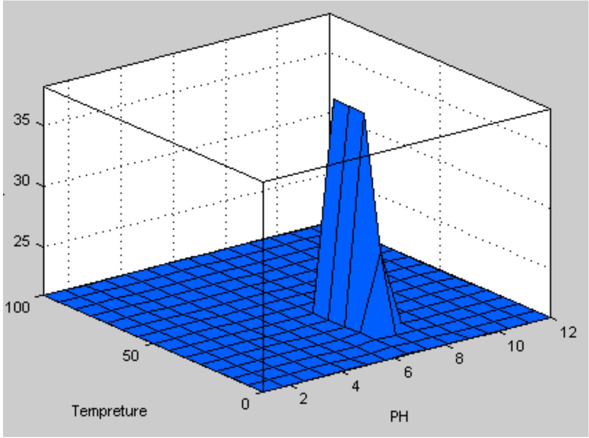


Fig. 22. The effects of pH and temperature on the adsorption percentage.

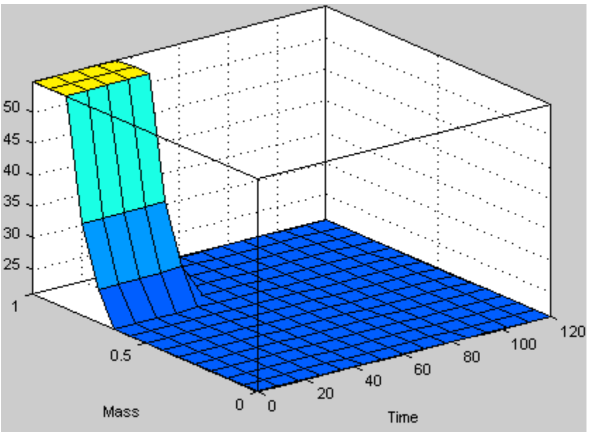


Fig. 23. The effects of adsorbent dose and time on the adsorption percentage.

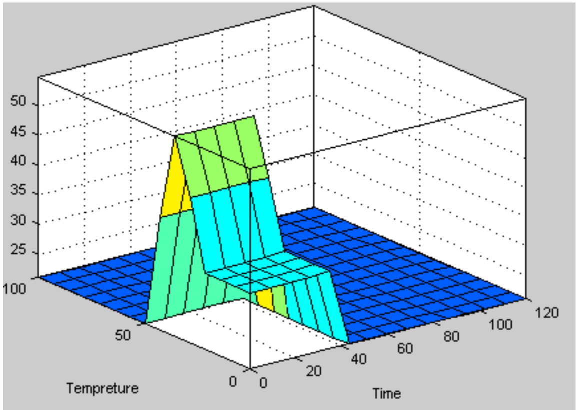


Fig. 24. The effects of temperature and time on the adsorption percentage.

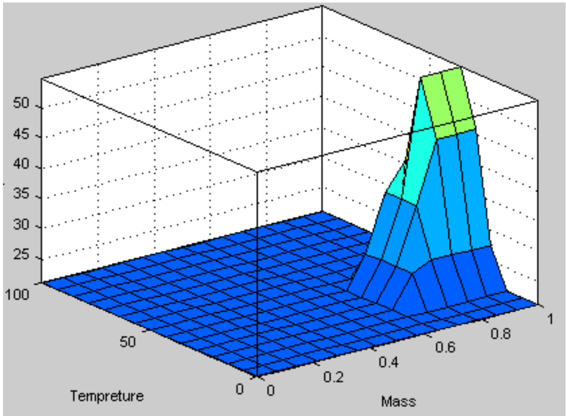


Fig. 25. The effects of temperature and adsorbent dose on the adsorption percentage.

mg/L and temperature of 40°C. The results show that this adsorption for lithium ion on the modified zeolite with Freundlich isotherm has more similar factors with kinetics model. Investigations on the thermodynamic parameters revealed that adsorption process is spontaneous and endothermic. Based on kinetics and BET analysis, it can be inferred that adsorption process is dependent to lithium ion and adsorption sites. The quick process of adsorption on modified zeolite reveals that chemical reactions such as ion transformation, ion exchange and complexation limit the speed of the process. Lithium ion adsorption on zeolite surface by ligand does not have any significant effect on the adsorption mechanism. Statistical results from fuzzy logic and experimental data in MATLAB software reveal that fuzzy logic has more abilities to model the surface adsorption process of lithium ion.

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