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Kinetics of Potassium Desorption from the Loess Soil, Soil Mixed with Zeolite and the Clinoptilolite Zeolite as Influenced by Calcium and Ammonium

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Abstract: The rate of K^+ release from soils can significantly influence K^+ fertility of soils. The objectives of this study were investigated the effect of different calcium concentrations (0, 0.028, 0.057, 0.085, 0.128 and 0.171 $mg L^{-1}$) and different ammonium concentrations (0, 40, 60, 90, 120 and 140 $mg L^{-1}$) on potassium isothermal desorption kinetics of diluted suspensions of a soil, the Iranian natural clinoptilolite zeolite and their incorporation (within 2 and 1800 h), application of some kinetic models and correlation between potassium desorption kinetic coefficients of the best models with the calcium concentration. Potassium desorption was initially fast (first 192 h) with Ca^{2+} and NH_4^+ addition and continued during next stage (192-1800 h) with low speed until the end of the experiment. Also, increasing the Ca^{2+} and NH_4^+ solution concentration increased the potassium desorption in all of treatments. The potassium released from NH_4^+ treatments was more than Ca^{2+} treatment in equal equivalent of Ca^{2+} and NH_4^+ . Zeolite decreased K^+ desorption rate by incorporation with soil. The kinetic equations used to estimate data were zero order, first order, simple Elovich, parabolic diffusion and power function. The Elovich model described the desorption processes on soil and soil+zeolite and zeolite in NH_4^+ treatment ($0.628 < r^2 < 0.990$). Elovich, first order, zero order and power function models described desorption processes, respectively for zeolite well ($0.87 < r^2 < 0.97$). The models indicated that K^+ desorption was diffusion controlled. Result shows that zeolite release K^+ slowly.

Key words: Clinoptilolite zeolite, illitic loess soil, potassium desorption, ammonium, calcium

INTRODUCTION

Potassium is one of the most important plant nutrients in soils and has thus been studied extensively. 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. It is believed that the soils of arid and semiarid regions contain sufficient exchange K^+ (exchange with NH_4^+ acetate) and K^+ -bearing minerals able to release enough K^+ to meet crop requirements.

Adsorption and desorption are most important chemical processes in soils and soil constituents. Desorption kinetics of K^+ have been determined by using different extraction methods. In calcareous soils, Ca^{2+} is the most common cation replacing interlayer K^+ . The K^+ in the interlayer of illite can be exchanged by hydrated cations such as Ca^{2+} and NH_4^+ (Zhau and Huang, 2007; Scott, 1968). In addition, the presence of NH_4^+ cation of fertilizer (Mustscher, 1995) and Ca^{2+} in irrigation water and of soil minerals able to release K^+ .

Natural clinoptilolite zeolite has a three-dimensional crystal structure and its typical unit cell formula (Tehrani and Salari, 2005; Rezaei and Movahedi Naeini, 2009). 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. 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; Rezaei and Movahedi Naeini, 2009). 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^+ desorption on clinoptilolite (Cooney *et al.*, 1999; Weatherley and Miladinovic, 2004). Their selectivity of ionexchange on clinoptilolite was determined in an order of $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$ (Guo *et al.*, 2008). 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 desorption behaviors of K^+ on natural zeolite and incorporation with loess soil.

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) (Rezaei and Movahedi Naeini, 2008, 2009). 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.

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 work was not possible. However, the comprehensive comparison and screening of kinetic models for effects of NH_4^+ and Ca^{2+} concentration on K^+ desorption on loess soils, clinoptilolite zeolite and the consequent alterations with zeolite additions in Golestan Province loess soils were not documented yet. This study has the following objectives:

- To investigate the K^+ desorption kinetics with NH_4^+ and Ca^{2+} on zeolite and loess soil with prevailing illite clay
- To determine the effects of zeolite on desorption kinetics of K^+ on the incorporation of loess soil
- To apply five kinetic models on K^+ desorption

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 almost over 80% clinoptilolite and the remainder consisted of bantonite (Rezaei and Movahedi Naeini, 2009).

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).

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 (3.571 g) zeolite per (1000 g) soil ($20\ t\ ha^{-1}$) zeolite into soil to obtaining our aims. Samples (soil, zeolite and soil+zeolite) pH and EC were determined using 1:2 soil to water suspension with a glass electrode (Rhodes, 1996) and particle size was determined

by the hydrometer method (Klute, 1986). Organic matter was determined by dichromate oxidation (Walkley and Black, 1934). Cation Exchange Capacity (CEC) of the samples were determined by the (1 Molar 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 NH_4 OAC) 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 K saturation and heat was determined by X-ray diffraction analysis and using a Bruker D8 X-ray diffractometer using Cu-K α 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 NH_4^+ and Ca^{2+} 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 desorption: Desorption of K^+ tests conducted during February 2007 to September 2008 with batch method (Selim and Archer, 1997; Wilson *et al.*, 2004; Rezaei and Movahedi Naeini, 2009) by NH_4^+ and Ca^{2+} solutions in Gorgan University of Agricultural Sciences and Natural Resources soil laboratory. Kinetics of K^+ desorption was studied by successive extraction (Sparks and Libhardt, 1981; Lopez-Pineiro and Navarro, 1997; Jalali, 2007; Rezaei and Movahedi Naeini, 2008, 2009). We weighed 1.0 g of soil, soil+zeolite 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 NH_4^+ concentrations (40, 60, 90, 120 and 140 $mg\ L^{-1}$) from ammonium chloride for NH_4^+ treatments and Ca^{2+} (0.028, 0.057, 0.085, 0.128 and 0.171 $mg\ L^{-1}$) from calcium nitrate for Ca^{2+} treatments. We used 10 times (2, 4, 8, 12, 48, 192, 240, 720, 1440 and 1800 h) for two 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 and Schuffelen, 1963) and room temperature ($25\pm 2^\circ C$) (Jalali, 2006). At the end of the adsorption times (each time) tubes centrifuged at 3000 x g for 10 min (Kithome *et al.*, 1998). The quantity of K^+ release by soil, soil+zeolite and zeolite was calculated in the extracted solution.

Kinetic models: Different kinetic models described in Eq. 1-5, were used to describe K⁺ adsorption and desorption by the natural clinoptilolite zeolite, soil and soil+zeolite clinoptilolite.

First order model $\ln (K_0 - K_t) = b - at$ (1)

Zero order model $(K_0 - K_t) = b - at$ (2)

Elovich model $K_t = b + a \ln t$ (3)

Parabolic diffusion model $K_t / K_0 = b + at^{1/2}$ (4)

Power fraction model $\ln K_t = b + a \ln t$ (5)

where, K_t is the amount of cumulative K⁺ desorbed or adsorbed at time t, t the time of adsorb or desorb, K₀ is the maximum K⁺ adsorbed or desorbed (final equilibrium), 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 (r²) were obtained by least square regression of measured versus predicted values. A relatively high r² and low (SE) values for the relationship between measured and predicted 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 r² 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:

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

where, K_t 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 was calcareous with large silt and clay contents (silty clay loam) and zeolite was

sandy. The exchangeable form of K and zeolite was 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 1). The predominate clays in soil were 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 (less than 20%).

The soil sample had 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⁺, (2) the management and cropping of the site prior to sampling (Rezaei and Movahedi Naeini, 2009).

Kinetics of potassium desorption: Potassium desorption was initially fast (first 192 h, first stage) but continued with low speed (after 192 h) until the end of the experiment (second stage). Potassium desorption for soil, soil with zeolite and zeolite was 85.3 to 1496.9, 46.3 to 1380.6 and 14 to 559.9 mg kg⁻¹, respectively for all NH₄⁺ concentration (0 to 140 mg L⁻¹). The amount of K⁺ desorbed was greatest in the soil (Fig. 1a-c). The natural clinoptilolite zeolite addition to soil decreased K desorption than soil treatment. The amount of K desorption increased with increasing NH₄⁺ concentration in initial solution in all treatments. K desorbed amount was over than 60% total desorption in rapid stag.

Figure 2a-c show potassium desorption process at Ca²⁺ concentration treatment in soil, soil+zeolite and zeolite by passing of time. Like NH₄⁺ treatment the desorption was initially rapid followed by a slower reaction. Potassium desorption for soil, soil with zeolite and zeolite was 85.3 to 978.0, 46.3 to 889.0 and 14 to 432.21 mg kg⁻¹, respectively for all Ca²⁺ concentration (0 to 0.171 mg L⁻¹).

It seems, increasing Ca²⁺ initial concentration increased K desorption at Ca²⁺ 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 total K desorption in first stag (first 192 h)

Table 1: Some chemical and physical properties of soil, zeolite and soil+zeolite

Treatments	Textures	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

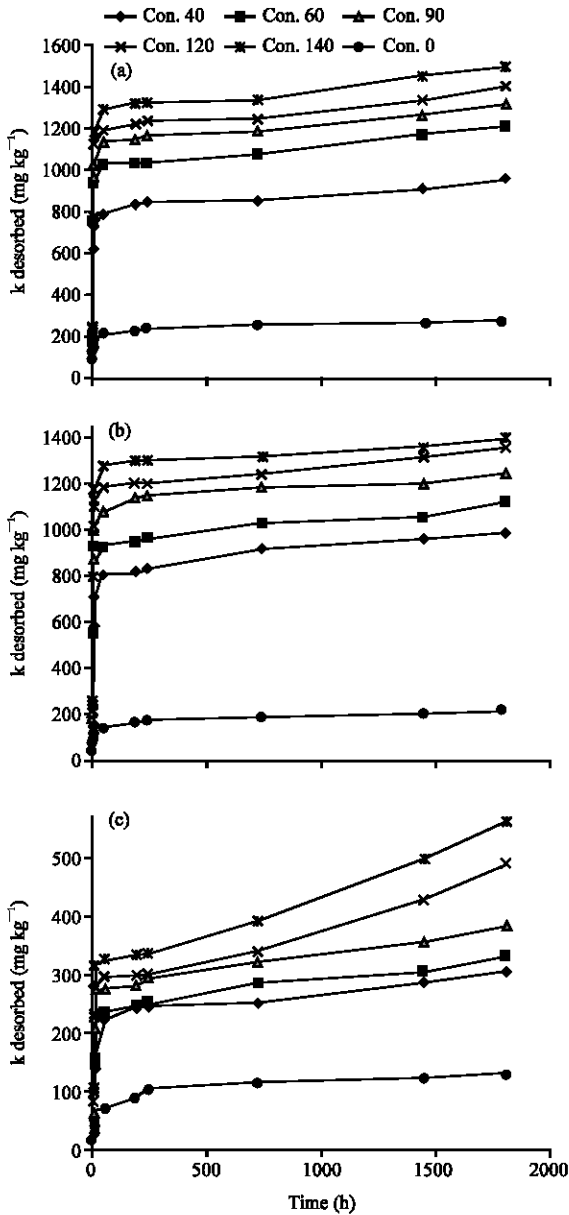


Fig. 1: Cumulative potassium desorbed by (a) soil, (b) soil+zeolite and (c) zeolite with time at NH_4^+ treatment

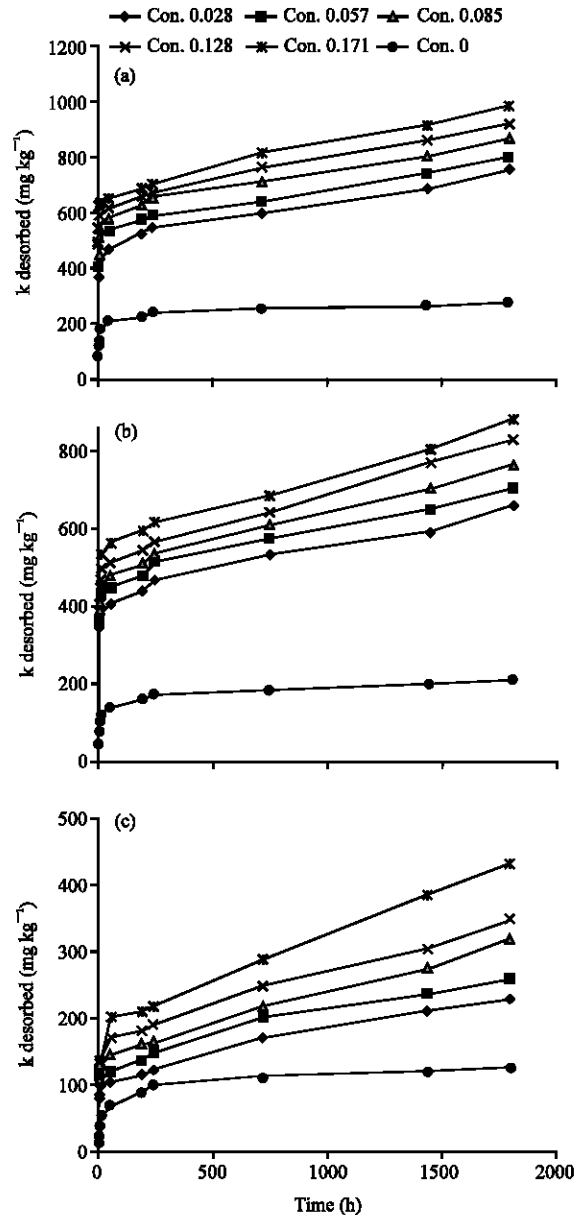


Fig. 2: Cumulative potassium desorbed by (a) soil, (b) soil+zeolite and (c) zeolite with time at Ca^{2+} treatment

for soil and soil+zeolite and it was 50% from total K desorption for zeolite. Result showed K desorption in Ca^{2+} treatment for zeolite was very low. In similar equivalent concentrations of NH_4^+ and Ca^{2+} , K^+ desorption in NH_4^+ treatment greater than Ca^{2+} in zeolite treatment.

The changes in the amount of K^+ desorption in the loess soil with prevailing illite clay and soil+zeolite with desorb time in different treatments and solution at $25 \pm 2^\circ\text{C}$ indicating that the K^+ desorption in different Ca^{2+}

and NH_4^+ solutions during the initial period (2-192 h) was faster than that in the latter period of over 192 h. Zhou and Huang (2007) founded the same result like these result. The K^+ desorption from the illite of soil and zeolite apparently did not proceed through a single reaction rate process during the reaction period (0-1800 h); the exchange reaction appeared to greatly contribute to K^+ desorption in the period of 0-192 h in all of treatment (especially zeolite).

With Ca^{2+} and NH_4^+ 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 Rezaei and Movahedi Naeini (2009) on studied of K^+ adsorption and desorption. this biphasic is characteristic of a diffusion control process and has previously been observed for K^+ (Martin and Sparks, 1983) and other similar ion, lik NH_4^+ (Steffens and Sparks, 1997).

Zhou and Huang (2007) showed that the reactions of K^+ release from the illite in $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ 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 (Ca^{2+} and NH_4^+) indicates that the cations (NH_4^+ and Ca^{2+}) affected the rate of K desorption. Comparing K^+ desorbed from the Ca^{2+} and NH_4 treatments indicated K^+ desorption from NH_4^+ treatment was more than K desorption in Ca^{2+} treatment. Rezaie and Movahedi Naeini (2009) suggested 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.

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 (Ca^{2+} 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°) is larger than hydrate K^+ (3.3A°) (Rao *et al.*, 1999). But at the NH_4^+ - K^+ - Ca^{2+} system (NH_4 treatment), the size of hydrate NH_4^+ (2.9A°) 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.

For most cases of this study, the desorption of potassium on all treatments didn't finish to 1800 h in the experimental condition. In stage 2 of Ca^{2+} treatment the slop of K^+ release mort than NH_4^+ treatment. In zeolite in second stage the rate of K^+ desorption was more than initial stage. This result shows that zeolite release K^+ slowly. The higher desorption kinetics for potassium by various NH_4^+ in zeolite is of significant importance to apply fertilizer and zeolite for supplay potassium and other nutrients.

Application of data to kinetic models

Desorption process: Different kinetic models were used to describe K^+ desorped in soil, soil+zeolite and zeolite. The desorption data in NH_4^+ 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. Table 2 shows the coefficients of determination (r^2), Standard Errors (SE) and parameters (a and b) of Elovich model for soil, soil with zeolite and zeolite. The coefficients of determination ranged 0.640-0.768, 0.649-0.801 and 0.809-0.949 for soil, soil+zeolite and zeolite, respectively. In all of treatments, Standard Errors (SE) of Elovich model increased with increasing initial NH_4^+ concentration (increasing trended).

In Ca^{2+} treatment the Elovich, zero order and power function models describe the K desorption with soil and soil+zeolite (Table 3). The Power function, zero order and first order models describe the K desorption with zeolite in Ca^{2+} treatment and all of concentration. Table 4 shows parameters of those models. Increasing initial Ca^{2+} and NH_4^+ concentration increased parameters (slop and intercept) of describing models on soil, soil+zeolite and zeolite (Table 3, 4). Zeolite decreased these parameters on

Table 2: Parameters coefficient of determination (r^2) and standard error of the estimate (SE) of the Elovich model, the best model to describe of K^+ desorption kinetics in soil, soil+zeolite and zeolite, at NH_4^+ treatment

Treatments	NH_4^+ concentration (mg L ⁻¹)	a (mg/kg/h)	b (mg kg ⁻¹)	SE	r^2
Soil	0	25.45	91.86	120.6	0.940
	40	101.78	249.34	469.0	0.740
	60	129.64	306.67	603.4	0.745
	90	135.17	386.91	628.9	0.690
	120	136.16	454.95	639.8	0.640
	140	165.81	360.62	762.9	0.768
Soil+zeolite	0	21.52	50.48	103.8	0.960
	40	109.09	277.91	494.8	0.801
	60	121.02	309.35	585.4	0.751
	90	125.99	393.05	605.4	0.649
	120	131.87	462.07	629.1	0.628
	140	150.89	384.63	824.6	0.724
Zeolite	0	16.60	4.74	876.9	0.990
	40	36.00	39.09	494.8	0.912
	60	38.16	41.38	585.4	0.949
	90	39.94	79.33	605.4	0.809
	120	47.69	76.17	629.1	0.852
	140	55.77	79.10	824.6	0.867

a: Slop, b: Intercept

Table 3: Parameters coefficient of determination (r^2) and standard error of the estimate (SE) of the power fraction, Elovich and zero order models, the best models to describe of K^+ desorption kinetics in soil and soil+zeolite, at Ca^{2+} treatment

Ca^{2+} concentration	Power fraction				Elovich				Zero order			
	a*	b*	SE	r^2	a*	b*	SE	r^2	a*	b*	SE	r^2
0	1.453	23.17	204.5	0.86	25.45	91.86	120.6	0.940	-0.057	74.38	197.8	0.10
0.028	0.946	35.17	552.8	0.96	49.16	308.24	259.8	0.920	-0.182	314.63	410.5	0.87
0.057	0.808	36.84	614.4	0.90	46.28	376.62	244.9	0.880	-0.173	299.36	464.5	0.85
Soil												
0.085	0.807	37.70	668.0	0.94	50.73	48.35	269.6	0.910	-0.189	323.77	507.9	0.87
0.128	0.787	38.39	710.6	0.94	52.81	37.79	285.0	0.900	-0.200	336.48	544.8	0.90
0.171	0.807	38.89	757.3	0.91	57.20	459.71	309.8	0.880	-0.218	371.77	571.2	0.88
0	1.785	18.05	14.3	0.86	21.52	50.48	103.8	0.960	-0.065	99.86	126.3	0.60
0.028	0.806	34.67	486.9	0.90	38.29	298.52	232.5	0.850	-0.152	269.36	368.0	0.94
Soil+zeolite												
0.057	0.859	35.19	528.4	0.94	43.47	312.79	235.3	0.890	-0.166	282.05	400.8	0.91
0.085	0.919	35.48	562.2	0.93	49.3	317.43	268.3	0.890	-0.190	325.20	419.2	0.92
0.128	0.907	26.27	621.3	0.91	52.77	343.47	290.2	0.850	-0.209	359.03	449.2	0.93
0.171	0.885	37.10	656.2	0.93	54.82	376.82	295.8	0.870	-0.212	373.27	477.5	0.91

a: Slop, b: Intercept. *a: $mg\ kg^{-1}$, *b: $mg/kg/h$

Table 4: Parameters coefficient of determination (r^2) and standard error of the estimate (SE) of the zero order, power function and first order the best models to describe of K^+ desorption kinetics in zeolite, at Ca^{2+} treatment

Ca^{2+} concentration	Power fraction				Zero order				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	-0.050	74.23	79.7	0.63	-0.021	20.08	92.0	0.90
0.028	2.72	11.47	138.8	0.98	-0.089	146.50	122.3	0.96	-0.015	27.33	141.9	0.98
0.057	1.32	21.07	155.9	0.99	-0.086	143.24	132.6	0.95	-0.014	27.20	164.0	0.99
0.085	1.46	21.70	183.2	0.98	-0.109	192.68	157.4	0.96	-0.011	29.93	188.2	0.98
0.128	1.63	21.79	205.4	0.98	-0.230	211.75	178.4	0.92	-0.011	30.87	209.4	0.97
0.171	1.84	22.20	250.3	0.98	-0.164	280.59	232.6	0.93	-0.012	33.84	253.2	0.97

a: Slop, b: Intercept. *For power fraction zero order and first order models. *a: $mg\ kg^{-1}$, *b: $mg/kg/h$

corporation with soil. In Ca^{2+} treatment the trend of slop values of zero order and first order was less than 1 $mg/kg/h$ (Table 4).

DISCUSSION

According to results the Elovich model was the best model to describe desorption data for potassium, for soil and zeolite amended soil and zeolite in Ca^{2+} and NH_4^+ treatments. Successful presentation of the Elovich equation for non-exchangeable K^+ release from soils has been reported by Jalali (2006, 2007). Aharoni *et al.* (1991) and Aharoni and Sparks (1991) have noted that a conformity of experimental data to Elovich equation indicated by a relatively high r^2 value during an entire excrement could suggest a heterogeneous diffusion process. The slops of the Elovich model for the desorption processes for all Ca^{2+} and NH_4^+ suggesting heterogeneous diffusion (Aharoni and Sparks, 1991; Kithome *et al.*, 1998; Rezai and Movahedi Naeini, 2009).

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 Ca^{2+} and NH_4^+ treatments.

The cumulative K^+ desorption was fitted to the first order model in zeolite at Ca^{2+} 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. Since, the zero-order and first-order rate equations were virtually the same in fitting the data of K release. The zero-order rate equation described the data quite well as shown by the SE and r^2 values. The results indicate that the K release, which was induced by Ca^{2+} , apparently followed the same rate process in the reaction period of 2-1800 h.

The results shown a significant positive correlation between ammonium concentration and potassium desorption coefficient rate of Elovich with zeolite treatment ($p = 0.05, 0.88$), a non significant positive correlation for soil ($p = 0.11, 0.78$) and also mixture of soil and zeolite ($p = 0.8, 0.83$). The Increasing correlation (mixture of soil and zeolite toward soil) suggested the effect of ammonium concentration and zeolite addition on potassium desorption in soil by passing of time. Also, the

results of this study shown significant positive correlation between calcium concentration and potassium desorption coefficient rate of Elovich model with soil treatment ($p = 0.014, 0.94$) and the mixture of soil and zeolite ($p = 0.003, 0.98$) and also zero order for zeolite ($p = 0.008, 0.96$).

CONCLUSIONS

Arid and semiarid region soils generally contain large quantities of exchangeable and non-exchangeable K^+ . Increasing of Ca^{2+} and NH_4^+ concentration increased rate of K^+ desorption in soil, zeolite and their incorporation and zeolite decreased desorption rate by incorporation with soil. Result shows that zeolite release K^+ slowly.

The power function, zero order and first order models suggested that the process of K desorption by all of treatments in Ca^{2+} was controlled as slow diffusion and mass action. A good fit with Elovich, suggests diffusion as the principle mechanism at least for the later stages of K^+ desorption kinetic of the studied elements (soil, soil+zeolite and zeolite). Intercept increased with zeolite incorporation in NH_4^+ treatment and some of concentration in Ca^{2+} treatment which might suggest increased potassium availability in soils with limited diffusion to the bulk solution due to a truncated double layer.

In this study, although (a) the rate constant and (b) intercept for potassium expressed differently between two treatments, one fact should be notified that desorb rates of potassium on Ca^{2+} treatment less than NH_4^+ treatment occurred on soil, soil+zeolite and zeolite. The Increasing correlation between ammonium and potassium desorbed (mixture of soil and zeolite toward soil) suggested the effect of ammonium concentration and zeolite addition on potassium desorption in soil by passing of time.

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REFERENCES

Aharoni, C. and D.L. Sparks, 1991. Kinetics of Soil Chemical Processes: A Theoretical Treatment. In: Rate of Soil Chemical Processes, Sparks, D.L. and D.L. Suarez (Eds.). SSSA Special Publication Series No. 27, Madison, WI., ISBN: 0-12-656445-0, pp: 1-18.

Aharoni, C., D.L. Sparks, S. Levinson and I. Ravina, 1991. Kinetics of soil chemical reactions: Relationships between empirical equation and diffusion models. *Soil Sci. Soc. Am. J.*, 55: 1307-1312.

Allen, E.R. and D.W. Ming, 1995. Recent progress in the use of natural zeolites in agronomy and horticulture. *Natu. Zeolites*, 93: 477-490.

Carter, D.L., M.D. Heilman and C.L. Gonzalez, 1965. Ethelene glycol monoethyl ether for determining surface area of silicate minerals. *Soil Sci.*, 100: 356-360.

Chapman, H.D., 1965. Cation-Exchange Capacity. American Society of Agronomy, Madison, WI, pp: 151-157.

Cooney, E., N.A. Booker, D.C. Shallcross and G.W. Stevens, 1999. Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process. *Separ. Sci. Technol.*, 34: 2741-2760.

Dhillon, S.K. and K.S. Dhillon, 1990. Kinetics of release of non-exchangeable potassium by cation-saturated resins from red (Alfisols), Black (Vertisols) and Alluvial (Inceptisols) soils of India. *Geoderma*, 47: 283-300.

Guo, X., L. Zenga, X. Li and H.S. Park, 2008. Ammonium and potassium removal for anaerobically digested wastewater using natural clinoptilolite followed by membrane pretreatment. *J. Hazardous Mater.*, 151: 125-133.

Havlin, J.L., D.G. westfall and S.R. Olsen, 1985. Mathematical models for potassium release kinetics in calcareous soils. *Soil Sci. Soc. Am. J.*, 49: 366-370.

Jalali, M., 2006. Kinetics of non-exchangeable potassium release and availability in some calcareous soils of Western Iran. *Geoderma*, 135: 63-71.

Jalali, M., 2007. Spatial variability in potassium release among calcareous soils of Western Iran. *Geoderma*, 140: 42-51.

Jardin, P.M. and D.L. Sparks, 1984. Potassium-calcium exchange in multireactive soil system: I. Kinetics. *Soil Sci. Am. J.*, 48: 39-45.

Kithome, M., J.W. Paul, L.M. Lavkulich and A.A. Bomke, 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Sci. Soc. Am. J.*, 62: 622-629.

Kittrick, J.A. and E.W. Hope, 1963. A procedure for the Particle size separation of soils for X-ray diffraction analysis. *Soil Sci.*, 96: 312-325.

Klute, A., 1986. Methods of Soil Analysis, Part I. Physical and Mineralogical Methods. 2nd Edn., ASA and SSSA, Madison, WS, USA., pp: 1189.

- Lopez-Pineiro, A. and A.G. Navarro, 1997. Potassium release kinetics and availability in unfertilized vertisols of Southwestern Spain. *J. Soil Sci.*, 162: 912-918.
- Martin, H.W. and D.L. Sparks, 1983. Kinetics of nonexchangeable potassium release from two coastal plain soils. *Soil Sci. Soc. Am. J.*, 47: 883-887.
- Mehra, O.P. and M.L. Jackson, 1960. Iron oxide removal from soils and clays by a dithionite. Citrate system buffered with sodium bicarbonate. *Clay Mine.*, 7: 317-327.
- Mustscher, H., 1995. Measurement and assessment of soil potassium. *International Potash Institute Research Topical*, 4.
- Rao, S.S., A. Swarup, A.R. Subba and V. Goptal, 1999. Kinetics of nonexchangeable potassium release from a Tropaquept as influenced by long-term cropping, fertilization and manuring. *Aust. J. Soil Res.*, 37: 317-328.
- Rezaei, M. and S.A.R. Movahedi Naeeni, 2008. Zeolite in Soil and its Effect on Potassium Quantity-intensity (Q/I) Relationship and their Parameters Regression with Soil Properties. In: *First Iran International Zeolite Conference*, Kazemian, H. (Ed.), Amir Kabir University Press, Tehran, Iran, pp: 508 (In Persian).
- Rezaei, M., D. Akhbari, A. Keshavarzi, M.Z. Alaedin, V. Taheri and S.A.R. Movahedi Naeeni, 2008. Zeolite and Ammonium Effect on Release and Availability of Potassium. In: *1st Iran International Zeolite Conference*, Kazemian, H. (Ed.). Amir Kabir University Press, Tehran, Iran, pp: 510 (In Persian).
- Rezaei, M. and S.A.R. Movahedi Naeini, 2009. Effects of ammonium and Iranian natural zeolite on potassium adsorption and desorption kinetics in the loess soil. *Int. J. Soil Sci.*, 4: 1-19.
- Rhoades, J.D., 1996. Salinity: Electrical Conductivity and Total Dissolved Solids. In: *Methods of Soil Analysis, Part 3. Chemical Methods*, Sparks, D.L. (Ed.). Soil Science Society of America, Inc. American Society Agronomy, Inc., Madison, WI, USA., pp: 417-435.
- Schouwenburg, J., Ch. Van and A.C. Schuffelen, 1963. Potassium-exchange behavior of an illite. *Neth. J. Agric. Sci.*, 11: 13-20.
- Scott, A.D., 1968. Effect of particle size on interlayer potassium exchange in Mca. *Int. Cong. Soil Sci. Trans.*, 9: 649-660.
- Selim, H.M. and M.C. Archer, 1997. Reactivity and transport of heavy metal in soils. CRC/Lewis, Boca Raton, FL.
- Sparks, D.L. and W.C. Liebhardt, 1981. Effect of long-term lime and potassium application on quantity-intensity relationships in sandy soil. *Soil Sci. Soc. Am. J.*, 45: 786-790.
- Sparks, D.L., 1989. *Kinetics of Soil Chemical Processes*. Academic Press, San Diego.
- Steffens, D. and D.L. Sparks, 1997. Kinetics of nonexchangeable ammonium release from soils. *Soil Sci. Soc. Am. J.*, 61: 455-462.
- Tehrani, R.M.A. and A.A. Salari, 2005. The study of dehumidifying of carbon monoxide and ammonia adsorption by Iranian natural clinoptilolite zeolite. *Applied Surface Sci.*, 252: 866-870.
- Walkey, A. and I.A. Black, 1934. An examination of Degtjareff method for determination soil organic matter and a proposed modification of the chromic acid in soil analysis. I. *Experimental. J. Soil Sci.*, 79: 459-465.
- Weatherley, L.R. and N.D. Miladinovic, 2004. Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Res.*, 38: 4305-4312.
- Wilson, G.V., F.E. Rhoton and H.M. Selim, 2004. Modeling the impact of ferrihydrite on adsorption-desorption of soil phosphorus. *Soil Sci.*, 169: 271-282.
- Zhou, J.M. and P.M. Huang, 2007. Kinetics of potassium release from illite as influenced by different phosphates. *Geoderma*, 138: 221-228.