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Release of Potassium, Calcium, and Magnesium from Vermiculite Clay Soil of the Jiroft Mine

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ABSTRACT

Abstract: The purpose of this research was to investigate the release of non-exchangeable potassium (K), magnesium (Mg), and calcium (Ca) from vermiculite clay soil using different extractants as a natural source to achieve sustainable agriculture. The treatments included four extractants: hydrochloric acid, calcium chloride, citric acid, and oxalic acid, each at a concentration of 0.01 M, applied in ten half-hour intervals. The cumulative release of K, Mg, and Ca from the vermiculite clay soil was measured, and the data were fitted to five kinetic equations. The results of the analysis of variance indicated that the effect of the extractant on the release of K, Mg, and Ca was significant ($p < 0.01$). The maximum cumulative releases for HCl, calcium chloride, citric acid, and oxalic acid solutions were found to be 160.7, 62.1, 140.1, and 95.2 mg kg^{-1}, respectively, for K element and 192, 1872, 1776 and 528 mg kg^{-1}, respectively, for Mg release and cumulative release maximums for HCl, citric acid, and oxalic acid solutions were estimated to be 1600, 3040, and 1120 mg kg^{-1} respectively, for Ca release. The highest and lowest release amounts for K were related to HCl and calcium chloride, respectively, as the extractant. The power function ($r = 0.95$ to 0.99, $p<0.01$), parabolic diffusion ($r = 0.76$ to 0.99, $p<0.01$), and Elovich models ($r = 0.85$ to 0.89, $p<0.01$) were identified as the most effective equations for predicting the release of three elements from vermiculite clay soil. Mineralogical results indicated that the component of the vermiculite was transformed to smectite clay in two HCl and citric acid extractants. In conclusion, vermiculite clay soil can serve as a natural source to meet the K and Mg requirements of plants.

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1. Introduction

Potassium (K) is an essential nutrient for plants and plays a significant role in agriculture. Among the various forms of K, soluble and exchangeable forms are readily available to plants, while non-exchangeable K is slowly available, and structural K is unavailable to plants (Sparks and Huang, 1985). Non-exchangeable K is not chemically bonded to minerals; instead, it is retained within the hexagonal voids between adjacent tetrahedral sheets in micas and vermiculites (Sparks, 1987). The primary sources of K in soils are aluminosilicates, such as K feldspars and micas, along with their weathering products, including vermiculite, which together account for 98% of soil K (Al-Zubaidi, 2008). Studies on soil K show that the amount and rate of K release are influenced by soil texture and the types of constituent particles. Magnesium (Mg), the eighth most abundant element in the Earth's crust, is an essential nutrient for plants and plays a vital role in their growth. The release of Mg from clay minerals and its availability to plants are affected by factors such as soil pH, particle size, and weather conditions. Soil pH directly influences the release of Mg from clay minerals and its uptake by plants (Hailes *et al*., 1997). The majority of soil Mg (90-98%) is contained within the crystal lattice structure of minerals, making it unavailable for plant uptake. Due to significant variations in Mg content in raw materials and the degree of weathering, the total Mg content in soil can range from 0.05% to 0.5% (Gransee and Führs, 2013).

Netto-Ferreira *et al.* (2023) demonstrated that incorporating organic materials into mineral particles enhances the availability of K and phosphorus. Soil components, including clay, sand, and silt, contribute differently to the release of soil K, with clay particles being particularly recognized for their role in supplying K essential for plant growth. The release of K from various solutions-such as saline solutions (e.g., dilute $CaCl_2$), inorganic acids (e.g., HCl, H_2SO_4, and HNO_3), organic acids (e.g., oxalic, citric, acetic, and malic acids), and sodium tetraphenylborate—depends significantly on several factors. These factors include the quantity and type of clay minerals, mineral particle size, calcium carbonate ($CaCO_3$) content, quartz content, soil fertility, and weathering conditions (Tu *et al.*, 2007). Pohlman and McCall (1986) stated in their study on the release of magnesium, potassium, and aluminum from forest soils that the rate of release by organic acids (complexing agents) is higher than in their absence.

Vermiculite is a phyllosilicate clay mineral characterized by a negative layer charge ranging from -0.6 to -0.9 per formula unit. It exhibits a high cation exchange capacity, typically between 120 and 200 cmolc kg^{-1}, which is among the highest of soil clay minerals. Its specific surface area is approximately 800 m^2/g (Kumari & Mohan, 2021). Consequently, it effectively retains certain ions, including NH_4^+ and K^+. Silicate clay minerals, particularly 2:1 types such as vermiculite, significantly influence K availability in soil (Hongo *et al*., 2012). Mg-vermiculite exhibits a series of reflections in X-ray diffraction patterns at the following angles: $2\theta = 6.45°$ (d (001) = 1.45 nm), 7.19° (d (002) = 1.23 nm), 17.9° (d (003) = 0.49 nm), 25.4° (d (004) = 0.35 nm), and 30.9° (d (005) = 0.296 nm). Thermal treatment of vermiculite reduces the interplanar distance, with the extent of reduction depending on the heating temperature. The first-order peak corresponds to Mg-vermiculite, while the second peak is attributed to partially dehydrated magnesium within the vermiculite interlayer space (Marcos *et al*., 2009).

Hatami *et al*. (2014) investigated the release of soluble, exchangeable, and non-exchangeable K from silicate minerals. They found that phlogopite and biotite exhibited the highest release of soluble, exchangeable, and non-exchangeable K, respectively, while muscovite showed the lowest release for all three forms of K. Additionally, a study on K release in calcareous soils identified two distinct phases—slow and fast—during ten extraction steps using 0.01 M $CaCl_2$ in both control and K-treated soils. The fast phase indicates the release of K from the wedge position, while the slow phase reflects K release from the interlayer positions of the fractured K mineral (Najafi-Ghiri *et al*., 2020). Srinivasarao *et al*. (1999) demonstrated that citric acid released more K in illite soils compared to hydrochloric acid and calcium chloride, and more than in smectite and kaolinite soils. Mousavi *et al*. (2014) found that, when comparing calcium chloride with organic extractants—including oxalic and citric acids—on pure feldspar and muscovite minerals, organic acids released between 2.5 and 3 times more K than calcium chloride. This increased release can be attributed to the use of pure minerals rather than soil. The authors argued that oxalic acid can effectively release K through decomposition or substitution, without interference from impurities such as calcium. Najafi-Ghiri *et al*. (2018) found that oxalic acid extracted more K than other solutions over the long term, while calcium chloride released the least amount of K. In the short term, citric acid was found to release more K. The ability of the solutions to extract K in both short-term and long-term experiments was ranked as follows: calcium chloride < HCl < citric acid < oxalic acid. Similarly, Li *et al*. (2015) reported that hot HCl can extract more than 30% of non-exchangeable K from biotite without altering the mineral structure in the short term, through the exchange of H^+ ion with interlayer K. Their findings indicated that biotite and vermiculite phyllosilicates can be effectively utilized as traditional K fertilizers. Oze *et al*. (2019) demonstrated that glaucony sediments serve as a source of K and heavy metals, such as chromium, revealing that the release rate of K was higher than that of other elements. Additionally, they found that increased acidity correlates with a greater release of K. Their findings indicated that approximately 2.5 grams of K were released from 1 kg of glaucony sediment after one year. They proposed glaucony as a viable source of K for agricultural applications. Hashemi and Najafi-Ghiri (2024) further illustrated that the K release rate may decrease following the removal of carbonates from vermiculite clay soil, and $CaCl_2$ is more effective at extracting K from vermiculite clay soil than citric acid.

The study of K, Mg, and calcium (Ca) release from vermiculite clay soil as nutrient sources is crucial for arid and semiarid regions. Using clay soil extracted from mines as a fertilizer containing Mg and K offers a novel solution to enhance the availability of these nutrients in agriculture. This natural material can serve as an effective alternative to chemical fertilizers. To utilize this clay as a fertilizer rich in K and Mg for potassium-loving plants, it is essential to evaluate the release rates and the changes that occur after nutrient release. Implementing new methods to lower the pH of the rhizosphere and facilitate the release of K and Mg from clay minerals—particularly in calcareous soils with high pH—can significantly enhance their uptake by plants. The objectives of this research are: (1) to investigate the release of K, Ca, and Mg from vermiculite clay soil after continuous extraction with various extractants in a short-term analysis, to recommend it as a natural fertilizer; and (2) to identify the most effective extractant for releasing these specific elements from vermiculite clay soil.

2. Materials and methods

2.1. Vermiculite Sampling and Characteristics

The vermiculite sample used in this study was obtained from the Jiroft Mine in Kerman Province, Iran. The Jiroft Plain is part of the structural sedimentary basin of central Iran, shaped by tectonic forces that have created fractures and faults in the region. Vermiculite clay soil was collected from fine-grained materials in the central area within the subsidence layers. The vermiculite clay soil was ground using a steel grinder and then passed through a #10 mesh sieve (particles smaller than 2 mm), achieving a purity of approximately 70%, as determined by X-ray diffraction (XRD), X-ray fluorescence (XRF), and energy-dispersive X-ray spectroscopy (EDX) analyses. The current clay sample contains several impurities, including approximately 16% lime and 5% gypsum, as well as other mixed minerals identified through various analyses. The X-ray analysis confirmed the presence of mixed minerals, including muscovite, talc, and quartz, with vermiculite identified as the dominant mineral in this sample. Several chemical properties were assessed, such as cation exchange capacity (Chapman, 1965), calcium carbonate equivalent (Allison and Moodie, 1962), soil pH (Thomas, 1996), electrical conductivity (Thomas, 1996), and specific surface area using the N2-BET method (Carter, 1996). Different forms of K, including solution, exchangeable, non-exchangeable, and total K, were quantified (Sparks, 1987). All extracted samples were analyzed for K content using flame photometry (Jenway PFP7).

2.2. Release Kinetics of K, Mg, and Ca from Vermiculite

This experiment was conducted using a completely randomized design with three replicates. The treatments consisted of vermiculite clay soil combined with four extractants: 0.01 M $CaCl_2$, HCl, oxalic acid, and citric acid. The extraction process was carried out over ten continuous time intervals: 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 hours. For the K, Mg, and Ca release experiment, 10 g of vermiculite samples (in triplicate) were first equilibrated with 100 mL of 1 M $CaCl_2$ for 24 hours to remove native soluble and exchangeable K. The samples were then washed with deionized water to eliminate any residual $CaCl_2$ and air-dried. Two grams of the dried sample were suspended in 20 mL of 0.01 M extractant solutions and shaken at 25°C on a reciprocating shaker for 30 minutes. The mixture was centrifuged, and the K concentration in the clear solution was determined using a flame photometer (Jenway PFP7). A new portion of extractant was added to the remaining samples, which were then shaken for 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 hours, after which the K concentration was measured. Mg and Ca concentrations were determined using standard methods (Rowell, 1994). Throughout the entire experiment, the temperature was maintained at 25°C.

To describe the kinetics of K release from samples into various solutions, five mathematical models were fitted:

1) Elovich equation (Sparks, 1989): $Y = a + b \ln t$
2) Parabolic law (Havlin *et al*., 1985) $Y = a + b\sqrt{t}$
3) Zero-order kinetic (Martin and Sparks, 1983) $Y^{\circ} - Y = a - bt$
4) First-order kinetic (Martin and Sparks, 1983) $\ln\ (Y^{o} - Y) = a - bt$
5) Power function (Havlin *et al*., 1985) $\ln Y = \ln a + b \ln t$

In these equations, Y represents the quantity of the element released (mg) at time t; a is the intercept of the equation at the origin; b is the slope of the equation; and t is the release duration (h). Y0 is the maximum quantity of the element released (mg).

We calculated the coefficient of determination (R^2) using least squares regression and evaluated the standard error (SE) of the estimate using the appropriate formula:

$$\mathrm{SE} = \sqrt{\frac{\sum (X - X^{*})^{2}}{n - 2}} \qquad (1)$$

Where X and X* are the measured and calculated quantities of the element released at time t, respectively (mg kg^{-1}), and n is the total number of data points.

2.3. Data Analysis

The statistical analysis of the data was conducted using SPSS version 21.0. For multiple treatment comparisons, we employed Analysis of Variance (ANOVA) followed by Tukey's Honestly Significant Difference (HSD) post hoc test ($p < 0.01$). Average comparisons between treatments (extractants) were performed for all three studied elements. Microsoft Excel 2019 was used to generate graphs of the kinetic models.

3. Results

3.1. Physicochemical and mineralogical properties

Table 1 presents various physical and chemical properties of the vermiculite clay soil used in the initial research. As shown, the total K content in the sample is elevated, indicating the presence of additional minerals beyond vermiculite in the clay. The elemental composition of the clay sample was also identified using XRF analysis (Table 2). The X-ray diffractograms of the sample extracted from the mine are shown in Figure 1. The diffractograms display the second (7.2 Å) and third (3.59 Å) peaks, confirming the presence of vermiculite. Other minerals, such as quartz (3.4 Å) and dolomite (2.8 Å), were detected as impurities. The presence of vermiculite particles in the analyzed samples is further illustrated by the SEM image (b) and the EDX spectrum (c) in Figure 1.

Table 1. Some physicochemical properties of the vermiculite clay soil

Specific surface area (m^2g^{-1})	CEC (cmol(+) kg^{-1})	EC (dS m^{-1})	CCE (%)	pH	Soluble K (mg kg^{-1})	Exchangeable K (mg kg^{-1})	NEK (mg kg^{-1})	Total K (mg kg^{-1})
118.00	75.00	0.20	16.30	8.10	21.70	113.40	1100.40	21280.00

Abbreviations: NEK: non-exchangeable K

Table 2. Analysis of vermiculite clay soil according to X-ray fluorescence

Chemical Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	MnO	LOI
	49.00	3.50	5.78	4.76	0.82	28.10	2.10	0.03	0.13	7.30

3.2. Cumulative K Release

The release data indicated that the cumulative K released over intervals of 30 to 300 minutes ranged from 18.8 to 160.7 mg kg^{-1} in the HCl extract, 9.4 to 62.1 mg kg^{-1} in the calcium chloride extract, 13 to 140.1 mg kg^{-1} in the citric acid extract, and 11.7 to 95.2 mg kg^{-1} in the oxalic acid extract (Table 3). The analysis of variance revealed that the effect of the extractant on the amount of released K is significant ($p < 0.01$) (Table 4). According to the mean comparison results (Table 5), HCl and calcium chloride were the most and least effective extractants for K release from vermiculite clay soil, respectively. Organic acids, specifically citric acid and oxalic acid, demonstrated a higher release rate compared to calcium chloride. Additionally, no significant difference was observed between HCl and citric acid. The K release from vermiculite clay soil during ten consecutive extractions using different extractants is illustrated in Figure 2.

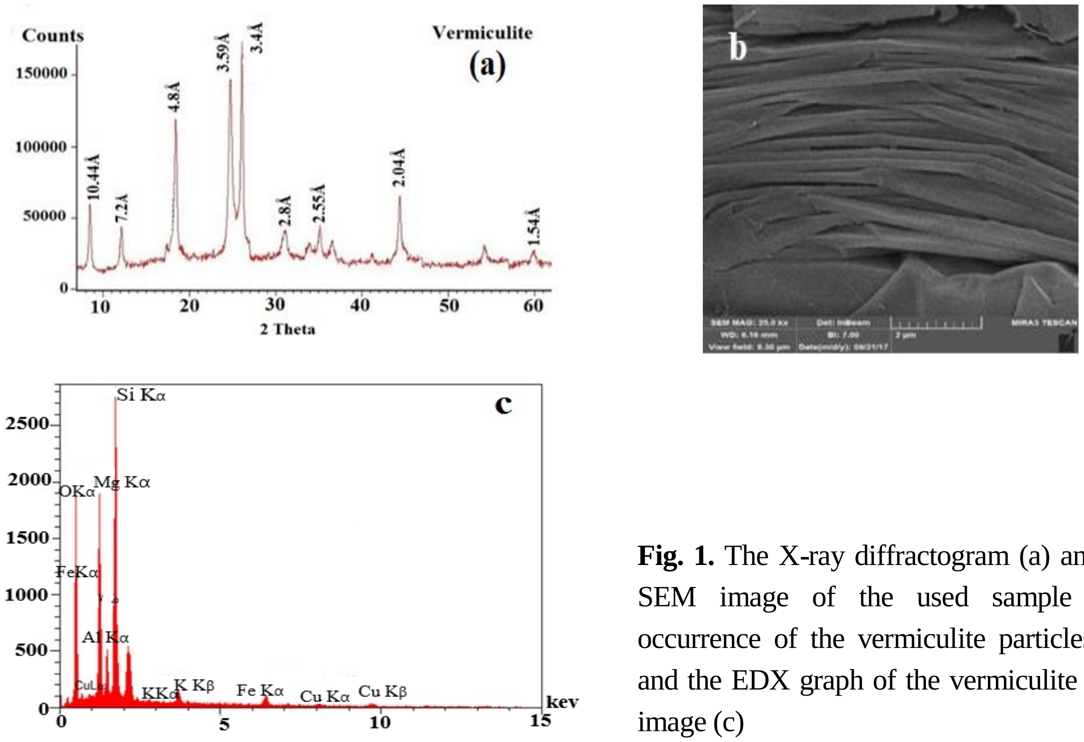

Fig. 1. The X-ray diffractogram (a) and the SEM image of the used sample with occurrence of the vermiculite particles (b), and the EDX graph of the vermiculite SEM image (c)

Table 3. The range of cumulative K, Ca, and Mg release from vermiculite clay soil with different extractants

Treatments	Cumulative K release (mg kg^{-1})	Cumulative Ca release (mg kg^{-1})	Cumulative Mg release (mg kg^{-1})
HCl	18.8-160.7	160-1600	96-192
$CaCl_2$	9.4-62.1	1520-29920	240-1872
Citric acid	13.0-140.1	320-3040	336-1776
Oxalic acid	11.7-95.2	160-1120	48-528

Table 4. Analysis of variance of cumulative K, Ca, and Mg release from vermiculite clay soil in different extractants

Source of variation	df	Mean square	F	Significance
K release	4	5521.293	20.894	0.000**
Ca release	4	4814425173.300	25.780	0.001**
Mg release	4	1627848.600	35.760	0.001**

*and **represent 0.05 and 0.01 levels of significance, respectively.

Table 5. Mean comparison of cumulative K, Ca, and Mg release from vermiculite clay soil in different extract solutions during 5h

Extractant	Cumulative K release (mg kg^{-1})	Cumulative Ca release (mg kg^{-1})	Cumulative Mg release (mg kg^{-1})
HCl	160.70a	1533.3b	195c
$CaCl_2$	63.00c	-	1856a
Citric acid	140.30a	2986.6a	1728a
Oxalic acid	94.76b	1066.6c	480b

Means with different letters in each column are significantly different according to Tukey's test at a significance level of $p < 0.05$.

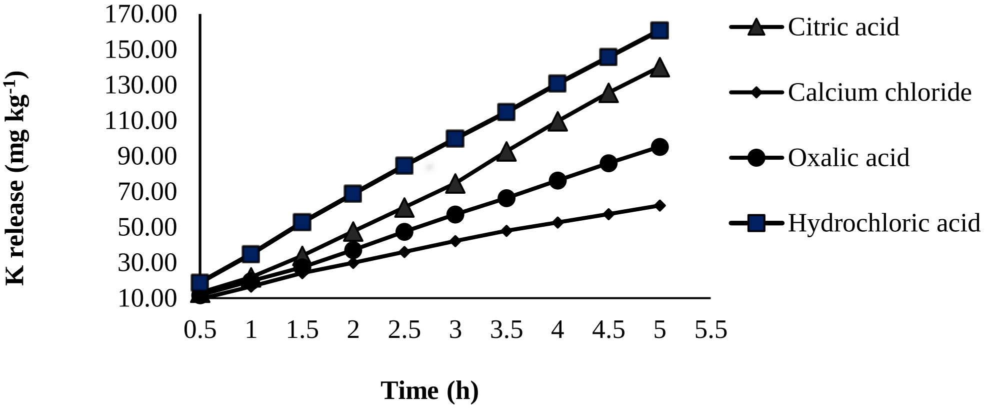

Fig. 2. K release rate from vermiculite clay soil to four extractants during 5h

3.3. Cumulative Ca release

Given that calcium chloride is not a reliable extractant for obtaining the element Ca, the results derived from this method for calcium should be disregarded. The release data (Table 3) show that the cumulative amount of Ca released over time intervals ranging from 30 to 300 minutes varied from 160 mg kg-1 to 1600 mg kg-1 in the HCl extractant, 320 mg kg-1 to 3040 mg kg-1 in the citric acid extractant, and 160 mg kg-1 to 1120 mg kg-1 in the oxalic acid extractant. The analysis of variance revealed that the effect of the extractant on the amount of released Ca was significant (Table 4). According to the mean comparison results presented in Table 5, the citric acid extractant produced the highest Ca release in vermiculite clay soil. Additionally, citric acid showed the greatest Ca release in the sample overall. In contrast, the oxalic acid extractant resulted in the lowest Ca release. Among the two organic acids, citric acid demonstrated a significantly higher release rate than oxalic acid ($p < 0.01$). Additionally, the difference between HCl and citric acid treatments was significant. The pattern of Ca release during ten continuous extraction steps from vermiculite clay soil using different extractants is illustrated in Figure 3. According to the figure, the Ca release process in all extractants, except for calcium chloride, exhibited a gradual increasing trend. The difference in release rates between the calcium chloride treatment and the other extractants is attributed to the type of extractant used, rather than the properties of the vermiculite clay soil itself.

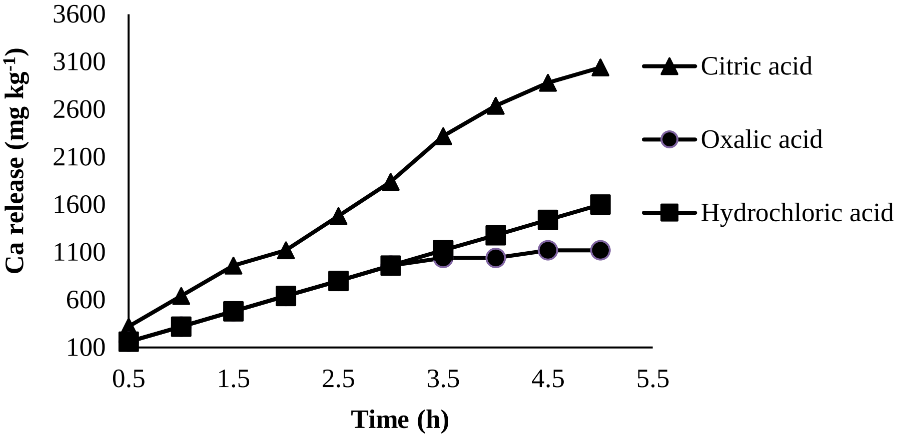

Fig. 3. Calcium release from vermiculite clay soil to four extractants during 5h

3.4. Cumulative Mg Release

The release data presented in Table 3 indicate that the cumulative Mg released from vermiculite clay soil ranged from 96 mg kg^{-1} after half an hour to 192 mg kg^{-1}after five hours when using HCl as the extractant. In contrast, the cumulative Mg release ranged from 240 to 1872 mg kg^{-1} with calcium chloride, 336 to 1776 mg kg^{-1} with citric acid, and 48 to 528 mg kg^{-1} with oxalic acid. The results of the variance analysis (Table 4) indicate that the effect of the extractant on the amount of released Mg is significant ($p < 0.01$). According to the mean comparison results (Table 5), calcium chloride extractant exhibits the highest Mg release rate in vermiculite clay soil, whereas oxalic acid extractant shows the lowest release rate. Among the organic acids tested, citric acid exhibited a higher release rate than oxalic acid. The mean comparison results indicated that the difference between the HCl treatment and oxalic acid was significant; however, the difference between calcium chloride and citric acid extractants was not significant (Table 5). Figure 4 illustrates the variation in Mg concentration in vermiculite clay soil over ten consecutive extraction steps using different extractants. The Mg concentration varied among the extractants, with calcium chloride showing the highest efficacy in extracting Mg, while HCl exhibited the lowest. During the release process, calcium chloride and citric acid showed an increasing trend in Mg concentration, whereas treatment with oxalic acid displayed a relatively decreasing trend (Fig. 4).

Conversely, in the HCl extractants, the release rate nearly reached equilibrium after three hours, and the amount released became negligible.

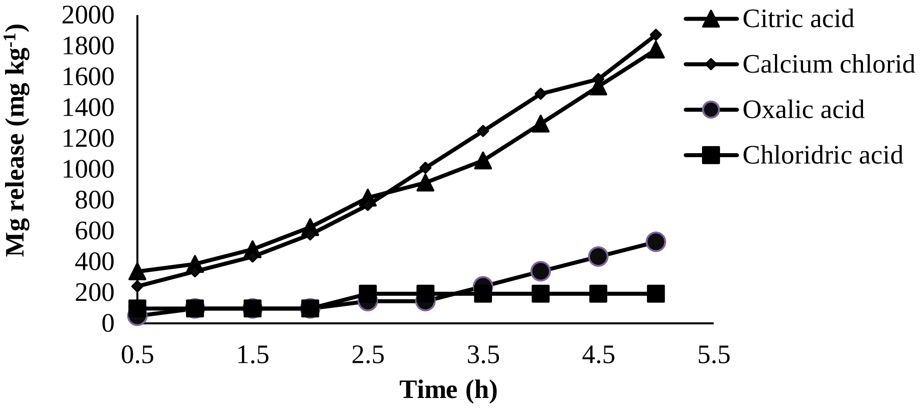

Fig. 4. Mg release from vermiculite clay soil to four extractants during 5h

3.5. Description of K, Ca, and Mg Release by Different Kinetic Models

The data on element release stages were analyzed using Elovich, parabolic diffusion, power function, zero-order, and first-order equations to evaluate the rate of element release (see Table 6). Based on the coefficient of determination and the standard error of the kinetic models employed, the power function, parabolic diffusion, and Elovich models demonstrated superior ability to accurately represent the release rates of K, Ca, and Mg. Although the zero-order equation exhibited a high coefficient of determination, it was unable to adequately describe nutrient release due to its high standard error. The first-order equation also failed to adequately describe the release because of its low coefficient of determination; therefore, it was not discussed further. As shown, for the K element, the power function equation demonstrated the highest coefficient of determination—an average of 0.99 across all extractants—and the lowest standard error, making it the most effective model. Specifically, the HCl extractant exhibited the highest coefficient of determination ($R^2 = 0.99$) and the lowest standard error (SE = 0.4), corresponding to the greatest release rate. The parabolic diffusion equation exhibited the highest coefficients of determination for the various extractants: calcium chloride ($R^2 = 0.99$), HCl ($R^2 = 0.98$), oxalic acid ($R^2 = 0.97$), and citric acid ($R^2 = 0.95$), respectively. In the Elovich equation, the highest coefficient of determination ($R^2 = 0.94$) and the lowest standard error (SE = 4.5) were observed with the $CaCl_2$ extractant.

In the case of the Ca element, the highest coefficient of determination and the lowest error corresponded to the power function equation, parabolic difusion, and the Elovich equation, respectively. The power function equation exhibited the highest coefficient of determination ($R^2 = 1$) and the lowest standard error (SE = 0.02) when applied to the HCl extractant.

In the Ca element diffusion equation, the highest coefficient of determination ($R^2 = 0.97$) was observed for hydrochloric acid and oxalic acid extractants. Similarly, the Elovich equation showed its highest coefficient of determination ($R^2 = 0.96$) with the oxalic acid extractant. The lowest coefficient of determination ($R^2 = 0.85$), accompanied by the highest standard error (SE = 4090), was observed for the Elovich equation in the $CaCl_2$ extractant. As mentioned earlier, the data related to the calcium chloride extractant cannot be relied upon to estimate Ca content due to the properties of the extractant.

An examination of the coefficients in the equations for the magnesium element showed that the power function, parabolic, and Elovich equations were able to describe the release rate of Mg effectively, respectively (see Table 6).

In the power function equation, the coefficients of determination (R^2) and standard errors (SE) for the various extractants were as follows: HCl had an R^2 of 0.70 and an SE of 26.9; $CaCl_2$ had an R^2 of 0.95 and an SE of 121.1; citric acid had an R^2 of 0.92 and an SE of 151.4; and oxalic acid had an R^2 of 0.84 and an SE of 81.5. Therefore, the $CaCl_2$ extractant, with the highest coefficient of determination, was able to more accurately describe the release of Mg despite having a relatively high standard error. In the parabolic dispersion equation, the highest coefficient of determination ($R^2 = 0.92$) was observed with the calcium chloride extractant. The lowest coefficient of determination ($R^2 = 0.63$), accompanied by a standard error of 104, was observed with the oxalic acid extractant in the Elovich equation. In general, the power function equation provided the best description of the release for all three elements. Specifically, K release was best described using HCl as the extractant; Ca release was best described using both HCl and citric acid extractants; and Mg release was best described using the citric acid extractant.

Table 6. Determination coefficients and standard error of kinetic models for K, Ca, and Mg release of vermiculite clay soil

Kinetic models	Element	0.01 M HCl		0.01 M $CaCl_2$		0.01 M citric acid		0.01 M Oxalic acid	
		R^2	SE	R^2	SE	R^2	SE	R^2	SE
Elovich	K	0.91	14.60	0.94	4.5	0.85	17.60	0.88	10.1
Parabolic diffusion		0.98	6.40	0.99	1.4	0.95	10.30	0.97	5.2
Power function		0.99	0.40	0.99	0.6	0.99	4.30	0.99	2.0
Elovich	Ca	0.90	157.80	0.85	4090.0	0.86	373.00	0.96	68.7
Parabolic diffusion		0.97	75.30	0.94	2405.0	0.95	226.00	0.97	59.7
Power function		1.00	0.02	0.98	592.0	0.98	140.08	0.97	99.2
Elovich	Mg	0.70	241.00	0.82	254.3	0.79	238.00	0.63	104
Parabolic diffusion		0.74	26.50	0.92	161.7	0.90	161.00	0.76	83.3
Power function		0.70	26.90	0.95	121.0	0.90	151.04	0.84	81.5

The constants of the kinetic equations used to describe the release rates of K, Ca, and Mg are presented in Table 7. In this context, the slope of the equation (b) represents the rate of interlayer element release, while the intercept (a) indicates the maximum or initial rate of nutrient release. As shown, for the K element, the highest release rate (b) in the parabolic equation was associated with the HCl extractant, measuring 94.3 mg kg^{-1} $h^{-1/2}$, while the lowest release rate (b) was linked to the $CaCl_2$ extractant, recorded at 35.2 mg kg^{-1} $h^{-1/2}$. In the parabolic equation, the highest initial release (a) was observed in the vermiculite treatment with the citric acid extractant, at 64.4 mg kg^{-1}, whereas the lowest release was seen with the $CaCl_2$ extractant, at 18.1 mg kg^{-1}. In the Elovich equation, the highest K release rate was observed with the HCl extractant, measuring 62.2 mg $kg^{-1}h^{-1}$, while the lowest rate was observed with the $CaCl_2$ extractant, measuring 23.4 mg $kg^{-1}h^{-1}$. The highest initial release rate (a) in this equation was also obtained with the HCl extractant, equal to 40.2 mg kg^{-1}. In the power function equation, the highest release rate (0.9 mg $kg^{-1}h^{-1}$) and initial release (3.5 mg kg^{-1}) were observed with the HCl extractant.

The constants of the kinetic equations used to determine the Ca release rate showed that the highest release rate (b) in the parabolic equation was associated with the citric acid extractant (1900 mg $kg^{-1}h^{-1/2}$), while the lowest release rate was linked to the oxalic acid extractant (869.8 mg $kg^{-1}h^{-1/2}$). The highest initial release rate (a) was observed in the parabolic model using citric acid as the extractant (1314.7 mg kg^{-1}), while the lowest initial release rate was recorded in the parabolic model with oxalic acid as the extractant (327.9 mg kg^{-1}). The highest release rate in the Elovich equation was observed with the citric acid extractant (1241 mg kg^{-1} h^{-1}), while the lowest was observed with the oxalic acid extractant (469.4 mg kg^{-1} h^{-1}). The highest initial release was also recorded for citric acid (689.6 mg kg^{-1}), and the lowest initial release was observed with HCl (366 mg kg^{-1}). In the power function equation, the results were consistent, with citric acid exhibiting the highest release rate and initial release.

Table 7. Kinetic models constants for K, Ca, and Mg release of vermiculite clay soil

Extractant	Element	Power function		Parabolic diffusion		Elovich	
		a mg kg^{-1}	b mg $kg^{-1}h^{-1}$	a mg kg^{-1}	b mg $kg^{-1}h^{-1/2}$	a mg kg^{-1}	b mg $kg^{-1}h^{-1}$
HCl	K	3.5	0.9	58.8	94.3	40.2	62.2
$CaCl_2$		2.8	0.8	18.1	35.2	18.7	23.4
Citric acid		3.1	1.0	64.4	85.9	26.4	55.7
Oxalic acid		3.0	0.9	36.9	56.2	22.3	37.8
HCl	Ca	5.7	1.0	-639.6	956.5	366.0	628.9
$CaCl_2$		8.0	1.3	-1663.0	19535.0	4081.8	1255.0
Citric acid		6.4	0.9	1314.7	1900.0	689.6	1241.0
Oxalic acid		5.7	0.8	-327.9	869.8	384.3	469.4
HCl	Mg	4.6	0.4	17.9	85.3	170.0	56.8
$CaCl_2$		5.8	0.9	-796.6	1102.7	374.8	710.0
Citric acid		6.0	0.7	-567.0	937.0	431.5	599.6
Oxalic acid		4.3	0.9	-238.8	286.3	70.0	178.0

The constants of the kinetic equations used to describe the Mg release rate indicated that the highest release rate (b) was associated with the $CaCl_2$ extractant, measuring 1102.7 mg $kg^{-1}h^{-1/2}$ in the parabolic equation. Conversely, the lowest release rate was recorded for the HCl extractant, at 85.3 mg $kg^{-1}h^{-1/2}$. The highest and lowest initial release values (a) in the parabolic equation were observed with the $CaCl_2$ extractant, at 796.6 mg kg^{-1}, and the HCl extractant, at 17.9 mg kg^{-1}, respectively. In the Elovich equation, the highst release rate of 710 mg kg^{-1} h^{-1} was observed with the $CaCl_2$ extractant, while the lowest release rate of 178 mg $kg^{-1}h^{-1}$ was observed with the oxalic acid extractant. Similarly, the highest initial release (374.8 mg kg^{-1}) occurred with $CaCl_2$, and the lowest with oxalic acid. The results from the power function equation were consistent with these findings, indicating that $CaCl_2$ had the highest release rate and initial release.

3. 6. Clay Mineralogy of Vermiculite Clay Soil under Different Extractants

Semi-quantitative X-ray diffraction analysis before treatment reveals vermiculite as the primary phase (61%), accompanied by muscovite (13%), talc (5%), dolomite (5%), calcite (8%), and gypsum (1%) as minor impurities (Fig. 1). The presence of vermiculite is confirmed by reflection peak intensities at 7.2, 3.59, and 1.69 Å. Peaks at 3.4 and 2.8 Å, corresponding to quartz and dolomite, respectively, are also observed as impurities (Fig. 1). As shown in Figure 5, the mineralogical results illustrate the rapid release of K and Mg from vermiculite clay soil using various extractants. Comparing the graphs for each extractant with the pre-treatment data reveals changes in the vermiculite clay content. The peaks at 2.85, 3.3, and 4.6 Å indicate the presence of dolomite and quartz minerals, which are clearly visible impurities in all treatments. In Figure 5a, the peak at 6.9° 2θ observed in the Mg and ethylene glycol treatment indicates the presence of vermiculite clay in the HCl treatment. The peaks at 9.8 and 9.12 Å, appearing at angles between 7.8° and 9.5°, correspond to the second-order reflections of smectite minerals, exhibiting very high counting intensities (above 160,000) following HCl treatment. The gradual increase in HCl concentration over ten steps resulted in the replacement of K ions with hydrogen ions, causing the expansion of vermiculite layers and the release of K from between the layers. Consequently, this process induced significant changes in vermiculite clay within a very short time. It can be concluded that this led to the formation of a vermiculite-smectite mixed mineral.

The second phase of vermiculite (6.9 Å) is faintly visible in the magnesium saturation treatment, but its size remains unchanged in the ethylene glycol treatment. Therefore, it can be concluded that, under the influence of HCl, the clay has transformed into an intermediate vermiculite-smectite clay. Figure 5b pertains to the $CaCl_2$ treatment, where the peak intensity is significantly lower than that of the HCl treatment (40,000 counts compared to 160,000), indicating a substantially reduced release of K in the $CaCl_2$ treatment. The third-order peak of vermiculite in the $CaCl_2$ treatment remains unchanged in intensity compared to before the treatment. In this extract, the quartz peaks at 3.3 and 4.6 Å, as well as the dolomite peak at 2.85 Å, are still present.

In Figure 5c, the presence of a 9.8 Å peak at an angle between 8.7° and 9.5° indicates the second-order reflection of the smectite mineral, exhibiting a very high-count intensity (above 160,000) in the citric acid treatment. The intensity of the second-order reflection of vermiculite has decreased, falling below 20,000. In contrast, the intensity of the smectite second-order peak

(8 to 9 Å) is significantly higher in the citric acid treatment (approximately 160,000) compared to the $CaCl_2$ treatment (approximately 50,000) (Figure 5c). The release of K in the citric acid and HCl treatments is greater than that in the $CaCl_2$ treatment and the oxalic acid sample (Figure 5d), enabling for a clearer observation of changes in the amount of vermiculite.

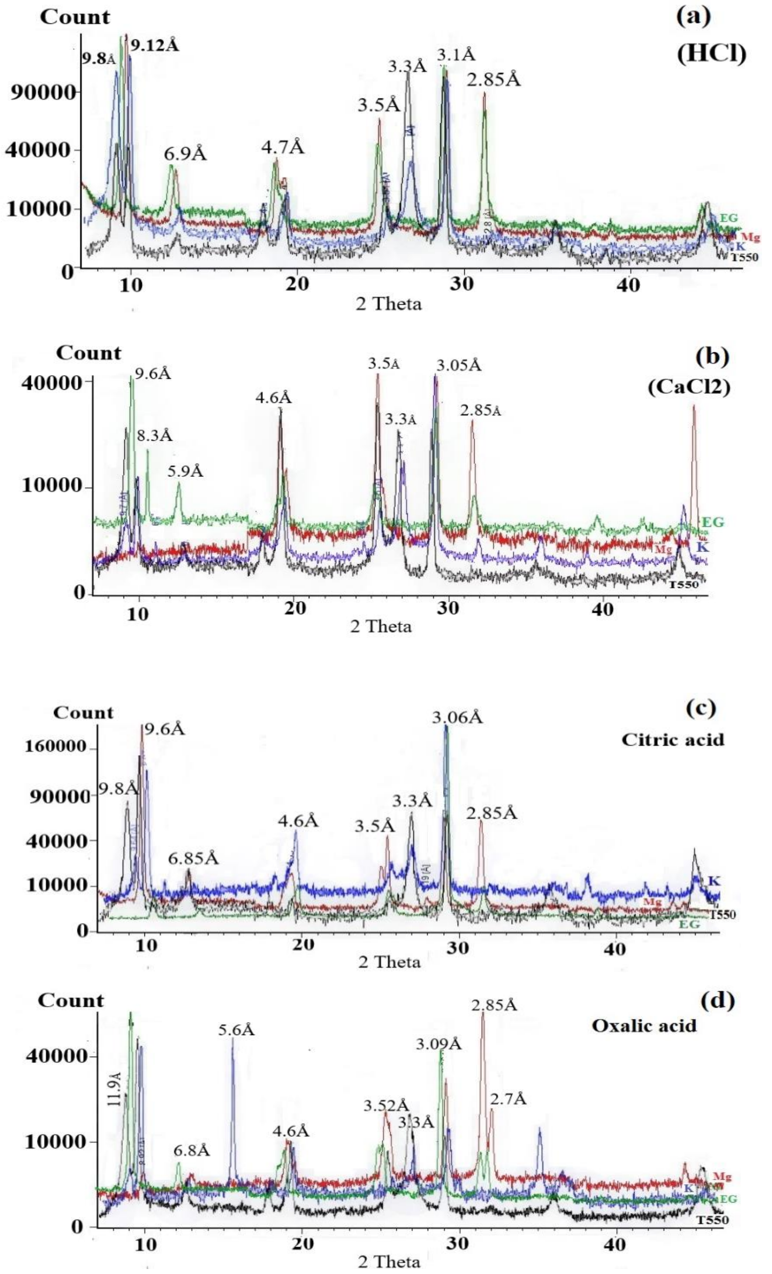

Fig. 5. X-ray diffraction pattern of vermiculite clay samples after treatment with different extractants.

4. Discussion

According to the mean comparison results among treatments, HCl and $CaCl_2$ extractants exhibited the highest and lowest K release amounts from vermiculite clay soil, respectively. In the short-term experiment, HCl, citric acid, $CaCl_2$, and oxalic acid extracted 14.6%, 12.7%, 5.7%, and 8.6%, of non-exchangeable K, respectively, indicating that HCl was more effective than the other solutions in extracting K from vermiculite clay soil. Organic acids, specifically citric acid and oxalic acid, exhibited higher K release rates compared to $CaCl_2$. Notably, citric acid was more effective in releasing K than oxalic acid, with release rates of 12.7% and 8.6%, respectively. Different solutions extracted K from minerals through cation exchange or mineral dissolution mechanisms. Hashemi and Najafi-Ghiri (2024) reported that the amount of K released increased with $CaCl_2$ extractant over the long term, which contrasts with the findings of the present study conducted over a shorter duration (256 hours vs. 5 hours). As shown in Table 5, the primary factor controlling the release rate is the type and concentration of the extractant used. Kong *et al*. (2014) noted that the ability of inorganic acids, such as HCl and sulfuric acids, to dissolve soil minerals and release soil K may be equal to or greater than that of organic acids like citric and oxalic acids. Researchers (Bahreini Touhan *et al.,* 2010; Mousavi *et al.,* 2014) have reported that organic acids, particularly citric acid, are more effective than calcium chloride at releasing K from calcareous soils and K-containing minerals. The release of K from vermiculite clay soil during ten continuous extractions demonstrated that the rate of K release is high in the initial stages and may continue at a constant rate after five hours, if it persists. The initial rapid release is attributed to the edge and wedge-shaped regions of the minerals. Additionally, the decrease in the release rate can be linked to the higher energy level of K absorption between the layers, the greater distance of K ions from the edges of minerals such as mica, vermiculite, and mixed clays, and the increased diffusion distance (Srinivasarao *et al*., 1999; Najafi-Ghiri *et al.,* 2020). Since the K present at the edge of the mineral is released first in vermiculite clay soil, it is expected that the maximum slope of the release curve will occur at the beginning of the experiment. Similar findings regarding this process have been reported in other studies on K release (Hashemi and Najafi-Ghiri, 2024). Basak *et al*. (2021) investigated the use of mineral rock powders as fertilizers for the release of K and several micronutrients. They found that the release rate of K was initially very high but sharply decreased after 45 days. This decline continued gradually until the 90th day. The highest cumulative release of K was observed in the powder sample with the smallest particle size. Overall, the results indicate that the primary mechanism for K release from calcareous soils during acid extractions, as well as in solutions containing Ca, involves the exchange reaction of K with Ca and Mg, which contribute to carbonate dissolution. Additionally, citrate can dissolve minerals containing K and release K in slightly calcareous soils (Li *et al*., 2015). Similar mechanisms of K release have been observed in vermiculite clay soils.

The analysis of variance revealed that the effect of the extractant on the amount of released Ca is significant. According to the mean comparison results for Ca, the citric acid extractant exhibited the highest release of Ca in vermiculite clay soil, regardless of the results obtained with $CaCl_2$. This may be attributed to the fact that the $CaCl_2$ extractant itself has been reported to contain higher levels of Ca. Moreover, the oxalic acid extract exhibited the lowest amount of Ca release. Citric acid demonstrated a higher release rate compared to both oxalic acid and HCl, with significant differences observed. Li *et al.* (2015) reported an increase in Ca release due to organic acids (citric acid and oxalic acid) in calcareous soils. The concentration of Ca in the oxalic acid extract was lower than that in HCl, which may be attributed to the precipitation of calcium oxalate (Strom *et al.,* 2005).

The results of the variance analysis indicated that the effect of the extractant on the amount of released Mg was significant. According to the mean comparison of Mg across different treatments, the $CaCl_2$ extractant exhibited the highest Mg release rate in vermiculite clay soil, while the HCl extractant demonstrated the lowest release rate. Additionally, citric acid exhibited a higher release rate compared to oxalic acid. The mean comparison results revealed that the differences between the treatments with HCl and oxalic acid were significant. The presence of Mg ions in the $CaCl_2$ extract may result from the release of Mg from the fine pores of the soil and the dissolution of magnesium carbonates (Najafi-Ghiri *et al*., 2018). Although hydronium ions (H^+) released from HCl and citric acid can dissolve soil carbonates and release Ca^{2+} and Mg^{2+} ions, citrate can complex with Mg^{2+} ions in clay minerals such as smectite and illite, thereby increasing their concentration in solution (Golubev *et al*., 2006). Consequently, citric acid is more effective than HCl in extracting Mg from vermiculite clay soil. In the release of Ca and Mg following $CaCl_2$ treatment, citric acid has demonstrated greater efficacy compared to other treatments. The release rate of elements is influenced by both the specific element being studied and the type of acid used. Specifically, citric acid facilitates a greater release of Ca compared to oxalic acid. Organic acids with low molecular weights that contain a higher number of carboxyl and hydroxyl functional groups exhibit a stronger tendency to form complexes with certain metal ions found in mineral structures, thereby enhancing their analysis (Jones, 1998). Based on this information, citric acid, which contains six carboxyl functional groups, appears to be more effective at releasing Ca and Mg from the vermiculite clay structure than oxalic acid, which has only two functional groups (Albert and Serjean, 1984). Furthermore, a comparison of the dissociation constants of the two organic acids—oxalic acid (pKa1 = 1.25 and pKa2 = 3.81) and citric acid (pKa1 = 3.13 and pKa2 = 4.76)—indicates that oxalic acid is more acidic. Therefore, if the release rate of Ca and Mg from the studied mineral depends on the strength of the acid used, we would expect the release rate of these elements in the sample treated with oxalic acid to be greater than that in the sample treated with citric acid. However, the results of this study indicate that the release rate of Ca is actually higher in the citric acid treatment. Mohammad Jafari *et al.* (2015) investigated the effect of two types of organic acids on the release rate of Mg from sepiolite mineral. The results indicated that the amount of Mg released from samples treated with citric acid was higher than that from samples treated with oxalic acid. The findings of the current study further corroborate these results. Genagh *et al.* (2016) investigated the effects of two types of organic acids on the release of silicon, Mg, and iron from bentonite minerals. They concluded that the release of Mg in samples treated with citric acid was significantly higher than in those treated with oxalic acid. Conversely, the release of silicon and iron in samples treated with oxalic acid was significantly higher than in those treated with citric acid. The results indicated that the $CaCl_2$ extractant had the highest capacity for extracting Mg, while the HCl extractant showed the lowest capacity.

As shown in the results, the power function, parabolic diffusion, and Elovich models effectively describe the release rates of K, Ca, and Mg in a more systematic manner (Hashemi and Najafi-Ghiri, 2024). Another study on K release from soil incubated with organic manures indicated that the first-order, Elovich, and power function equations not only provided the best fit but also exhibited high K release rate (b) values (Taiwo *et al*., 2018).

The high R^2 value in the power function equation, followed by parabolic diffusion for the K, Ca, and Mg, indicates the release of these elements from interlayer sites and their diffusion into the solution. The release of non-exchangeable K in this clay soil is primarily governed by the dispersion process (da Silva *et al*., 2013). Additionally, the high coefficients of the Elovich equation for Ca suggest that surface adsorption mechanisms contribute to Ca release, but, in certain specific circumstances, the publication process has also played a complementary role.

The values of b, which represent the K release rate, are critical in equations that more accurately reflect the kinetics of K release. The highest b value in the parabolic equation corresponded to the HCl extractant, whereas the lowest value in the power function equation was associated with the $CaCl_2$ extractant. Acidification caused by the H^+ ions from hydrochloric acid destabilizes the mineral surfaces of clay and releases cations, such as K, from the mineral structure (Lei *et al*., 2015). In the power function equation, the coefficient b for the extractants is less than one, indicating that the rate of non-exchangeable K release decreases over time. The parameter a represents the release rate of K during the initial time period (0.5 hours) or the initial amount of K released. Consequently, the highest and lowest release rates (a) were observed in the parabolic and power function equations, respectively, for vermiculite treated with citric acid and $CaCl_2$ extractants. Hashemi and Najafi-Ghiri (2024) concluded that the highest K release rate in the Elovich equation was associated with the treatment of vermiculite using lime in the $CaCl_2$ extractant, measuring 261 mg $kg^{-1}h^{-1}$. Conversely, the lowest release rate was observed in the treatment of vermiculite without lime using the citric acid extractant, which was 63.8 mg $kg^{-1}h^{-1}$. da Silva *et al*. (2013) conducted a study on K release from phlogopite clay, utilizing three kinetic models: parabolic, power function, and Elovich equations. The power function exhibited the highest coefficient of determination and the lowest standard error. The results showed that the slow release of K from interlayer positions in mica, including vermiculite, is the primary process controlling the release rate.

Based on the coefficient of determination and the standard error of the kinetic models, the HCl extractant demonstrated the greatest ability to facilitate the release of Ca, as evidenced by the highest coefficient of determination and the lowest standard error. Furthermore, the highest and lowest release rates (b) were observed with citric acid and oxalic acid extractants, respectively, in the parabolic and power function equations. The carboxyl groups in citric acid interact with mineral surfaces, facilitating the leaching and release of nutrients, including Ca, into the soil solution (Liu *et al*., 2016; Njafi Ghiri *et al*., 2018). The lower release rate observed with oxalic acid is attributed to the precipitation of Ca as calcium oxalate (Strom *et al*., 2005). The highest initial release rate (a) was observed in the parabolic equation using citric acid as the extractant, while the lowest release rate was recorded in the parabolic equation with HCl as the extractant.

The Elovich, parabolic, and power function equations effectively described Mg release. Among the extractants, CaCl2 exhibited the highest coefficient of determination and the lowest standard error, indicating its superior ability to explain Mg release. The highest and lowest b values were associated with the $CaCl_2$ and HCl extractants in the parabolic and power function equations, respectively. Additionally, the highest and lowest initial release rates (a) were observed in the Elovich and parabolic equations, respectively. The presence of Mg ions in the $CaCl_2$ extract may result from the release of Mg from the soil's fine pores and the dissolution of magnesium carbonates. Additionally, hydronium ions (H^+) derived from hydrochloric acid and citric acid can dissolve soil carbonates, releasing both Ca and Mg. Citrate can complex with Mg ions from clay minerals such as smectite and illite, thereby increasing their concentration in the solution (Golubev *et al*., 2006). Therefore, the ability of citric acid to extract Mg from vermiculite ore is greater than that of HCl (Najafi-Ghiri *et al*., 2018). The release of Mg from the vermiculite clay soil is primarily influenced by the complexation properties of the organic acids under study.

The results showed that sequential release partially converted vermiculite into smectite mineral. Although the conversion was incomplete, a mixed vermiculite-smectite mineral was formed. The extent of this conversion was greater with the two extractants, citric acid and HCl. The peaks at 2.85, 3.3, and 4.6 Å indicate the presence of dolomite and quartz minerals, which are clearly visible impurities in all treatments (Moore & Reynolds, 1989). The second phase of vermiculite (7.12 Å) is faintly visible in the magnesium saturation treatment, but its size remains unchanged in the ethylene glycol treatment. The gradual increase in HCl concentration over ten stages led to the replacement of K^+ ions with H^+ ions, causing the vermiculite layers to expand and releasing K^+ from between the layers. This process rapidly induced significant changes and transformations in the vermiculite, resulting in the formation of a mixed vermiculite-smectite mineral (Li *et al.*, 2015; Hashemi and Najafighiri, 2024). The acidic conditions created by HCl and citric acid play a crucial role in the transformation of vermiculite into mixed minerals. Some researchers have also stated that minerals may dissolve and release elements when H^+ ions infiltrate their structures (Li *et al.*, 2015). Research has shown that sequential extraction of K and Mg using citric acid over 15 cycles leads to the dissolution of trioctahedral minerals present in the silt and clay fractions of the soil. This process subsequently transforms dioctahedral mica minerals into vermiculite (Simard *et al.*, 1992). The increase in the intensity of the second-order smectite peaks (9.12 to 9.8 Å), coupled with the decrease in the second- (7.2 Å) and third-order peaks (3.54 Å) associated with vermiculite, as revealed by X-ray analysis of HCl and citric acid extracts, clearly indicates a greater release of K and Mg by these acids. Additionally, the carboxyl groups in citric acid interact with mineral surfaces, facilitating the release and mobilization of nutrients into the soil solution (Shabtai *et al.*, 2024). The release of K from wedge-shaped regions and interlayer positions during the short-term period leads to the expansion of the smectite layer due to the increased presence of Ca and Mg ions in the solution (Srinivasarao *et al.*, 1999; Najafi Giri *et al.*, 2018). However, because the release period is brief, the conversion is not complete. If the release continues for an extended period, mineral transformation will occur.

In general, the comparison of graphs related to different extractants confirms the results of K and Mg release from vermiculite clay. In the $CaCl_2$ extractor, the reduction in the intensity of the second and third vermiculite peaks was less pronounced; however, an increase in the intensity of the smectite peaks was observed. Therefore, it can be concluded that K release in this extractor was lower, whereas Mg release occurred. The presence of Mg ions in $CaCl_2$ extraction may result from the diffusion of Mg from soil micropores and the dissolution of magnesium carbonates. (Najafi Giri *et al.*, 2018). The primary mechanism driving the release of these elements is the transformation of vermiculite into smectite and vermiculite–smectite mixed minerals.

5. Conclusion

Organic and inorganic extractants were used to release potassium (K) and magnesium (Mg), essential nutrients for plants, from a naturally available source—vermiculite clay soil. The study results showed that, within a short period, hydrochloric acid extractant had the greatest effect on releasing K, while $CaCl_2$ was most effective in releasing Mg. Among the two organic acids used, citric acid was more effective than oxalic acid in releasing all three elements. These results indicate that the slow release of K from the interlayer positions of vermiculite clay soil is the primary mechanism controlling the release rate. The high coefficients in the parabolic equation for both K and Mg indicate that the release of these elements is governed by diffusion. The release of K and Mg causes the vermiculite mineral to transform into intermediate minerals and smectite, thereby reducing the amount of this clay.

In summary, these findings can guide informed decisions regarding the use of vermiculite clay soil as a natural source of K, and Mg nutrients needed for plants. Since citric acid is a more effective extractant for all three elements, it is advisable to investigate its use in extracting these nutrients in a test plot for plants with high nutritional demands for K and Mg.

Authors' contribution

Conceptualization, S.S.H. and Y.Ch.; methodology, S.S.H.; software, S.S.H. and Y.Ch.; validation, S.S.H and Y.Ch.; formal analysis, S.S.H. and Y.Ch.; investigation, S.S.H. and Y.Ch.; resources, S.S.H. and Y.Ch.; data curation, S.S.H. and Y.Ch.; writing—original draft preparation, S.S.H.; writing—review and editing, S.S.H.; visualization, S.S.H.; supervision, S.S.H; project administration, S.S.H.; funding acquisition, S.S.H., Y.Ch., and Z.V.Kh.; All authors have read and agreed to the published version of the manuscript.

Data availability

Data available on request from the authors.

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Ethical considerations

The authors avoided from data fabrication and falsification.

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Conflict of interest

The authors declare no conflicts of interest

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