Adsorption Reaction and Kinetics of Zn on Zeolite Mineral Comparing with Two Calcareous Soils

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Abstract: A laboratory experiment was conducted to study zinc adsorption at eight concentrations (0, 25, 50, 100, 150, 200, 250 and 300 mg.L^{-1}) by using $ZnSO_4.7H_2O$. with two replicates were used for each concentration, where 20 mL of zinc solution was added to 1 gram of natural zeolite, synthetic zeolite, soil 1, and soil 2. Langmuir equation was used to describe the relationship between zinc adsorption and its concentration. Additionally, the Freundlich equation was used to describe adsorption of ions. Freundlich equation was found to be more important than Langmuir equation, as the values of k and b in Freundlich equation and the R^2 values for natural and synthetic zeolites were higher in both soils. The second experiment involved kinetics. Zeolite and soil were kept moist at field capacity throughout the incubation period. Zinc was extracted using DTPA after each incubation period, with two replicates to study the rate of zinc release from zeolite and soil over time and its concentration in the solution. results showed a decrease in the availability of added zinc with increasing incubation time. The highest concentration of available zinc was found when zinc was added to synthetic zeolite, reaching 346 µg $Zn^{+2}.ml^{-1}$ at the end of the incubation period. The second-order equation was the most effective in describing the behavior of zinc and its reaction rate during the incubation period, representing the period of crop growth.

Keywords: Adsorption, Calcareous soil, Zeolite, Zinc.

Introduction

Adsorption is a physicochemical reaction where particles, atoms, or ions of the adsorbate substance accumulate or adhere to the solid surfaces of the adsorbent materia (Al-Mamoori *et al*., 2017). The presence of active sites depends on the size and nature of the adsorbent material, as well as the surface area of the adsorbent material (LeVan *et al*., 2012**)** Layers of particles, ions, or atoms are formed and concentrated on the surface of the adsorbent material (Petrovic *et al*., 2021) Adsorption determines the quantity of plant nutrients and their movement in soil solution, as well as the amount retained on the solid phase(Campillo-Cora *et al*., 2020); for this reason, adsorption is considered a fundamental process that controls the transfer of different nutrients and compounds in the soil (Dandanmozd & Hosseinpur, 2010). Kausar *et al.* (2018) defined adsorption as the accumulation of the adsorbate substance on the surface of the adsorbent material. Adsorption can be classified into two types based on the strength of attraction: the first

type is chemical, resulting from electron exchange, while the second type is physical, resulting from physical forces such as polarity and Vander Waals forces. Hamidpour *et al.* (2019) explained that the adsorption of nutrients, especially trace elements, occurs on clay minerals or solid organic materials, thus controlling their bioavailability, movement, and fate in the soil. The adsorption of zinc and essential trace elements occurs in two stages: the first stage lasts for two hours, during which the adsorption rate is high, while the second stage shows a sharp decrease over time (Rassaei *et al.*, 2020). Adsorption is considered one of the most important reactions that occur in the soil because it limits the movement of nutrients, organic compounds, and minerals (Dandanmozd & Hosseinpur, 2010). Zinc is an essential nutrient for plants, and its availability is often affected by factors such as soil pH, clay mineral types, and cation exchange capacity (Arias *et al.,* 2005).

The presence of calcium carbonate ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$) also affects the availability of zinc and alters its pathway in the soil through adsorption or raising the pH of the soil solution (Zarga *et al.,* 2013). The phenomenon of adsorption and nutrient release in the soil, as well as its importance for plants, has been described by various equations such as Freundlich, Temkin, Gunary, and Langmuir, and others (Mam-Rasul, 2020). The study of the kinetics of adsorption and release reactions serves as an important entry point for understanding the mechanisms and direction of chemical reactions in adsorption and release processes (Thajeel, 2013). The steps and mechanisms of the adsorption process can be determined through mathematical equations. It is necessary to determine the rate of adsorption or release of an element in order to predict the

conditions that lead to its adsorption on the solid phase or its persistence in the equilibrium solution, and to assess its availability to plants in the soil (Norde, 1986) The processes of nutrient retention by soil involve ion exchange, adsorption, and precipitation, so it is important to match the obtained results with different kinetic and equilibrium equations (Mukkanti *et al.*, 1985).

Recently, zeolite has been used in various industries due to its unique properties and the presence of water molecules within its structure. When water is removed, the resulting empty spaces can be occupied by other molecules. The occupation of these spaces by molecules is called adsorption (Pérez-Botella *at al.*, 2022). The interest in zeolite has been growing, especially in the ion exchange process; Ion exchange is used in the treatment of natural water, wastewater, and has gained widespread attention in the removal of salts, ammonia, treatment of certain radioactive wastes, and the treatment of wastewater containing heavy metals (Zanin *et al.,* 2017). Several recent studies have confirmed the exceptional performance of natural zeolite and its effectiveness in reducing high concentrations of positive and negative ions in drinking water, as well as treating surface and groundwater and sewage water, as it belongs to the group of positive exchangers (Nakhli *et al.,* 2017). Suleiman, (2016) conducted a study on the removal of heavy metals (zinc and lead) from industrial water using Syrian natural zeolite. This study demonstrated that the removal process is ion exchange-based and natural zeolite exhibits high efficiency in removing these elements. In another study, the synthesis of zeolite from alkaline-modified kaolin using NaOH and hydrothermal treatment showed that the prepared zeolite exhibited excellent adsorption properties for both single-

component and multi-component solutions. It was concluded that synthetic zeolite could be used as a cost-effective and relatively efficient adsorbent for removing heavy metals from industrial wastewater containing them (Meng *et al.,* 2016).

This research aims to study adsorption reaction and kinetics of Zn on natural and synthetic zeolites and comparing with two calcareous soils synthetic zeolite, compared to two calcareous soils.

Materials & Method

Natural zeolite, which is of Jordanian origin, and synthetic zeolite prepared from kaolin were used. The kaolin clay was obtained from the General Commission for Geological Survey and is available in the Al-Dweikheleh area in western Anbar.

Preparation of zeolite

Samples of kaolin were taken, crushed, and ground into powder form, then sieved using a laboratory sieve with a diameter of 75 μm. The kaolin was subjected to thermal treatment according to the method proposed by Breck (1973), at a temperature of 600°C for 3 hours to convert it to metakaolin. The metakaolin was treated with a 4M sodium hydroxide solution in a ratio of 5:1. After 24 hours, the solution was stirred and heated using a magnetic stirrer heater. The reaction mixture was placed in a volumetric flask with a thermometer to measure the temperature of the solution and adjust it to 80°C for 2 hours to prepare the synthetic zeolite from metakaolin. After heating, the mixture was filtered using a Büchner funnel with a suction pump and washed with distilled water to remove excess alkali. The washing process was repeated several times until reaching a pH of 10.5. The product was then dried in an electric oven at a temperature of 100°C for

four hours, followed by grinding and sieving through a sieve with a diameter of 63 μm.

Adsorption experiment

Samples of natural zeolite, synthetic zeolite, soil 1, and soil 2 and their characteristics are shown in table (1) showed the characteristics were taken, each weighing 1 g, and placed in test tubes with a capacity of 50 ml. Eight concentrations of zinc (0, 25, 50, 100, 150, 200, 250 and 300 mg.L^{-1}) were added to each tube from its source, $ZnSO_4.7H_2O$. 20 mL of each prepared concentration was added to each test tube, and they were shaken for two hours using a shaker. The samples were then filtered to separate the solution using Whatman filter paper (type 42). The zinc content in the filtrate was measured using an atomic absorption spectrophotometer. The amount of zinc adsorbed was calculated by subtracting the amount of zinc in the extract after zinc shaking and filtration from the amount of zinc added of the original solution. The adsorption of zinc in natural zeolite, synthetic zeolite, and two types of calcareous soil for comparison was determined using the Langmuir equation, which describes the relationship between adsorbed zinc and its concentration in the equilibrium solution (C), and the Freundlich equation, which describes ion adsorption on solid surfaces. Zinc adsorption was evaluated in natural zeolites, synthetic zeolites and two types of calcareous soils for comparison.

1-Langmuir equation

$$C/X/m = 1/Kb + 1/b.C$$

Where X/m is the amount of adsorbed element (μg of $Zn^{+2}.g^{-1}$ of soil), C is the concentration of the element at equilibrium (μg of $Zn^{+2}.ml^{-1}$), K is the binding energy

(ml^{-1}.μg of Zn^{+2}), and b is the maximum adsorption (μg of Zn^{+2}.g^{-1} of soil).

2- Freundlich equation

log X/m = log K + b log C

Where X/m is the amount of adsorbed element at equilibrium (μg of Zn^{+2} g^{-1} of soil), K is the adsorbed quantity (μg of Zn^{+2} .g^{-1} of soil), and b is the binding energy (ml^{-1} . μg of Zn^{+2}).

Table (1): Some properties of the soil and zeolite used in the experiment.

	Unit	Natural Zeolite	Synthetic Zeolite	Soil 1	Soil 2
EC1:1	dSm^{-1}	2.53	7.21	1.2	1.9
pH	-	8.1	11.2	8.2	8.3
Organic matter	g. Kg^{-1}	0.595	1.241	0.284	0.414
CaCO$_3$	g. Kg^{-1}	12	35	22	32
Soluble Ions					
Na		5.21	12.5	2.21	3.21
K		0.55	0.32	0.45	0.51
Ca		7.55	16.52	4.50	5.21
Mg	Mmol. l^{-1}	2.25	13.51	1.81	2.74
Cl$^-$		5.21	15.35	3.12	4.55
HCO^{-3}		5.11	18.68	3.58	3.73
SO4$^=$		7.62	17.20	3.23	5.61
CO$_3^=$		-	-	-	-
Sand		-	-	394	413
Silt	g. Kg^{-1}	-	-	465	346
Clay		-	-	141	241

Kinetics experiment

Samples of natural zeolite, synthetic zeolite, soil 1, and soil 2 were taken with a weight of 40 grams. Zinc was added to them at concentrations of 100 and 1000 mg.ml^{-1}, prepared from ZnSO$_4$.7H$_2$O. They were placed in plastic containers for the following periods:0 , 1, 5, 10, 20, 30, 40, 60, and 80 days, and moistened to field capacity throughout the incubation period. Zinc was extracted using DTPA after each incubation period according to the method described by Lindsay & Norvell (1978). The experiment was repeated to study the rate of zinc release from the soil as a function of time and its concentration in the soil solution. The experimental results were analyzed using kinetic equations, including those based on principles of chemical kinetics, such as:

Zero-order equation: $Ct = C0 - Kt$

First-order equation: $\ln Ct = \ln C0 - Kt$

Second-order equation: $1/Ct = 1/C0 + Kt1$

There are also equations that rely on experimental physical principles, such as:

Elovich equation: $Ct = C0 - K \ln t$

In the above equations:

C0 represents the initial concentration, which is the concentration of zinc in the soil solution at time zero.

Ct represents the concentration of zinc in the solution at the specified time.

K is the rate constant of zinc release.

t is the time. Parabolic diffusion equation:

$Ct = C0 - Kt^{1/2}$

Results & Discussion

Zinc adsorption

The adsorption process is crucial for determining the fate of nutrients present in the soil and their bioavailability. The study of thermally symmetrical adsorption of zinc was conducted by adding different concentrations of zinc to natural zeolite (Fig 1-A). It illustrates the relationship between the equilibrium zinc concentration in the solution and the adsorbed quantity on the natural zeolite minutes at a temperature of 298 Kelvin. When zinc was added in the form of zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) at different concentrations. It is observed that the adsorption of zinc increases with an increase in the added concentration, and the zinc adsorption curve follows an S-shaped isotherm, according to the classification of thermally symmetrical adsorption curves (Sposito, 1984). This type of curve is characterized by a small initial slope that increases with the adsorbate concentration, indicating a division of zinc ions between the equilibrium solution at low concentrations and the adsorption on the surface of natural zeolite minutes. There is no high affinity for one phase over the other. It is also noted that the zinc ions exhibit a small initial slope that increases with the zinc concentration in the solution. This slope indicates that the surface affinity of the zeolite (natural zeolite minutes) for zinc ions at low concentrations is lower than the affinity of the solution. As the zinc concentration increases, the zinc ions start to adsorb on the surface of the minutes in larger quantities, and the affinity becomes stronger than that of the solution due to the high adsorption capacity of zeolite, facilitated by the channels in its structure and its high cation exchange capacity. The adsorption capacity is significant from the beginning of adding zinc at low concentrations and increases with the added zinc concentration until the exchange sites on the surface of natural zeolite (the active surface) are saturated. After that point, the adsorbed quantity from the solution starts to decrease, resulting in a decreasing slope of the curve with increasing concentration in the solution

All adsorption sites on the surfaces of the minutes are active at the beginning of adding zinc. The adsorption capacity of natural zeolite is large, and zinc adsorption is significant at low concentrations of zinc. In the case of zinc adsorption, the curve slope continues from the lowest concentration to the highest concentration added 300 micrograms Zn^{+2} ml^{-1}, and the amount of adsorbed zinc increases with the increase in the added zinc concentration. This is primarily due to the fact that higher zinc concentrations create a higher concentration gradient for the dissolved substance, providing the necessary driving force for zinc ions to replace exchangeable cations on the surface and within the fine

internal pores of natural zeolite (Du *et al.,* 2019).

As for fig. (1-B), it illustrates the relationship between the equilibrium zinc concentration in the solution, added in the form of zinc sulfate at different concentrations, and the adsorbed quantity of zinc on the surface of synthetic zeolite minutes. It is observed that the adsorption curve follows an S-shaped isotherm, similar to the S-type classification by Sposito (1984). This type indicates the division of zinc ions between the equilibrium solution at low concentrations and the adsorption on the surface of zeolite minutes. There is no high affinity for one phase over the other. It is also noted that the zinc ions exhibit a small initial slope that increases with the zinc concentration in the solution. This slope indicates that the surface affinity of the mineral particles for zinc ions at low concentrations is lower than the affinity of the solution. As the zinc concentration increases, the zinc ions start to adsorb on the surface of the particles in larger quantities, and the affinity becomes stronger than that of the solution. Fig. (1-C) which shows the relationship between the zinc concentration in the equilibrium solution added in the form of zinc sulfate at different concentrations and the amount of zinc adsorbed on the surface of soil particles 1-D- as the adsorption curve is similar to the type L (L-shaped isotherm) according to the classification of adsorption curves (Sposito, 1984) indicating the high affinity of soil particles for zinc ion adsorption at low concentrations. The amount of adsorbed zinc increases with the concentration in the solution, as the solid phase affinity for zinc adsorption is greater than that of the solution, especially at low concentrations

where most adsorption sites are empty. After covering the adsorption sites with a layer of zinc ions, the curve slope increases with the concentration in the equilibrium solution, and the affinity of zinc ions to the equilibrium solution becomes greater than the solid phase affinity for zinc adsorption.

sing the Langmuir equation to describe zinc adsorption

To describe the process of zinc adsorption on natural zeolite, synthetic zeolite, soil 1, and soil 2, the Langmuir equation was used. The relationship between $(C/x/m)$ µg Zn^{+2} .g^{-1}, which represents the amount of adsorbed zinc according to the Langmuir equation, and (C) µg Zn^{+2} ml^{-1}, the concentration of zinc in the equilibrium solution, was plotted. Table (2) and ig (2) shows that the synthetic zeolite outperformed in providing the highest determination coefficient (R^2) value, reaching 0.987. It was followed by natural zeolite, which gave 0.985 for (R^2), while soil 1 had an (R^2) value of 0.983. Soil 2 had the lowest (R^2) value of 0.971. As for the maximum adsorption capacity (b) of zinc, the natural zeolite had the highest value at 1960.87 µg Zn^{+2}.g^{-1} zeolite, and the highest binding energy (k) at -0.00066 than synthetic zeolite adsorption capacity (b) of zinc was -1923.07 µg Zn^{+2}.g^{-1} and binding energy (k) 0.273 µg Zn^{+2}. This exceeded both soil 1 and soil 2, which gave values of (b) 1538.46 and 1388.88 µg Zn^{+2}.g^{-1} (soil) respectively, and binding energy (k) of 0.0464, and 0.0600 µg Zn^{+2} respectively. This is mainly due to the fact that at high zinc concentrations, there is a higher solute concentration gradient, and this provides the necessary driving force for zinc ions to replace the exchangeable cations on the surface and from the internal micropores of natural zeolite (Du *et al*., 2019).
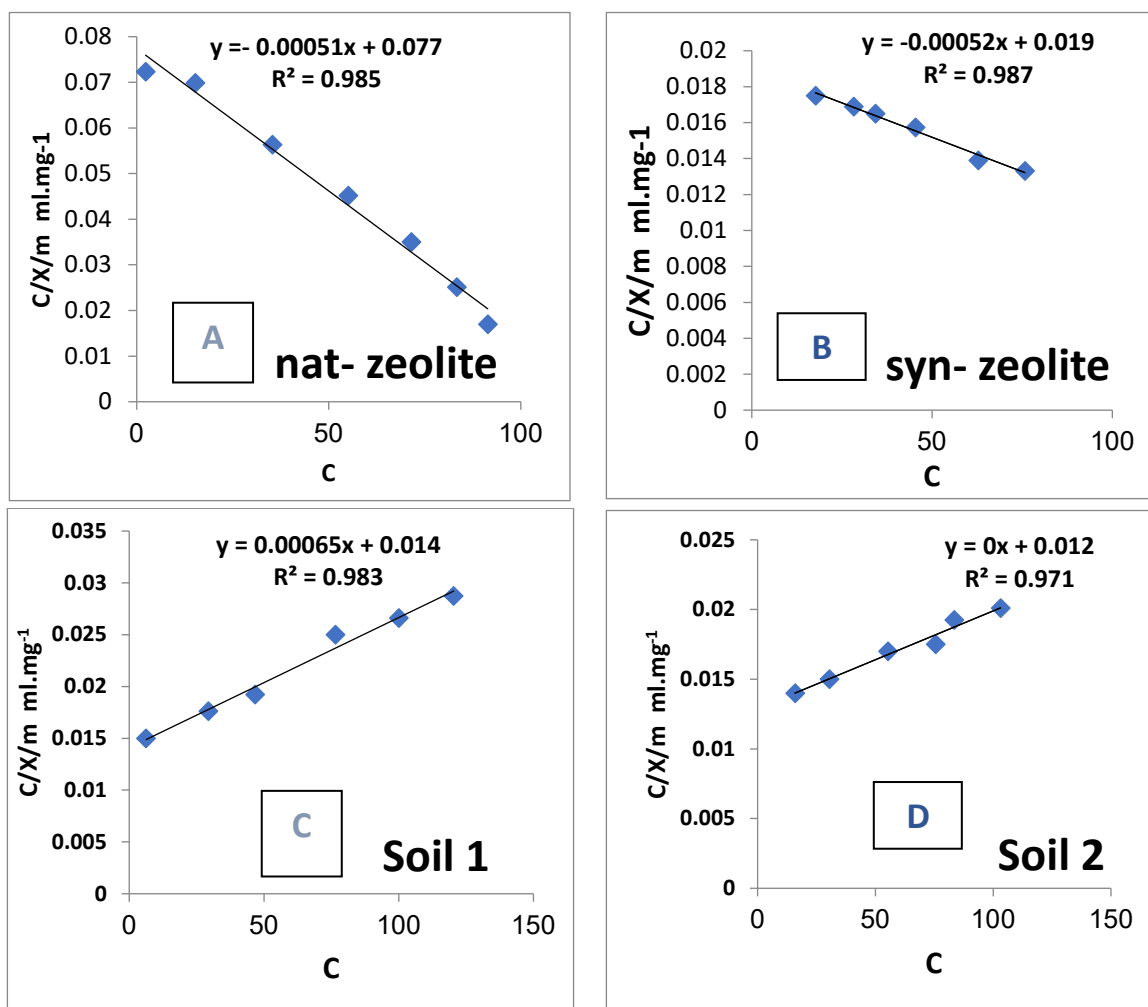
Fig. (1): The relationship between the concentration of zinc in the equilibrium solution (µg Zn^{+2}.ml^{-1}) and the amount adsorbed (µg Zn^{+2}.gm^{-1} (A-natural zeolite, B-synthetic zeolite, C-soil 1, D-soil 2).

The Freundlich equation was used to describe and evaluate zinc adsorption at a temperature of 298 Kelvin. The relationship between Log X/m and Log C values was plotted to obtain the constants of the Freundlich equation, which are K representing the intercept that indicates the adsorbed quantity in µg Zn^{+2}.g^{-1} of soil, and b representing the binding energy in µg Zn^{+2} .ml^{-1}. Table (2) and fig. (2) show the adsorption equations, determination coefficient values, and Freundlich equation constants for zinc added to zeolite and soil at a temperature of 298 Kelvin.

Between table (1) and fig. (3) for zinc, the highest determination coefficient value (R^2) was 0.995 in soil 2, closely followed by the determination coefficient of natural zeolite, which was 0.994. Synthetic zeolite and soil 1 had values of 0.988 and 0.983, respectively. As for the value of b, which represents the adsorbed quantity of zinc on natural zeolite, it recorded 7.634 µg Zn^{+2}.g^{-1} soil and 4.348 µg Zn^{+2}.g^{-1} for synthetic zeolite, and 10.92 and 14.81µg Zn^{+2}.g^{-1} for soil 1 and soil 2, respectively.
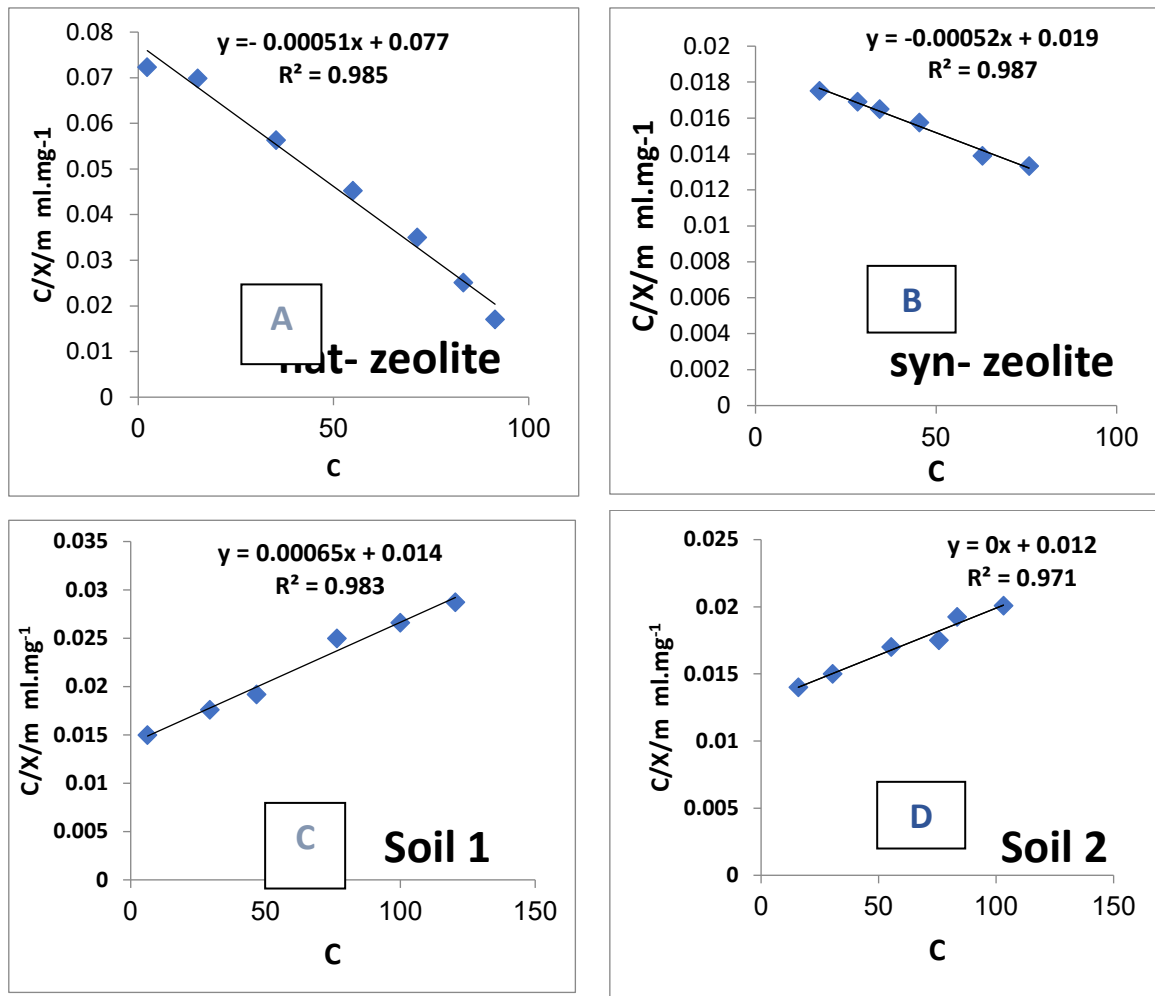
Fig. (2): The relationship between the concentration of the equilibrium solution (c) and the amount adsorbed (c/x/m) according to the Lancgmeyer equation.Using the Freundlich equation to describe zinc adsorption.

Regarding the binding energy (k), according to table (2), the highest binding energy value for zinc was 7.706 $\mu g\ Zn^{+2}$ in natural zeolite, followed by 1.59 $\mu g\ Zn^{+2}$ in synthetic zeolite. The lowest value was 0.232 $\mu g\ Zn^{+2}$ in soil2, and the lowest value was0.311 in soil 1. An increase in the initial concentration of zinc resulted in an increase in the adsorbed quantity of zinc per gram of zeolite. This is mainly attributed to the high concentrations of zinc, which create a gradient in the solution concentration, providing the necessary driving force for zinc ions to replace exchangeable cations on the surface and within the internal pores of the zeolite (Abadzic & Ryan, 2001; Du *et al.,* 2005). who demonstrated that it is possible to describe adsorption with a high degree of accuracy using the Freundlich equation. Additionally, several researchers have used the Freundlich equation to describe adsorption experiments (Alvarez-Ayuso, 2003; Cincotti *et al.,* 2006; Gunay *et al.*, 2007).

Table (2): Equations and indices for zinc adsorption according to Freundlich at 298 K.

Fertilizer source	Langmuir equations	R^2	b The maximum adsorption $\mu g.Zn^{+2}.g^{-1}$	k(The binding energy) $\mu g\ Zn^{+2}\ g^{-1}$
Natural zeolite	y =- 0.00051x + 0.077	0.985	1960.78	0.00066
Synthetic zeolite	y = -0.00052x + 0.019	0.987	1923.07	0.0273
Soil 1	y = 0.00065x + 0.014	0.983	1538.46	0.0464
soil 2	y = 0.0072x + 0.012	0.971	1388.88	0.0600
	Freundlich equations			
Natural zeolite	y = 1.353x + 1.041	0.994	7.634	7.706
Synthetic zeolite	y = 1.700x + 0.718	0.988	4.348	1.59
Soil 1	y = 0.810x + 1.968	0.983	10.92	0.311
Soil 2	y = 0.856x + 1.950	0.995	14.81	0.232

Kinetics experiment

Effect of incubation period on extracted zinc concentration

Fig. (4) explained that the extracted zinc from natural zeolite, synthetic zeolite, soil 1, and soil 2 with DTPA extractant decreases with increasing incubation period. When added to natural zeolite, the highest concentration of extracted zinc was 32.84 µg Zn^{+2} ml^{-1} at an incubation period of 0 days. The concentration gradually decreased with longer incubation periods, reaching 26.10, 20.71, 15.27, 14.59, 12.15, 9.89, 8.75 µg Zn^{+2} ml^{-1} respectively until the end of the 80-day incubation period, where the concentration became 7.64 µg Zn^{+2} ml^{-1}. This represents a percentage decrease of 67.16%, 73.90%, 79.29%, 84.73%, 85.41%, 87.85%, 90.11%, 91.25%, and 92.36%, respectively, compared to the initial concentration of 100 mg $L^{-1.}$

Similarly, a decrease in the concentration of extracted zinc added to synthetic zeolite is observed from the same figure. The initial concentration of extracted zinc at an incubation period of 0 days was 49.2 µg Zn^{+2} ml^{-1}, with a percentage decrease of 50.80%.

The concentration continued to decrease with longer incubation periods until the end of the 80-day period, reaching 10.03 µg Zn^{+2} ml^{-1}, representing a percentage decrease of 89.79%. The highest concentration of extracted zinc added to soil 1 was 10.21 µg Zn^{+2} ml^{-1} at an incubation period of 0 days, with a percentage decrease of 89.97% compared to the initial concentration of 100 mg. L^{-1}. The concentration continued to decrease with longer incubation periods, reaching 3.895 µg Zn^{+2} ml^{-1} after 80 days of incubation, corresponding to a percentage decrease of 96.11%.

Regarding soil 2, the highest decrease in extracted zinc concentration was observed after 80 days, where it reached 2.57 µg Zn^{+2} ml^{-1}, representing a percentage decrease of 97.43%. The highest concentration of extracted zinc at an incubation period of 0 days was 11.27 µg Zn^{+2} ml^{-1}, with a percentage decrease of 88.73%. This is due to the high soil reaction pH, which has an important and influential role in the solubility of calcareous soils, as Taalab *et al*. (2019) confirmed increasing the soil reaction from 5.5 to 7 reduced the readiness of zinc by approximately 30-40 times.
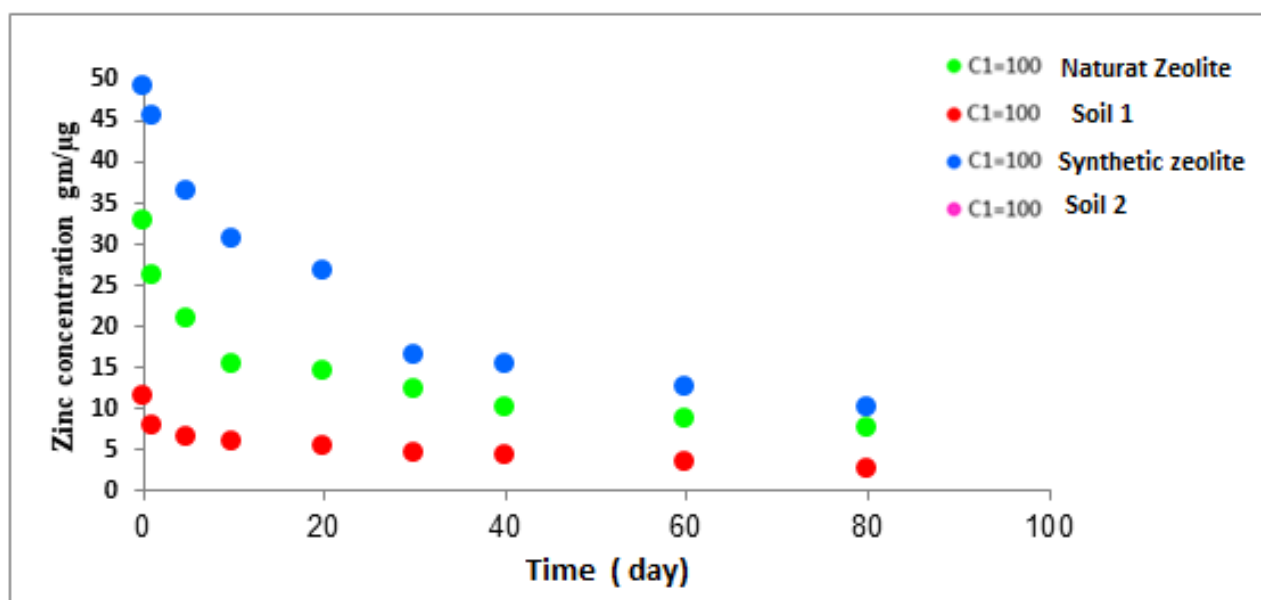
Fig. (4): The relationship between available zinc (100 μg Zn^{+2} ml^{-1}) with time (day) in natural zeolite, synthetic zeolite, soil 1 and soil 2

Fig (5) shows that the extracted zinc in DTPA solution decreases with increasing incubation period. When added to natural zeolite, the lowest concentration of extracted zinc was 28.2 μg $Zn^{+2}.ml^{-1}$, representing a percentage decrease of 97.18% at the end of the incubation period (80 days). The highest concentration of extracted zinc was 237.3 μg $Zn^{+2}.ml^{-1}$, with a percentage decrease of 76.27% compared to the initial concentration of 1000 mg. L^{-1}.

In the case of synthetic zeolite, the highest concentration of extracted zinc was 346 μg Zn^{+2} ml^{-1}, with a percentage decrease of 65.4%. The concentration continued to decrease with longer incubation periods, reaching the lowest concentration of 30.56 μg Zn^{+2} ml^{-1} and a percentage decrease of 96.94% at an incubation period of 0 day. The highest percentage decrease in zinc concentration was observed when added to

soil 1, reaching 98.28%. The highest concentration of extracted zinc in soil 1 was 17.25 μg $Zn^{+2}.ml^{-1}$, with a percentage decrease of 98.28%. The concentration continued to decrease, reaching the lowest concentration of 4.44 μg $Zn^{+2}.ml^{-1}$ and a percentage decrease of 99.56% at an incubation period of 0 day. When added to soil 2, the highest decrease in zinc concentration was observed, reaching 3.745 μg Zn^{+2} ml^{-1}, with a percentage decrease of 99.63%. The highest concentration was 15.8 μg Zn^{+2} ml^{-1} at an incubation period of 0 days, with a percentage decrease of 98.42%. This may be due to the role of calcium carbonate in calcareous soil conditions and its effect on the precipitation and stabilization of zinc, as zinc can be exchanged with calcium ions easily if it is abundant in the soil solution (Xing *et al*., 2023).
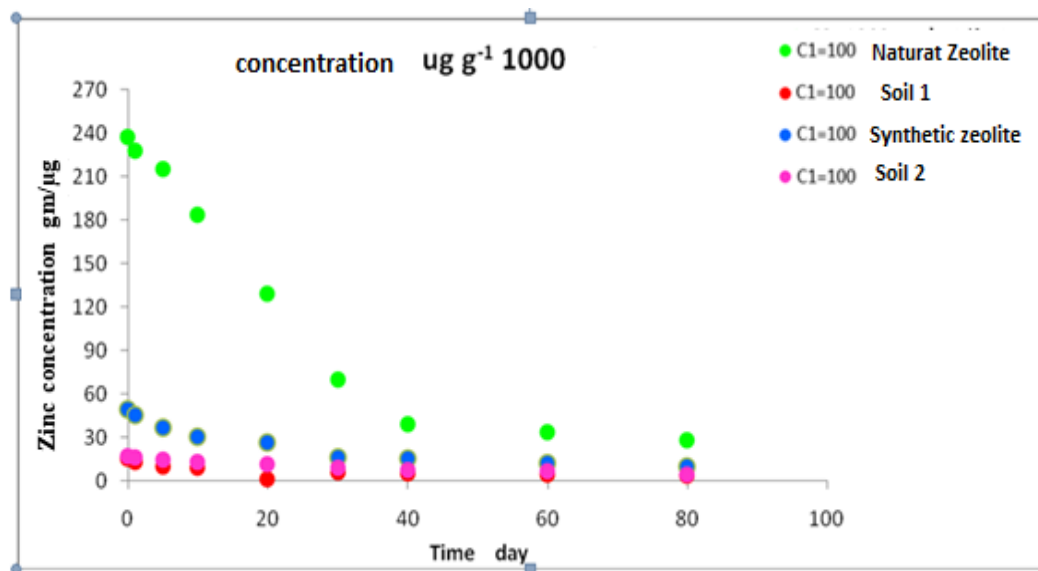
Fig. (5): The relationship between ready zinc (1000 μg Zn^{+2} ml $^{-1}$) with time (day) in natural zeolite, synthetic zeolite, and soil 1 soil 2.

Zinc release kinetics

Determining the relationship between zinc behavior and its reaction rates in natural zeolite, synthetic zeolite, soil 1, and soil 2 during an incubation period representative of crop growth in the field is accomplished using five mathematical equations. Some of these equations rely on the principles of chemical kinetics, such as zero-order kinetics, first-order kinetics, and second-order kinetics, while others are based on natural principles like the diffusion equation. Experimental equations, such as the Elovich equation, are also used. Table (3) displayed that the second-order kinetics equation is the most effective equation among the studied equations in describing the nature of the relationship between the releases of available zinc over time. It yielded the highest determination coefficient of 0.96 and the lowest standard error (SEe) of 0.008875. This means that the second-order kinetics equation I/Ct = 1/C0 + Kt is the most suitable for describing the relationship between zinc behavior and its reactions over time when sourced from (ZnSO$_4$.7H$_2$O) in the release kinetics of zinc from natural zeolite, synthetic zeolite, soil 1, and soil 2. This finding is consistent with Behroozi *et al.* (2020), who found the superiority of the second-order kinetics equation in describing the release kinetics of zinc associated with cation elements in smectite clay in Tunisia. Similarly, Mhamdi *et al.* (2013) found that the second-order kinetics equation outper formed all other equations used in the study to describe zinc release in Syrian soil.

Table (3): Indicators of the kinetic equations for the release of zinc added at two different concentrations.

Treatment	index	Zero- Order	1^{St}- Order	2nd- Order	Diffusion	Elovich
Natural zeolite C1=100	R^2	0.673	0.836	0.949	0.890	0.949
	SE	5.217	0.215	0.008	3.016	2.043
	T	-3.797	-5.973	11.449	-7.557	-11.520
Soil (1) C1=100	R^2	0.676	0.871	0.968	0.871	0.875
	SE	1.599	0.170	0.017	1.009	0.994
	T	-3.827	-6.894	14.638	-6.885	-7.005
Synthetic zeolite C1=100	R^2	0.796	0.917	0.981	0.957	0.975
	SE	6.979	0.178	0.004	3.186	2.410
	T	-5.241	-8.807	19.502	-12.586	-16.795
Soil (2) C1=1000	R^2	0.894	0.937	0.923	0.957	0.899
	SE	0.680	0.078	0.014	0.430	0.665
	T	-7.720	-10.263	9.181	-12.620	-7.920
Natural zeolite C2=1000	R^2	0.833	0.919	0.955	0.934	0.893
	SE	38.536	0.267	0.002	24.154	30.872
	T	-5.930	-8.936	12.210	-10.016	-7.661
Soil (1) C2=1000	R^2	0.478	0.245	0.968	0.695	0.803
	SE	3.641	0.732	0.012	2.780	2.235
	T	-2.532	-1.511	14.779	-4.000	-5.346
Synthetic zeolite C2=1000	R^2	0.679	0.929	0.988	0.889	0.904
	SE	61.963	0.226	0.001	36.420	33.746
	T	-3.851	-9.612	24.062	-7.496	-8.161
Soil (2) C2=1000	R^2	0.928	0.979	0.948	0.988	0.915
	SE	1.280	0.069	0.013	0.516	1.389
	T	-9.523	-18.371	11.341	-24.385	8.720
Mean	R^2	0.744625	0.829125	0.96	0.897625	0.901625
	SE	14.98688	0.241875	0.008875	8.938875	9.29425
	T	-5.302625	-8.795875	14.64525	-10.69313	-9.141

As for figs. (6 and 7), they illustrate the relationship between the reciprocal of zinc concentration and the incubation time in days. According to the second-order kinetics equation, I/Ct = 1/C0 + Kt, for natural zeolite, synthetic zeolite, soil 1, and soil 2 successively, when applying this equation in fig (6) specifically for zinc and during a 40-day incubation period, the extracted zinc amounts are 9.88, 15.52, 6.33, and 4.08 micrograms Zn^{+2} $gram^{-1}$, respectively. By applying it to fig. (6) for natural zeolite, synthetic zeolite, soil 1, and soil 2, the extracted zinc amounts after the same incubation period are 0.187, 0.119, 0.292, and 0.454 µg $Zn^{+2}.g^{-1}$, respectively. According to the half-life (t1/2) for natural zeolite, synthetic zeolite, soil 1, and soil 2, calculated using the equation t1/2 = 1/K [A]0, where (K) represents the rate constant of release and [A]0 is the initial concentration, the values obtained are 8.33, 10, 3.33, and 5.26 mg. g^{-1}, respectively
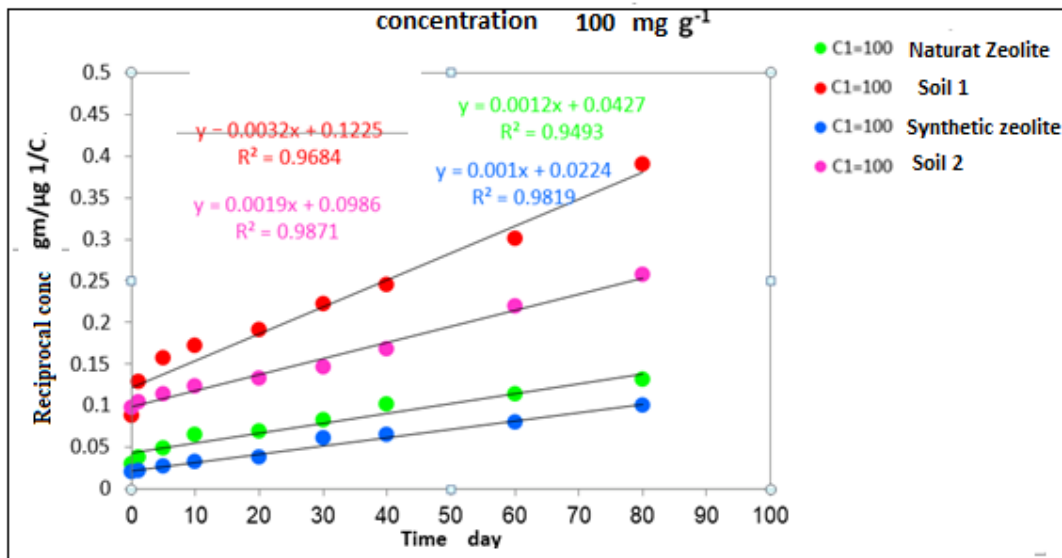
Fig. (6): The relationship between the Reciprocal of zinc concentration (100 µg Zn^{+2} g^{-1}) for natural zeolite, synthetic zeolite, soil 1 and soil 2, and incubation time (day).

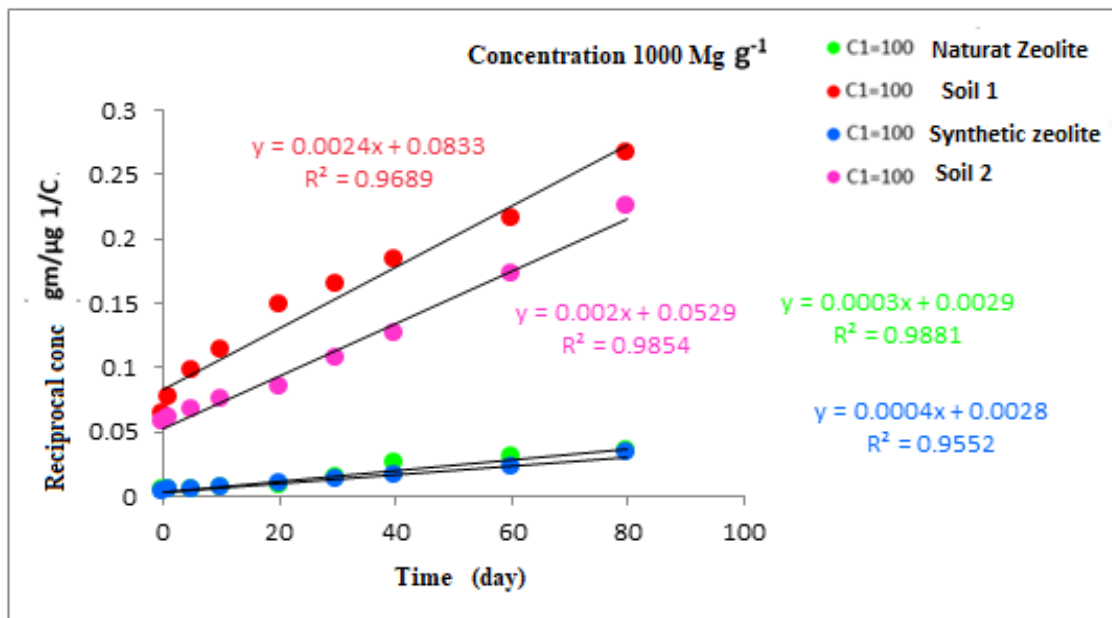**Fig. (7): The relationship between the reciprocal of zinc concentration (1000 µg Zn^{+2} .g^{-1}) for natural zeolite, synthetic zeolite, soil 1 and soil 2, and incubation time per day.**

Applying the half-life equation to fig (7) to find the half-life for natural zeolite, synthetic zeolite, soil 1, and soil 2 yielded the following values in mg. g^{-1}, respectively: 3.33, 2.5, 0.42, and 0.5. This difference in the extracted zinc quantity can be attributed to the fact that zinc released from zeolite remains for a long period, reaching up to 1176 hours, while zinc released from ZnSO$_4$ stays for duration of 216 hours. Therefore, zeolite is capable of retaining and slowly releasing zinc into the solution (Yuvaraj *et al*., 2018).

Conclusion

The Lanckmayer and Freundlich equations were suitable for studying and evaluating the adsorption process of zinc on natural zeolites, synthetic zeolites, and calcareous soils. 3- The kinetic equations are efficient in describing the speed and path of zinc liberation on

natural zeolite, synthetic zeolite, and two calcareous soils of different textures, and that the second-order equation was the most efficient of all equations.The adsorption capacity of natural zeolite and synthetic zeolite is higher than the adsorption capacity of traditional zinc sources.

Acknowledgements

We are so grateful to the head of the Department of Soil Sciences and Water Resources, and the deanery of our college for providing all laboratory equipment and chemicals.

Contributions of authors

M.A.R.: Sample collection, Laboratory methodology, and writing the manuscript.

A.A.H.: Suggest a title of the research, graphs, and statistical analysis.

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Conflicts of interest

The authors declare that they have no conflict of interests.

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الامتزاز وحركيات الزنك على معدن الزيولايت بالمقارنة مع تربتين كلسيتين

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المستخلص: اجريت تجربة مختبرية لدراسة امتزاز عنصر الزنك بثمان تراكيز 0 و 25 و 50 و100 و 150 و 200 و 250 و 300 ملغم لتر $^{-1}$ من كبريتات الزنك المائية ZnSO₄.7H2O وبواقع مكررين لكل تركيز اذ اضيف 20 مل من محلول الزنك الى 1 غم من الزيولايت الطبيعي والزيولايت الصناعي وتربة 1 وتربة 2 وقدرت الكمية الممتزة واستعملت معادلة لانكماير لوصف العلاقة بين الزنك الممتز وتركيزه في المحلول، كما استخدمت معادلة فروندلخ لوصف امتزاز الايونات على السطح الصلب وكانت معادلة فروندلخ اكثر اهمية منها في معادلة لانكماير اذ ان قيم k و b في معادلة فروندلخ وقيم R^2 للزيولايت الطبيعي والصناعي اعلى كمية منها في التربتين. اما التجربة الثانية هي تجربة الحركيات , اخذت نماذج من الزيولايت طبيعي و الزيولايت الصناعي وتربة 1 وتربة 2 بوزن 40 غم اضيف اليها الزنك بتركيز (1000،100 ملغم لتر $^{-1}$) المحضر من ZnSO₄.7H₂O ووضعت في عبوات بلاستيكية لفترات (0،1،5،10،20،30،40،60 و 80 يوماً). رُطب الزيولايت والتربة الى السعة الحقلية طيلة فترة التحضين. ويستخلص الزنك بـ DTPA بعد اكتمال كل فترة من فترات التحضين وبواقع مكررين ولدراسة سرعة تحرر الزنك من الزيولايت والتربة مع الزمن وتركيزه في المحلول. واظهرت النتائج انخفاض جاهزية الزنك المضاف مع زيادة زمن الحضن وكان اعلى تركيز للزنك الجاهز عند اضافة الزنك الى الزيولايت الصناعي 346 مايكروغرام Zn^{+2} مل$^{-1}$ عند نهاية فترة الحضن وكانت معادلة الرتبة الثانية المعادلة الاكفأ في وصف سلوك الزنك وسرعة تفاعلاته طوال فترة الحضن الممثلة لفترة نمو المحصول.

الكلمات المفتاحية: الامتزاز ، ترب كلسية، الزيولايت، الزنك.