The effect of the leaching process on the kinetics of magnesium dissolution for soils of different use

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ABSTRACT

The study was conducted to describe the behavioral processes that liberate magnesium as a result of its dissolution from salts and minerals carrying it in unconsulted natural soil columns. Not exploited agriculturally ("abandoned") and leached with different types of water (distilled water, river water, well water) and for six porous volumes by the method of continuous and intermittent leaching, The results showed an increase in the amount of magnesium liberated from the process of dissolving salts and minerals and supplying the equilibrium solution with the duration of water flow through the soil columns by increasing the ionic strength, as well water outperformed the rest of the used water types, and the intermittent leaching treatment showed more liberation than the continuous leaching factor, as the amount of magnesium reached The liberated from dissolution by continuous leaching was (0.042-1.872) cmol kg^{-1} of soil in the site of the abandoned soil, while it reached (0.032-3.282) cmol kg^{-1} of soil by intermittent leaching in the site of soil treated with well water, The mathematical description of the liberation process showed the presence of two paths controlling the dissolution process, the first being a rapid reaction representing the easy-to-dissolve salts, and the second in which the dissolution paths were consecutive and took a straight shape representing the liberation from the melting of the metal. And the force function equation, The Elovich equation showed the lowest value of the melt speed coefficient, which reached (47.0 and 17.0) cmol kg^{-1} min^{-1} in the abandoned soil treated with distilled water by the continuous and intermittent leaching method, respectively, while the highest value of the melt speed coefficient reached (9877.0-4880.0) cm kg^{-1} min^{-1} at the site of vegetable soil treated with well water by continuous and intermittent leaching method, respectively.

Key Words : Magnesium, Leaching, Continuous, Discontinuous

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Introduction

Leaching is the process of transferring salts from the soil during the water entering the soil body and penetrating it to its depths. This process includes two stages, the first includes the process of dissolving salts, ions and soluble mineral components inside the soil body during and after entering the water and filling the pores of the soil. The second is the removal of these mineral components and the leaching of ions or dissolved salts and their displacement and transfer outside the soil body and movement or removal of the leaching water after it has exceeded the limit of soil saturation (Alhadede et al., 2022). The process of dissolution of salts and other ionic species takes place when water enters the soil pores, and displacement occurs when the leaching water is drained out of the soil body, as the volume of water required and necessary for leaching and dissolving is divided into two parts. It means the ability of the soil to retain water. As for the second part, it expresses the volume needed to displace the solute from the layer to be leached or the brine, and it is greater than the capacity of the soil to retain water in order to achieve its removal and transfer of dissolved salts (Al-Hassani, 2007), The leaching process is one of the complex processes that occur between the soil and the leaching water, as it includes continuous interactions between the leaching water and the soil colloids and their mutual positive ions. Leaching water after saturating the soil (Al-Hadethi and Al-Falahi, 2019), Research conducted on the reclamation of saline soils indicates that there are two types of leaching, the first being (Continues) and the second intermittent (Discontinues). In order to obtain salt leaching in the shortest period of time, regardless of the volume of the leaching water, continuous leaching is the most efficient, and if the opposite is desired, the intermittent leaching method is the most efficient (Abboud and Salman, 2014). The use of water, whether for irrigation or reclamation, will lead to changes in the ionic composition of the soil solution, resulting in the liberation of ions such as sodium, potassium, calcium and magnesium, and their leaching depending on the ionic composition of the water passing through the soil body through the ion exchange that occurs during a short period or the dissolution of minerals in the long term (Al-Obaidi et al., 2012 and al-Obaidi et al., 2017). And the dissolution of salts and the liberation of different ionic species or their precipitation and thus their separation from the liquid soil phase depending on the properties of the soil. The passage of water in the soil body and the volumes of drained water (Nafawah et al., 2007 and Al-Hadidi, 2021), The amount of magnesium carried by the water that enters the soil body, whether it comes from water or dissolved manure, will affect the processes of liberation and adsorption, which are considered among the dominant and influential processes in the balance of dissolved magnesium, as the sites and surfaces remain with heterogeneous concentrations due to the lack of complete mixing between the added amount of magnesium Water and soil, which encourage the diffusion process (Alrawi and Alhadede, 2022). Ghosh and Debjani (2010) indicated that a decrease in the dissolved and mutual content due to biological leaching and depletion processes below the release threshold will promote demineralization, Accordingly, there will be an expansion of the intermetallic distances of the metals at their worn edges, and the primary metals will turn into secondary metals (Mengel, 2007). And the speed of its liberation by weathering does not depend on the soil content of primary minerals only, but also on the type of mineral layers, its crystalline dimensions, the arrangement of hydroxyl groups, the chemical composition of the mineral, the layer charge variation and its relationship to weathering (Sparks, 2003). While Datta and Satary (1989) see that the continued depletion of ions and the decrease of their content in the liquid soil phase to the threshold level (Threshold value) is the determining factor for the renewal of the soil solution through the release of non-exchanged ions, which is heading towards the reciprocal phase to be liberated again to water current based on Capon's coefficient of preference (Ghosh and Debjani, 2010), The intermittent leaching process gave a period of rest for the melting of the scarce salts according to the phenomenon of (salt inheritance) compared to continuous leaching, which made it more efficient than continuous leaching (Al-Hadidi and Al-Obaidi, 2021), Mengel (2007) indicated that it is necessary to calculate the liberated amount of the elements for the solid phase and use the rate coefficient to study the release of nutrients from the soil. The duration of water flow is an important factor in explaining many of the kinetic reactions of the processes of liberating ions, including magnesium from the soil, and given the importance of water in agriculture and its role in many interactions, including (ion exchange, dissolution, sedimentation), the study aims at the role and quality of water in The liberation of magnesium by dissolving the metals carrying it by the method of continuous and intermittent leaching according to the kinetic approach with determining the speed of dissolution.

Research materials and methods

Four location were selected in Nineveh Governorate / northern Iraq on the basis of the variation in the nature of agricultural exploitation (two location in the Baybukht area of Bashiqa district, the first planted with wheat and irrigated by rain water, the second planted with vegetables irrigated with well water, the third location for agriculturally unexploited (abandoned) soil, and the fourth site in the forests of Mosul), A composite soil sample was taken from each location in addition to natural (unconsulted) soil columns with a length of 20 cm and a radius of 3.5 cm and treated with different types of water (distilled water, Tigris river water, well water) to study the behavior and release of magnesium by flow method Quiet at different pore sizes by the methods of continuous and intermittent leaching. The physical and chemical analyzes of soil and water samples were carried out according to the methods mentioned in (Salem and Shawky, 2017), including: pH, EC, Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{-2}, $CaCO_3$, CEC, Organic matter, soil texture Table (1), and water samples were classified according to the American Salinity Laboratory (Richards, 1954) Table (2), the water samples were allowed to pass quietly through the soil columns for the purpose of leaching the column while maintaining a constant level of the compressor water column (5) cm above the soil surface in the continuous immersion system, The time of the first equilibrium filtrate drop was recorded until the first pore volume was collected, which was divided into four stages (Pv0.25, Pv0.5, Pv0.75, and Pv1.0) for all soil location. The time of reaching each pore size of the columns, but in the case of intermittent leaching, the same process was repeated until the first pore size was reached. Then the soil column is left for ten days to dry and then re-moistened until the second pore size is obtained. This process was repeated six times until the sixth pore size and the time required to collect each pore size was recorded. In both washings, the following was done:

1- Determination of the amount of magnesium in the equilibrium solution by titration method with EDTA-2Na standard solution and expressed as S(Mg).
2- Calculating the amount of exchanged magnesium X(Mg) according to the equation proposed by (Levy, 1980) which states:

$$X(Mg) = ESP \times \frac{CEC}{100} \qquad \text{.............(1)}$$

After calculating the following indicators:

A- Calculate the values of the sodium adsorption ratios (SAR) for equilibrium solutions at each time period from the following equation:

$$SAR = \frac{[Na]}{\sqrt{\frac{[Ca+Mg]}{2}}} \qquad \text{.............(2)}$$

B- Calculate the values of the percentage of exchanged sodium (ESP) at each time period from the following equation:

$$\mathrm{ESP} = 100\,\mathrm{K}\frac{\mathrm{SAR}}{1+\mathrm{SAR}} \quad \text{.............(3)}$$

Where:

K = constant as

3- Calculating the amount of magnesium liberated from the melting of the bearing metals, expressed in the symbol M(Mg), according to the following equation:

M(Mg) = S(Mg) – X(Mg) ……………..(4)

3- The velocity coefficient of the release of the magnesium ion was calculated as a result of the dissolution of the minerals carrying it by subjecting the results to the Eluvig equation, considering the time of water flow through the soil column as a function of the release of ions according to the following relationship:

$C_t = C_0 + \mathrm{KLnt}$ ……………..(5)

Where:

Ct = releasing concentration of magnesium due to metal solubility at time (t)

K = coefficient of velocity of release

t = time (minutes)

Table (1): Some physical and chemical properties of the study soils.

Characteristic	Location				Unit
	Baybukht (vegetables)	Baybukht (wheat)	Waterfalls (abandoned)	Mosul forests	
Clay	502.0	67.5	160.0	364.5	gm kg^{-1}
Silt	312.5	772.0	679.5	257.5	
Sand	185.5	160.5	160.5	378.0	
$CaCO_3$	400	450	455	225	
Organic matter	21.85	13.11	8.40	107.57	
EC	3.35	0.70	1.85	1.55	dS m^{-1}
pH	7.2	7.5	7.4	6.8	
CEC	22.94	20.16	15.30	29.20	c.mol$_c$ kg^{-1}
Ca^{+2}	22.00	5.00	9.50	10.00	mol m^{-3}
Mg^{+2}	11.00	2.04	8.00	4.00	
Na^+	0.36	0.28	1.26	0.75	
K^+	0.18	0.23	0.39	2.07	
Cl^-	2.50	1.50	7.50	7.50	
HCO_3^-	11.10	5.00	8.80	8.50	
SO_4^{-2}	19.94	1.10	1.85	0.82	

Table (2): Chemical analysis of water samples used for leaching

Location	PH	EC	Soluble ions (mmol charge L^{-1})	SAR	classification

		dS.m^{-1}	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}		
river water	7.7	0.5	2.8	2.1	0.5	0.10	3.0	1.8	0.7	0.32	C_2-S_1
water well	7.4	1.2	8.5	3.5	0.2	0.02	6.5	2.5	3.2	0.08	C_3-S_1

Results and discussion

Magnesium liberated from dissolving metals: Table (3 and 4) shows the values of cumulatively liberated magnesium as a result of dissolving the bearing minerals, these values were obtained from the difference between the amount of magnesium measured in the water of the six pore volumes and the values liberated from the exchange sites for the same volumes. The results showed that the amount of magnesium liberated as a result of metal dissolution ranged from (0.042-1.872) cmol kg^{-1}, it was the lowest amount liberated (0.042) cmol kg^{-1} in the left soil treated with distilled water, while the highest amount was recorded (1.872) cmol kg^{-1} In the soil of the vegetable site treated with well water in the case of continuous leaching, while in the case of intermittent leaching**.** The results showed that the amount of magnesium liberated as a result of metal dissolution ranged from (0.032-3.382) cmol kg^{-1}, it was the lowest amount liberated (0.032) cmol kg^{-1} in the left soil treated with distilled water, while the highest amount was recorded (3.382) cmol kg^{-1} In the soil of the vegetable site treated with well water, The difference of soils in the amount of magnesium liberated as a result of the dissolution of minerals is due to the different soils in their mineral and ionic composition, as well as the ionic strength of the water used in the leaching process (Al-Obaidi et al., 2014). It is clear from the results that the amount of magnesium liberated as a result of the dissolution of the minerals carrying it was few in the early stages during the passage of water through the soil columns, while it increased with the successive washing processes and continued until the sixth pore size. This confirms that the liberation process as a result of metal melting is slow and requires long periods of time, and this is consistent with what I obtained (Sultani, 2015). In general, it is noted that the intermittent leaching method is superior to continuous leaching in the amount of magnesium that is collectively liberated as a result of the dissolution of minerals. Increasing the ionic strength directly affects the speed of dissolving carbonate minerals and leaching the ions into the soil solution, meaning that the ionic strength of the water used in the leaching process will be related to the process of dissolving ion-bearing minerals and salts and thus affect the speed of their dissolution and this leads to a change in the ionic composition of the soil solution (kopittke et al., 2006). This is in line with the results of our study, which showed that well water with high ionic strength led to leaching out larger amounts of magnesium compared to river water and distilled water with low ionic strength.

Table (3): The effect of water quality on the amount of liberated magnesium (cmol kg^{-1} soil) by the continuous leaching method.

Location	distilled water			river water			water well		
	S(Mg)	X(Mg)	M(Mg)	S(Mg)	X(Mg)	M(Mg)	S(Mg)	X(Mg)	M(Mg)
vegetables	1.535	0.392	1.143	2.020	0.223	1.797	2.080	0.208	1.872
wheat	0.870	0.358	0.512	0.800	0.137	0.663	0.950	0.208	0.742
abandoned	0.192	0.150	0.042	1.036	0.705	0.331	0.816	0.365	0.451
Forests	0.777	0.508	0.269	1.775	1.468	0.307	1.260	0.850	0.410

S(Mg) = the amount of total magnesium released.
X(Mg) = the amount of magnesium released from the exchange location.
M(Mg) = the amount of magnesium liberated from metal solubility.

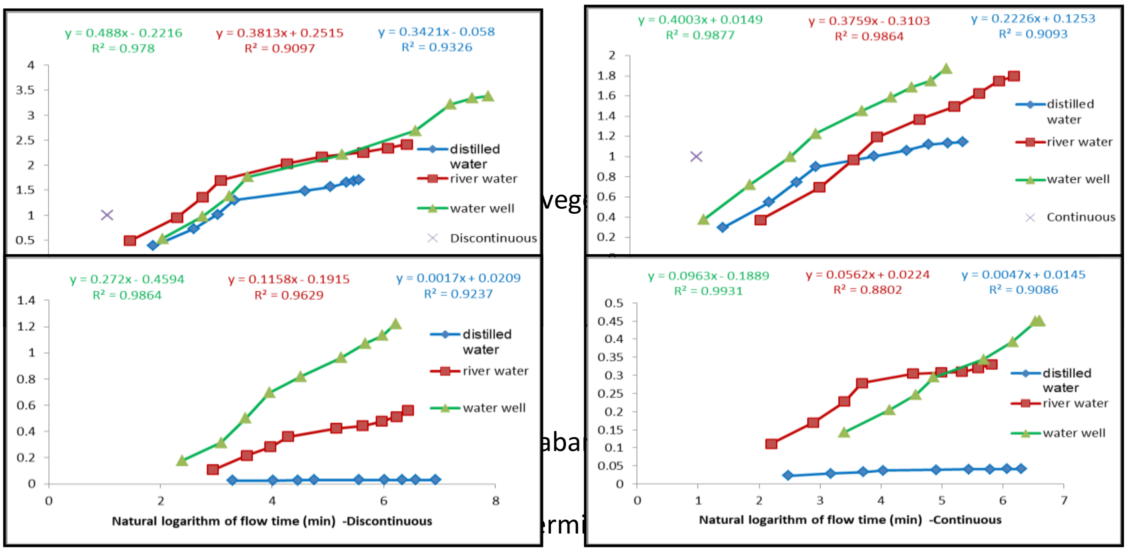
Table (4): The effect of water quality on the amount of liberated magnesium (cmol kg^{-1} soil) by the intermittent leaching method.

Location	distilled water			river water			water well		
	S(Mg)	X(Mg)	M(Mg)	S(Mg)	X(Mg)	M(Mg)	S(Mg)	X(Mg)	M(Mg)
vegetables	1.853	0.143	1.710	2.539	0.121	2.418	3.598	0.216	3.382
wheat	0.727	0.478	0.249	1.189	0.103	1.086	1.665	0.260	1.405
abandoned	0.563	0.531	0.032	1.100	0.537	0.563	1.815	0.591	1.224
Forests	1.452	0.975	0.477	1.894	1.331	0.563	1.890	1.179	0.711

Kinetic description of the process of dissolving and releasing magnesium: The application of the kinetic chemistry approach can provide a description of the dissolution and liberation of many elements, including magnesium, by introducing the time factor with the liberated or dissolved quantity and describing it with a mathematical equation (Sparks, 1985). This is expressed by the rat coefficient, which is a kinetic value that describes the speed of liberation of elements or ions through the use of a number of mathematical or kinetic coefficients. To apply this concept to the dissolution and liberation of magnesium, Kinetic equations were used to describe the process of dissolving magnesium and releasing it from the soil under study as a result of the dissolution of the minerals carrying it and treatment with distilled water, river water and well water, The amount of liberated magnesium was used as a function of time and kinetic equations were tested to describe the results and to find the best equation describing the mechanics of dissolving and releasing magnesium and the equations used. It is the zero-order equation, the first-order equation, the diffusion equation, the power function equation (exponential) and the Elovich equation. To determine the best equation, statistical indicators were used, namely the coefficient of determination (R^2) and the standard error (SE). In order to apply this concept, we will deal with Figures (1-4), which show the behavior of magnesium dissolution and liberation according to the Elovich equation, which gave the best description of the rest of the other equations is that the process of dissolution to liberate magnesium passes through two stages, The first is a rapid reaction (rapid dissolution), which is characterized by the fast-dissolving salts containing magnesium, and the second is a straight line indicating the stability of the dissolution process in the last stages of time, which is associated with the magnesium in minerals that have slow dissolution (Sposito, 2008 and Yacoub, 2019). It is noted from Figures (1-4) that the process of dissolution of magnesium in all study sites was characterized by the presence of two stages of dissolution, the first is fast and the second is slow and stable, except for the site of the abandoned soil treated with distilled water. And it took a straight shape. The results shown in Tables (5-6) indicate that all the kinetic equations described well the liberation of magnesium, as the values of the coefficient of determination were high for all equations, and the equations can be arranged according to their preference in the liberation process as follows:

Elovich equation>Diffusion equation>first order equation>zero order equation>force function equation.

That is, the best equations to describe the release of magnesium is the Elovich equation, which gave the highest coefficient of determination (R^2) and the lowest standard error (SE) for all study sites and for the continuous and intermittent leaching methods, respectively.



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kinetic equations used to describe the solubility of magnesium by the continuous leaching method.

Treatment	zero order equation		first order equation		Diffusion equation		Elovich equation		force function equation	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE
Vegetables										
distilled water	0.61	0.48	0.76	0.23	0.76	1.15	0.90	3.82	0.80	5.96
river water	0.75	0.66	0.96	0.20	0.88	3.10	0.98	1.43	0.90	14.90
water well	0.76	0.73	0.92	0.34	0.89	1.90	0.98	5.39	0.90	5.69
Wheat										
distilled water	0.96	0.32	0.98	0.05	0.99	1.44	0.96	.980	0.95	38.97
river water	0.80	0.26	0.92	0.13	0.92	0.59	0.98	1.42	0.92	4.99
water well	0.75	0.25	0.88	0.10	0.85	0.59	0.94	1.67	0.86	4.19
Abandoned										
distilled water	0.59	0.01	0.89	0.85	0.74	0.05	0.90	0.31	0.86	11.01
river water	0.57	0.12	0.76	0.50	0.72	0.47	0.88	2.35	0.81	12.02
water well	0.90	0.15	0.94	0.45	0.96	1.52	0.99	1.76	0.97	41.99
Forests										
distilled water	0.35	0.10	0.52	0.87	0.49	0.23	0.67	1.43	0.63	7.45
river water	0.60	0.10	0.88	0.49	0.71	0.38	0.83	2.53	0.76	11.76
water well	0.31	0.15	0.52	0.73	0.45	0.51	0.68	3.82	0.63	14.03

Table (6): values of the coefficient of determination (R^2) and standard error (SE) of the kinetic equations used to describe the solubility of magnesium by the intermittent leaching method.

Treatment	zero order equation		first order equation		Diffusion equation		Elovich equation		force function equation	
	R^2	SE	R^2	SE	R^2	SE	R^2	SE	R^2	SE
Vegetables										
distilled water	0.73	0.72	0.86	0.33	0.83	2.56	0.93	.121	0.83	10.56
river water	0.54	0.94	0.75	0.52	0.71	3.45	0.90	.051	0.78	12.50
water well	0.74	1.16	0.98	0.54	0.88	11.54	0.97	0.91	0.87	51.53
Wheat										
distilled water	0.91	0.09	0.90	0.31	0.94	0.50	0.94	.011	0.91	23.78
river water	0.62	0.46	0.76	0.20	0.78	1.25	0.93	.721	0.83	8.15
water well	0.87	0.49	0.91	0.01	0.94	3.89	0.97	.332	0.92	36.23
Abandoned										
distilled water	0.63	0.01	0.81	1.23	0.78	0.02	0.92	0.21	0.91	8.52
river water	0.77	0.24	0.90	0.22	0.87	1.40	0.96	0.93	0.85	32.31
water well	0.78	0.51	0.92	0.11	0.90	2.83	0.98	1.60	0.90	28.04
Forests										
distilled water	0.54	0.17	0.81	0.48	0.68	0.95	0.85	0.71	0.73	25.21
river water	0.69	0.19	0.72	0.04	0.76	0.88	0.83	0.63	0.75	16.55
water well	0.60	0.25	0.95	0.06	0.75	1.80	0.90	0.70	0.81	34.24

Dissolution rate coefficient: It expresses the rate of the reaction at the rate of change in the concentration of the reactants or products resulting from the reaction with respect to time, for example, an increase in the concentration of one of the products per unit time or a decrease in the concentration of one of the reactants per unit time (Al-Dabbagh, 2010). In order to apply this approach to the soil under study to determine the rate of melting and leaching of magnesium using kinetic equations, we will review the results in Table (7-8), including the values of the coefficient of magnesium liberation from dissolving minerals in the study soils treated with different types of water calculated from the slope of the straight lines For linear kinetic equations, The results indicated that the test of five kinetic equations showed variation and difference in the values of the velocity coefficient of release, that the criterion in the variation of kinetic behavior is the constant velocity of liberation and the half-life of liberation, which in practice means that half of the amount of the liberated element was liberated in the soil within the calculated time period ($t^{½}$) (Sparks, 1998). And the values of the velocity coefficient of magnesium liberation obtained from the Elovich equation, which was more appropriate in describing the kinetics of liberation of magnesium from the dissolution of its bearing minerals, and that the soil treatment gave the lowest velocity coefficient of dissolution of magnesium using distilled water. The coefficient of liberation velocity was (47×10^{-4}, 17×10^{-4}) cmol kg^{-1} min^{-1} for the location of soils left for continuous and intermittent leaching, respectively. Whereas, the highest coefficient of dissolution and liberation of magnesium ion was recorded using well water, which was (9877×10^{-4}, 4880×10^{-4}) cmol kg^{-1} min^{-1} for vegetable soils for continuous and intermittent leaching, respectively. It is noted from the results that the continuous leaching method recorded higher values of the melt speed coefficient compared to the intermittent leaching method, and this is consistent with what was indicated by (Al-hadethi and Al-Alwani, 2020).

In this regard, Pichu (2018) indicated that there is a relationship between the ionic strength of water and the intensity of weathering that increases the dissolution of minerals and salts, and that increasing the ionic strength directly affects the speed of dissolution of carbonate minerals and the liberation of ions into the soil solution. That is, the ionic strength of water will be related to the process of dissolving ion-bearing minerals and salts, and consequently the speed of their dissolution, which is reflected in the dissolution velocity coefficient, which resulted in the well water's superiority in the dissolution velocity coefficient values over river water and distilled water with lower ionic strength, The variation in the values of the rate of dissolution of magnesium in the study soils can be explained by the variation in the soil content of clay, organic matter, magnesium formulas, and the degree of electrical conductivity, as well as the adsorption capacity of the magnesium ion on soil particles and organic matter. Which is one of the important factors in liberating the ion through its binding energy with the solid phase of the soil. The results of this study are consistent with the results obtained (Nafawah, 2017 and Alhadede et al., 2022).

Table (7): The values of the dissolution velocity coefficient of magnesium K×10^{-4} (cmol kg^{-1} min^{-1}) by the continuous leaching method according to the kinetic equations used.

Treatment	zero order equation	first order equation	Diffusion equation	Elovich equation	force function equation
Vegetables					
distilled water	46.0	87.0	711.0	2226.0	3177.0
river water	39.0	76.0	869.0	3759.0	3813.0
water well	113.0	150.0	1515.0	9877.0	3954.0
Wheat					
distilled water	10.0	16.0	257.0	1345.0	6350.0
river water	59.0	239.0	680.0	1514.0	4280.0
water well	35.0	348.0	458.0	1219.0	2609.0
Abandoned					
distilled water	0.3	93.0	8.0	47.0	1413.0
river water	5.0	51.0	117.0	562.0	2607.0
water well	4.0	67.0	130.0	963.0	3351.0
Forests					
distilled water	2.0	32.0	45.0	6785.0	1252.0
river water	2.0	49.0	55.0	350.0	1508.0
water well	2.0	21.0	66.0	473.0	1642.0

Table (8): the values of the dissolution velocity coefficient of magnesium K×10^{-4} (cmol kg^{-1} min^{-1}) by the intermittent leaching method according to the kinetic equations used.

Treatment	zero order equation	first order equation	Diffusion equation	Elovich equation	force function equation
Vegetables					
distilled water	51	62	915	3421	3438
river water	30	36	806	3813	2797
water well	13	25	634	4880	2764
Wheat					

distilled water	4	48	107	594	4423
river water	36	68	645	2291	3619
water well	13	41	441	2938	3835
Abandoned					
distilled water	0.05	47	2	17	587
river water	6	19	183	1158	3862
water well	18	29	504	2720	4574
Forests					
distilled water	2	15	76	602	1888
river water	4	59	113	761	1944
water well	1	23	69	664	1267

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