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Recovery of K^+ from concentrates from brackish and seawater desalination with modified clinoptilolite

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ABSTRACT

Using modified clinoptilolite, column sorption–elution was carried out for recovering potassium from concentrates, a simulative by-product of brackish and seawater desalination. A breakthrough curve was obtained, and then the total and breakthrough capacity values of the modified clinoptilolite were calculated. The K^+ on the zeolite was quantitatively eluted with 25% NaCl solution, and the concentration of K^+ in the obtained primary K^+-enriched solution was 7.5730 g/L at levels above six times of raw concentrates. Three consecutive sorption–elution cycles were implemented, and the total capacity values remained almost constant, demonstrating the good reusability of modified clinoptilolite. Both Thomas and Yoon–Nelson models could describe the breakthrough curves well, and some column parameters required for the process design were determined. All these could give some contributions to utilization of chemical resources in seawater.

Keywords: Modified clinoptilolite; Potassium; Fixed bed; Seawater desalination; Concentrates

1. Introduction

Potassium is an essential resource for agriculture [1] and industry. There is about $1{,}480 \times 10^8\,t$ of potassium resources on land in the world, 90% of which is concentrated in a few countries including: Canada, Russia, Ukraine, Germany, Israel, Jordan, and USA. And most countries, especially agricultural countries, have to import a lot of potash to meet their need every year. For instance, China needs about one million tons potash (amount to K_2O) annually, and the half mainly imports from Canada, Russia, and Belarus, because the potassium in China is about 2.2% of the whole reserves (about 9,500 million tons K_2O) [2] in the world. However, there is about $550 \times 10^{12}\ t$ of potassium dissolved in seawater, the amount of which is 10 thousand times of that on land in the world.

Nowadays, with big-scale seawater desalination implementing, the discharge of concentrated seawater which is a by-product of seawater desalination was paid more attention for its environmental harm to the ocean, in particular to the semi-enclosed sea like Bohai of China. At the same time, direct emission is also unreasonable, because the concentrate stream contains many useful and scarce minerals at levels about two times raw seawater concentrations. So the utilization of chemical resources in concentrates becomes a tendency [3,4]. In the past 100 years, many researchers have developed a myriad of technologies to exploit potassium resources in seawater including: chemical

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precipitation, solvent extraction, membrane separation, ion exchange, and adsorption. And the technology of ion exchange and adsorption is considered the most attractive process for extracting potassium from seawater/concentrated seawater with cheap alternative materials like zeolite [5,6].

Zeolites are hydrous alumino silicates in which the SiO_4 tetrahedra form a three-dimensional cage-like framework. The substitution of Al^{3+} for Si^{4+} results in permanent net negative charges that are balanced by exchangeable cations (sodium, calcium, or potassium) [7–9]. This fact makes them particularly suitable for removing undesirable heavy metal ions and eutrophic ammonium ions from industrial and civilian effluent waters, and recovering/extracting valuable ions from solutions. Clinoptilolite, which has a high affinity for the K^+ [10] and the NH_4^+ [11,12], is one of the most important zeolites. Its approximate chemical formula is: $(Ca, Na, K)_6Al_6Si_{30}O_{72}·24H_2O$. In particular, there is a great deal of public attention on potassium extraction from seawater by ion exchange and adsorption of zeolites [13–15]. Some works about ion exchange and adsorption have been done in potassium removal and recovery from solutions. Natural zeolite from Bear River Zeolite Company (Idaho, USA) was used to investigate the individual and simultaneous uptake isotherm and kinetics of ammonium and potassium of anaerobically digested cattle manure effluent [16]. Man-made molecular sieves [17], synthesized clinoptilolite [18], merlinoite [19], and magnetic P zeolites [15] are investigated for the ion exchange and adsorption capability to K^+ in the seawater, respectively. But all above works are mainly focus on the K^+ uptake of materials, and little faces practical application. Because more synthesized zeolites are powdery, it brings about some inevitable difficulties when treating huge volume seawater. Intension restricts their application all long, even though the man-made zeolites were granulated. The intension of natural clinoptilolite is enough to meet industrial need except relatively low K^+ uptake.

The column process is the most common and efficient ion exchange and adsorption method, and the fixed bed operation is the most frequently used system [20]. During the process, as the feed solution containing the cation(s) passes through the bed of packed material, like zeolite, the ion-exchange zone moves in the direction of the flow and reaches the exit in due course. The curve representing the cation exit concentration vs. time (or effluent volume) is called the breakthrough curve, and it is used to characterize the process. Fixed bed operation is influenced mainly by equilibrium (isotherm and capacity) and kinetic (diffusion coefficient) factors. Diffusion coefficients, equilibrium isotherms, and capacity are frequently determined in batch-type reactors. The operating capacity is defined as the amount of cations exchanged during fixed bed operation and determined by integration of the experimental breakthrough curve [21].

This study mainly describes the ion-exchange process in a fixed bed packed with modified clinoptilolite, which had a better K^+ uptake and was designed for potassium extraction from simulated concentrates. And Thomas and Yoon–Nelson models were applied to the results obtained from the fixed bed operation, and column capacities were also calculated. All these should give some contributions to efficient extraction of K^+ from concentrates from brackish and seawater desalination, and then promote the development of huge brackish and seawater desalination and remit the potassium crisis in some coastal countries to some extend in the future.

2. Experimental

The raw clinoptilolite used in this study was collected from a deposit in Inner Mongolia Autonomous Region, China. The chemical composition of the clinoptilolite is shown in Table 1 [11]. It was ground and sieved out the fraction 18–36 mesh (about 0.4–1.0 mm) and then was washed with water to remove very fine particles and dried in an electric drying oven at 60℃. Modified clinoptilolite was obtained by treating the above mineral with saturated NaCl solution at the boiling temperature for 2 h and repeated three times [22]. And X-ray powder diffraction (XRD) patterns of the raw and modified materials were collected with Cu Kα radiation at room temperature on Bruker D8 Focus diffractometer.

In this study, about 2,850 g modified clinoptilolite was packed into three glycerin-jacketed glass columns

Table 1
Chemical composition of clinoptilolite

Component	wt.%
SiO_2	68.27
Al_2O_3	7.48
MgO	1.87
CaO	2.61
K_2O	1.69
Na_2O	0.68
Fe_2O_3	1.95
H_2O	6.26
LOS**	7.86

**LOS means the mass loss on ignition at 1,000℃.

(28 mm in inner diameter with 1 mm wall thickness and 2,600 mm in length) on average. The fixed bed tests were carried out in a glycerin-jacketed glass column (Fig. 1) at room temperature for extraction and a higher temperature (about 90℃) for elution–regeneration.

The simulated concentrates (mainly containing 2.36 g/L KCl, 76.15 g/L NaCl, 3.27 g/L $CaCl_2$, 19.80 g/L $MgCl_2·6H_2O$, and 12.16 g/L $MgSO_4·7H_2O$), in which the concentration of ions is about three times of that in standard seawater and 1.5 times of that in by-product of seawater desalination, were delivered downflow in above three columns (packing layer height was 2.3 m for each column) at different flow rates (170, 200 and 230 mL/min) controlled by a peristaltic pump (Longer Pump, Baoding LanGe Constant Flow Pump Co., Ltd) to select optimized flow rates. From the outlet of the column, each successive 5,000 mL fractions of the effluent were collected. Breakthrough curves were obtained by analyzing the K^+ concentration of each fraction with tetraphenylboron sodium titration method. Column adsorption was terminated when the column reached exhaustion [23], and then fresh water was pumped for washing. The elution–regeneration step was then performed upflow by using 25% NaCl solution at different flow rates (70, 80, and 90 mL/min). Elution was completed when the elution profile was obtained by analyzing the 500 mL fractions of the effluent. And then a volume of primary potassium-enriched solution was gained, which is further taken for concentrating and then producing potash product after processes of evaporation and crystallization [24–26]. The washing step was carried out with fresh water, and another loading cycle was then carried out.

The recycle tests were conducted using the modified clinoptilolite as follows. Simulated concentrated seawater was passed through above columns in series at an optimized flow rate chosen from above experiments. After the elution step using 25% NaCl solution at an optimized flow rate obtained from above experiments, the modified clinoptilolite got regenerated, and another loading cycle was then carried out.

3. Results and discussion

3.1. XRD pattern of the clinoptilolites

XRD diffraction spectra of the raw and modified clinoptilolites are given in Fig. 2. It showed that the modified clinoptilolite has roughly the same crystal structure as raw material. Modification with 25% NaCl solution has no obvious effect on the crystal structure of the raw clinoptilolite. But the potassium uptake of the modified clinoptilolite is about 5 mg/g more than that of the raw one, which should attribute to the single component of Na forms clinoptiliote changed from multicomponent (mainly containing K, Ca, and Mg) one [27].

Meanwhile, the modified clinoptilolite has a prior K^+ uptake to some synthesized zeolites like *P* zeolites [15]. Its selectivity factor to K^+ in seawater is 18.52 [17], and its separation factor $\alpha^{K}_{Ca,Mg}$ is above 1,250 which is much higher than $\alpha^{Ca}_{K,Mg}$ (≤0.411) and

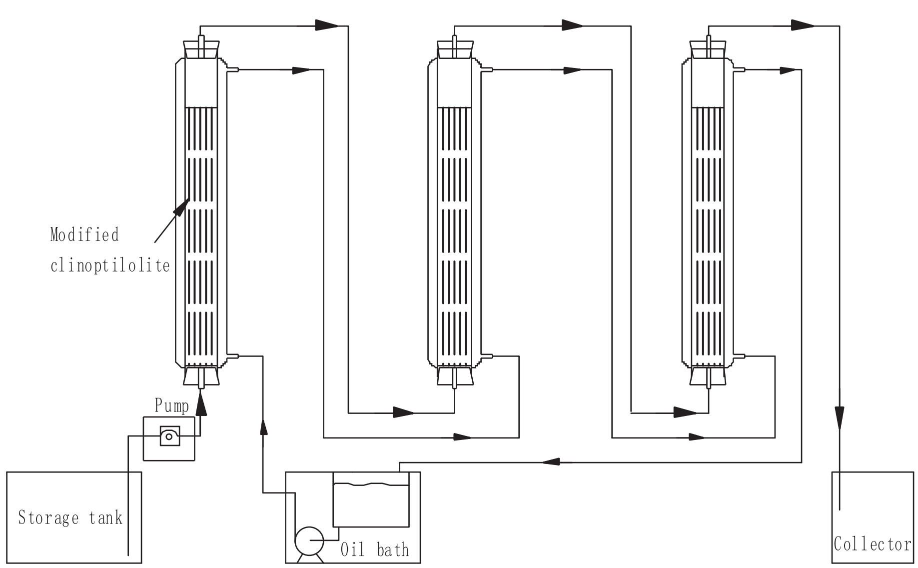

Fig. 1. Scheme of experimental system.

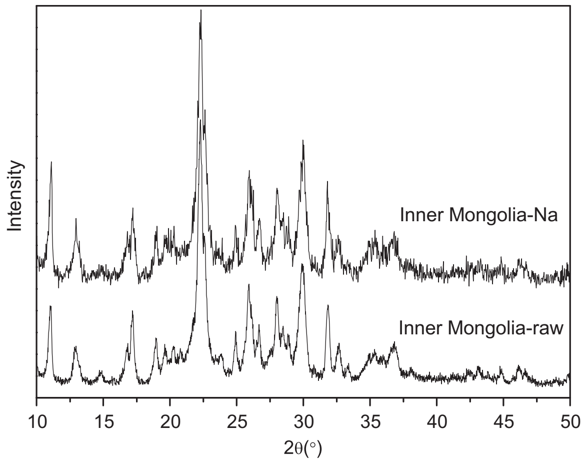

Fig. 2. X-ray diffraction patterns of the clinoptilolites.

$\alpha^{Mg}_{Ca,K}$ (≤0.014) at 25℃ [28]. In addition, there are some advantages such as cost and strength, even though their capacity for K^+ is slightly lower than man-made molecular sieve/clinoptilolite [18,29].

3.2. Effect of flow rates on column adsorption performance

Breakthrough curves generally permit a good description of the process in ion-exchange columns, since a breakthrough capacity characteristic of a column under given condition can be assigned to its curve. The breakthrough curves show the loading behavior of K^+ to be recovered from simulated seawater in a fixed bed (compared with K^+, the loading behavior of Ca^{2+} and Mg^{2+} to be recovered was not considered for the modified clinoptilolite's good selectivity for K^+), and is usually expressed in terms of sorbed K^+ concentration (C_p = inlet potassium ion concentration (C_{in}) – effluent K^+ concentration (C_{out}) or normalized concentration defined as the ratio of effluent K^+ concentration to inlet K^+ concentration (C_{in}/C_{out}) as a function of time (t) or volume of effluent ($V = Q \cdot t$, Q is the volume flow rates) for a given bed height. The area under the breakthrough curve obtained by integrating the sorbed concentration vs. the throughput volume plot can be used to define the total sorbed K^+ quantity (maximum column capacity). Sorption capacity of the bed (q_0 mg/g) is calculated by the following equations [30,31].

$$q_0 = \frac{\int_0^V (C_{in} - C_{out})\mathrm{d}V}{m} \tag{1}$$

$$q_0 = \frac{\sum_i^n (C_{in} - C_{out})V_i}{m} \tag{2}$$

where m is the mass of the ion exchanger (g), i.e. modified clinoptilolite; i is the number of i fractions collected; and n is the sum of fractions collected.

In this research, C_{out} was the average concentration of 5,000 mL fraction of the effluent collected, and t was the intermediate value of the collected time with the corresponding C_{out}. Fig. 3 shows the results of fixed beds adsorption for K^+ with various flow rates, and the corresponding elution flow rate was 80 mL/min. The column capacity values of the modified clinoptilolite are given in Table 2, which are obtained from Eq. (2). The sorption capacity of the modified clinoptilolite is the greatest, when the flow rate is 200 mL/min in this research. The flow rate is too slow to meet the need of commercial production, and it is too high to react completely with the clinoptilolite. Column utilization which is also named

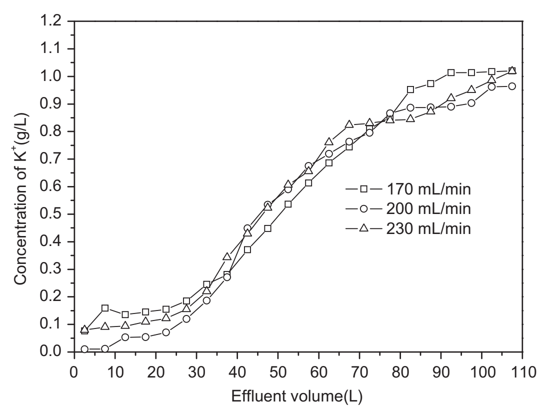

Fig. 3. Effect of flow rate on breakthrough capacity of modified clinoptilolite.

Table 2
Column adsorption performance of modified clinoptilolite at different flow rates

Flow rate (mL/min)	Sorption capacity, q_0 (mg/g)	Total capacity, q_T (mg/g)	Column utilization (%)	Adsorption ratio of K^+ (%)
170	19.1	21.4	89.34	46.69
200	20.5		95.68	50.00
230	19.4		90.67	47.38

*Total capacity (q_T) was obtained in preliminary tests according to Ref. [22].

the use ratio of the modified clinoptilolite could reach 95.7%, and extraction ratio of K^+ in the concentrated seawater is about 50%.

3.3. Elution performance of the fixed beds at different flow rates

The loaded column adsorbed at 200 mL/min was eluted with 25% NaCl solution under different elution flow rates, and the elution profile of the modified clinoptilolite is shown in Fig. 4 and Table 3. It was shown 80 mL/min is the optimal flow rate for elution in this research under considered experimental conditions, and the elution efficiency of K^+ was above 80%. It was speculated that the elution process is governed by film diffusion and particle diffusion.

The average K^+ concentration of the 5 L elution, which was collected in the elution process, could reach 7.5730 g/L, which was above six times higher than that of the feed solution. The intermediate materials are also qualified as a feed for further concentrating to make K^+-enriched solution, in which K^+ concentration should be above 35 g/L, and then potash product can be obtained after evaporation and crystallization [23,25,26].

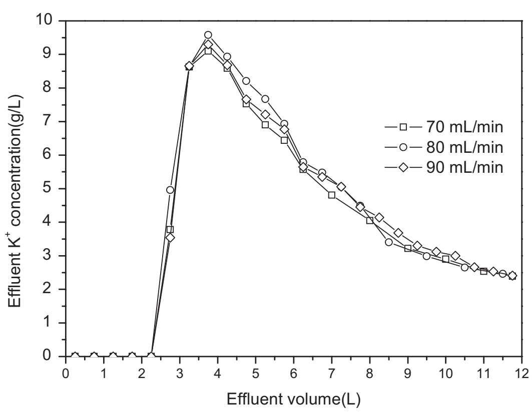

Fig. 4. Elution profiles of K^+ at different flow rates.

Table 3
Column elution performance of modified clinoptilolite at different flow rates

Flow rate (mL/min)	Sorption capacity (g)	Elution capacity (g)	Elution efficiency of K^+ (%)
70	59.73	48.18	80.66
80	57.02	49.37	86.57
90	58.16	48.59	83.54

3.4. Reusability of the modified clinoptilolite

In order to demonstrate the reusability of the modified clinoptilolite and the reliability of the foregoing data, the adsorption–washing–elution/regeneration-washing cycle was repeated three times. According to above results, recycle use of the modified clinoptilolite was studied at 200 mL/min adsorption flow rate and 80 mL/min elution flow rate. The resulting breakthrough curves are given in Figs. 5 and 6, and the column capacity values of the modified clinoptilolite for each cycle are given in Table 4.

According to Figs. 5 and 6 and Table 4, the breakthrough capacity of the modified clinoptilolite maintained constant to some extent for each cycle, which could testify the stability of the modified clinoptilolite. At the same time, adsorption ratio and elution efficiency for K^+ remained almost the same during the three cycles. Therefore, the modified clinoptilolite has strong repeatability, when the surveying point and its surroundings keep unchanged.

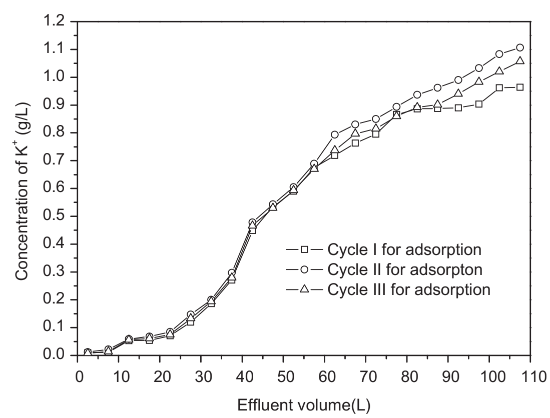

Fig. 5. Recycle use of modified clinoptilolite for adsorption.

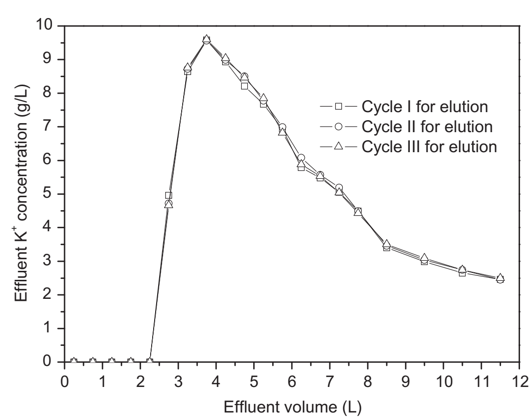

Fig. 6. Recycle use of modified clinoptilolite for elution.

Table 4
Column performance of modified clinoptilolite for each cycle

Process	Performance	Cycle		
		I	II	III
Adsorption	Initializing K^+ concentration, C_{in} (g/L)	1.06	1.12	1.09
	Sorption capacity, q_0 (mg/g)	20.5	21.0	20.9
	Total capacity, q_T (mg/g)	21.4		
	Column utilization (%)	95.68	98.12	97.63
	Adsorption ratio of K^+ (%)	50.00	48.53	49.62
Elution	Sorption capacity (g)	58.30	59.79	59.49
	Elution capacity (g)	49.37	49.99	49.87
	Elution efficiency of K^+ (%)	84.67	83.60	83.82

3.5. Column characteristic analysis with Thomas and Yoon–Nelson models

Successful design of a column adsorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum adsorption capacity of an adsorbent is also needed in design. Traditionally, both Thomas model and Yoon–Nelson model were used to fulfill the purpose.

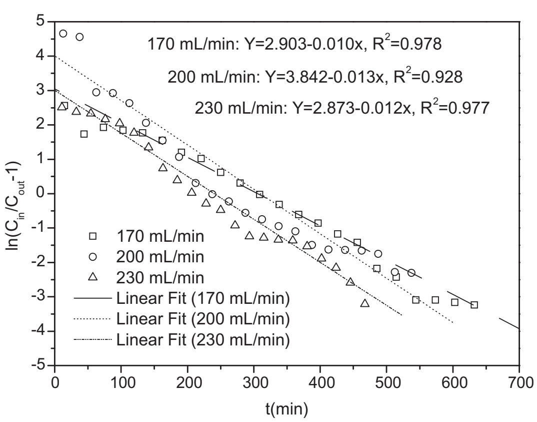

Fig. 7. ln $[(C_{in}/C_{out}) - 1]$ against t and its fit to Thomas model at different flow rates.

3.5.1. Thomas model

Thomas model, the most general and widely used methods in column performance theory, whose advantages include its simplicity and reasonable accuracy in predicting the breakthrough curves under various operating conditions, is represented by the following equation [31–33]:

$$\ln\left[(C_{in}/C_{out}) - 1\right] = K_{Th}q_0m/Q - K_{Th}C_{in}V/Q \quad (3)$$

where K_{Th} is the Thomas rate constant (L/(min g)) and Q is the volumetric flow rate (L/min). K_{Th} and q_0 can be determined from a plot of $\ln\left[(C_{in}/C_{out}) - 1\right]$ against time ($t = V/Q$) at a given flow rate Q (Fig. 7). Each of the regressed lines indicated that they were all acceptable fits with linear regression coefficients ranging from 0.928 to 0.978. The Thomas equation coefficients for potassium sorption are given in Table 5, and the theoretical predictions based on the model parameters are compared with the observed data in Fig. 8.

According to Table 5, the optimal capacity value was obtained as 22.2 mg/g at 200 mL/min using Thomas model. The theoretical model and their parameters fitted the experimental breakthrough curve well as shown in Fig. 8, although some deviations of experimental data from predicted values were existing. The

Table 5
Coefficients of Thomas model for K^+ uptake on clinoptilolite at different flow rates

Flow rate (mL/min)	Coefficients of Thomas model			Experimental data
	K_{Th} (mL/(min mg))	q_0 (mg/g)	R^2	q_0 (mg/g)
170	0.009	18.4	0.978	19.1
200	0.012	22.2	0.928	20.5
230	0.012	19.7	0.977	19.4

Table 6
Coefficients of Yoon–Nelson model for K^+ uptake on modified clinoptilolite

Flow rate (mL/min)	Coefficients of Yoon–Nelson model				Experimental data
	$K_{Y–N}$ (min^{-1})	τ(min)	q_0 (mg/g)	R^2	q_0 (mg/g)
170	0.010	290.3	18.4	0.978	19.1
200	0.013	297.8	22.2	0.928	20.5
230	0.012	239.4	20.5	0.977	19.4

Thomas model is suitable for adsorption processes where the diffusion will not be the limiting step.

3.5.2. Yoon–Nelson model

Yoon–Nelson model is another simple one, which requires no detailed data concerning the characteristics of the adsorbate such as the type of the sorbent and the physical properties of the sorption bed. Its equation regarding a single-component system is expressed as [31,34]

$$\ln\,(C_{out}/(C_{in} - C_{out})) = K_{Y–N}t - \tau K_{Y–N} \tag{4}$$

where $K_{Y–N}$ is the rate constant (1/min) and τ is the time required for 50% adsorbate breakthrough (min). The values of $K_{Y–N}$ and τ were determined from $\ln\,(C_{out}/(C_{in} - C_{out}))$ against t plots at different flow rates (Fig. 9). And according to the symmetrical nature of the breakthrough curve, the amount of potassium sorbed by the modified clinoptilolite can be represented by the following equation:

$$q_0 = 1/2C_{in}Q(2\tau)/m = C_{in}Q\tau/m \tag{5}$$

Then, the values of $K_{Y–N}$, τ, and q_0 are listed in Table 6, and the theoretical curves are compared with the corresponding experimental data in Fig. 10.

According to Table 6, the optimal capacity value was obtained as 22.2 mg/g at 200 mL/min using Yoon–Nelson model. The theoretical curves are

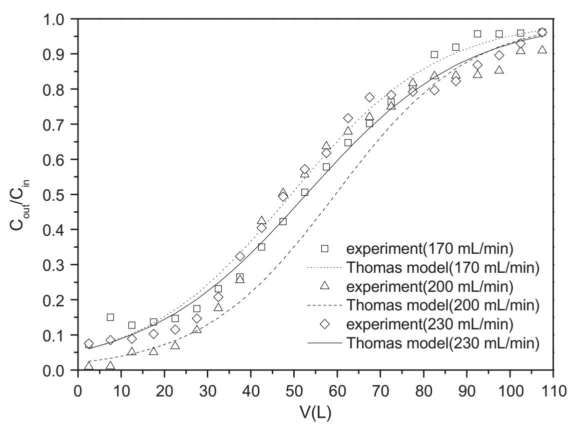

Fig. 8. Comparison of the experimental and predicted breakthrough curves according to Thomas model.

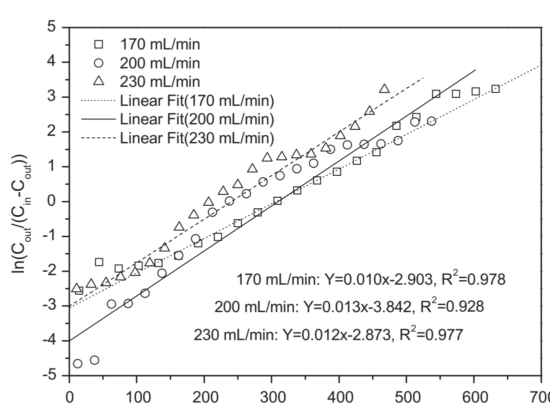

Fig. 9. $\ln\,(C_{out}/(C_{in} - C_{out}))$ against t and its fit to Yoon–Nelson model at different flow rates.

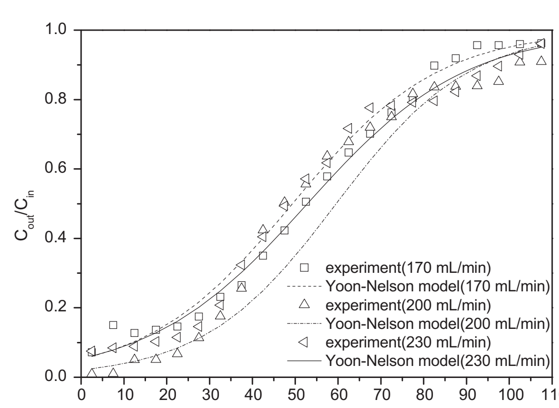

Fig. 10. Comparison of the experimental and predicted breakthrough curves according to Yoon–Nelson model.

compared with the corresponding experimental data in Fig. 10. The experimental breakthrough curves were very close to those predicted by Yoon–Nelson model in the C_{out}/C_{in} region from 0.07 up to 0.96. From the experimental results and data regression, the model proposed by Yoon–Nelson provided a good correlation of the effect of flow rate.

4. Conclusions

The modified clinoptilolite is promising for column extraction of potassium from concentrates, and the zeolite performed a quantitative recovery of K^+ from concentrates from brackish and seawater desalination.

The optimal flow rate is 200 mL/min in adsorption process under considered experimental conditions. The use ratio of the modified clinoptilolite could reach 95.7%, and the extraction ratio of K^+ in the concentrates is about 50%. And the K^+ concentration of primary K^+-enriched solution is 7.5730 g/L, which is above six times higher than that of the raw solution.

Both Thomas model and Yoon–Nelson model could predict the breakthrough curves well in various operating conditions in this paper.

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