

Kinetics of Copper Desorption of Selected Calcareous Soils from Iran

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Abstract: Desorption of copper (Cu) is an important factor in determining Cu availability in calcareous soils. Kinetics of native Cu desorption by DTPA from 12 calcareous (Entisols and Aridisols) soils of central Iran were studied in a laboratory experiment. Two- constant and simple Elovich rate equations were the best fitted equations among seven kinetic models used. The b rate constant in two constant equation showed significant correlation with CEC ($r = 0.70$, $n=12$). The a rate constant showed significant correlation with total calcite surface area ($r = 0.713$), non reactive calcite surface area ($r = 0.713$, $n=12$) and reactive calcite surface area ($r = 0.622$, $n=12$). The result for k_s rate constant of simple Elovich equation was similar to a of two-constant equation but its k_s did not show significant correlation with soil properties.

Key words: Aridisols % Calcareous soils % Copper % Desorption % Entisols

INTRODUCTION

Copper(Cu) is an essential nutrient for plants and animals [1], the availability of which is usually low in calcareous soils. Dudley *et al.* [2] observed that Cu was retained by a specific adsorption reaction in calcareous soils and presence of carbonates effectively immobilizes Cu by buffering the soil pH.

Maftoun *et al.* [3] reported that top dry weight, Cu concentration and Cu uptake were significantly greater in Cu treated plants than those of untreated plants in a greenhouse experiment with 26 calcareous soils from southern Iran. Ghasemi Fasaie *et al.* [4] noted that Cu desorption from 15 highly calcareous soils of southern Iran was higher in the first 2h followed by a slower release rate. They reported that diethylenetriaminopentaacetic acid (DTPA) extracted only one-fifth of added Cu after 20 d and that calcium carbonate equivalent (CCE), cation exchange capacity (CEC) and, clay content were the most important influential soil characteristics in determination of the rate constants of the kinetic models.

Desorption of Cu from exchange complex and its release from organic matter, crystalline minerals and other metastable compounds to the solution phase are the processes that control soil Cu mobility and determine the relative contribution of soil Cu to plant available Cu [5].

Jarvis [6] stated that prediction of Cu availability will remain difficult until more is known about the characteristics of Cu desorption from soils. Most of Cu desorption studies have been performed on pure soil components. Covelo *et al.* [7] reported that vermiculite preferentially sorbed and retained Cu. Undabeytia *et al.* [8] reported that heavy metal such as Cu was adsorbed by inner-sphere complexes on the edge sites of the montmorillonite. They determined a binding coefficient for Cu^{2+} on the edge sites $k = 2 \times 10^4 \text{ MG}^{-1}$, indicating a very high affinity of Cu^{2+} for these sites. The poor reversibility of Cu adsorption has considerable effects on Cu availability to plants [9]. Our knowledge of Cu adsorption desorption is based mainly on the study of equilibrium conditions using thermodynamic approaches that can predict only the final state of a soil system from an initial non equilibrium state. Kinetic data, on the other hand, may yield important information concerning the nature of the reaction at a given time [10]. Some researchers reported that Cu desorption in calcareous soils was related to pH, CEC and carbonates content of soils [11,12].

However, data on the kinetics of Cu desorption in calcareous soils is limited. The present experiment was, therefore, initiated to 1) study Cu desorption patterns and 2) determine the suitability of different models for description of the kinetics of Cu release in 12 calcareous soils.

MATERIALS AND METHODS

Twenty surface soil samples (0-30 cm) representing different fields of Gazvin and Tehran province of Iran were collected, air dried, sieved (<2mm sieve) and analyzed for pH, organic matter (OM), CEC and CCE according to Page *et al.* [13]. Active CaCO₃ equivalent (ACCE) after passing soil from <1mm sieve, which is the amount of fine particle calcite, was also determined by the NH₄⁻ oxalate method [14] because CCE is usually a poor measure of carbonate reactivity. Specific surface area of soil and Ca CO₃ was determined by the BET nitrogen sorption method [15]. The specific area related to total and active lime were determined by measuring specific area in the same soil samples before and after the removal of total and active limes.

Identification of clay and carbonate minerals was carried out by X-ray diffraction (XRD) using random powder and oriented clay on ceramic plates. Soil texture was determined by hydrometer method [16]. Selected characteristics of the soils used are shown in Table 1 showing that CCE and ACCE ranged from 46 to 228 and 16.08 to 99.8 gkg G¹, respectively and that illite, vermiculite and smectite were the dominant clay minerals in all of the soil samples (data not shown). Twelve soil samples representing the major soil series of studied regions were selected.

Desorption studies were carried out as follows: 50 g of each sample were placed in a polyethylene tube and added 100 ml of DTPA extractant, buffered at pH=7.3, 10 drops of toluene were added to suppress microbial activity and shaken on an end-over-end circulatory shaker for periods of 0.25, 0.5, 1, 2, 4, 6, 8, 12, 24, 36, 48, 60, 72, 84, 96, 120, 144, 168 or 192h at 25±1°C. At the end of shaking period, 5 ml of suspension was pipetted with a sterile syringe, passed through a 0.45 µm filter and Cu concentration was determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

Kinetic equations commonly used in soil desorption studies including zero-order [10,17], first-order [18], second-order [10,19], third-order [10,17], parabolic diffusion [20], two- constant rate [10] and simple Elovich [21]. (Table. 2). The equations thus obtained were tested for goodness of fit by least- square regression analysis. To select the equation that best fit the release of Cu in soils, the standard error of estimate(SE) was calculated as follows:

$$SE \neq \left[\frac{\sum (q - q')^2}{(N - 2)} \right]^{0.5} \quad [1]$$

Table 1: Selected characteristics of soils (Cont d).

Soil no	CEC (cmol.kgG ¹)	SSA. Soil	SSA. ACCE	SSA.CCE (m ² .gG ¹)	SSA. Non ACCE
1	16.4	26.0	99	157	208
2	12.4	10.0	44	111	143
3	19.2	20.0	124	83	61
4	16.3	18.6	28	50	68
5	17.7	18.2	20	151	450
6	15.3	8.5	36	28	26
8	30.0	20.3	197	94	58
10	20.2	39.0	26	79	114
12	19.8	18.0	13	124	228
14	19.2	38.6	132	102	84
15	32.0	11.8	25	21	19
17	19.6	18.6	39	84	98

OC=organic carbon, CCE=calcium carbonate equivalent, CEC=cation exchange capacity, SSA=soil surface area, SSA.ACCE=active calcium carbonate surface area, SSA.CCE=total calcium carbonate surface area, SSA.NonACCE=Non active calcium carbonate surface area

Table 1: Selected characteristics of soils.

Soil no	Soil Series	Clay	OC	CCE gkgG ¹	ACCE	pH ^r
1	Kooskak	325	8.2	80.0	38.40	7.63
2	Saeedabad	106	9.2	46.0	19.20	7.70
3	Ahmadabad	226	8.2	72.0	27.20	7.70
4	Kordamir	308	11.2	136.0	62.60	7.81
5	Daneskade	253	19.9	62.0	44.50	7.50
6	Absard	215	12.3	88.0	16.08	7.20
8	Boomhen	134	13.1	125.0	33.50	7.56
10	Firoozkooh1	307	15.0	228.0	99.80	7.77
12	Vardavrd	203	24.7	82.0	40.80	7.40
14	Damavand	410	9.2	94.0	40.80	7.60
15	Roodhen	134	6.3	194.0	58.50	7.51
17	Firoozkooh2	363	7.3	90.0	23.50	7.36

* pH in 1: 5 soil: 0.01M Cacl₂ suspension)

Table 2: Kinetic models used in the study

Model	Equation	Parameters
Zero order	q _t =q ₀ -k ₀ t	k ₀ , zero-order rate constant (mg CukgG ¹ sG ¹)
First order	Ln q _t =Lnq _∞ -k ₁ t	k ₁ , first-order rate constant (sG ¹)
Second order	1/q _t =1/q _∞ -k ₂ t	k ₂ , second-order rate constant [(mg CukgG ¹)G ¹]
Third order	1/q _t =1/q _∞ ² -k ₃ t	k ₃ , third-order rate constant [(mg CukgG ¹) ²]
Parabolic Diffusion	q _t =q _∞ +k _p t ^{0.5}	k _p , diffusion rate constant [(mg CukgG ¹) ^{0.5}]
Two constant rate	q _t =at ^b	a, initial Cu desorption rate constant (mg Cu kgG ¹ SG ¹) ^b and b, desorption rate coefficient
Simple Elovich	q _t = $\frac{1}{b_s} L_n$ a s b s + $\frac{1}{b_s} L_n t$	" _s , initial Cu desorption rate (mgCu kgG ¹ SG ¹) and \$ _s , Cu desorption constant [(mgCukgG ¹)G ¹]

Where q and q' are the measured and calculated amounts of Cu in soil at time t , respectively and N is the number of measurements. A relatively large coefficient of determination (r^2) and small SE were used as criteria for the best fit [10,21].

RESULTS AND DISCUSSION

Rate of Cu desorption was initially rapid but gradually declined with time. The Maximum amount of released Cu was from soil no. 17 with 12.77 mg Cu kg⁻¹ soil and minimum amount of released Cu was from soil no.6 with 2.3 mg Cu kg⁻¹ in 192 h (Fig.1). The zero order, first order, second order and third order equations did not describe Cu desorption from studied soils and from zero to third order coefficients of determination were decreased. Soil no.15 was exception in comparison with others. Its coefficient of determination (r^2) for zero order equation was higher than other equations (and had maximum $r^2=0.982$, Table 3) and it seems, that zero-order equation could describe Cu desorption in this soil (Fig. 3).

Comparisons of r^2 and SE values of different models indicated that the best models for describing the data in all studied soils were two-constant rate and simple Elovich equations. Also, the relationships between measured and predicted values of released Cu were close (Fig. 4 and 5). Singh *et al.* [5] reported that desorption of Cu in calcareous soils conformed to the linear form of Langmuir isotherm. Khater and Zaghloul [20] concluded that power function, parabolic- diffusion and first-order equations were the best fitted equations used to describe

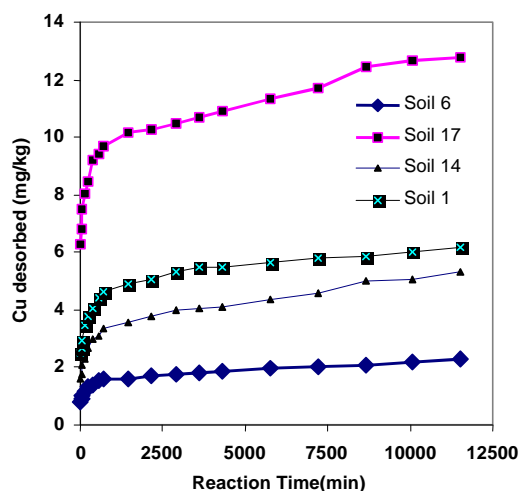


Fig. 1: Copper desorption by DTPA with time in calcareous soils

Table 3: Mean and range of coefficient of determination (r^2) and standard error of the estimate (SE) of various kinetic models for Cu desorption

Kinetic model	r^2 (n=12)		SE (mg Cu kg ⁻¹)	
	Range	Mean	Range	Mean
Zero order	0.673-0.982	0.784	0.2-0.94	0.44
First order	0.574-0.927	0.725	0.12-0.23	0.18
Second order	0.463-0.714	0.546	0.02-0.11	0.09
Third order	0.354-0.425	0.420	0.04-0.93	0.18
Parabolic diffusion	0.862-0.949	0.908	0.12-0.58	0.32
Simple Elovich	0.638-0.994	0.937	0.07-1.15	0.24
Two- constant rate	0.854-0.994	0.973	0.02-0.33	0.06

Table 4: Values of the rate constants for the kinetic models that best described Cu desorption

Soil no	Two constant rate			Simple Elovich		
	a (mgCukg ⁻¹ sG ¹)	b	ab (mgCukg ⁻¹ sG ¹)	" _s (mgCukg ⁻¹ sG ¹)	\$_s\$ (mgCukg ⁻¹ s)G ¹	" _s \$_s\$ ^t
1	1.76	0.140	0.2464	2.186	1.759	57.67
2	0.76	0.146	0.1109	0.583	3.512	30.71
3	0.91	0.135	0.1228	1.063	3.450	55.01
4	1.39	0.135	0.1876	1.676	2.240	56.32
5	1.36	0.123	0.1673	2.965	2.763	122.88
6	0.58	0.144	0.0835	0.524	4.819	37.88
8	0.55	0.157	0.0864	0.284	4.140	17.63
10	0.84	0.148	0.1243	0.593	3.049	27.12
12	1.66	0.141	0.2341	1.815	1.773	48.27
14	1.02	0.172	0.1754	0.3991	1.863	11.13
15	0.17	0.373	0.0634	0.0150	1.408	0.32
17	4.92	0.099	0.4871	46.85	1.088	764.60
Min	0.17	0.099	0.0634	0.0150	1.088	0.32
Max	4.92	0.373	0.4871	46.85	4.819	764.6
Mean	1.33	0.159	0.1741	4.9127	2.65	102.46

* calculated for t=15 min

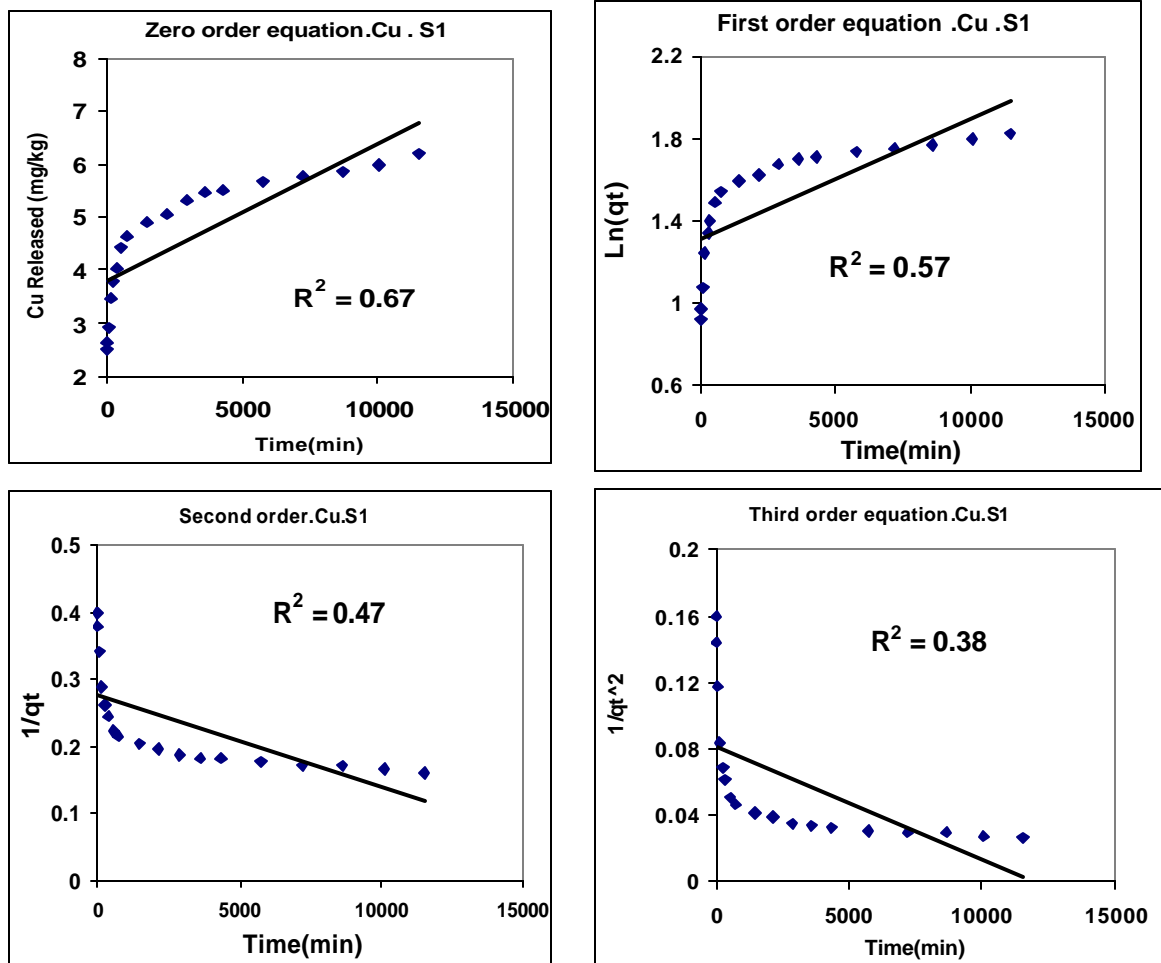


Fig. 2: Test of zero, first, second and third order kinetics for calcareous soil number 1

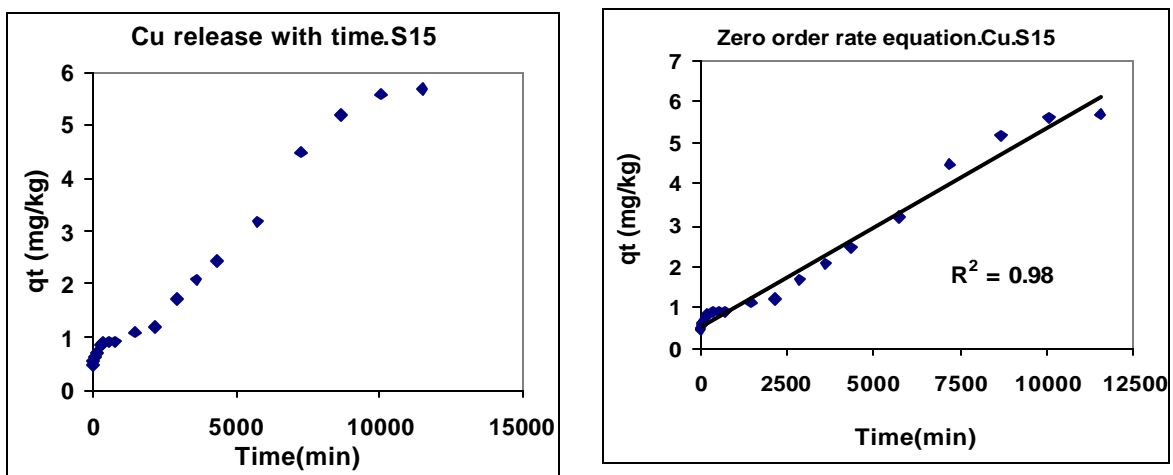


Fig. 3: Copper desorption by DTPA with time in calcareous soil number 15 and test of zero order kinetics equation

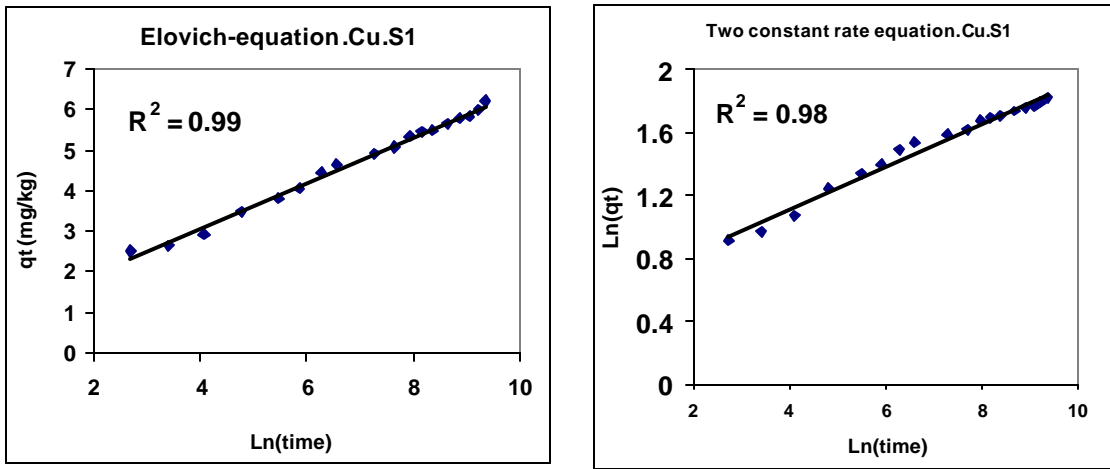


Fig. 4: Test of simple Elovich and two constant rate kinetics for calcareous soil number 1

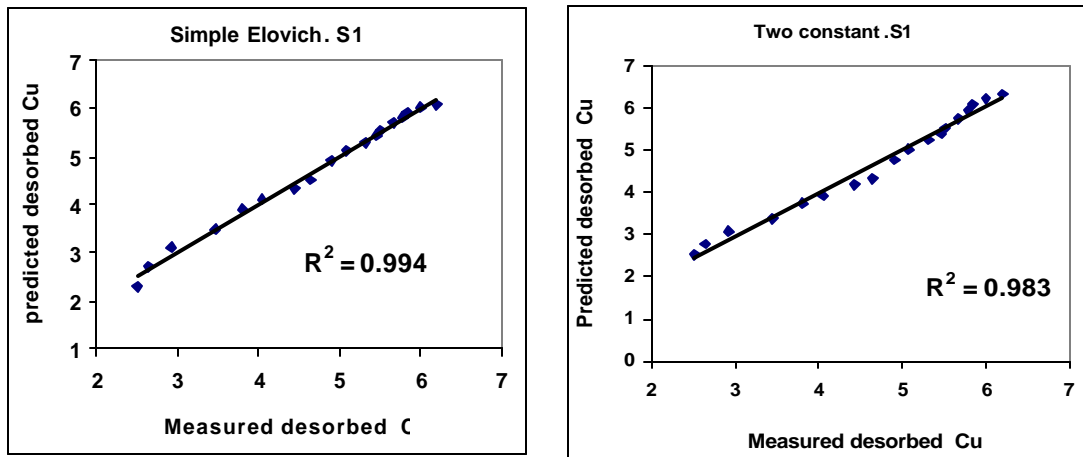


Fig. 5: Relationships between measured desorbed Cu and predicted by simple Elovich and two constant rate equation during 192 hours in calcareous soil

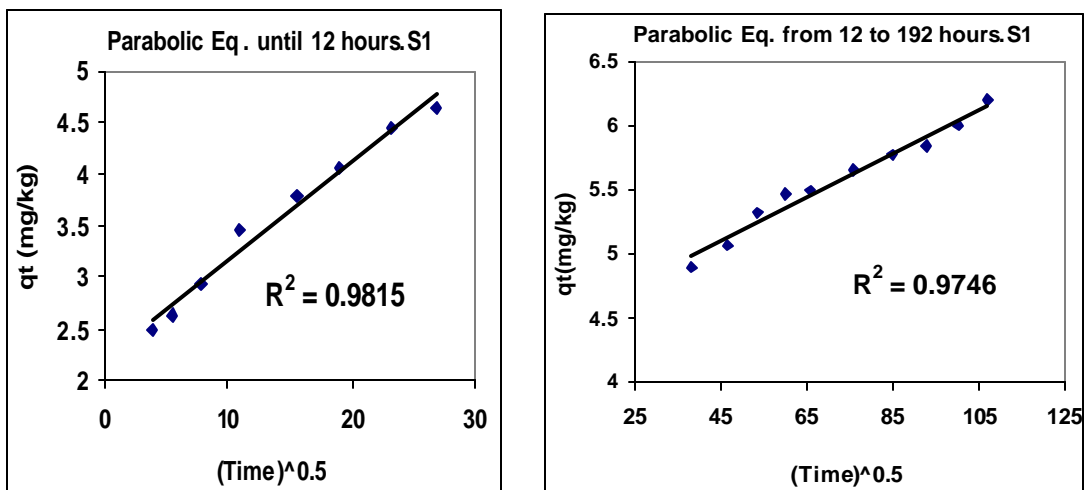


Fig. 6: Test of parabolic kinetics in two sections for soil number 1

Cu desorption. Ghasemi fasaei *et al.* [4] concluded that two-constant rate, Elovich and simple Elovich were the best- fitted equations used to describe Cu desorption from highly calcareous soils of southern Iran. They, also, reported a discontinuity in slope at 120 min in linear form of parabolic diffusion equation. Similar results were observed in our experiment except that the rate of Cu released from time 0 to 9 h was significantly higher than that from 9 to 192h in most soils (Fig.6 as an example). The trend observed suggest that probably two different mechanisms were involved. Because of continuous shaking of soil samples during desorption experiment, it is likely that two particle-diffusion mechanisms are involved [22]. Khater and Zaghoul [20] and Gasemi fasaei *et al.* [4] reported that Cu desorbed from macro aggregates or outer surface of micro aggregates in the first 2h are followed by desorption and diffusion of Cu from inside macro-or micro-aggregates. Also, it is possible that the energies of Cu desorption increase exponentially or as a power function as Cu is desorbed by DTPA from soil solids and diffuses into the soil solution [10]. Gasemi fasaei *et al.* [4] reported a higher rate of Cu desorption from highly calcareous soils of southern Iran in the first 2h and concluded that this may describe the reason why the DTPA soil test can effectively predict Cu availability in calcareous soils. This, however, needs further studies in our soils.

Lindsay and Norvell [23] considered a 2-h shaking period in their DTPA soil test. Findings of Chien and Clayton [24] revealed that the rate of Cu desorption increased when the value of s increased or S_s decreased. Likewise, Dang *et al.* [10] proposed that an increase in the value of a and decrease in the value of b in the two constant- rates equation probably indicate an increase in the rate of desorption from soils. Gasemi fasaei *et al.* [4] reported that means for a values were 0.24 and for b value were 0.282 and that s value was 18.44 and mean S_s was 3.61. Dalal [25] stated that simple Elovich equation was derived from Elovich equation with assumption of $s, S_s, t > 1$. The value of s, S_s is calculated for 15 minute and the values are shown in Table 4. Only for soil no. 15 is lower than 1 and for 30 minute the values of s, S_s, t is higher than 1 for all soils.

In the two-constant-rates equation, qt can be differentiated with respect to t, resulting in $dq/dt=tb-1$ and when $t=1$, the previous equation can be written as $dq/dt=ab$, [10] and ab may be taken as initial desorption rate of soil nutrient. The values of ab were calculated for 12 calcareous soils (Table 4). The mean value was calculated to be 0.1722 mg Cu kgG⁻¹ sG⁻¹ which is significantly higher than 0.0525, the value reported

Table 5: Correlation coefficient (r) between constant rates of kinetic models

Constant rates	Constant rates			
	a	B	ab	As
a (Two-constant rate)				
b (Two-constant rate)	NS			
ab (Two-constant rate)	0.986 **	NS		
s	0.940 **	NS	0.880 **	
S_s	NS	NS	-0.600*	NS

NS = Not significant

*, ** Significant at 0.05 and 0.01 levels of probability, respectively.

for highly calcareous soils of southern Iran by Gasemi fasaei *et al.* [4]. Results of the statistical analyses showed that b rate constant is significantly correlated with CEC ($r=0.70, n=12$) and, if soil no.17 is excluded, a rate constant, showed significant correlation total calcite surface area ($r=0.713, n=11$) and nonreactive calcite surface area ($r=0.622, n=11$). The results for s rate constant was similar to those of a, namely, as showed significant correlation with total calcite surface area ($r=0.670, n=12$) and nonreactive calcite surface area ($r=0.847, n=11$). S_s did not show significant correlation with soil properties in our study. Clay content was the only soil property that showed significant correlation with ab and that predicted the values of ab from the two-constant-rates equation. According to Dalal [25], ab values may be taken as an initial desorption rate of soil nutrient. Therefore, it seems that initial desorption rate of Cu in the soils is controlled mainly by clay content. Maftoun *et al.* [26] reported that the Cu-adsorption maximum, b, 20 calcareous soils from southern Iran, calculated from Langmuir isotherm, was positively correlated with Clay, CEC and CCE. They believed that the sites of Cu adsorption of the calcareous soils were clay, calcium carbonate and organic matter.

The values of the rate constants for the two constant rates equation were correlated with the value of the rate constant of simple Elovich equation. There was significant correlation between a and ab with s (Table5).

CONCLUSIONS

The results of this study showed that two-constant-rates and simple Elovich were the best equations for description of Cu- desorption of calcareous soils of central Iran. The Cu desorption pattern based on parabolic diffusion equation indicated that the rate native Cu desorption was higher in the first 9h followed by a slower release rate, indicating that two different mechanisms are involved. Results of statistical analysis indicated that clay content and surface area of calcite are

the most important soil characteristics that could be used to predict the rate constants of the kinetic models. It seems that clay content and surface area of CaCO₃ are the most influential factors in controlling Cu release from calcareous soils of central Iran.

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