Journal of
Particle Science and Technology

J | P | S | T

Xenon and krypton separation in a chromatographic column packed with granulated nano NaY zeolite

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HIGHLIGHTS

- Nano NaY zeolite was synthesized by the clear solution method

- Nano NaY zeolite was granulated into homogeneously uniform granules

- New HETP correlation was proposed for the synthesized packing

- Calculated HETP values revealed to be in good agreements with experimental data

GRAPHICAL ABSTRACT
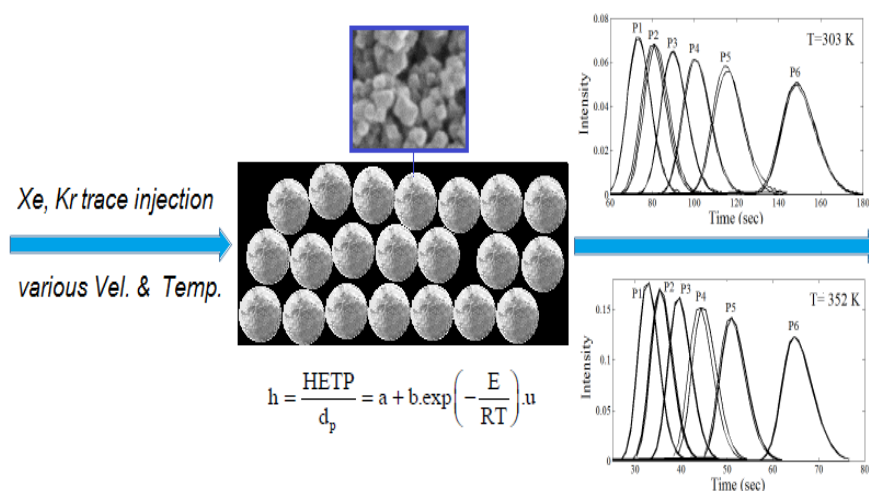
$$h = \frac{HETP}{d_p} = a + b.\exp\left(-\frac{E}{RT}\right).u$$

ABSTRACT

In order to investigate the gas separation ability of a column packed with nanozeolitic material, nano NaY zeolite was synthesized and granulated. These uniform granules packed in a chromatographic column were utilized for separation of Xe and Kr under various operating conditions. With regards to the response peaks obtained from trace injections of Xe and Kr into the column, the first and second normalized moments of peaks were calculated. Moreover, the height equivalent to a theoretical plate (HETP) for the column was determined. The results illustrated that the retention time of Xe was remarkably greater than Kr indicating that, the nano NaY zeolite was a good choice as an adsorbent in Kr and Xe separation process. Moreover, a simple and temperature dependent correlation was derived to predict the HETP for the packed column. Ultimately, the calculated HETP values were in a good agreement with experimental data.

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1. Introduction

Zeolites considered as valuable materials acting as molecular sieves, ion-exchangers and catalysts. These materials broadly utilized in gas separation processes as the adsorbent or inorganic and mixed matrix membranes [1].

Nano sized adsorbent utilizations led to increased external surface areas and shortened diffusion path lengths enhancing the adsorption kinetics. Hydrothermal clear solution method is a common technique to produce nanozeolites [3]. In this method the crystallization processes carried out at lower temperatures for longer times. It was noteworthy that, as-synthesized nanozeolites in their original sizes might have not been applied for industrial adsorption processes due to causing very high pressure drops in the column. Shaping of zeolitic nanopowders in the form of granules might have alleviated some of the technical problems associated with nanoparticles including; losses as dust, caking and lump formations; changing of the flow properties, handling of hazards, low surface to volume ratio and porosity as well as, high pressure drops through the reactor [4]. Therefore, size enlargement of the zeolitic nanoparticles particularly in the form of granules might be necessary to promote their industrial applications as adsorbents and catalysts. Traditional approaches for size enlargement of the micron sized zeolites usually consisted to be mixing of the powders with 1–50wt.% of the inorganic binders (e.g. bentonite, kaolanite) and some fillers (e.g., starch or carboxy-methyl-cellulose (CMC)) followed by applying a shaping technique such as agitation (i.e., mixing or tumbling agglomerates), fluidization, spray drying, pressing, extruding and thermal or liquid agglomeration methods in order to form the particles as granules, pellets, rods, etc. [5]. In addition, some other techniques existed for the size enhancement of micron sized zeolite powders not applicable to the nanozeolites [6].Granulation of nanozeolites however; might be done through different methods [7-8]. In some of these methods, the mechanical strength obtained by utilizing inorganic binder such as clay [9]. The knowledge of the various adsorption and diffusion parameters for these granulated adsorbents considered necessary to simulate the chromatographic separation method in turn, needed for the process optimization purpose. One older chromatographic theory described column efficiency was the plate theory developed by Martin and Synge [10]. In this theory column was divided into a number of hypothetical adjacent segments called theoretical plates. Within each theoretical plate complete equilibrium of analyt between stationary and mobile phases occurred. According to this theory greater separation in a given length of chromatographic column occurred in a column with smaller plate height or namely height equivalent to theoretical plate (HETP). In other words, having more theoretical plates increased the efficacy of the separation process [10].

In this paper, first nano NaY zeolite was synthesized and characterized. Then a chromatographic column was packed with this material and utilized for separation of Xe and Kr. As a further novelty of this work, a new HETP tempera ture dependent correlation for this system was derived and shown to well agree with the experimental data.

2. Theoretical background

In order to calculate the HETP, the column response to a small pulse injections of a solute under trace conditions in the Henry's law limit was investigated. For such conditions, the statistical moments of the response peak were used to characterize the chromatographic behavior [10]. According to the first and second moments of the response peaks the number of plates, *Np*, and the height equivalent to a theoretical plate, HETP, defined as follow:

$$N_p = \mu_1^2 / \mu_2^2 \tag{1}$$

$$HETP = (\mu_1^2 L) / \mu_2^2 \tag{2}$$

Moreover, the first normalized moment (μ_1) and the second central moment (μ_2) were calculated as follows:

$$\mu_1 = \frac{\int_0^\infty t \cdot C_b(z,t)dt}{\int_0^\infty C_b(z,t)dt} = \frac{\sum_{i=1}^n t_i C_i \Delta t}{\sum_{i=1}^n C_i \Delta t} \tag{3}$$

$$\mu_2 = \frac{\int_0^\infty (t-\mu_1)^2 C_b(z,t)dt}{\int_0^\infty C_b(z,t)dt} = \frac{\sum_{i=1}^n (t_i-\mu_1)^2 C_i \Delta t}{\sum_{i=1}^n C_i \Delta t} \tag{4}$$

Where C_i was the concentration of solute in the column outlet at the time t.

With regards to the general rate model [10] proposed for the liquid chromatography, HETP of a column was the sum of the independent contributions due to the film mass transfer, intercrystalline and intracrystalline

resistances raised due to the diffusion of sorbates through the external film and the macropores and micropores of the granulated adsorbent. According to this theory HETP was defined as the simple classical Van Deemter equation given as followings [10]:

$$HETP = A + Bu + c/u \qquad (5)$$

Where, u was the linear velocity (m/s) of the carrier gas inside the column, A was related to eddy diffusion parameters, B was resistance to the mass transfer coefficient of the analyte between mobile and stationary phases including solid diffusion of solute in pores of stationary phase and B was the axial dispersion coefficient in the longitudinal direction.

3. Experimental

3.1. Materials

Aluminum isopropoxide, tetraethyl orthosilicate (TEOS), sodium hydroxide, tetramethylammonium hydroxide (TMAOH), barium chloride as well as; strontium nitrate were provided by the Merck Chemicals. Low viscosity sodium alginate was purchased from the Sigma Chemicals.
Bentonite was provided by the Kabir Bentonite Co. from the mines located in Mehrigan (Iran). All the chemicals were used as received without any further purifications.

3.2. Synthesis of nanozeolites

Nanoparticles of NaY zeolite were synthesized by means of a clear solution method according to the batch composition of $2.46(TMA)_2O$: $0.032Na_2O$: $1Al_2O_3$: $3.40SiO_2$: $370H_2O$ reported by Creaser and co-workers [11]. First, 38.5g of aluminum isopropoxide, 518.3g of distilled water; 0.242g of NaOH and 84.5g of the TMAOH solution were mixed and stirred at 0°C in an ice bath to get a clear solution (Sol A). Then 66.7g of TEOS and 84.5g of TMAOH solution were mixed (Sol B). Sol B was added dropwise to the sol A. The resulting mixture was aged overnight while it was mixing with a magnetic stirrer. Then, the aged mixture was transferred into a PTFE-lined stainless steel autoclave reactor. The crystallization reaction was carried out at 100°C for 10 days. After seven days of reaction; in order to increase the crystallization yield; eight portions of 8 ml of 1.0 M NaOH solution was added to the reaction mixture at 8h intervals. The autoclave was then removed from the oven, cooled down to room temperature and nanopowders of

Na-Y zeolite were recovered from the resulted milky, colloidal suspension by centrifuging at 20000 rpm for 10min. In order to remove the un-reacted chemicals, the centrifugation process was repeated 3 times by re-dispersing of the precipitate in fresh distilled water using ultrasonic waves. The as-synthesized nanopowders were air dried at room temperature for 24h. The organic template molecules (*i.e.*, TMA cations) were removed from the zeolite pores using an ion exchange treatment. To do this, 0.3wt.% of zeolite powders was mixed with a 1.0M solution of sodium nitrate at 90 °C for 12h. The ion exchanged powder was then separated from supernatant and washed by means of repeated centrifugation approach.

3.3. Granulation of nanozeolites

An appropriate amounts of alginate/zeolite+clay were granulated while the weight ratios of clay/zeolite were 25wt.% . To do this, two grams of synthesized nanozeolite powder and sufficient amounts of clay were dispersed in 5ml of water using vigorous ultrasonication for 15min. The resultant suspension was then added to a sufficient amount of a 2wt.% sodium alginate gel. The resulted slurry was well mixed by means of a magnetic stirrer for 1h. The resulted homogenous gel was then aged for 1h without shaking in order to separate any trapped air bubbles. Afterward, the agglomerates of sodium alginates were separated by centrifuging at 2500 rpm for 10min. To form the granules, the aforementioned slurry consisted of the nanozeolite, sodium alginate, and the clay in water, was dropped into a 0.1M solution of barium chloride as a mean of a homemade granulation setup. A peristaltic pump was utilized to send the slurry into a pipe having a needle at the end. The air was passed around the needle causing to cut droplets into spherical shape. The gel droplets were dripped into a beaker containing a 0.1M solution of $BaCl_2$ under stirring in order to homogeneously and uniformly shape granules resulted due to the cross-linking reaction. To complete the cross-linking reaction, the resulted spherical granules were kept in $BaCl_2$ solution for two more hours under gentle stirring. The formed granules were washed several times with distilled water to remove unreacted chemicals and then dried by immersing in acetone for 1h to extract water content of the granules. As a final drying step, granules were kept at room temperature for about 24h, then calcined at 600°C for 44h in an electric furnace using a controlled heating program to decompose the alginate content of the granules.

3.4. Separation of xenon and krypton

A Buck Scientific gas chromatograph, model 910, system equipped with thermal conductivity detector (TCD) and a suitable computer recording system was utilized. A vacuumed stainless steel tube (*i.e.*, taken as the column) was well packed with granulated NaY nano-sized zeolites under continuous mechanical vibration. The temperature of the chromatographic system's oven was carefully calibrated and controlled to within ±1°C. Prior to

the experimental runs, the chromatography column conditioning was performed at 473K for 24h while helium gas flowed through the column. The experiments were carried out with trace injection

of xenon and krypton in the carrier gas of helium using a ten port valve equipped with a sample loop of 100μl. The pulse injection of xenon and krypton into the carrier gas of helium were carried out at different upstream pressures of carrier gas in the range of 12–28 psig and different temperatures in the range of 30–110°C. The flow rate was measured by a soap bubble meter which placed at the exit pipe of the detector.

3.5. Characterization

Crystallinity of the as-synthesized Y zeolite was studied by means of a STOE STAD-MP x-ray diffractometer (XRD) using Cu (Kα) at 40 kV and 30 mA. Morphology and size of the nanozeolite spheres, the as-synthesized nanozeolites and commercial NaY zeolite (*i.e.*, CPA100) were studied by means of a Philips XL 30 scanning electron microscope (SEM) equipped with an energy dispersive x-ray analysis system (EDX) to measure the Si/Al ratio of the zeolitic samples.

4. Results and discussion

4.1. Characterization of granulated NaY zeolite nanoparticles

The XRD pattern of the prepared binderless granules (*i.e.*, zeolite–alginate composite after calcination) was demonstrated in Fig. 1. This pattern was very similar to those of the reference faujasite zeolite structure. In addition, the SiO_2/Al_2O_3 ratio of these granules obtained by the EDX analysis determined to be 1.96 revealing that, the tested granules were composed of the NaY zeolite type.

Typical SEM micrographs of the samples were illustrated in Fig. 2. According to the SEM image (Fig. 2a), the synthesized NaY zeolite particles were substantially finer than 100nm. Employing the image processing ability of the MATLAB software, the estimated average size of zeolitic crystallites was determined to be 98.6nm. The images of the produced nanostructured granules with 25wt.% bentonite (as the binder) illustrated in Fig. 2b. According to the SEM micrographs, the produced granules retained their spherical shape after calcination.

In Figures 3 and 4 response peaks of the chromatographic column packed with the prepared granulated nanozeolite illustrated. As revealed through this Figures the retention time of Xe is considerably greater than those of Kr emphasizing the separation of these gases was readily possible by utilizing adsorption columns. In order to describe the efficiency of columnpacked with granulated nanozeolites, height equivalent to a theoretical plate (HETP) at various operating conditions was calculated as explained earlier in this paper.
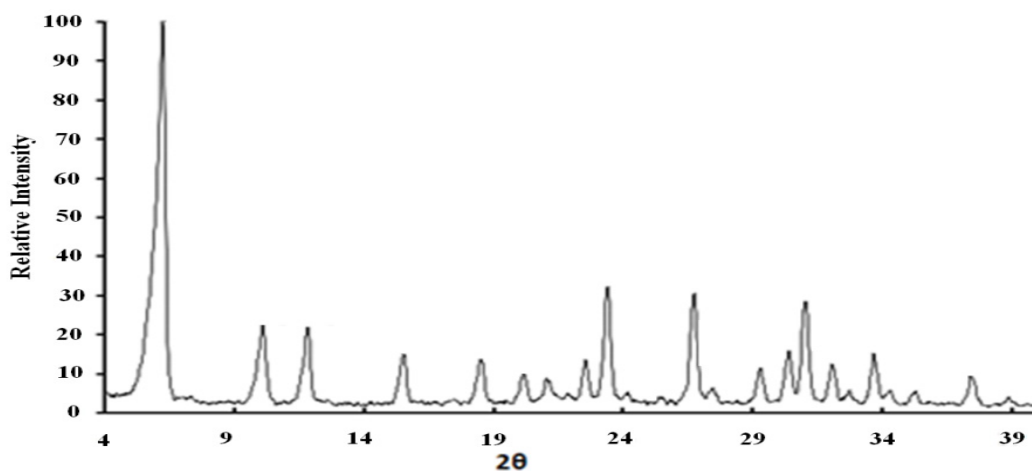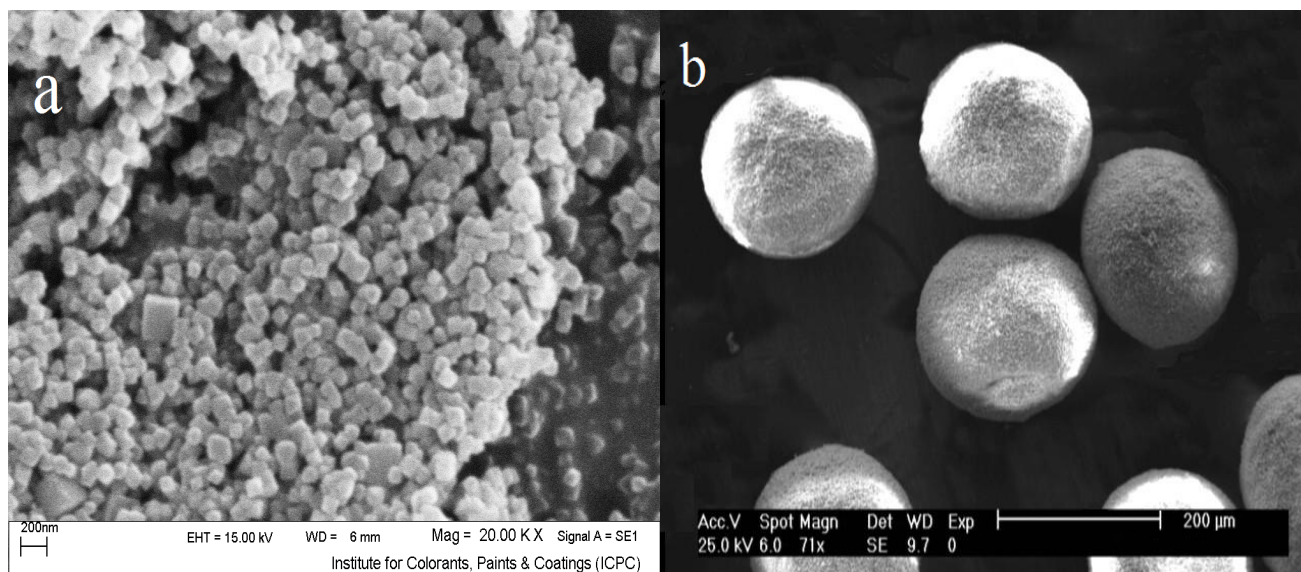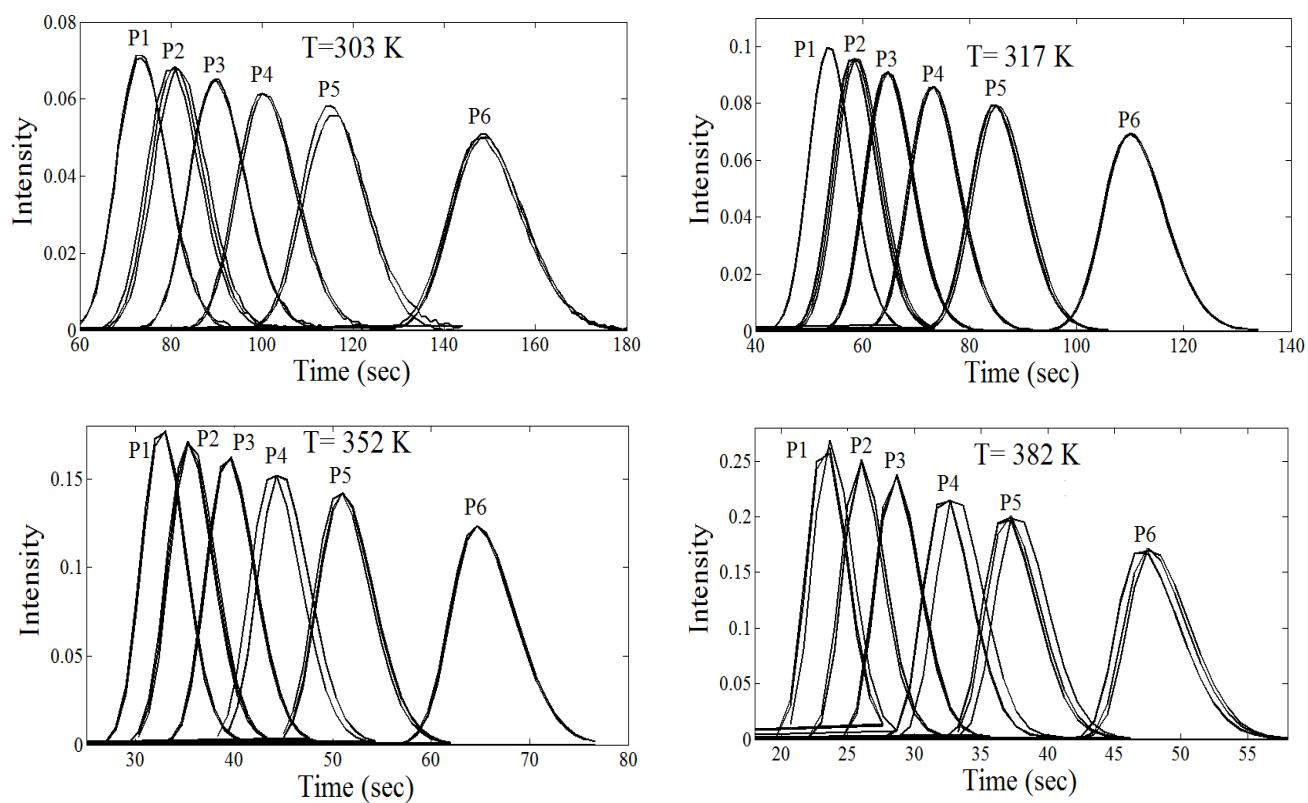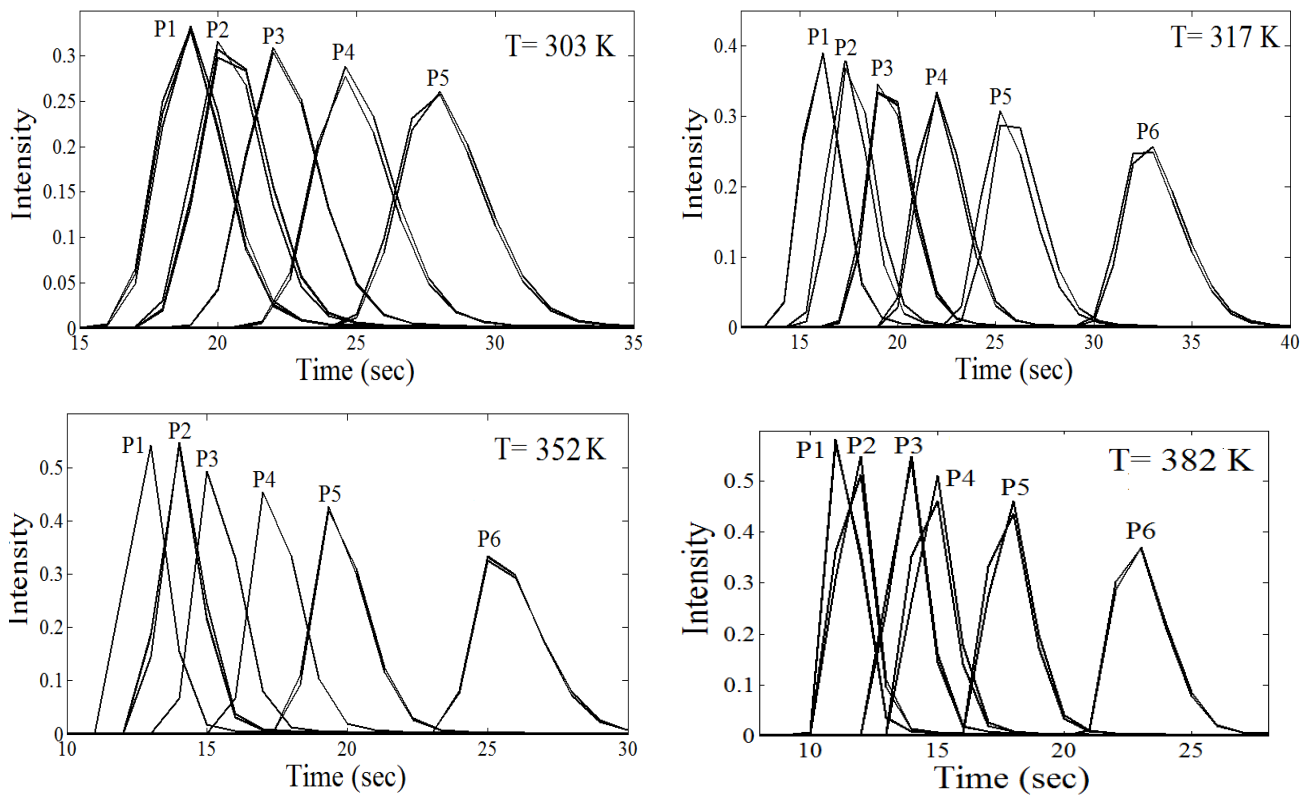

**Fig. 1.** The XRD pattern of the binderless granulated NaY nanozeolite.

Fig. 2. The SEM image of the nano-NaY (a) and the TEM photograph of granulated nanozeolite material (b).


Fig. 3. Effect of the temperature upon the retention time of Xe at various inlet pressures of P_1=12, P_2=16, P_3=19, P_4=22, P_5=25 and P_6=28 psig.

Fig. 4. Effect of the temperature upon the retention time of Kr at various inlet pressures of P_1=12, P_2=16, P_3=19, P_4=22, P_5=25 and P_6=28 psig.
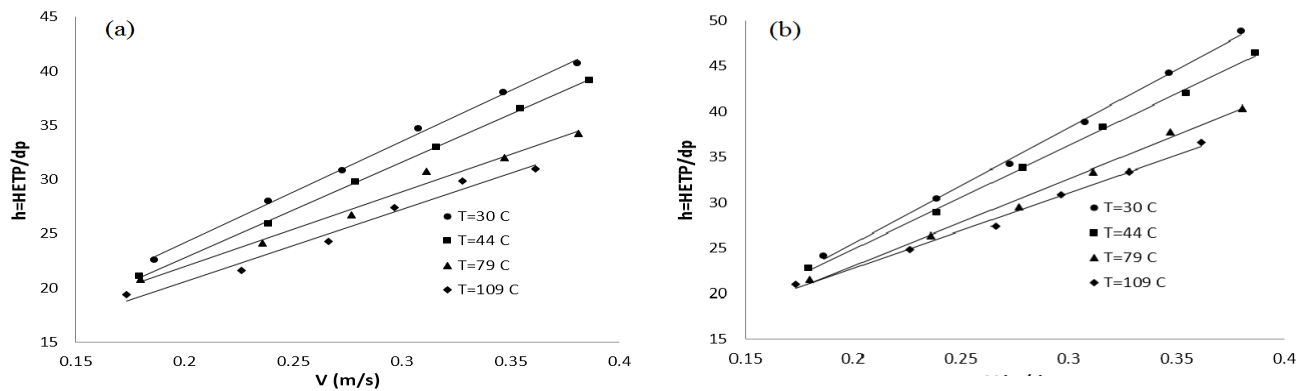
Fig. 5. The reduced HETP of column packed with granulated nano NaY at various temperatures and gas velocities, Xe (a) and Kr (b).
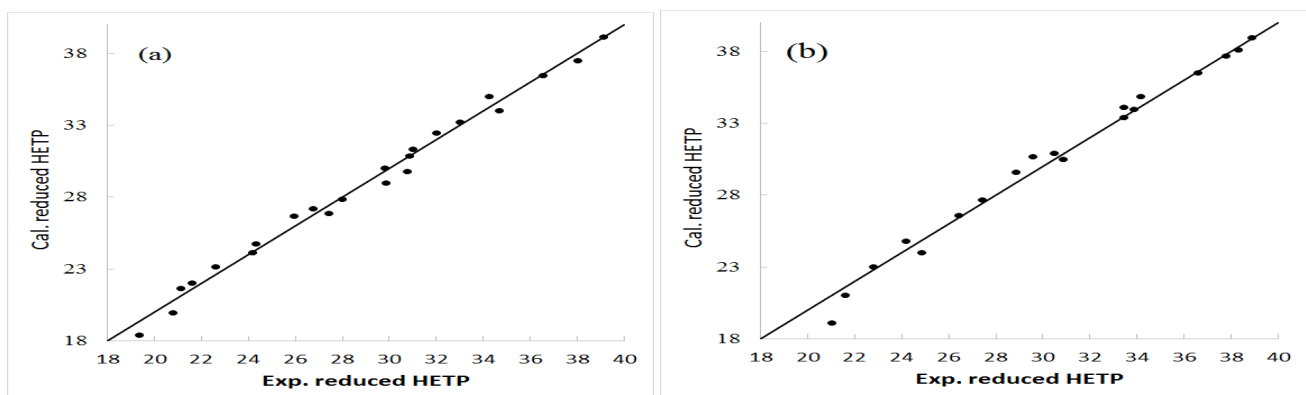
Fig. 6. The parity plots for the comparison of experimental and calculated HETP, Xe (a) and Kr (b).

In this work, a new correlation was proposed to predict the HETP of chromatographic columns. This simple correlation established according to the theoretical aspect of the general law model. According to general rate model in equation 5, B was proportional to the inverse of the solid diffusion coefficient. Moreover, according to results shown in Figure 5, the third term of equation 5 may be considered negligible for the range of velocities selected in this work. Thus, the equation 5 might be simplified into the following new temperature dependent correlation:

$$h = \frac{HETP}{d_p} = a + b.exp\left(-\frac{E}{RT}\right).u \qquad (6)$$

By utilizing 3D curve fitting tool of Matlab2010 software, constant parameters of equation 6 were determined and summarized in Table 1. The predicted HETP values at various temperatures and gas velocities were provided through Figure 5 by the solid lines. The results indicated (see Figure 6 please) that, there is a good agreement between calculated and experimental HETP values possessing average error of less than 1.8% for both Kr and Xe separations (see table 1 please).

Table 1
constant parameters of equation 6.

solute	A	b (s/m)	E (J/mol)	AARE%
Kr	6.529	24.92	3216.687	1.74
Xe	3.16	37.92	2823.434	1.79

5. Conclusions

Nano NaY zeolite was successfully synthesized by the clear solution method and granulated into homogeneously uniform granules. These materials were packed into a chromatographic column and utilized to determine the response peaks of the trace injection for the Xe and Kr. With regards to the obtained response peaks, the first and second normalized moments were calculated. Results demonstrated that, the retention time of Xe was considerably greater than that of Kr. Thus, separation of Xe from its gaseous mixture with Kr was readily feasible through preparative chromatographic method utilizing this material. Moreover, the HETP values of the column were calculated according to a simple temperature dependent relationship. Then a new HETP correlation was proposed for the synthesized packing

of this study. Ultimately, the calculated HETP values revealed to be in good agreements with experimental data. This research was an initial major step towards optimizing the chromatographic separation of Xe and Kr materials.

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