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Effects of Ammonium and Iranian Natural Zeolite on Potassium Adsorption and Desorption Kinetics in the Loess Soil

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Abstract: Information about the adsorption and desorption kinetics of potassium and the consequent alterations with zeolite additions are limited in Golestan Province loess soils with illite dominance in the clay fraction. The kinetics of potassium adsorption and desorption with different KCl concentrations (0, 40, 60, 80, 110 and 140 mg L⁻¹) and KCl+NH₄Cl concentrations (K80,N60; K80,N120; K60,N60; K110, N120; K80, N90 and K110, N90 mg L⁻¹) on the soil, the zeolite and their incorporation (within 2 and 1800 h) were investigated with this research using batch method. Potassium adsorption and desorption was initially fast (first 48 h) but continued with low speed (after 48 h) until the end of the experiment. Results shown increasing of K⁺ concentration increased rate of adsorption and desorption in soil, zeolite and their incorporation and zeolite increased adsorption and decreased desorption rate by incorporation with soil. Ammonium presence decreased potassium adsorption and it increased potassium desorption. K/NH₄ desorption rate did not follow exactly K/NH₄ adsorption ratio for all treatments. The kinetic equations used to estimate data were zero order, first order, simple Elovich, parabolic diffusion and power function. The Elovich model described the adsorption and desorption processes on soil and soil with zeolite (0.88<R²<0.99). Elovich and power function models described adsorption and desorption processes, respectively for zeolite well (0.65<R²<0.97). The models indicated that K⁺ adsorption and desorption was diffusion controlled. Potassium adsorption and release by batch method did not simulate potassium uptake by wheat.

Key words: Clinoptilolite zeolite, illitic loess soil, potassium, ammonium, adsorption and desorption, kinetic models

INTRODUCTION

Potassium (K⁺) is one of the most plentiful nutrients in the soil surface with important physiological roles in plant, improving their quality (Marschner, 1995). Although the distribution of K⁺ forms differs from soil to soil as a function of the dominant soil minerals present, total soil K⁺ reserves are generally large. Soil K⁺ is typically divided into four forms: soil solution K⁺, exchangeable K⁺, non-exchangeable K⁺ and K⁺ in soil minerals. There are dynamic, equilibrium reactions between different forms of K⁺. It is believed that the soils of arid and semiarid regions contain sufficient exchangeable K⁺ (exchange with NH₄⁺ acetate) and K⁺-bearing minerals able to release enough K⁺ to meet crop requirements. Although these regions may contain large quantities of exchangeable and non-exchangeable K⁺ (Jalali, 2005), the exchangeable K⁺ may become depleted in these regions due to the intensive crop production (Jalali and Zarabi, 2006). The estimation of K⁺ available to crops as well as most of the K⁺ fertilizer recommendations is based on soil analysis (Parker *et al.*, 1989).

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Zeolites are crystalline aluminosilicate minerals with three dimensional network of open structure. Natural clinoptilolite (zeolite) has a three-dimensional crystal structure and its typical unit cell formula is given either as $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$ or $(\text{Na}_x \text{K}_y \text{Ca}_z \text{Mg}_3)[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$ (Tehrani and Salari, 2005; Haggerty and Bowman, 1994). Their cation exchange capacities is high and have a remarkable tendency for adsorption of cations within their crystalline network which are plant available through an exchange reaction by roots. Allen and Ming (1995) proved zeolites released ions slowly. The most important of which are in adsorption and desorption, separation and ion exchange operations as well as catalysis (Kirk and Othmer, 1998). Processing and optimum application of this mineral in Iran, sporadic explorations in areas such Semnan have led to valuable zeolite resources of the eight documented reports regarding zeolite rich areas in Iran (Rezaei *et al.*, 2008; Tehrani and Salari, 2005). Co-existed cations such as Na^+ , K^+ , Ca^{2+} , NH_4^+ and Mg^{2+} are typically presented with K^+ and NH_4^+ , the presence of these competing cations could affect K^+ and NH_4^+ adsorption and desorption on clinoptilolite (Cooney *et al.*, 1999; Weatherley and Miladinovic, 2004; Hankins *et al.*, 2004). Although, different potassium exchange capacities under the influence of those competing cations have been measured by the above named researchers, so far little information is available for the investigations of adsorption and desorption behaviors of K^+ on natural zeolite and incorporation with loess soil.

Adsorption and desorption are most important chemical processes in soils and soil constituents. In Golestan Province (Pardis Estate) with Loess soil with prevailing illite clay, exchangeable K^+ is not always a reliable measurement of plant availability. This region soils can't supply K to plant growth despite they are containing 270-580 mg kg^{-1} exchangeable K^+ (exchange with NH_4^+ acetate and Rezaei and Movahedi Naeeni (2008) showed maximum potassium adsorption and potential buffering capacity obtained by zeolite treatment and maximum wheat N^+ and K^+ uptake and yield was also with the zeolite treatment as a slow release source of these ions. Adsorption and desorption kinetics of K^+ have been determined by using different extraction methods. The K^+ in the interlayer of illite can be exchanged by hydrated cations such as Ca^{2+} and NH_4^+ (Rausell-Colom *et al.*, 1965; Scott and Smith, 1966; Scott, 1968). In addition, the presence of NH_4^+ cation of fertilizer (Mutscher, 1995) and Ca^{2+} in irrigation water and of soil minerals able to release Ca^{2+} are important in determining the amounts of K^+ leached from soils in arid and semiarid regions (Jalali and Rowell, 2003). Several kinetic studies have been conducted on soils and pure minerals, to elucidate mechanisms and release rates of non-exchangeable K (Huang, 2005). The available K^+ status after fertilizer application is also dependent upon the K^+ sorption and desorption capacity of soil. An alternative approach to soil testing is to consider K^+ extractable and release rate of K^+ simultaneously to improve fertilizer application.

Understanding the adsorption and desorption kinetics of K^+ in calcareous soils is important to determine fertilizer application and appropriate management of soils. However, the comprehensive comparison and screening of kinetic models for K^+ and effects of ammonium concentration on K^+ adsorption and desorption on loess soils, clinoptilolite zeolite and the consequent alterations with zeolite additions in Golestan Province loess soil were not documented yet. This research has the following objectives:

- To investigate the K^+ adsorption and desorption kinetics on zeolite and loess soil with prevailing illite clay
- To determine the effects of zeolite on adsorption and desorption kinetics of K^+ on the incorporation of loess soil
- To apply five kinetic models on K^+ sorption and desorption
- To survey various $\text{NH}_4\text{Cl}+\text{KCl}$ concentration on K^+ adsorption and desorption kinetics

MATERIALS AND METHODS

Zeolite and Soil

The natural zeolite used in experiments was sourced from North of Semnan Province, Iran. Composition of the natural clinoptilolite used in this study was characterized by X-Ray Diffractometry (XRD). As it can be shown from Fig. 1, X-ray diffraction analysis showed that this material was almost over 80% clinoptilolite and the remainder consisted of bantonite. Table 1 shows its elemental analysis.

The soil samples with a loess origin, obtained from a Typic Calcixerols (Rahmat Abad Series) of silty clay loam texture from the estate of Gorgan University of Agricultural Sciences and Natural Resources at Golestan Province, Iran (approx. 37°45'N, 54°30'E). Illite prevailed in the clay fraction (Fig. 1).

Analysis of Soil and Zeolite

The soil and zeolite samples were air dried and ground to pass through a 2 mm sieve for laboratory experiments. We added 3571 mg zeolite per 1 kg soil (20 t ha⁻¹) zeolite into soil. Samples (soil, zeolit and soil+zeolit) pH and EC were determined using 1:2 soil to water suspension with a glass electrode (Rhoades, 1996) and particle size was determined by the hydrometer method (Klute, 1986). Organic matter was determined by dichromate oxidation (Walkey and Black, 1934). Cation Exchange Capacity (CEC) of the samples were determined by the 1 M NaOAC, pH 8.2 method (Chapman, 1965) and specific surface area determined with Ethelene glycol monoethyl ether method (Carter *et al.*, 1965). The following extraction solution were used for determination of solution: extraction with a soil-water ratio 1:20 for 30 min and exchangeable form: extraction with 1 M NH₄OAC solution, pH 7 at a solution ratio 1:20 with an extraction time of 30 min. The semi-quantitative mineralogical composition of the clay fraction treated by Mg-saturation, Mg-plus ethyleneglycol- saturation, K-saturation and heat was determined by X-ray diffraction analysis and using a Bruker D8 X-ray diffractometer using Cu-Ka radiation (40 kV and 30 mA), at a step size of 0.02°2 Theta and a step time of 1 sec. (Mehra and Jackson, 1960; Kittrick and Hope, 1963). Pearson's correlations co-efficient were used to determine the relationship between K⁺ and NH₄⁺ concentration with the constants a and b of the best model (to describe the adsorption and desorption of K⁺) represent the intercept and the slope of the linear curves.

Kinetics of Potassium Adsorption

Adsorption and desorption of K⁺ tests conducted during February 2007 to September 2008 with batch method (Selim and Amcher, 1997; Wilson *et al.*, 2004) by KCl and NH₄Cl+KCl solutions in Gorgan University of Agricultural Sciences and Natural Resources Soil Laboratory. We studied the kinetics of K adsorption at five potassium concentrations (K treatments) from KCl source and six

Table 1: Elemental analysis results of raw clinoptilolite zeolite

Chemical composition	Percentage
SiO ₂	64.40
Al ₂ O ₃	12.80
Fe ₂ O ₃	1.31
TiO ₂	0.31
CuO	2.37
MgO	1.15
Na ₂ O	1.13
K ₂ O	2.64
P ₂ O ₅	0.21
LOI*	13.19

*Loss on ignition

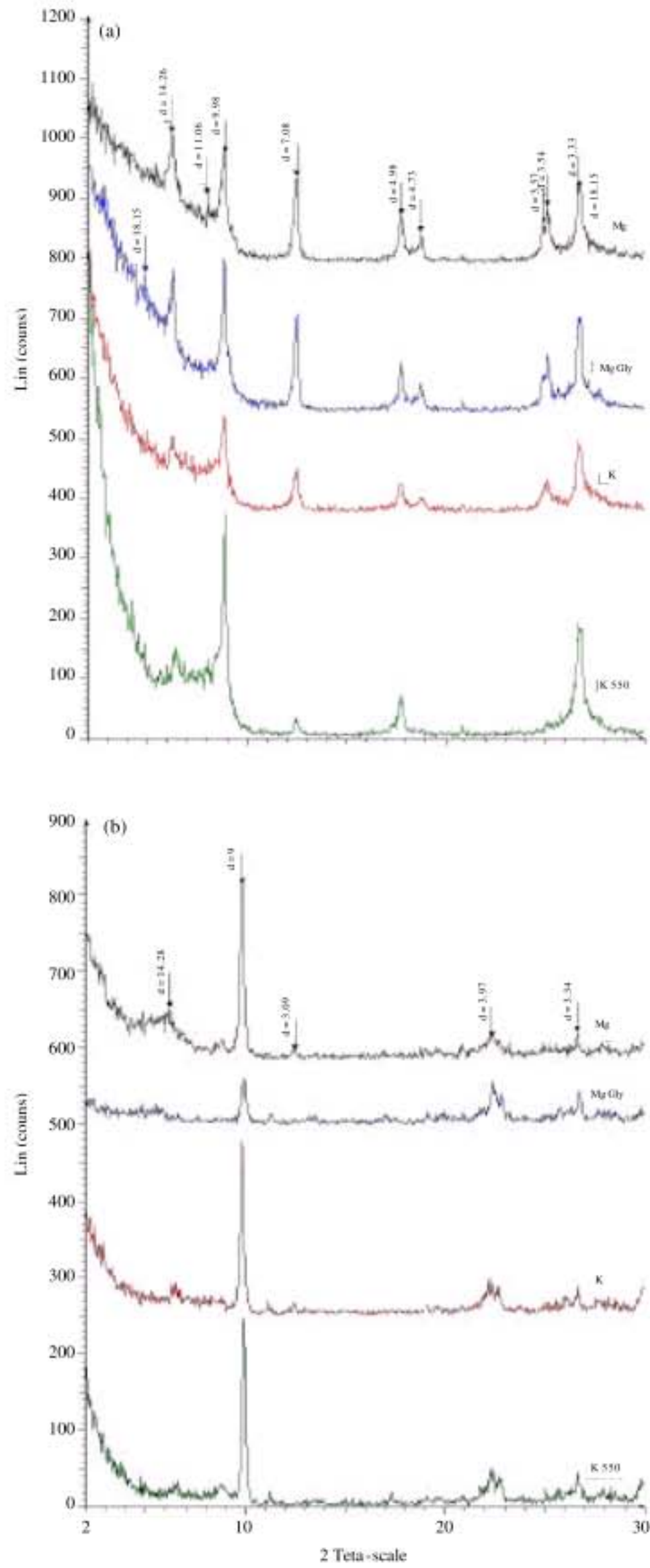


Fig. 1: X-ray diffractograms of (a) soil sample and (b) zeolite sample

potassium+ammonium concentrations (NH_4^+ + K^+ treatments) from $\text{KCl}+\text{NH}_4\text{Cl}$ sources. We weighed 1.0 g of soil, soil+zeolit and zeolite in 50 mL polypropylene centrifuge tubes in 2 repetition and added 10 mL of with an ionic strength and pH equivalent to Pardis saturated soil paste extract containing potassium concentrations 40, 60, 80, 110 and 140 mg L^{-1} for K treatments and potassium+ammonium concentrations, K80, N60; K80, N120; K60, N60; K110, N120; K80, N90 and 6. K110, N90 mg L^{-1} for $\text{NH}_4\text{Cl}+\text{KCl}$ treatments. We used 10 times 2, 4, 8, 12, 48, 192, 240, 720, 1440 and 1800 h for K^+ treatments and 8 times 2, 4, 8, 12, 192, 240 and 720 h for NH_4^+ + K^+ treatments. A few drops of chloroform were added to the tubes to suppress microbial growth. The centrifuge tubes were capped and shaken for 1 h in each time at 150 rpm (Schouwenburg *et al.*, 1963) and room temperature ($25\pm 2^\circ\text{C}$) (Jalali, 2006). At the end of the adsorption times (each time) tubes centrifuged at $3000 \times g$ for 10 min (Kithome *et al.*, 1998). The quantity of K^+ uptake by soil, soil+zeolite and zeolite was calculated from the decrease of its concentration in solution (Guo *et al.*, 2008).

Kinetics of Potassium Desorption

We conducted desorption studies after finishing of K^+ adsorption time (1800 h for K^+ and 720 h for $\text{NH}_4\text{Cl}+\text{KCl}$ treatments) for all of concentration exactly. Kinetics of K^+ desorption was studied by successive extraction (Sparks and Libhardt, 1981; Lopez-Pineiro and Navarro, 1997; Jalali, 2007; Rezaei and Movahedi Naeni, 2008) with 10 mL of 0.0034 M. CaCl_2 solution with an ionic strength and pH equivalent to Pardis saturated soil paste extract solution for blew times for finaling samples of adsorption experiments and also zero concentration of K^+ or NH_4^+ + K^+ treatments. For approach kinetics of K^+ desorption, we used 10 times 2, 4, 8, 12, 48, 192, 240, 720, 1440 and 1800 h for K^+ treatments and 8 times 2, 4, 8, 12, 192, 240 and 720 h for $\text{NH}_4\text{Cl}+\text{KCl}$ treatments. The centrifuge tubes were capped and shaken for 1 h in each time at 150 rpm (Schouwenburg *et al.*, 1963) and room temperature ($25\pm 2^\circ\text{C}$) (Jalali, 2006). At the end of the desorption times (each time) tubes centrifuged at $3000 \times g$ for 10 min (Kithome *et al.*, 1998).

Kinetic Models

Different kinetic models described blew were used to describe K^+ adsorption and desorption by the natrul clinoptilolite zeolite, soil and soil+zeolit clinoptilolite.

$$\text{First order model} \quad : \quad \ln (K_0 - K_t) = b - at \quad (1)$$

$$\text{Zero order model} \quad : \quad (K_0 - K_t) = b - at \quad (2)$$

$$\text{Elovich model} \quad : \quad K_t = b + a \ln t \quad (3)$$

$$\text{Parabolic diffusion model} \quad : \quad K_t / K_0 = b + a t^{1/2} \quad (4)$$

$$\text{Power fraction model} \quad : \quad \ln K_t = b + a \ln t \quad (5)$$

where, K_t is the amount of cumulative K^+ desorbed or adsorbed at time t, t is the time of adsorb or desorb, K_0 is the maximum K^+ adsorbed or desorbed (final equilibrium) and a and b are constants.

An important term of these equations is the constant a, which is indicative of the adsorb and/or desorb rate of K^+ . These mathematical models were tested by least square regression analysis to determine which equation best described K^+ adsorb and/or desorb by treatments. Coefficients of determination (R^2) were obtained by least square regression of measured versus predicted values. A relatively high R^2 and low (SE) values for the relationship between measured and predicated K^+ adsorption or desorption data indicate that the model successfully describe the kinetics of K^+

adsorption and desorption by soil, soil+clinoptilolite zeolite and clinoptilolite zeolite. It should be noted that a high R^2 value for a particular kinetic model does not necessarily mean that this model is the best (Sparks, 1989). A model also cannot be used to definitively determine the mechanisms of K^+ adsorption or desorption. Standard errors of the estimate were calculated by:

$$SE = [\sum(K_i - K^*)^2 / (n - 2)]^{1/2} \quad (6)$$

where, K_i and K^* represent the measured and predicted K^+ adsorb and/or desorb, respectively and n is the number of data points evaluated.

RESULTS

Samples Properties

The soil is calcareous with large silt and clay contents (silty clay loam) and zeolite is sandy. The exchangeable form of K and zeolite is also relatively high in the studied samples. The soil was neutral to slightly alkaline and low in EC and organic matter. Like soil, zeolite was alkaline and Low in organic matter but high in EC. Clinoptilolite zeolite increased CEC, EC exchangeable K^+ and decrease organic matter, solution K^+ and specific surface area in soil+zeolite treatment (Table 2). The predominate clays in soil are illite, chlorite, smectite. X-ray diffraction spectrum showed the standard peak for clinoptilolite zeolite was identical with that in the raw sample and that the zeolite was of relatively high purity (over 80%) and clinoptilolite containing bantonit (<20%). More details of mineralogy composition of soil and zeolite are shown in Fig. 1.

The soil sample has adequate K^+ to supply the needs of cereal crops, but inputs of K^+ are required to maintain the availability of K^+ and zeolite containing high exchangeable K^+ (1983.3 $mg\ kg^{-1}$) can help to reach that aim. Levels of exchangeable K^+ reflect (1) the ability of the soil minerals to weather and release K^+ and (2) the management and cropping of the site prior to sampling.

Kinetics of Potassium Adsorption

Potassium adsorption was initially fast (first 48 h, first stage) but continued with low speed (after 48 h) until the end of the experiment (second stage). Potassium adsorption for soil, soil with zeolite and zeolite was 156 to 998, 161 to 1046 and 300.7 to 1399 $mg\ kg^{-1}$, respectively. From the results shown, K^+ adsorption increased rapidly in zeolite. The K adsorption process was virtually complete in 40 and 60 $mg\ KCl\ L^{-1}$ treated zeolite samples within 720 h but in higher concentrations such as 80 $mg\ KCl\ L^{-1}$ adsorption process continued within 1800 h. Amount of K adsorb was over than 70% KCl in initial solution for soil and soil +zeolite and it was 90% for zeolite in first stage. Also the amount of K adsorbed increased as the initial KCl concentration increased in all of samples (soil, soil+zeolite and zeolite). In soil+zeolite treatment K adsorption was more than soil treatment because of zeolite added into soil (Fig. 2).

The results shown zeolite addition to soil increased potassium adsorption in soil+zeolite although ammonium combined with it. In first time (first 12 h) potassium adsorption was fast and after that continued with low speed. Amount of K adsorption was 35% from 60% total K adsorbed for soil and

Table 2: Some chemical and physical properties of soil, zeolite and soil+zeolite

Treatment	Texture	OM* (%)	CEC* (cmolc kg^{-1})	pH	EC* (dS m^{-1})	SSA* ($m^2\ g^{-1}$)	Solution K^+ ($mg\ L^{-1}$)	Extractable K^+ ($mg\ kg^{-1}$)
Soil	Si.C.L	1.880	16.730	7.45	0.753	130	9.358	289.44
Soil+zeolite	Si.C.L	1.810	18.716	7.40	0.792	125	7.210	296.63
zeolite	S	0.043	74.836	7.34	2.810	35	6.976	1983.3

*CEC: Cation Exchange Capacity, SSA: Specific Surface Area, OM: Organic Matter, EC: Electrical Conductivity

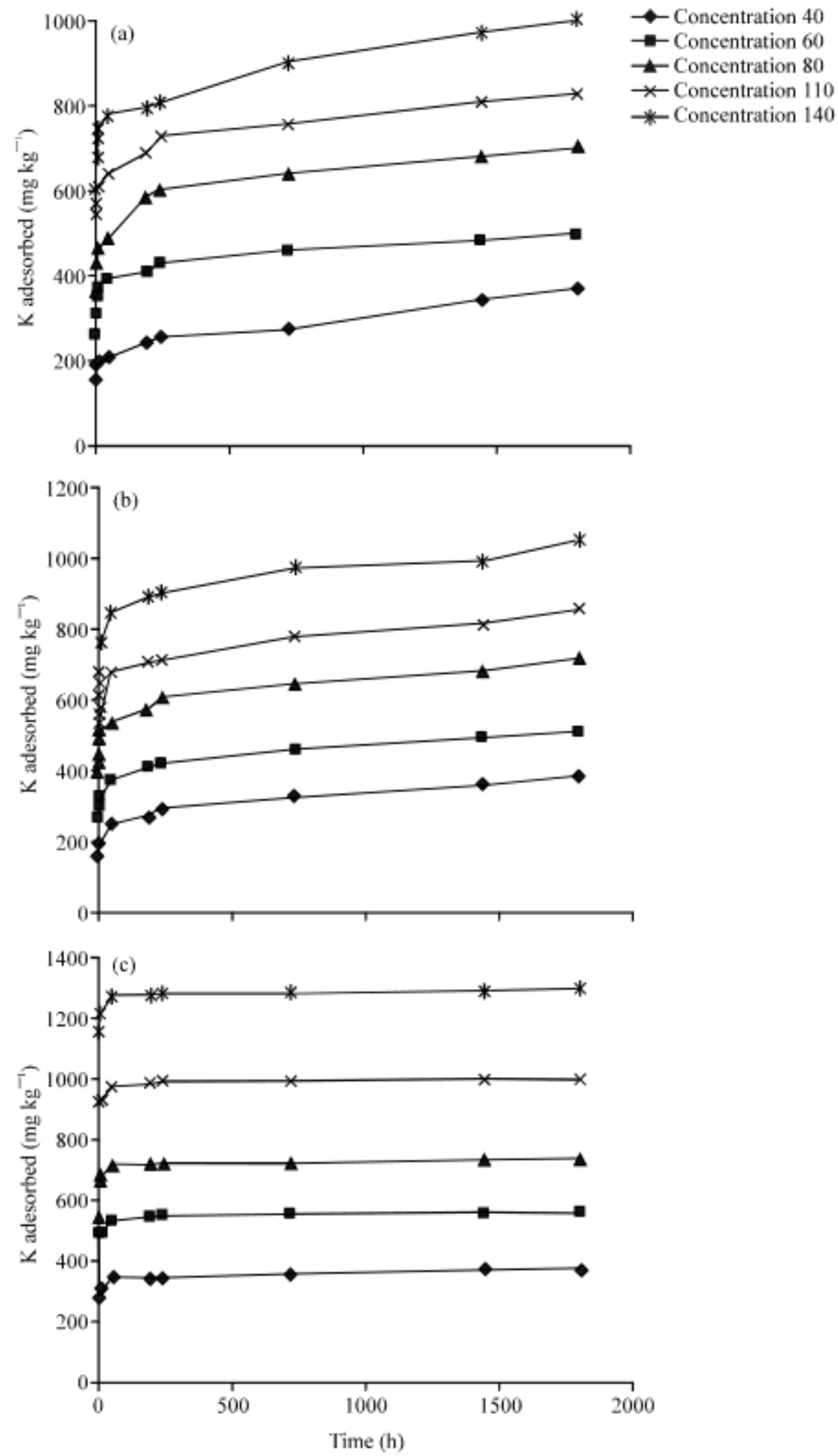


Fig. 2: Potassium adsorbed by (a) soil, (b) soil+zeolite and (c) zeolite with time at KCl treatment

soil+zeolite and it was 80% from 95% total K adsorbed for zeolite in KCl+NH₄Cl treatment. In this treatment (KCl+NH₄Cl treatment) potassium adsorption increased with increased initial KCl concentration in soil, soil with zeolite and zeolite (Fig. 3).

Result indicated K adsorption in KCl treatment (for example K adsorbed with soil, soil+zeolite and zeolite was 631.1, 644.4 and 778.5 mg kg⁻¹, respectively for 80 mg L⁻¹ KCl at 720 h) greater than

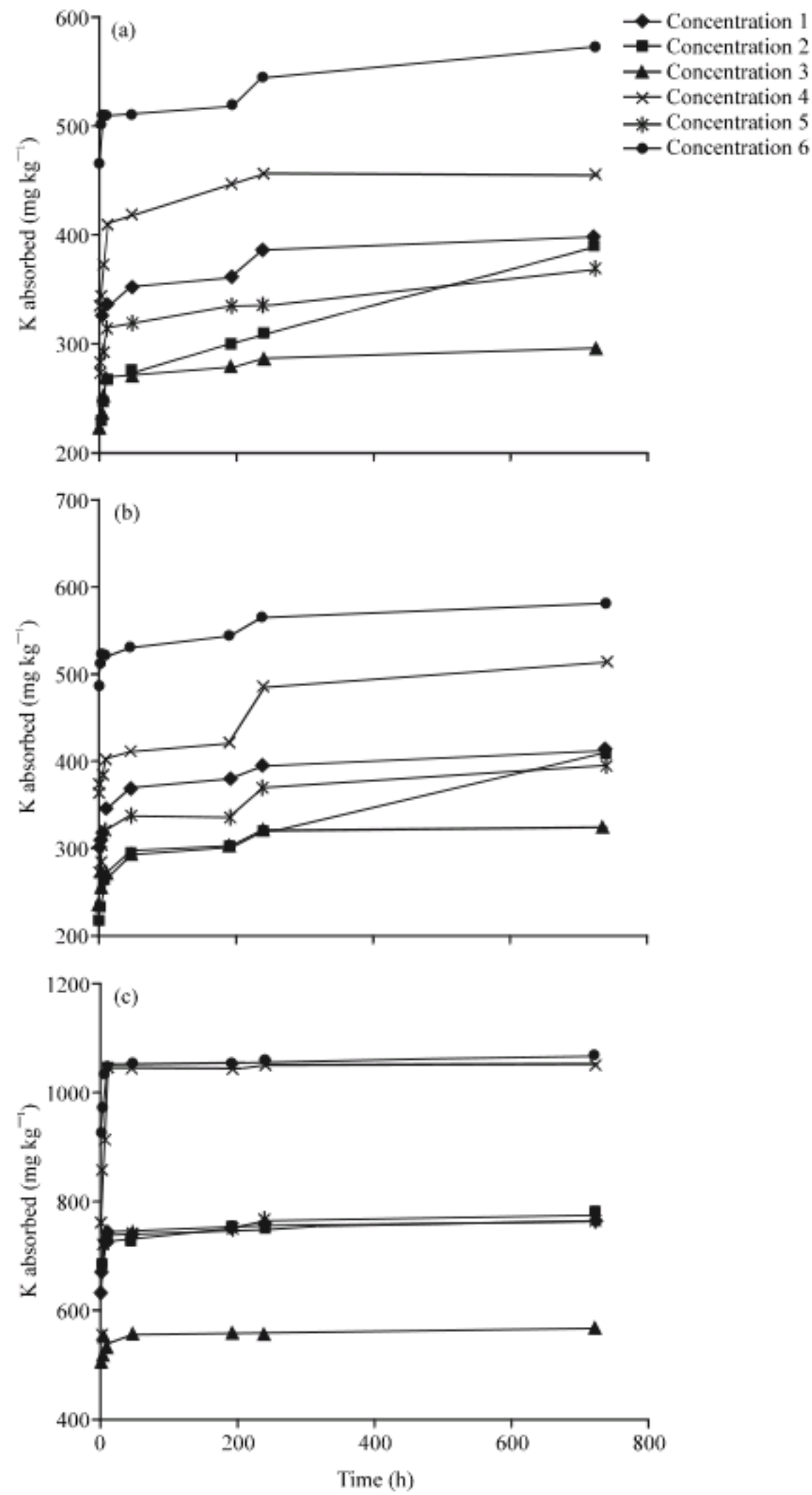


Fig. 3: Potassium adsorbed by (a) soil, (b) soil+zeolite and (c) zeolite with time at KCl+NH₄Cl treatment

K adsorption in KCl+NH₄ treatment (for example, K adsorbed was 398, 388.8 and 369.9 mg kg⁻¹ with soil, 582.2, 411.1 and 407.7 mg kg⁻¹ with soil+zeolite and 764.4, 775.5 and 497.6 mg kg⁻¹ with zeolite for 80 mg L⁻¹ KCl and 60, 90 and 120 mg kg⁻¹ NH₄Cl, respectively).

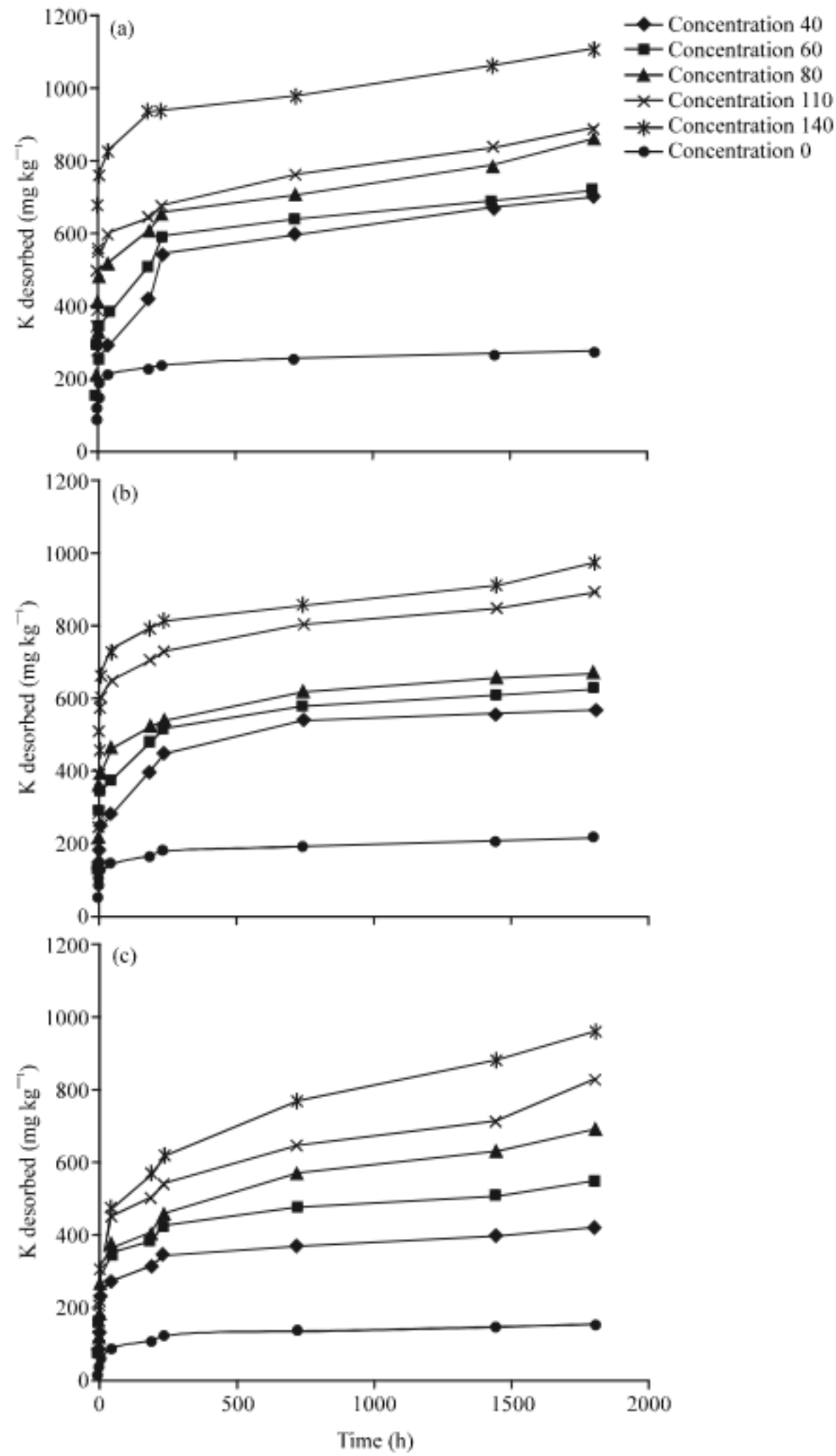


Fig. 4: Cumulative potassium desorbed by (a) soil, (b) soil+zeolite and (c) zeolite with time at KCl treatment

Kinetics of Potassium Desorption

The adsorption was initially rapid followed by a slower reaction. The rapid release continued for 48 h. There was slower, continued desorb of K⁺ after the above time. Potassium desorption for soil, soil with zeolite and zeolite was 85.3 to 1111.4, 46.3 to 970.8 and 14 to 794.8 mg kg⁻¹, respectively for all KCl concentration (0 to 140 mgL⁻¹). The amount of K⁺ desorbed was greatest in the soil (Fig. 4). The natural clinoptilolite zeolite addition to soil decreased K desorption than soil treatment.

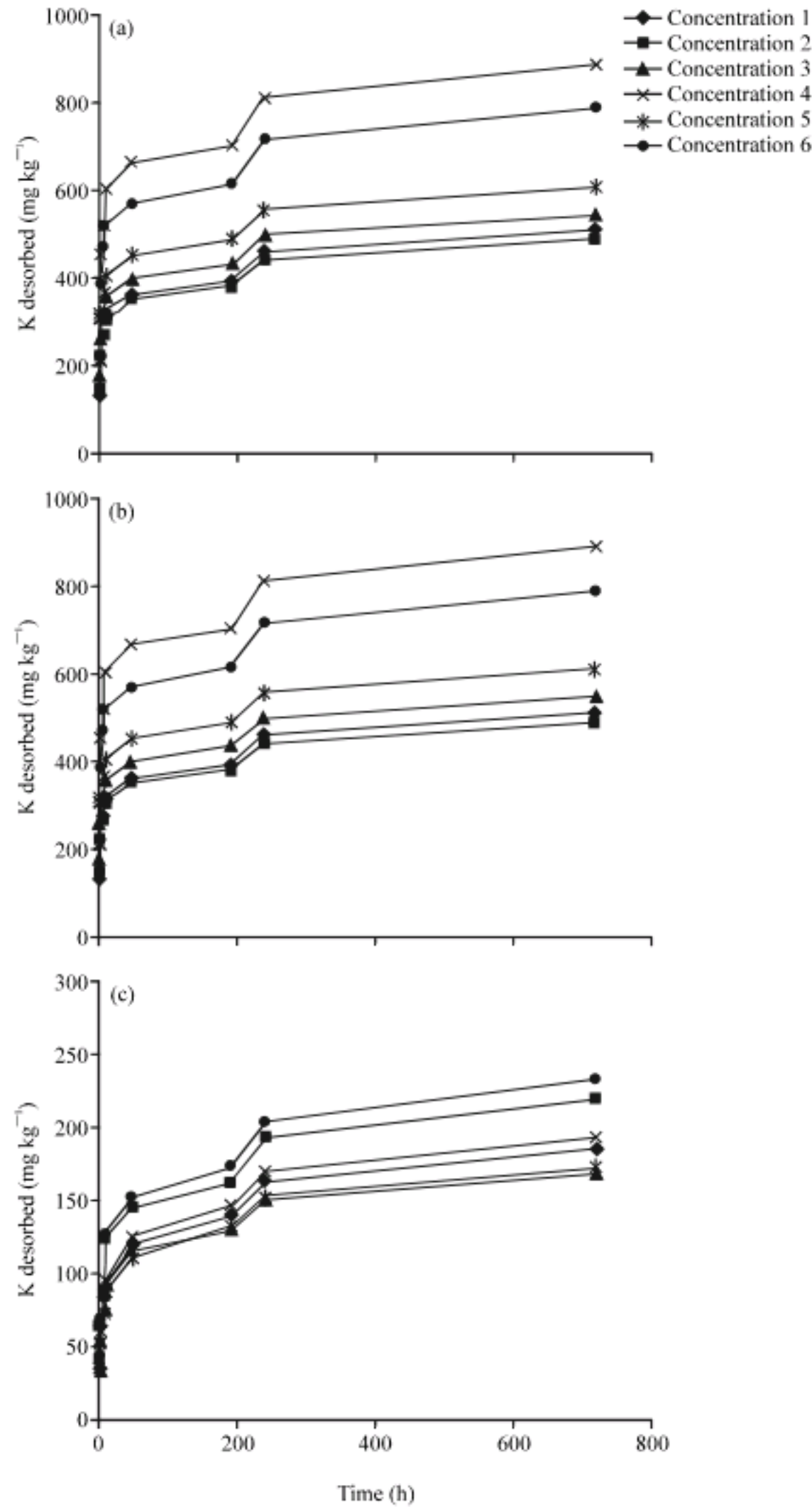


Fig. 5: Cumulative potassium desorbed by (a) soil, (b) soil+zeolite and (c) zeolite with time at KCl+NH₄Cl treatment

The amount of K desorption increased with increasing KCl concentration in initial solution at adsorption process in all treatments. K desorbed amount was 60% total desorption in rapid stage.

Figure 5 shows potassium desorption process at KCl+NH₄Cl concentration treatment in soil, soil+zeolite and zeolite by passing of time. Like KCl treatment the adsorption was initially rapid

followed by a slower reaction. It seems, increasing K initial concentration increased K desorption at KCl+NH₄Cl treatment. The amount of K desorbed with natural clinoptilolite zeolite was less than soil+zeolite and it was less than soil. K desorbed amount was 60% from 90% total K desorption in first stage (first 48 h) for soil and soil+zeolite and it was 15% from 30% total K desorption for zeolite.

Result showed K desorption in KCl treatment (for example K desorbed with soil, soil +zeolite and zeolite was 710.6, 667.6 and 476.1 mg kg⁻¹, respectively for 80 mg L⁻¹ KCl at 720 h) greater than K desorption in KCl+NH₄ treatment (for example, K desorbed was 509.1, 608.6 and 486.2 mg kg⁻¹ with soil, 640.7, 576.5 and 812.9 mg kg⁻¹ with soil+zeolite and 185.5, 218.6 and 172.9 mg kg⁻¹ with zeolite for 80 mg L⁻¹ KCl and 60, 90 and 120 mg kg⁻¹ NH₄Cl, respectively) expect high NH₄Cl concentration in soil+zeolite treatment.

APPLICATION OF DATA TO KINETIC MODELS

Adsorption Process

Different kinetic models were used to describe K⁺ adsorb in soil, soil+zeolite and zeolite. The adsorption data in KCl treatment and all of concentration were found to conform to the Elovich model on soil, soil with zeolite and zeolite, other models were also tested but did not fit the data and therefore are not discussed. The coefficients of determination ranged 0.88-0.98, 0.96-0.99 and 0.61-0.95 for soil, soil+zeolite and zeolite, respectively. In zeolite, Standard Errors (SE) of Elovich model decreased with increasing initial KCl concentration (decreasing trended). Standard Errors (SE) of Elovich model for zeolite less than soil+zeolite and it was for soil+zeolite less than soil. Thus zeolite addition to soil increased slope and intercept of Elovich model at KCl treatment (Table 3).

In KCl+NH₄ treatment Elovich model the best model to describe the K⁺ adsorption in soil and soil+zeolite, also but no model fit the K⁺ adsorption data for zeolite after testing, in all of concentration. The coefficients of determination ranged 0.80-0.93 for soil and 0.85-0.96 for soil+zeolite (Table 4).

Desorption Process

Desorption data plotted according to Elovich kinetic model showed considerable deviation from linearly, with R² values ranging 0.91-0.98 for soil and 0.90-0.98 for soil+zeolite in KCl treatment (Table 5). The Power function, Parabolic diffusion and First order models describe the K desorption with zeolite in KCl treatment and all of concentration (Table 6). Increasing initial KCl concentration increased parameters (slope and intercept) of describing models on soil, soil+zeolite and zeolite

Table 3: Parameters (a, b), coefficient of determination (R²) and standard error of the estimate (SE) of the Elovich model, the best model to describe of K⁺ adsorption kinetics in soil, soil+zeolite and zeolite, at KCl treatment

Treatment	K ⁺ concentration (mg L ⁻¹)	a (mg/kg/h)	b (mg kg ⁻¹)	SE	R ²
Soil	40	26.139	131.82	139.9	0.88
	60	29.064	272.92	347.9	0.94
	80	25.922	342.49	205.5	0.98
	110	42.102	489.40	600.4	0.97
	140	48.156	592.89	253.5	0.92
Soil+zeolite	40	30.165	134.66	156.1	0.96
	60	33.252	243.23	167.5	0.99
	80	44.436	360.60	222.7	0.98
	110	48.774	461.44	244.8	0.98
	140	60.663	572.87	297.9	0.97
Zeolite	40	14.546	296.49	170.6	0.95
	60	13.633	508.40	155.7	0.89
	80	19.643	662.12	141.3	0.61
	110	13.071	982.95	106.6	0.93
	140	18.784	1265.10	86.4	0.86

a: Slope, b: Intercept

Table 4: Parameters (a, b) coefficient of determination (R²) and standard error of the estimate (SE) of the Elovich model, the best model to describe of K⁺ adsorption kinetics in soil and soil+zeolite, at KCl+NH₄Cl treatment

Treatment	Concentration No.	a (mg/kg/h)	b (mg kg ⁻¹)	SE	R ²
Soil	1	12.736	306.85	52.9	0.90
	2	23.051	199.71	103.4	0.86
	3	10.917	225.91	40.4	0.88
	4	22.153	327.77	78.2	0.91
	5	14.398	264.52	58.8	0.93
	6	13.419	470.89	57.7	0.80
Soil+zeolit	1	19.189	286.12	73.1	0.96
	2	26.848	191.06	118.3	0.87
	3	14.335	233.81	52.6	0.96
	4	22.995	337.97	98.7	0.85
	5	18.699	290.95	75.8	0.92
	6	13.970	438.03	56.2	0.92

a: Slop, b: Intercept

Table 5: Parameters (a, b), coefficient of determination (R²) and standard error of the estimate (SE) of the Elovich model, the best model to describe of K⁺ desorption kinetics in soil and soil+zeolit, at KCl treatment

Treatment	K ⁺ concentration (mg L ⁻¹)	a (mg/kg/h)	b (mg kg ⁻¹)	SE	R ²
Soil	0	25.45	91.86	120.6	0.94
	40	22.67	87.25	370.2	0.98
	60	79.02	118.68	392.1	0.97
	80	81.03	211.37	400.9	0.96
	110	76.09	284.09	378.3	0.94
	140	91.52	428.22	432.9	0.91
Soil+zeolit	0	21.52	50.48	103.8	0.96
	40	43.26	70.73	303.8	0.98
	60	68.16	122.49	331.7	0.97
	80	68.86	164.69	333.4	0.95
	110	78.97	299.32	380.2	0.92
	140	81.60	356.54	385.9	0.90

a: Slop, b: Intercept

Table 6: Parameters (a, b), coefficient of determination (R²) and standard error of the estimate (SE) of the Power fraction, Parabolic diffusion and First order models, the best models to describe of K⁺ desorption kinetics in zeolit, at KCl treatment

K ⁺ concentration	Power fraction*				Parabolic diffusion*				First order*			
	a	b	SE	R ²	a	b	SE	R ²	a	b	SE	R ²
0	2.84	6.01	81.3	0.89	0.194	2.95	89.6	0.82	-0.021	20.08	92.00	0.90
40	3.51	12.63	247.2	0.65	0.182	3.28	265.5	0.70	-0.016	29.10	253.7	0.76
60	2.64	20.02	313.5	0.87	0.180	3.22	336.0	0.78	-0.015	32.12	320.8	0.79
80	2.67	21.27	370.4	0.93	0.189	2.61	394.0	0.89	-0.015	36.00	375.2	0.91
110	2.74	22.49	438.2	0.92	0.182	2.57	463.5	0.87	-0.012	37.65	440.6	0.83
140	2.63	24.60	512.6	0.97	0.191	2.45	539.4	0.92	-0.015	39.70	516.9	0.94

a: Slop, b: Intercept. *For Power fraction and First order models, a (mg kg⁻¹) and b (mg/kg/h) and for Parabolic diffusion model a (mg/kg/h^{1/2}) and b (mg kg⁻¹)

(Table 5, 6). Zeolite increased these parameters on corporation with soil. In KCl treatment the trend of slop values of First order and Parabolic diffusion was less than 1 mg/kg/h and mg/kg/h^{1/2}, respectively (Table 6).

The desorption data in KCl+NH₄Cl treatment were found to conform to the Elovich model on soil and soil with zeolit and Power function model described the K desorption data on zeolite in all of concentration. In Table 7 and 8 showed the coefficients of determination (R²), Standard Errors (SE) and parameters (a and b) of Elovich model for soil and soil with zeolit and Power function for zeolite.

At last correlation between addition of KCl concentrations and parameters of the best models to describe K⁺ adsorption and desorption kinetics in soil, soil+zeolite and zeolite, at KCl treatment was investigated (Table 9). Elovich suggests a significant positive correlation between K⁺ concentration and

Table 7: Parameters (a, b), coefficient of determination (R²) and standard error of the estimate (SE) of the Elovich model, the best model to describe of K⁺ desorption kinetics in soil, zeolite and soil+zeolite, at KCl+NH₄Cl treatment

Treatment	Concentration No.	a (mg/kg/h)	b (mg kg ⁻¹)	SE	R ²
Soil	1	56.918	132.95	216.6	0.93
	2	52.478	140.98	199.1	0.95
	3	54.809	183.09	208.2	0.94
	4	88.961	318.21	327.4	0.93
	5	59.319	217.34	225.3	0.94
	6	80.268	256.20	305.8	0.91
Soil+zeolit	1	66.393	201.86	252.8	0.93
	2	62.347	164.12	237.5	0.92
	3	42.879	155.04	163.3	0.93
	4	63.799	281.63	243.2	0.91
	5	70.758	344.24	270.0	0.91
	6	98.306	281.69	374.8	0.93

a: Slop, b: Intercept

Table 8: Parameters (a, b), coefficient of determination (R²) and standard error of the estimate (SE) of the Power function model, the best model to describe of K⁺ desorption kinetics in zeolite, at KCl+NH₄Cl treatment

Concentration No.	a (mg/kg/h)	b (mg kg ⁻¹)	SE	R ²
1	2.536	13.642	111.0	0.91
2	2.610	15.101	134.8	0.88
3	2.409	13.758	102.5	0.89
4	2.626	3.737	116.3	0.90
5	2.502	13.317	103.2	0.91
6	2.561	15.901	143.7	0.90

Table 9: Correlation coefficients (r) between addition of K concentrations and parameters of the best models to describe K adsorption and desorption kinetics in soil, soil+zeolite and zeolite, at various K concentration

Treatment	Model parameter	Soil		Soil+zeolite		Zeolite		Power fraction	
		Elovich		Elovich		Elovich		Power fraction	
		a	b	a	b	a	b	a	b
Adsorption	r	0.920	0.9900	0.980	0.9900	0.38	0.15	-	-
	p	0.025	0.0007	0.002	0.0007	0.52	0.80	-	-
Desorption	r	0.730	0.9800	0.880	0.9900	-	-	-0.63	0.88
	p	0.150	0.0013	0.040	0.0010	-	-	0.24	0.04

Table 10: Correlation coefficients (r) between addition of K+NH₄ concentrations and parameters of the best models to describe K adsorption and desorption kinetics in soil, soil+zeolite and zeolite, at KCl treatment

Treatment	Model parameter	Soil		Soil+zeolite		Zeolite		
		Elovich		Elovich		Power fraction		
		a	b	a	b	a	b	
Adsorption	K	r	0.4020	0.785	0.0990	0.7910	-	-
		p	0.4280	0.064	0.8510	0.0609	-	-
	NH ₄	r	0.9500	-0.371	0.8850	-0.3460	-	-
		p	0.0020	0.467	0.0188	0.5010	-	-
Desorption	K	r	0.9150	0.749	0.7420	0.5730	0.676	-0.026
		p	0.0104	0.086	0.0909	0.2340	0.140	0.96
	NH ₄	r	0.1610	0.271	-0.1590	0.1210	0.216	-0.283
		p	0.7590	0.602	0.7630	0.8180	0.680	0.585

potassium adsorption rate and also intercept with soil and soil incorporated zeolite treatments (p<0.01). Intercept values of Elovich model for desorption had a significant positive correlation with concentrations for the three treatments (p<0.05) but this correlation was not significant by kinetic coefficients for soil and zeolite treatments. Adsorption kinetic coefficients for zeolite were not correlated with concentrations.

Also, correlation between addition of KCl and NH₄Cl concentrations and parameters of the best models to describe K adsorption and desorption kinetics in soil, soil+zeolite and zeolite, at KCl+NH₄ treatment was investigated (Table 10).

The results of this study showed that weak correlation between potassium and ammonium concentration and potassium adsorption and desorption coefficient rate of models in all of treatments. But we can see a significant positive correlation with NH₄⁺ concentrations and slope (rate) of Elovich model ($p < 0.05$) for soil and soil+zeolite treatments.

DISCUSSION

Potassium Adsorption

With KCl and KCl+NH₄ treatment, initial K⁺ and NH₄⁺ concentration affected the amount of K adsorbed by the soil, soil+zeolite and zeolite. Similar observations were made by Kithome *et al.* (1998) on studied of NH₄⁺, which behaves similar to K. The natural clinoptilolite zeolite increased the amount of K⁺ adsorbed (about 20 to 60 mg kg⁻¹ increase for low and high concentration) on soil+zeolite in KCl treatment. The reason of the result was likely related to the specifically adsorptive properties of the employed zeolite.

For most cases of this study, the adsorption of potassium on the natural zeolite approached equilibrium over 720 h in the experimental condition. The higher adsorption kinetics for potassium by various KCl and KCl+NH₄Cl concentration in zeolite is of significant importance to apply fertilizer and zeolite for supply potassium and other nutrients. With zeolite K⁺ adsorption completed at greater than 720 h but these findings are in disagreement with those Kithome *et al.* (1998) and Guo *et al.* (2008), who observed that sorption of NH₄⁺ and K⁺ by natural zeolite was essentially complete after shaking for greater 1 to 2 h. Despite the rapid reactivity observed in zeolite, equilibrium had not been attained even after 720 or 1440 h in soil and soil+zeolite. Similar observations were made by Wilson *et al.* (2004).

With soil treatments with a low CEC, the NH₄⁺ presence decreased K⁺ adsorption. With zeolite treatment, presence and concentration of ammonium did not affect potassium adsorption (especially 60 and 90 mg L⁻¹ NH₄Cl) against soil and soil+zeolite. These results and the high K⁺ adsorption and low desorption with zeolite indicated that the natural zeolite had a high affinity for potassium. The K adsorption rate followed the molar ratio of ammonium/potassium. In Golestan soils especially Pardis with loess soil with prevailing illite clay, anion adsorption an high specific surface area suggesting a truncated diffuse double layer containing a high salt concentration, soil solution monovalent K⁺ adsorption exceeds possibly divalent Ca, decreasing equilibrium solution potassium intensity, increasing K⁺ adsorption and decreasing labile K⁺.

According to the results the Elovich model was the best model to describe adsorption data for potassium, for soil, zeolite (just KCl treatment) and zeolite amended soil. A good fit with Elovich, suggests diffusion as the principle mechanism at least for the later stages of kinetic adsorption of the studied elements. The good fit of this model for empirical prediction. As noted by Parravano and Boudant (1955), the Elovich model may describe a number of different processes, including bulk and surface diffusion, as well as activation and inactivation of catalytic surfaces. However, prediction is still marginal at very low and very high surface coverages (Kithom *et al.*, 1998). Some investigators have used Elovich parameters to estimate reaction rates. Chien and Clayton (1980) suggested that a (a) an increase or (b) decrease in should enhance the reaction rate. This may be questionable because the slope of this model changes with the level of added ion in all of treatment and adding zeolite into soil, as was observed in this study and with the solution/adsorbent ratio (Sharply, 1983). Consequently, these slopes and intercepts are not always characteristic of the adsorbents but depend on various experimental conditions (Sparks, 1986).

Potassium Desorption

The changes in the amount of K^+ desorption in the loess soil with prevailing illite clay and soil+zeolite with desorb (after adsorption) time in different treatments and solution at $25\pm 2^\circ C$ indicating that the K^+ desorption in different K^+ and $KCl+NH_4Cl$ solutions during the initial period (2-48 h) was faster than that in the latter period of over 48 h. Zhou and Huang (2007) found the same result like these results. The K^+ desorption from the illite of soil and zeolite apparently did not proceed through a single reaction rate process during the reaction period (0-720 or 0-1800 h); the exchange reaction appeared to greatly contribute to K^+ desorption in the period of 0-48 h in all of treatment (especially zeolite).

With KCl and $KCl+NH_4Cl$ treatment, initial K^+ and NH_4^+ concentration affected the amount of K^+ desorbed by the soil, soil+zeolite and zeolite. Similar observations were made by Kithome *et al.* (1998) on studied of NH_4^+ , which behaves similar to K . this biphasic is characteristic of a diffusion control process and has previously been observed for K^+ (Feigenbaum *et al.*, 1981; Martin and Sparks, 1983) and other similar ion, like NH_4^+ (Steffens and Sparks, 1997).

Zhou and Huang (2007) showed that the reactions of K^+ release from the illite in $Ca(H_2PO_4)_2$ and $NH_4H_2PO_4$ systems had a similar activation energy, indicating that these two systems had a similar mechanism for the K^+ release and the cation and pH also affected the rate of K^+ release. Therefore, the variation in the rates of K desorption in different treatments (KCl and $KCl+NH_4Cl$) indicates that the cations (NH_4^+ and K^+) affected the rate of K desorption. Comparing K^+ desorbed from the KCl and $KCl+NH_4Cl$ treatments indicated K^+ desorption from soil was more than K adsorption in $KCl+NH_4Cl$ treatment against K^+ desorbed in KCl treatment. These result suggesting no potassium preferential adsorption due to clay edge or inner positioning with bath experiment or K may be located in a truncated diffuse double layer soil.

With $K^++NH_4^+$ solution, K^+/NH_4^+ desorption rate did not follow exactly K^+/NH_4^+ adsorption ratio for all treatments. Ammonium presence decreased K desorption with zeolite treatment but did not affect K adsorption.

Lower values of K^+ desorption amount could be due to exchange of K^+ by Ca^{2+} on surface site of clay structure in the $Ca^{2+}-K^+$ system (KCl treatment). Once K^+ is exchanged on these sites, further exchange of K^+ by Ca^{2+} would be slower, as the size of hydrate Ca^{2+} ($4.3A^\circ$) is larger than hydrate K^+ ($3.3A^\circ$) (Rao *et al.*, 1999). But at the $NH_4^+-K^+-Ca^{2+}$ system ($KCl+NH_4Cl$ treatment), the size of hydrate NH_4^+ ($2.9A^\circ$) is close hydrate K^+ . Martin and Sparks (1983) indicated that wedge zones would selectivity screen out the Ca^{2+} ion because of its larger size.

According to results the Elovich model was the best model to describe desorption data for potassium, for soil and zeolite amended soil in two treatments. Successful presentation of the Elovich equation for non-exchangeable K^+ release from soils has been reported by Mengel and Uhlenbecker (1993) and Jalali (2006, 2007). Aharoni and Sparks (1991) and Aharoni *et al.* (1991) have noted that a conformity of experimental data to Elovich equation indicated by a relatively high R^2 value during an entire experiment could suggest a heterogeneous diffusion process. The slopes of the Elovich model for the adsorption and desorption processes for all KCl and $KCl+NH_4Cl$ suggesting heterogeneous diffusion (Aharoni and Sparks, 1991; Kithome *et al.*, 1998).

Since both power function and parabolic diffusion models describe the rate process and then the latter may also represent slow diffusion of K^+ from mica interlayer positions (Havlin *et al.*, 1985). The Power function described slow diffusion desorption of K^+ by the natural clinoptilolite zeolite on KCl and $KCl+NH_4Cl$ treatments. Conformity to the Parabolic diffusion model suggested that the process of K desorption by the natural zeolite in KCl treatment was diffusion controlled and either intraparticle diffusion or surface diffusion may be rate limiting (Crank, 1976; Kithom *et al.*, 1998). The former diffusional process is a transport of the desorbing ion through the liquid associated with less accessible exchange sites of the adsorbing or desorbing ion along the walls of the less accessible space of the

adsorbent or desorbent. When particle resistance determines the adsorption or desorption velocity. Surface diffusion is generally the rate-controlling mechanism (Jardin and Sparks, 1984) intraparticle surfaces in the natural zeolite clinoptilolite arise from intracrystal spaces within the mineral assemblage and from the network of channels and cage within the crystal structure. Even though zeolites are tectosilicates, the exchange of one counter ion for another of different size could affect the ease of motion for adsorbing or desorbing ions and in so doing lead to variation of the diffusion coefficients as we observed in this study (Table 6).

Also, the cumulative K^+ was fitted to the first order model in zeolite at KCl treatment. Successful description of K^+ release by the first order model was previously reported by Dhillon and Dhillon (1990). This was expected since several mass action rate processes may have been occurring independently the possibility of multiple First order reactions corresponding multiple independent retention sites in the zeolite mineral, similar to the multiple reactions suggested by Kithom *et al.* (1998) and Jardin and Sparks (1984) was not justified by the data.

A positive and significant correlation between K^+ adsorption and desorption parameters of the Elovich model and the potassium concentration ($p < 0.05$) with soil and soil incorporated zeolite treatments and non correlation for zeolite (in KCl treatment) indicated potassium adsorption and release by batch method did not simulate potassium uptake by wheat. With low solution concentrations, zeolite mixed with soil increased intercept with the Elovich linear model for potassium desorption that result maybe indicated zeolite supply K among wheat growth. The results of this study shown weak correlation between potassium and ammonium concentration and potassium adsorption and desorption coefficient rate of models in KCl+ NH_4Cl treatment because K^+/NH_4 was important factor in adsorption. There wasn't correlation between adsorption and desorption because cation exchange capacity of porous material is important in addition to rate of adsorption.

No earlier reports on the rate constants for potassium adsorption or desorption by natural zeolite, soil and their incorporation were found (especially in Iran), hence, comparisons with a similar study was not possible.

CONCLUSION

In Iran, as irrigated crop production systems intensify, utilization of these K^+ reserves will increase. Increasing of K^+ concentration increased rate of adsorption and desorption in soil, zeolite and their incorporation and zeolite increased adsorption and decreased desorption rate by incorporation with soil. Ammonium presence decreased potassium adsorption and it increased potassium desorption.

A good fit with Elovich, suggests diffusion as the principle mechanism at least for the later stages of kinetic adsorption and desorption of the studied elements (soil, soil+zeolite and zeolite). The Power function, Parabolic diffusion and First order models suggested that the process of K desorption by the natural zeolite was controlled as slow diffusion, diffusion and mass action, respectively. Intercept increased with zeolite incorporation which might suggest increased potassium availability in soils with limited diffusion to the bulk solution due to a truncated double layer.

Anyway, although the rate constant (a) and intercept (b) for potassium expressed differently between two treatments, one fact should be notified that desorb rates of potassium on KCl treatment less than KCl+ NH_4Cl treatment occurred on soil and soil+zeolite.

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