Kinetics of Cation Exchange Capacity of Homoionic Sodium Form Nay Zeolite

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ABSTRACT: Batch experiments have been performed on samples of synthetic homoionic sodium form NaY zeolites to measure their cation exchange capacity (CEC) and the kinetic parameters associated the exchange process. The kinetic data of the ion exchange of homoionic sodium form NaY zeolite/ Ca aqueous solutions systems at different temperatures was best fitted to Pseudo second order kinetic model. The results indicated that diffusion is the only mechanism that describes mass transfer from the particle surface to the exchangeable site, and intraparticle transport is the only rate –limiting step in the process of cation exchange.

KEYWORDS: Cation exchange capacity, Cation Exchange kinetic models, mass transfer mechanism, NaY zeolite.

I. INTRODUCTION

Zeolites are crystalline microporous aluminosilicates, built up of a 3-dimentional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, linked by sharing oxygen atoms, and weakly bonded (readily exchangeable) cations and water molecules in the pores and voids of the structure. Industrialization is the back bone of every nation's economy and the enhancement of citizenry well-being [1]. Zeolites are commonly used in environmental remediation for selective removal of toxic materials by cation exchange process. The CEC results from the presence of loosely bound cations of alkali and alkaline earths elements, often called exchangeable cations, in the structure of the zeolites. These loosely bound cations are easily exchanged when zeolites are in contact with solutions of saturating or indexing ions. The cation exchange rate can be limited by the speed of ion motion towards the zeolite. Zeolites are used in environmental remediation due to their high ion exchange capacity, molecular-sieve properties, which can be easily modified to make them selective of certain ion sizes [2, 3].

CEC is directly related to the amount of aluminum present in the framework. Properties such as Si/Al ratio, specific to the cationic species in solution and the anionic associated to them, solvent, pH, and temperature must be observed for good exchange efficiency. The exchange process is described as [4]:

$$M1 (Z) + M2(S) \leftrightarrow M 2 (Z) + M1(S) \qquad (1)$$

WhereM1 (Z) is the exchangeable cation present in zeolites Z, and M2 is the saturating ion in solution. Many methods are known for the determination of CEC. Ammonium acetate, $BaCl_2$ or $CaCl_2$ compulsive exchange, tetra ethylene amine, complex of Cu(II) with triethylenetetramine, Co hexamine trichloride and methylene blue. $CaCl_2$ and ammonium acetate method was the most widely used methods.

Ion-exchange kinetics, though of considerable importance in zeolite applications such as catalysis and in detergent action, has not been as extensively studied because of the complexity of the process. Diffusion of ions can be rate limiting within the crystal (particle-controlled diffusion) or in passing through the zeolite-fluid boundary (surface diffusion), with the latter becoming more important for smaller crystallite size. Within the crystal, diffusion is promoted by concentration gradients as well as influenced by electrical potential gradients due to the charge density differences of the exchanging ions [5-6]. The methods of ammonium acetate saturation (AMAS) and methylene blue absorption (MBA) are commonly used to measure the CEC of finely crystalline materials.

II. RELATED WORK

A comprehensive study of alkaline earth ion exchange in zeolites X and Y over the temperature range of 5–50°C was made by the ion exchange capacities of Na for Cr/K, Cr/Mg and Cr/Ca in Y and X zeolites by using breakthrough curves [5].

Liu et al [7] studies NaY zeolites which are in-situ synthesized from coal-based kaolin via the hydrothermal method. The ion exchange isotherms of Cr^{3+}, Mg^{2+}, Ca^{2+} and K^+ in binary mixtures (Cr/K, Cr/Ca, Cr/Mg) using NaY zeolite at 30, 45 and 60°C is reported by Barros at 2005 [8]. They found that ion exchange behavior of all systems seems to be very dependent on temperature, nature and interaction of in-going cations. This investigation concentrates on examination of kinetics of CEC of different zeolite samples using empirical kinetic models, comparison of their CEC and establishing the exchange mechanism of ions included in the ion exchange process.

III. MATERIALS AND METHODS

Zeolite Synthesis
In our previous investigation a simple and easy method was employed to synthesize of homoionic sodium from of Nay Zeolite to measure its CEC kinetically [9,10].

Kinetics of CEC measurement
Experiments have been performed on sample of synthetic homoionic sodium from of Nay zeolite prepared to measure its CEC and the kinetic parameters associated the exchange process [11].

Batch model was selected because of its simplicity and reliability. The ion exchange experiments were carried out in a series polyethylene tubes containing zeolite and $CaCl_2$ suspensions at constant temperatures.

Preliminary studies of CEC for NaY zeolite indicated that the process was characterized by a rapid change during 12-14 hs of contact time followed by more than one week to be sufficient to achieve the equilibrium.

The CEC measurement experiments were conducted by equilibrating 5 g of the prepared zeolite, in 50 ml centrifuge tubes, with 25 ml of 2M solution of $CaCl_2$. The mixtures were shaken continuously for 9 days at temperature controlled (303, 318 and 328 K) water bath with shaker at 185 rpm. When equilibrium time was achieved the supernatants were removed by centrifugation at 3500 rpm for 20 minutes. The supernatants of four replicates were collected together and analyzed spectrophotometrically for Na^{+1} and Ca^{+2}.

IV. CALCULATION

Based on the results for concentrations obtained from the examination of ion exchange kinetics, the amount of Ca^{2+} bound at selected solid/liquid contact times q_t and at equilibrium, q_e, has been calculated from [12]:

$$q_t = (C_0 - C_t)V/m \qquad (2)$$

The exchange capacity (q_e) was determined using the mass balance expression:

$$q_e = (C_0 - C_e)V/m \qquad (3)$$

Where C_o and C_t are the Ca^{2+} concentrations in liquid phase at the initial and time t (in ppm) respectively, m is the weight of the zeolite (in g), and V is the volume of the solution (in ml).

V. RESULTS AND DISCUSSION

Cation exchange Process
Kinetics Exchangeable cations are those that can be changed by a cation of added solution, or that is, any added cation will exchange the zeolite cation. The basic exchangeable cation in NaY zeolite is Na^{1+}, which was exchanged by Ca^{2+}.The ion exchange kinetics of Na Y zeolite/Ca aqueous solution system was done for the studied NaY zeolites.

Effect of contact time
Examination of ion exchange kinetics of Ca^{2+} was performed by means of the batch method in Na Y zeolite/ Ca aqueous solutions systems. Contact time is inevitably a fundamental parameter in all transfer phenomena such as cation exchange process.

The experimental results of CEC kinetics were illustrated in Fig. 1 represents the data obtained from Na^{1+} exchanged by Ca^{2+} in Na Y zeolite. The data showed that a contact time of 9 days was required to achieve the equilibrium. The ion

exchange of Ca^{2+} shown is rapid at initial times with prolonged slower exchange until equilibrium. During the first hours of Na Y zeolite/Ca aqueous solutions contact (12-24 h), the rate of cation exchange is found to be very rapid, and thereafter, the rate of metal ions exchange decreased.

During the initial stage of the process, a large number of Na^{1+} is available for exchange. After lapse of sometime, the ingoing metal ions (Ca^{2+}) are binded into the mesopores that get almost saturated with in-going metal ions during the initial stage of exchange. Our results were in good agreement with that reported in literature [13-14].
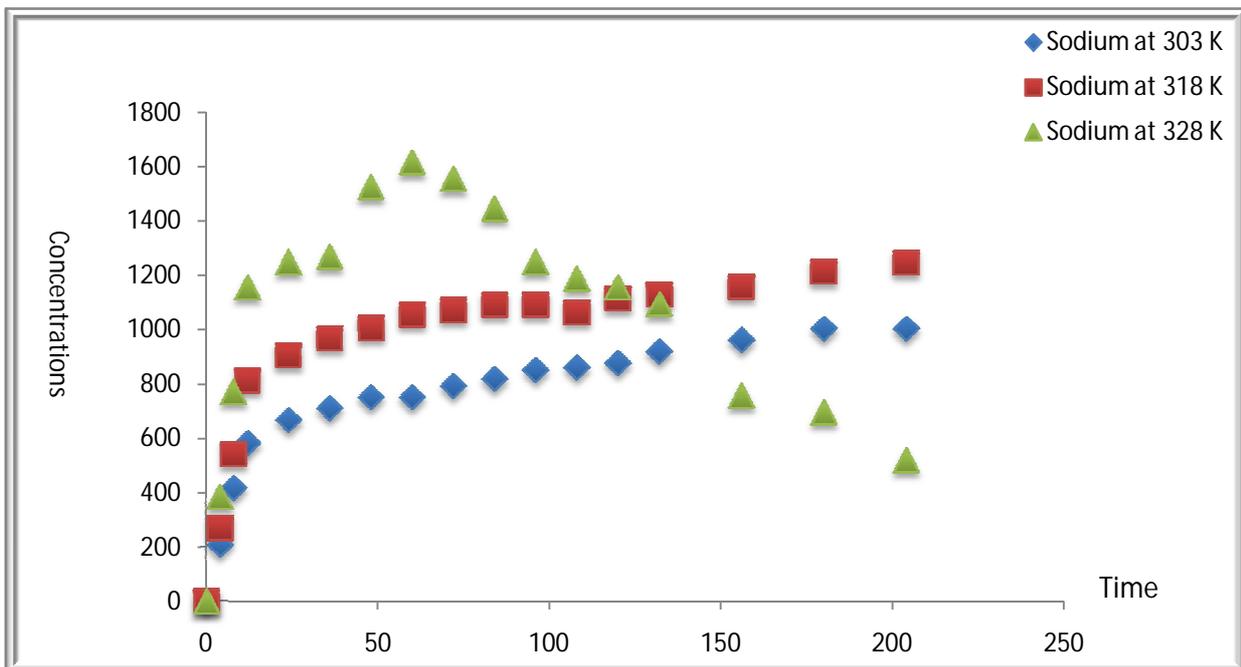
Fig. 1 Determination of the equilibrium contact time for Na $^{1+}$ exchange in NaY zeolite at different temperatures.

Kinetic Models
Pseudo first-order Model
Lagergrens pseudo first-order equation is the earliest known one describing the exchange rate based on the exchange capacity. The linear form of Lagergren,s pseudo first-order equation is generally expressed as[14]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\, t \qquad (4)$$

Where q_e and q_t were defined previously, k_1 is the pseudo first-order rate constant of the process (h^{-1}). The values of k_1 and q_e were calculated from the slope and the intercept of the lagergren plot of log (q_e - q_t) versus t as shown in Fig. 2. The pseudo first-order rate constant k_1, amount of Ca^{2+} exchanged calculated at equilibrium ,q_e, the experimental values of q_e, exchange rate, R, and the correlation coefficients ,R^2, obtained from the pseudo first-order rate model were all gathered in Table 1. The large differences between the experimental and the calculated values of q_e indicated that pseudo first-order mechanism is not fully followed in this process.

y = -0.050x + 5.521
R² = 0.925

y = -0.062x + 5.436
R² = 0.957

y = -0.081x + 5.453
R² = 0.987
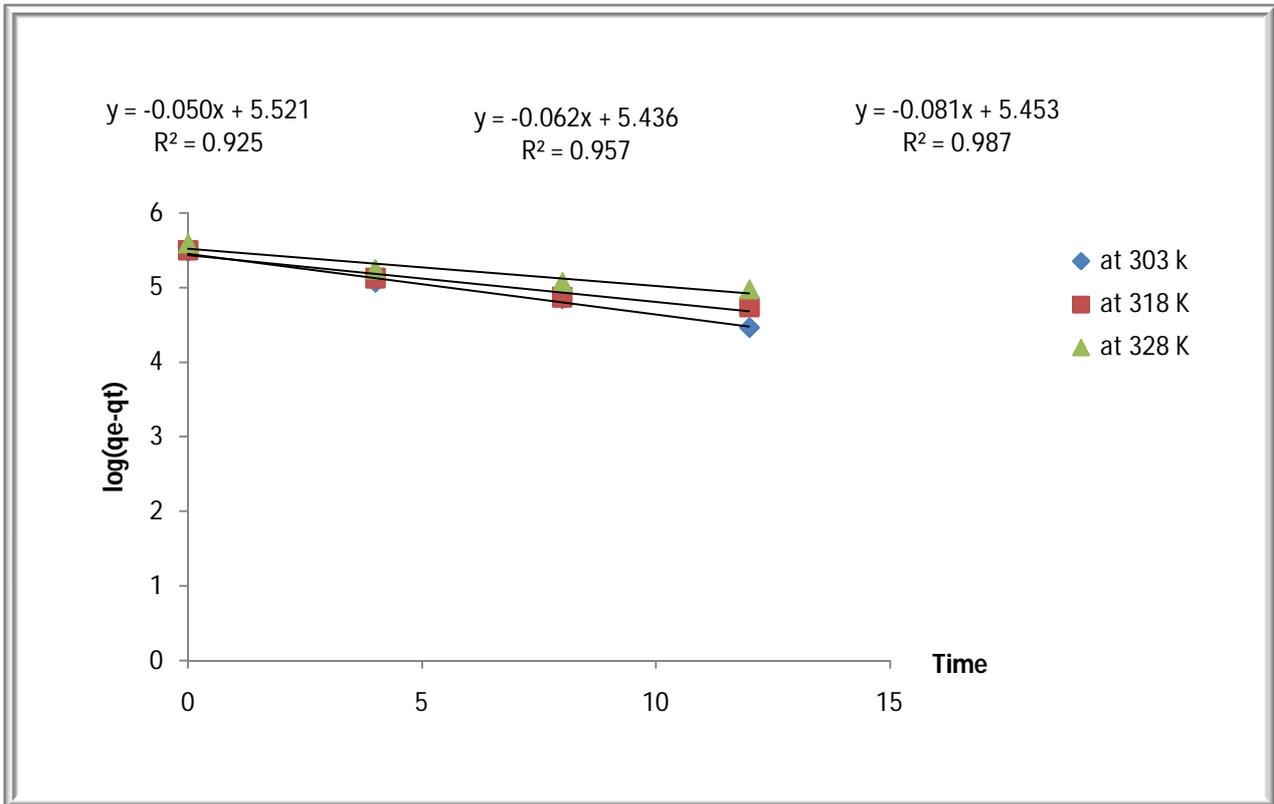
Fig. 2 .Lagergren plots for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems at different temperatures.

Table (1): Lagergren kinetic parameters for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems at different temperatures.

temp.(K)	Time(hrs.)	q_e(calc.) $(\mu g.g^{-1})$	q_e(exp.) $(\mu g.g^{-1})$	$k(h^{-1})$	R	R^2
303	204	283791.9	301180	0.186	2984.0	0.987
318	204	272897.7	312625	0.144	2318.4	0.957
328	204	331894.4	388500	0.115	1840.0	0.925

Pseudo second-order Model

Pseudo –second order kinetic rate expression was developed for the exchange system of divalent metal ions in its linear form as [15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

Where k_2 is the rate constant for the pseudo second order transport process $(g\mu g^{-1}h^{-1})$. The linear variation of t/qt with t for the studied system at different temperatures was shown in Fig.3. The initial exchange rate, h, (h^{-1}) is expressed as:

$$h = k_2 * q_e^2 \qquad (6)$$

Values of both constants k_2 and h together with values of q_e can be calculated from the intercept and slope of the line obtained by plotting t/qt versus t. The values of model parameters (k_2, h, and q_e), calculated values of q_e as well as experimentally measured values, and the pseudo second order regression of coefficients of determination (R^2) were all given in Table2.

It can be seen that cation exchange kinetic of Na Y zeolite/ Ca aqueous solutions systems follows this model with correlation coefficients higher than 0.99 and the calculated values q_e agreed well with the experimentally measured values. So the experimental kinetic data was best fitted to the pseudo second order kinetic model. Similar results have been reported in literature [16].
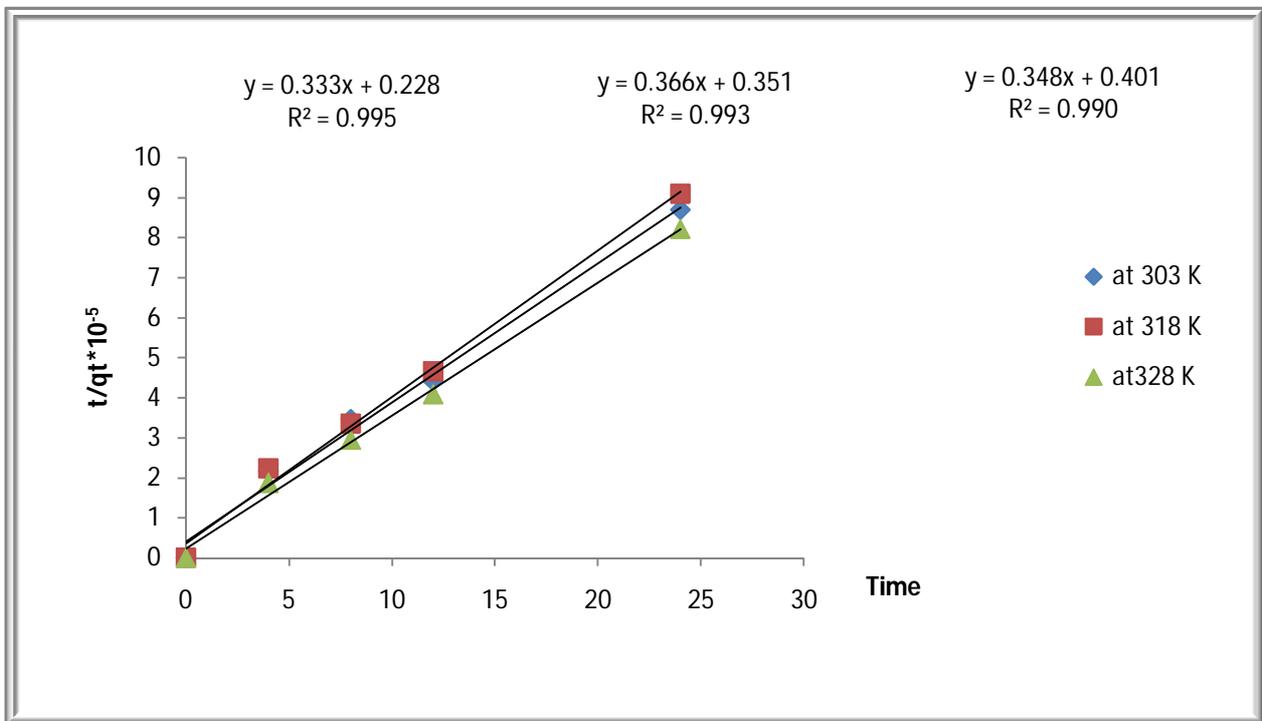
Fig. 3. Pseudo second order kinetic plots for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems at different temperatures.

Table (2): Pseudo second order kinetic parameters for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions system at different temperatures.

temp.(K)	Time(hrs.)	q_e(calc.) ($\mu g.g^{-1}$)	q_e(exp.) ($\mu g.g^{-1}$)	k_2(g $\mu g^{-1} h^{-1}$)	h(h^{-1})	R^2
303	204	287350	301180	30200	$2.49*10^{15}$	0.990
318	204	273224	312625	38200	$2.85*10^{15}$	0.993
328	204	300300	388500	48732	$4.39*10^{15}$	0.995

Elovich Model The simple Elovich kinetic model may be expressed in the following form [17]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (7)$$

Where α is an ion exchange initial rate (g.g^{-1}h^{-1}) and β is the revers rate (g.g^{-1}h^{-1}). The experimental results for cation exchange kinetic of Na Y zeolite/ Ca aqueous solutions system were analysed using the Elovich model, a plot of q_t versus ln t, as shown in Fig.4. Values of q_t, α, β, and R^2 were all summarized in Table 3.

The values of correlation coefficient (R^2) were $\geq$ 0969 which means that experimental results for cation exchange kinetic of Na Y zeolite/ Ca aqueous solutions systems were obey the Elovich model.

The general explanations for this form of kinetic equation involves a variation of the energetic of the exchange process with the active sites are heterogeneous in NaY zeolite/ Ca aqueous solutions system. It will be seen that applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation was able to describe the kinetics of the ion exchange of Na Y zeolite/ Ca aqueous solutions systems.
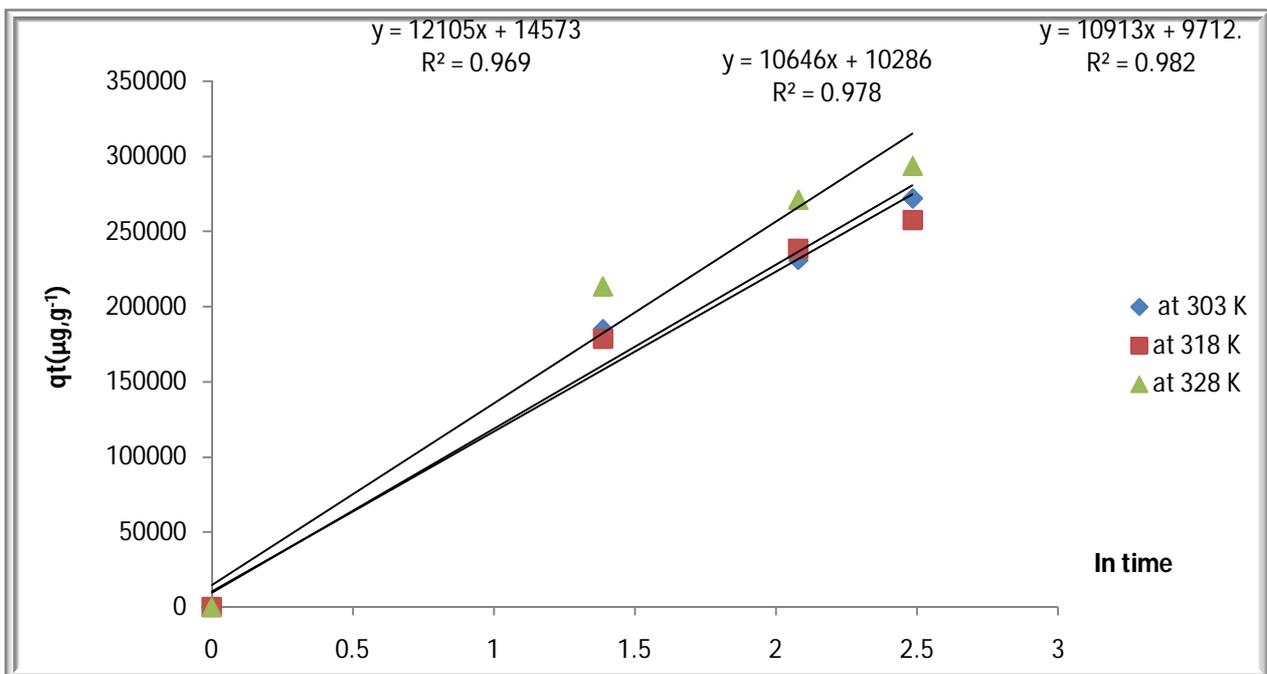
Fig. 4. . Elovich kinetic model plots for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems at different temperature.

Table (3) Elovich kinetic model parameters for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems at different temperature.

temp.(K)	Time(hrs.)	α g.g^{-1}h^{-1}	β g.g^{-1}h^{-1}	R^2
303	204	0.02655	$9.163*10^{-11}$	0.982
318	204	0.02729	$9.393*10^{-11}$	0.978
328	204	0.04031	$8.261*10^{-11}$	0.969

Intra Particle diffusion kinetic model

When the Ca^{2+} solution is mixed with zeolite, transport of Ca^{2+} from the solution through the interface between the solution and the zeolite occurs into pores in the particles. There are four main stages in the ion exchange process [12]:
(i) Ca^{2+} transfer from the bulk solution to the boundary film that surrounds the zeolite's surface, (ii) Ca^{2+} transport from the boundary film to the zeolite's surface, (iii) Ca^{2+} transfer the zeolites surface to active intraparticular sites, and
(iv) exchange between the in-going Ca^{2+} and the available out-going Na^{1+} on these sites.

One or more of these four steps control the rate at which Ca^{2+} exchanged. Intraparticular diffusion of Ca^{2+} was characterized using the relationship between amount Ca^{2+} exchanged and the square root of contact time ($t^{1/2}$). This relation is expressed as follows [18,19].

$$q_t = K_d \, t^{1/2} + C \qquad (8)$$

Where Kd is the initial rate of intraparticlar diffusion ($\mu gml^{-1} \, min^{-1/2}$) and C is the y- intercept. Fig.5 shows the diffusion of Ca^{2+} within the zeolite as a function of time. Values of intraparticular diffusion constants (K_d) for the studied zeolite and at all temperatures are given in (Table 4).

Values of K_d showed that Ca^{2+} diffused quickly among the zeolite particles. Figure 4 shows that all lines passed through the origin (i.e. no y-intercept) which indicates that intraparticle transport is the only rate – limiting step in the process of cation exchange of Na Y zeolite/ Ca aqueous solutions systems. That indicates that diffusion is only mechanism that describes mass transfer from the particle surface to the exchangeable site.
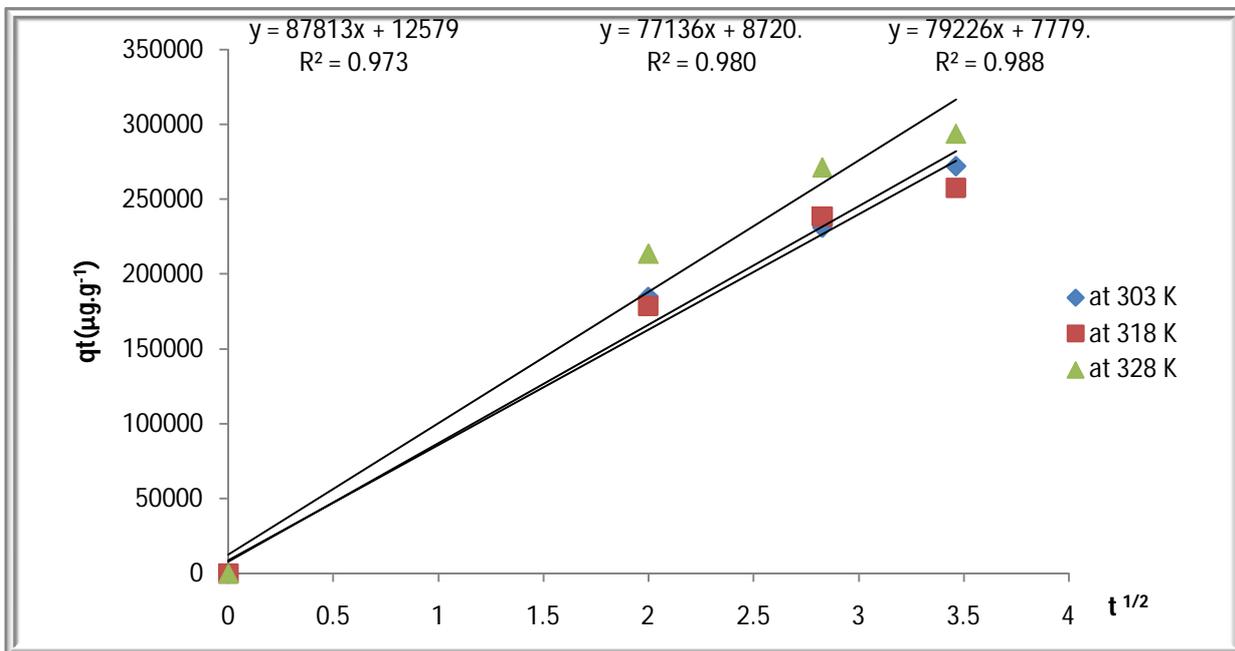
Fig. 5. Intra particle diffusion kinetic model plots for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems.

Table 4 Intra particle diffusion kinetic model parameters for the ion exchange of Ca^{2+} Na Y zeolite/ Ca aqueous solutions systems.

temp.(K)	Time(hrs.)	$K_d(\mu gg^{-1}h^{1/2})$	$I(\mu gg^{-1})$	R^2
303	204	79226	7779	0.988
318	204	77136	8720	0.980
328	204	87813	12579	0.973

Cation Exchange Mechanism

The rate of the ion exchange of Ca^{2+}Na Y zeolite/ Ca aqueous solutions systems at different temperatures was rapid initially, but it gradually becomes slower with passage of time reaching a maximum in contact time of 9 days. The initial faster rate may be due to the availability of uncovered surface area of zeolite initially, since ion exchange kinetics depends on the surface area of the zeolite. It is likely that several mechanisms are responsible for the slow exchange reaction these may include diffusion, precipitation, and\or adsorption reactions on sites that have higher activation energy than the fast exchange sites. Moreover IntraParticle diffusion kinetic model parameters revealed that intraparticle transport is the rate – determining step in the process of cation exchange of Na Y zeolite/ Ca aqueous solutions systems [20].

The ion exchange kinetics of Na Y zeolite/Ca aqueous solution system prepared by different procedures may vary widely in purity, chemical composition, crystal size, porosity, pores diameter and other properties, as well as their ion exchange capacity. Experiments have been performed on samples of synthetic zeolites prepared by different procedures to measure their CEC and the kinetic parameters associated the process.

VI. CONCLUSION

The CEC of Synthesized NaY zeolite was found to be dependent on contact time. The data was found to fit well to all with exceptional to the pseudo first order kinetic (Lagergren) model. The kinetic of the ion exchange of Na Y zeolite/ Ca aqueous solutions systems at different temperatures was best fitted to Pseudo second order kinetic. The diffusion is only mechanism that describes mass transfer from the particle surface to the exchangeable sites of the studied samples.

REFERENCES

[1] Gin, W.A., Jimoh, A.*, Abdulkareem, A.S. and Giwa, A. Kinetics and Isotherm Studies of Heavy Metal Removals from Electroplating Wastewater Using Cassava Peel Activated Carbon, *International Journal of Engineering Research & Technology (IJERT), 3* (1), 2014.

[2] Omar H. Elsayed-Ali, Tareq M. Abdel-Fattah, Hani E. Elsayed-Ali, Cation Exchange in Zeolites Placed in an Electro kinetic Cell, Proc. of the 6th WSEAS Int. Conf. on Environment, Ecosystems and Development (WICEED), 2008.

[3] Pierre Naïder Fanfan , Nicolas Mabon , Philippe Thonart , Georges Lognay , Alfred Copin and Jean-Paul Barthélemy. Investigations on Cationic Exchange Capacity and Unused Bed Zone according to operational conditions in a Fixed Bed Reactor for water lead removal by a natural zeolite, Biotechnol. Agron. Soc. Environ. 10 (2), 93 – 99.2006.

[4] Konstations P.K. Cation-Exchange capacity (CEC) of zeolitic materials: Applicability of the ammonium acetate saturation (AMAS) methods, *Clays and clay minerals, 47*, (6), 688-696.1999.

[5] Pramatha Payra and Prabir K. Dutta, *Zeolites,* A Primer Marcel Dekker, Inc. The Ohio State University, Columbus, Ohio, U.S.A. 2003

[6] Barros M. Zola A. Arroyo P. Sousa-Aguiar E. Tavares C. Binary ion exchange of metal ions in Y and X zeolite, *Brazilian Journal of Chemical Engineering, 20*, (4), 413 – 421.2003.

[7] Liu Ximmei Yan, Zifeng Wang, Huaiping Luo Yantuo, In-situ Synthesis of NaY Zeolite with Coal-Based Kaolin, *Journal of Natural Gas Chemistry,12,* 63-70.2003.

[8] Barros M. Arroyo P. Sousa-Aguiar E. Tavares C. Binary ion exchange isotherms in NaY zeolite, 2nd Mercosur Congress on Chemical Engineering, 2005.

[9] Avin M. Kafia M. Synthesis and Comparison of Cation Exchange Capacity of NaY Zeolites: *Thermodynamic and Kinetic study*, Master Thesis, University of Salahaddin-Erbil, Kurdistan, Iraq, 2014.

[10] Md Jelas Haron, Saiful Adli Masdan, Mohd Zobir Hussein, Zulkarnain Zainal and Anuar Kassim. KINETICS AND THERMODYNAMIC FOR SORPTION OF ARSENATE BY LANTHANUM-EXCHANGED ZEOLITE. The Malaysian Journal of Analytical Sciences, Vol 11, No 1: 219-228.2007.

[11] K. M. Abd El-Rahman, M. R. El-Sourougy, N. M. Abdel-Monem, and I. M. Ismail, Modeling the Sorption Kinetics of Cesium and Strontium Ions on Zeolite A, *Journal of Nuclear and Radiochemical Sciences, 7*, (2) 21-27.2006.

[12] Wang, S.; Peng, Y. *Chem. Eng. J, 156*, 11-24.2010.

[13] M. Trgo, J. Peri, N. Vukojevi, Medvidovi, Comparative study of ion exchange kinetics in zinc/lead—modified zeolite-clinoptilolite systems, *Journal of Hazardous Materials B136*, 938–945.2006.

[14] S. M. Yakout, E. Elsherif, Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons, *Carbon – Sci. Tech. 1* , 144-153.2010

[15] D. Paliulis, *Journal of Environmental Engineering and Landscape Management, XIV*, 10-15.2006.

[16] V. C. Srivastava, I. D. Mall, I. M. Mishra, *Journal of Hazardous Materials, 134,*257-267.2006.

[17] E. S. Z. El-Ashtoukhy, N. K. Amin, O. Abdelwahab, Binary Ion Exchange Isotherms in NaY Zeolite, *Desalination, 223,* , 162-173. 2008.

[18] N. Renugadevi, R. Sangeetha and P. Lalitha, Kinetics of the adsorption of methylene blue from an industrial dyeing effluent onto activated carbon prepared from the fruits of Mimusops Elengi, *Applied Science Research, 3* (3), 492-498.2011.

[19] Pattaranun Thuadaij, Kedsarin Pimraksa and Apinon Nuntiya. Synthesis of High Cation Exchange Capacity Faujasite from High Calcium Fly Ash. Australian Journal of Basic and Applied Sciences, 6(10): 194-208, 2012.

[20] Baybars A.F, Recep B, Alper E, Rdem Y, Serkan B, Adsorption Kinetics and Isotherms for the Removal of Zinc Ions from Aqueous Solutions by an Ion-Exchange Resin, J. Chem. Soc. Pak., 34 (4), 841- 50.2012.