



Plant Archives

Journal homepage: <http://www.plantarchives.org>
doi link : <https://doi.org/10.51470/PLANTARCHIVES.2021.v21.S1.241>

THE EFFECT OF LEVELS OF ZEOLITE, PHOSPHOROUS AND SULFUR ON AVAILABILITY AND RELEASE OF PHOSPHOROUS IN SOIL

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ABSTRACT

A field experiment was conducted at the field of the college of Agriculture, Al-Muthanna University, to study the effect of levels of zeolite, sulfur, and phosphorous, and the interactions on availability phosphorous in the soil, during the 2019-2020 agricultural season, by Randomized complete Block design (RCBD) with three replicates. The experiment contains three factors, the first factor included two levels of zeolite added in volume 0 and 3%, the second factor were three levels of agricultural sulfur 0, 150 and 300 kg S ha⁻¹, and third factor were three levels of phosphorous were 0, 60 and 120 kg P ha⁻¹. The land was divided into plots with three blocks, the area of the experimental unit was 2×2 m², the experimental unit included 8 lines with a length of 2 m, the distance between one line and another was 20 cm, the distance was left 75 cm between one replicate and another. The seeds of wheat were planted with IBA cultivar on 11/18/2019 at the lines. The results indicated that the addition of zeolite had a significant effect in increasing the amount of availability phosphorous in the soil after 45 days of planting, its average highest was 30.9 mg P ha⁻¹. The binary interactions between phosphorous, sulfur, phosphorous, and zeolite have a significant effect in increasing the amount of availability phosphorous in the soil, the highest mean achieved of 45.3 and 43.9 mg P kg⁻¹ soil for treatments S1P2 and Z0P1, respectively, for 15 days of planting, and 38.0 and 38.5 mg p kg⁻¹ soil for Z2P2 and S0P2 treatments, respectively, for 30 days of planting. The triple interaction was significantly affected, the treatment Z0P2S2 was the highest average of availability phosphorous in the soil after 15 days of planting, which was 49.7 mg P kg⁻¹ soil. Zeolite, sulfur, and phosphorous levels and their interactions affected the amount of release phosphorous during plant growth periods (15-90 days). The Eelovich Equation surpassed the first-order equation, explaining and describing the mechanics and speed of release phosphorous in soil, gave the coefficient of release phosphorous velocity (Kd), ranged between 0.1240-0.2956. The highest coefficient, correlation (r), of 0.9879. The treatments S₂P₁ and S₂P₂ achieved the highest amount of freely combined phosphorous, the amount of 10.32 and 10.22 mg. P kg⁻¹ soil.

Keywords: zeolite, phosphorous, sulfur, availability and release accumulation phosphorous, soil.

Introduction

Phosphorous is one of the major macronutrients, the second most important element, after nitrogen, in the biological structure, plays an excellent role in transmitting energy, and cellular metabolism, including nutrient absorption, no life process can take place without this element. Most of the phosphorous was commonly available in the environment, it is in an oxidized state just like phosphate, it continuously forms insoluble chemical groups with calcium, iron and aluminum, makes it not ready to be absorbed by plants. Phosphorous was extracted globally from geological deposits, most of the extracted P was added to agricultural soil, to meet the urgent need for vegetable crops for agricultural productivity. The phosphorous recovery of plants was very low, a large amount of phosphorous is fixed to the soil, leads to the need to add phosphate fertilizers (Adhya *et al.*, 2015).

The use of minerals for agricultural purposes has become widespread. The zeolite mineral has a special place in this field, considered as a material enhancer for soil chemical properties and fertility, which helped preserve nutrients and provide plant moisture content in the soil environment (Hussain, 2019). Much research work deals

with the potential of zeolite, can be included in the list of effective and efficient soil remediation amendments, because of its large and important characteristics, zeolite represents an important alternative to reduce the effects of drought in arid and semi-arid regions, it can be used to improve soil, enhancing the effects of chemicals, organic matter, and fertilizers alike, and as a component of the substrate for the development of various crops (Najafi-Ghiri, 2014). The zeolite mineral was characterized by its high ability to retain water and nutrients, and supply the plant with it when needed and gradually, encouraged the use of this mineral in local conditions, suffering from water scarcity and low availability of nutrients throughout the growing season of the crop, zeolite mineral is also distinguished by raising the readiness of some nutrients in the main soil in the growth of most field crops (Abdul-Hassan, 2018).

Agricultural sulfur was used in soils at areas that tend to be alkaline, especially in the central and southern soils of Iraq of great importance, where agricultural (mineral) sulfur transforms, to sulfuric acid by the action of sulfur bacteria, works to equalize the degree of soil reaction, it will positively affect the plant's nutrition, as well as for the trace elements and other nutrients, as the availability of nutrients

increases in general around the break-even point (Abu Dahi and Younes, 1988).

To know the behavior of zeolite, sulfur and phosphorous in the soil and its relationship to availability phosphorous by using the wheat crop as a vegetable guide, this study was proposed to study the effect of zeolite, phosphorous, and sulfur and their interactions on phosphorous readiness in soil.

Materials and Methods

Site experience

A field experiment was carried out during the 2019-2020 agricultural season, at the Al-Bandar Research Station, College of Agriculture, Al-Muthanna University, to determine the effect of zeolite, phosphorous and sulfur levels on availability phosphorous. Soil samples were brought from the field from depth 0-30 cm, it was filtered, air dried, milled, and passed through a sieve with holes diameter (2 mm).

Land preparation and service operations

The field soil was plowed with a triplex plow to a depth of 25 cm, and graded by disc combs, settled and then opened the main and secondary lines, divided into three blocks, including one block, with 18 experimental units, the area of the experimental unit $2 \times 2 \text{ m}^2$. The experimental unit included eight lines, and the distance between one line and another was 20 cm, a distance of 50 cm was left between one and another. Phosphate fertilizer was added with levels P_0 , P_1 and P_2 , fertilizer which was 0, 60 and 120 kg. P ha^{-1} in the form of triple superphosphate fertilizer TSP (20% P) in one batch before planting. Potassium fertilizer at level 100 kg. ha^{-1} was added in the form of potassium sulfate fertilizer (41.5% K). Nitrogen at a level of 150 kg N. ha^{-1} in the form of urea (46% N), by two batches, first a week after planting, and the second one a month after the first (Ali and Abdel Razzaq, 2016). The zeolite was added volumetrically by knowing the length and width of the experimental unit and the depth and

density of the soil and making a box that carries these dimensions, zeolite was added to it before mixing with soil. Sulfur was also added before planting and mixed with soil on October 28, 2019, to give a chance to oxidize. All service operations were performed equally for all experimental transactions in the study, whenever the need arises.

Study treatments

The zeolite (Z) was added volumetrically at two levels (0 and 3)% with symbols Z_0 and Z_1 . Added pure agricultural sulfur (90% S), at three levels (0, 150 and 300) kg S ha^{-1} , which represent the levels S_0 , S_1 and S_2 respectively. Three levels of phosphorous (P) were added 0, 60 and 120 kg. P ha^{-1} taking the symbol P_0 , P_1 and P_2 , respectively. Triple superphosphate fertilizer (20% p) were used.

Conducted as a factorial according to a Randomized Complete Block Design (RCBD), included 18 and three replicates, bringing the total number of units to 54 experimental units.

Agriculture and crop management

Experiment soil was grown with IBA99 cultivar wheat seeds, then irrigated the first irrigation on 11/18/2019. The experiment took the sufficient amount of water according to the system of need during the growth period of the crop. The soil was cultivated from the bush manually, and more than once as needed. The crop was harvested after completion of maturity on 5/1/ 2020 Per treatment, treatments were dried, the total weight of the dry matter was estimated, the spikes were separated from the straw, and the grain was weighed.

Soil sampling

Soil samples were taken from each experimental unit, using the drill to a depth 1-20 cm from the surface, to estimate availability phosphorus in soil, for periods of time during plant growth stages 15, 30, 45, 60, 75 and 90 days of planting, to estimating some of the physical and chemical characteristics of the study soil shown in Table (1).

Table 1 : Some chemical and physical characteristics of the study soil before planting.

parameters	Value	unite	
pH	7.78		
EC	3.80	dSm ⁻¹	
Organic matter	5.30	g. kg ⁻¹	
Available nitrogen	26.00	mg kg ⁻¹	
Available phosphorus	11.70		
Available potassium	186.00		
Sulphates	214.00		
Partial density	2.64	mg. m ⁻³	
Bulk Density	1.38		
Porosity	47.72	%	
Soil separates	Sand	209.00	g. kg ⁻¹
	Silt	436.00	
	Clay	355.00	
textures	Silty loam sandy		

The amount of availability phosphorous in soil during plant growth periods (15, 30, 45, 60, 75 and 90) days after planting, by using sodium bicarbonate (0.05M NaHCO₃) pH 8.5 according to the Alson method, the color was developed with ammonium molybdate and ascorbic acid, it was estimated using a Spectrophotometer with a wavelength 882 nanometers, according to Page (1982).

Kinetics Mersurment of Phosphorus

Estimate the amount of released phosphorus in soil with citric acid

Estimated phosphorous release by the Simard *et al.* (1989 and 1992) method, for soil under study by alternating extraction of phosphorus with citric acid C₆H₈O₇.H₂O dilute

M 4-10 × 5, for periods of time (15, 30, 45, 60, 75 and 90) days from planting.

The amount of release phosphorus was calculated for the previous time periods, by taking a weight of 2 g. of dry soil for each treatment and period of growth, placed in an airtight centrifuge tube, 20 ml of citric acid (M) added 4-10 × 5 to obtain a ratio of (10: 1) soil: citric acid. The samples were agitated by a vibrator at a temperature of 20 ± 5 C for a period of (6) hours, then left for 18 hours for the equilibrium, the samples were placed in a centrifuge at 2000 cycles. Min^{-1} for a period of 10 minutes. The filtrate was separated during the filter paper (Whatman 42). The phosphorous was estimated using the color method using ammonium molybdates, ascorbic acid, and a spectrophotometer, with a wavelength of (882) nanometers, as reported in Page *et al.* (1982).

Release phosphorous curves

Plot the relationship between the amount of released phosphorous (Cumulative P). Extract with citric acid M (4-10 x 5) for all treatments, against the extraction time during the stages of plant growth for periods (15, 30, 45, 60, 75 and 90) days from planting, then the mathematical relationship was re-drawn to assess the release phosphorous index, which was a function of the extraction time, by adopting the following kinematic equations (the first-order and Elovich equation), and the adoption of the best of them in describing the liberation of phosphorous in drawing the relationship between release phosphorous and the extraction time, in order to know the effect of different factors on the soil's ability to release phosphorous.

Kinetics equations to describe release phosphorous with citric acid

The following kinematic equations indicated by Sparks (1985a and b), to calculate the amount of release phosphorus for the different treatments of the study soil, and find the best kinematic equation that describes the mechanism of its release, to find out the velocity coefficient, which (Kd) is released from the best equation, which was as follows:

First order equation:

$$\ln(C_0 - C_t) = \ln C_0 - Kt \quad \dots(2)$$

Elovich equation:

$$C_t = C_0 - K \ln t \quad \dots(4)$$

whereas

C₀: Phosphorus concentration at time zero.

C_t: Phosphorus concentration measured at time t.

C_t / C₀: the amount of phosphorous released and diffused at time t.

K: In units (Kp) the slope of the straight line and equal to the coefficient of phosphorous release velocity.

$$(\text{mg. Kg}^{-1}.\text{day}^{-1}) \text{ Or } (\text{mg. Kg}^{-1} \text{ min}^{-1})$$

Statistical analysis

The experiment data were analyzed statistically according to the (ANOVA) method, to study the impact of

each of the sources and levels of compost and the interaction between them, the averages of the coefficients were compared to the LSD test at the 0.05 level, the Genstat discovery edition program were used.

Results and Discussion

Availability phosphorus in the soil at the 15-day period after planting

Table (2) indicates that the addition of zeolite and sulfur separately did not achieve a significant difference in the values of availability phosphorus in the soil at the period of 15 days, and for different levels. The addition of phosphorus was significant to increase the values of availability phosphorus in the soil for the levels P₁ and P₂, as the amount of availability phosphorus in the soil was 32.6 and 42.4 kg. P ha⁻¹, compared to the control treatment P₀, which had availability phosphorous 17.4 kg. P ha⁻¹. The reason may be due to the amount of phosphorous added at high levels, the low degree of reaction in the first periods, increased the availability phosphorus in the soil, agreed with Awad (1987) and Al-Jabouri (1999).

The binary interactions between zeolite and phosphorous, sulfur and phosphorous, significant differences were achieved in the values of availability phosphorus in the soil, the interaction between zeolite and phosphorous in which the treatments of Z₀P₂ and Z₁P₂ prevailed in phosphorous readiness, achieving the highest values, which was 43.9 and 41.2 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous was 14.7 kg. P ha⁻¹ when treatment Z₁P₀, as for the rest of the transactions, they varied between the significant and the non-significant. The reason may be due to mixing the zeolite mineral with chemical fertilizers, it significantly affects the ion content of the soil and its readiness, by the influence of the cation exchange and adsorption properties of zeolite (Supapron *et al.*, 2002), the interaction between sulfur and phosphorous, the S₂P₂, S₁P₂ and S₁P₁ treatments had the highest availability phosphorous values (45.3, 44.1 and 40.2 kg. P ha⁻¹), while the lowest value of availability phosphorus was when the comparison treatment S₀P₀ (17.8 kg. P. ha⁻¹), may be due to the positive effect of adding sulfur to reducing the degree of soil reaction, led to an increase in the values of availability phosphorus in the soil (Imran *et al.*, 2016).

Many of the triple interactions of zeolite, sulfur and phosphorous had a significant effect on the amount of availability phosphorus in the soil for the 15 days after planting, as the treatment Z₀P₂S₂ showed the highest rate of availability phosphorous in the soil, which was 49.7 kg. P. ha⁻¹, did not differ significantly with the treatments Z₀P₂S₁ and Z₁P₁S₁ and Z₁P₂S₁ and Z₁P₂S₀, which achieved availability phosphorus amounts in the soil were 47.5, 46.4, 43.1 and 41.9 kg P. e-1, respectively, all of them achieved significant superiority over many other interactions, agreed with Hassoun (2010), which indicates the importance of zeolite and sulfur in raising the values of availability phosphorus in the soil, and improve soil fertility and increase its ability to retain nutrients, when mixing zeolites with chemical fertilizers and soil (Kavoosi, 2007).

Availability phosphorus in the soil at the 30-day period after planting

Table (3) indicates that the addition of zeolite and sulfur separately did not achieve a significant difference in the values of availability phosphorous in the soil at the 30-day period, and for the various levels. As for adding phosphorous alone, the treatment P₂ achieved significant superiority in the amount of availability phosphorous in the soil at the period of 30, it was 28.5 kg. P ha⁻¹, superior to the two treatments P₀ and P₁, therefore, they did not differ significantly between them in the amount of availability phosphorous in the soil, which amounted to 20.9 and 23.1 respectively. The reason may be that the addition of phosphorous to the soil transforms from the first changes to ready-to-dissolved forms in the soil, depending on many factors, including soil type, time, and the degree of soil interaction.

The binary interactions between zeolite and phosphorous, sulfur and phosphorous, significant differences were achieved in the values of availability phosphorous in the soil, the interaction between the zeolite and phosphorous was the treatment Z₁P₂, achieved the highest values of availability phosphorous (33.5 kg. P ha⁻¹), while the lowest value of availability phosphorous was when treatment Z₁P₁ (20.0 kg. P ha⁻¹). As for the other of the treatments, they did not differ significantly with the comparison treatment. The reason may be due to mixing the zeolite mineral with chemical fertilizers, it significantly affects the ion content of the soil and its readiness, by the influence of the cation exchange and adsorption properties of zeolite (Supapron *et al.*, 2002). As for the interaction between sulfur and phosphorous, the two parameters S₀P₂ and S₂P₂ achieved the highest availability phosphorous values, which were 30.7 and 29.0 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous was when the comparison treatment S₀P₀ (9.7 kg. P ha⁻¹). The reason may be due to the positive effect of adding sulfur to reducing the degree of soil reaction, led to an increase in the values of availability phosphorous in the soil (Imran *et al.*, 2016).

The triple interactions of zeolite, sulfur and phosphorous, the effect was significant on the amount of availability phosphorous in the soil for the 30 day period after planting, as the treatments Z₁P₂S₂ and Z₁P₂S₀ showed the highest rate of availability phosphorous in the soil, were 36.8 and 33.4 kg. P ha⁻¹, respectively. The other of the treatments were not significant, agreed with Hassoun (2010), which indicates the importance of zeolite and sulfur in raising the values of availability phosphorous in the soil, and improve soil fertility and increase its ability to retain nutrients, when mixing zeolites with chemical fertilizers and soil (Kavoosi, 2007).

Availability phosphorus in the soil at the period of 45 days after planting:

The results in Table (4) indicate that the addition of zeolite has a significant effect on the values of availability phosphorous in the soil at a period of 45 days. The Z₁ level was significantly superior to the non-additive level Z₀, a availability medium phosphorous investigator of 30.9 kg. P ha⁻¹. There was an important characteristic of the zeolite mineral in raising the availability phosphorous in the soil, by

reserving it without fixation and releasing the plant when needed (Abdi *et al.*, 2006). The addition of sulfur did not achieve a significant difference in the values of availability phosphorous in the soil at the period of 45 days and for different levels. The addition of phosphorous was significant in increasing the values of availability phosphorous in the soil for the levels P₂ and P₁, as the amount of availability phosphorous in the soil was 27.7 and 36.7 kg. P ha⁻¹, compared to the control treatment P₀, when the availability phosphorous reached 20.4 kg. P ha⁻¹. The reason may be due to the amount of phosphorous added at high levels, the low degree of reaction in the first periods, it increased the availability phosphorous in the soil (Awad, 1987 and Al-Jubouri, 1999)

The binary interactions between zeolite and phosphorous, sulfur and phosphorous achieved significant differences in the values of availability phosphorous in soil. The interaction between zeolite and phosphorous in which the coefficients of Z₀P₂, Z₁P₁ and Z₁P₂ prevailed in availability phosphorous, the highest values were achieved, which were 35.4, 32.1 and 38.0 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous was when the comparison treatment was Z₀P₀, which was 18.1 kg. P ha⁻¹. The reason may be due to mixing the zeolite mineral with chemical fertilizers, significantly affects the ion content of the soil, and increase its readiness due to the effect of cation exchange and adsorption properties of zeolite (Supapron *et al.*, 2002). As for the interaction between sulfur and phosphorous, the parameters S₀P₂, S₁P₂, S₂P₂ and S₀P₁ had the highest availability phosphorous values, these were 38.5, 36.7, 34.8 and 32.2 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous was when the comparison treatment S₀P₀, which was 18.7 kg. P ha⁻¹. The reason may be due to the positive effect of adding sulfur to reducing the degree of soil reaction, led to an increase in the values of availability phosphorous in the soil (Imran *et al.*, 2016).

Many of the triple interactions of zeolite, sulfur and phosphorous, the effect was significant on the amount of availability phosphorous in the soil for the period of 45 days after planting. As the treatment Z₁P₂S₀ showed the highest rate of availability phosphorous in the soil, which was 40.4 kg. P ha⁻¹, which did not differ significantly with the treatments Z₁P₁S₀, Z₁P₂S₁, Z₀P₂S₀, Z₁P₂S₂, Z₀P₂S₁ and Z₀P₂S₂, achieved availability phosphorous quantities in the soil were 38.8, 38.0, 36.6, 35.6, 35.4 and 34.1 kg. P ha⁻¹, respectively, all of them achieved a moral superiority over many other interactions, agreed with Hassoun (2010), which indicates the importance of zeolite and sulfur in raising the values of availability phosphorous in the soil, and improve soil fertility and increase its ability to retain nutrients, when mixing zeolites with chemical fertilizers and soil (Kavoosi, 2007).

Availability phosphorus in the soil at the period of 75 days after planting

In Table (5) the levels of phosphorous addition P₁ and P₂ showed no significant difference between them, however, it significantly outperformed the treatment by not adding P₀, for which the availability phosphorous was 15.6 kg. P ha⁻¹, due to the acidic organic secretions of plant roots, which

reduce the degree of soil reaction, which reflects positively on availability phosphorous (Al-Barakat 2016).

The binary interactions between zeolite and phosphorous, sulfur and phosphorous, significant differences were achieved in the values of availability phosphorus in the soil, the interaction between zeolite and phosphorous in which the treatments of Z_1P_2 and Z_1P_1 prevailed in availability phosphorous, the highest values were achieved, which were 34.1 and 30.4 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorus was 17.6 kg. P ha⁻¹ when the comparison treatment was Z_0P_0 . As for the rest of the treatments, they were not significant. The reason may be due to mixing the zeolite mineral with chemical fertilizers, it significantly affects the ion content of the soil, and increase its readiness due to the effect of cation exchange and adsorption properties of zeolite (Supapron *et al.*, 2002). As for the interaction between sulfur and phosphorous, it had a significant effect, as the treatments S_2P_2 , S_1P_1 , S_0P_2 and S_1P_2 were the highest availability phosphorus values, were 34.3, 33.4, 30.3 and 29.5 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous was when the comparison treatment S_0P_0 , which was 14.9 kg. P ha⁻¹. The reason may be due to the positive effect of adding sulfur to reducing the degree of soil reaction, led to an increase in the values of availability phosphorus in the soil (Imran *et al.*, 2016).

Many of the triple interactions of zeolite, sulfur and phosphorous, the effect was significant on the amount of availability phosphorus in the soil for the period 60 days after planting, as the treatment $Z_1P_2S_0$ showed the highest rate of availability phosphorus in the soil, which was 37.0 kg. P ha⁻¹, which did not differ significantly with treatment $Z_1P_1S_1$, achieved a availability phosphorous in soil of 36.8 kg. P ha⁻¹, it achieved a significant superiority over many other non-significant interactions, agreed with Hassoun (2010). Which indicates the importance of zeolite and sulfur in raising the values of availability phosphorus in the soil, and improve soil fertility and increase its ability to retain nutrients, when mixing zeolites with chemical fertilizers and soil (Kavoosi, 2007).

Availability phosphorus in the soil at the period of 75 days after planting

Table (6) indicates that the addition of zeolite and sulfur separately, they did not achieve a significant difference in the values of availability phosphorus in the soil at the period of 75 days, and for the various levels. The levels of P_1 and P_2 phosphorous addition showed no significant differences between them in the availability phosphorous in the soil, reaching 22.2 and 27.9 kg. P ha⁻¹, respectively, however, the two treatments P_1 and P_2 significantly outperformed the treatment without adding P_0 , for which the availability phosphorus in the soil was 12.8 kg. P ha⁻¹.

The binary interactions between zeolite and phosphorous, sulfur and phosphorous achieved significant differences in the values of availability phosphorous in soil. The interaction between zeolite and phosphorous in which treatment Z_1P_2 prevailed in availability phosphorous, achieving the highest values, which amounted to 30.2 kg. P ha⁻¹, while the lowest value of availability phosphorous was when the comparison treatment Z_0P_0 , which was 11.9 kg. P

ha⁻¹, the other of the treatments varied between the significant and the non-significant. The reason may be due to mixing the zeolite mineral with chemical fertilizers, significantly affects the ion content of soil and increases its readiness due to the effect of cation exchange and adsorption properties of zeolite (Supapron *et al.*, 2002). As for the interaction between sulfur and phosphorous, the treatments S_0P_2 , S_1P_2 and S_2P_2 had the highest availability phosphorous, which were 29.0, 28.7 and 25.8 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous, which amounted to 11.3 kg, was when treatment S_1P_0 . The reason may be due to the positive effect of adding sulfur to reducing the degree of soil reaction, led to an increase in the values of availability phosphorus in the soil (Imran *et al.*, 2016).

Many of the triple interactions of zeolite, sulfur and phosphorous had a significant effect on the amount of availability phosphorus in the soil for the period of 75 days after planting. As the treatment $Z_1P_2S_0$ showed the highest rate of availability phosphorus in the soil, which was 32.1 kg. P ha⁻¹, which did not differ significantly with the treatments $Z_1P_2S_1$ and $Z_1P_2S_2$ that achieved availability phosphorous quantities in soil of 30.2 and 28.4 kg. P ha⁻¹, respectively, all of them achieved a moral superiority over many other interventions, agreed with Hassoun (2010), which indicates the importance of zeolite and sulfur in raising the values of availability phosphorus in the soil, and improve soil fertility and increase its ability to retain nutrients, when mixing zeolites with chemical fertilizers and soil (Kavoosi, 2007).

Availability phosphorus in the soil at the period of 90 days after planting

Table (7) indicates that the addition of zeolite has a significant effect on the values of availability phosphorous in the soil at the period of 90 days. As Z_1 level achieved a availability phosphorous in the soil amounted to 18.15 kg. P ha⁻¹, superior to the Z_0 level, which achieved 14.14 kg. P ha⁻¹, agreed with Abdel-Hassan (2018) and Hussein (2019). The addition of sulfur did not achieve a significant difference in the values of availability phosphorus in the soil during the period of 90 days, and for different levels, as for the addition of phosphorous, the P_1 level achieved the highest amount of availability phosphorous, which reached 20.58 kg. P ha⁻¹ in the soil, significantly higher than the P_2 level, which had a availability phosphorous 16.76 kg. P ha⁻¹, both of them outperformed the comparison treatment, P_0 , which had 11.10 kg. P ha⁻¹.

The binary interactions between zeolite and phosphorous, sulfur and phosphorous achieved significant differences in the values of availability phosphorous in soil. The interaction between zeolite and phosphorous had significant parameters of Z_0P_1 , Z_0P_2 and Z_1P_1 in availability phosphorous, they achieved the highest values, which were 25.27, 19.27 and 15.89 kg. P ha⁻¹, respectively. while the lowest value of availability phosphorous when the comparison treatment was Z_0P_0 , which was 9.92 kg. P ha⁻¹, the reason may be due to mixing the zeolite mineral with chemical fertilizers, it significantly affects the ion content of the soil, and increase its readiness due to the effect of cation exchange and adsorption properties of zeolite (Supapron *et al.*, 2002). As for the interaction between sulfur and phosphorous, the

treatments S_1P_1 , S_2P_2 and S_0P_1 had the highest values of availability phosphorous, which were 25.27, 21.88 and 19.20 kg. P ha⁻¹, respectively, while the lowest value of availability phosphorous was when S_1P_0 was treated, which was 10.79 kg. P ha⁻¹. The reason may be due to the positive effect of adding sulfur to reducing the degree of soil reaction, led to an increase in the values of availability phosphorous in the soil (Imran *et al.*, 2016).

Many of the triple interactions of zeolite, sulfur and phosphorous, the effect was significant on the amount of availability phosphorous in the soil for the period 90 days after planting, as the treatment $Z_0P_1S_1$ showed the highest rate of availability phosphorous in the soil, amounted to 33.92 kg. P ha⁻¹, and that did not differ significantly with the treatments $Z_0P_1S_0$ and $Z_0P_2S_2$, which achieved availability phosphorous quantities in the soil were 29.19 and 24.97 kg. P ha⁻¹, respectively, all of them achieved significant superiority over many other interactions, agreed with Hassoun (2010), which indicates the importance of zeolite and sulfur in raising the values of availability phosphorous in the soil, and improve soil fertility and increase its ability to retain nutrients, when mixing zeolites with chemical fertilizers and soil (Kavoosi, 2007).

Release phosphorus in study soil:

Amount of accumulation release phosphorus

Tables (8 and 9) show the amount of accumulation release phosphorous extracted, after six successive extracts of citric acid (M-1 10 x 5), at extraction periods (15-90) days from planting in the soil, which was a kinetic standard synonymous with traditional criteria, t_{To} to express the availability phosphorous in the soil. The results indicate an increase in the amount of released phosphorous in the first stage (15-60) days after planting, and a decrease in the amount of released phosphorous in the last stages in all treatments, this applies with the need of the plant in the first growth stage, which requires large amounts of accumulation release phosphorous in the soil. S_2P_1 , S_2P_2 , S_2 , $Z_1P_1S_1$ and $Z_1P_2S_1$ treatments achieved, the highest amount of availability phosphorous, the rest was 10.32, 10.22, 9.16, 9.01 and 9.01 mg. P kg⁻¹ soil, respectively. As for the lowest amount of accumulation release phosphorous, it was obtained by equations 0, P_1 and Z_1 , for the rest of 4.9, 5.46, and 5.99 mg. P kg⁻¹, respectively. The priority of treatments can be arranged in the following order:

$$S_2P_1 > S_2P_2 > S_2 > Z_1P_1S_1 = Z_1P_2S_1$$

Kinematic equations for describing a released phosphorus and a coefficient of phosphorus release velocity (Kd):

Kinetic equations have been used to describe the release of phosphorus from soil, by the effect of adding zeolite and sulfur extracted with citric acid (M-1 10 x 5) over time in soil. The amount of released phosphorous was used as a function of time and tested the following kinematic equation, to describe the results and find the best equation describing

the release phosphorous mechanism: The first-order and Ilovege equations. used a statistical indicator to determine the best equation. They are the values of the correlation coefficient (r) and the release velocity coefficient (Kd).

The results in Table (10) refer to the kinematic equations and the values of the correlation coefficient (r), release phosphorous velocity coefficient (Kd), to describe the release of phosphorous in soil due to the effect of addition of zeolite and sulfur. The results show that the two equations described release phosphorous in all treatments, where the correlation coefficient (r) was highly significant for the two equations, but the best of these two equations to describe release phosphorous ws the Elovich equation, which gave the highest value of the correlation coefficient (r). The kinetic equation can be arranged to describe the release of phosphorus from soil, with the effect of adding zeolite and sulfur according to preference as follows:

$$\text{Elovich} > \text{First order}$$

The preference of a mechanical Elovich equation explains the release phosphorous of soil for the different treatments, it was found that the amount of released phosphorous from the soil under the influence of different treatments, correlates directly with time, the time factor is the determining and controlling the release and dissolution of phosphorus from the fertilizer added to the soil, leads to when developing phosphorus fertilization plans. Its dissolution is gradual in the first periods of plant growth and then increases with time, affected by the addition of sulfur, its oxidation stages, and zeolites.

Table (10) show the best kinematic equation, the values of the correlation coefficient (r) and the values of the release phosphorous velocity coefficient (Kd) for the different parameters, computed from the straight line equation of linear kinematic equation. The values of the release phosphorous velocity coefficient obtained from the Elovich equation ranged between 0.1240-0.2950 mg. P kg⁻¹ soil. Day⁻¹ for the two treatments (control and S_2P_2). The results indicate the advantage of the Elovich equation in describing the release of phosphorus in soil, it was found that the values of the release phosphorous velocity factor were between 0.0008-0.0011 mg. P kg⁻¹ soil. Day⁻¹, from the first-order equation for the two treatments (control, S_2 , S_1 and S_1P_1). The values varied with different experimental treatments, addition levels, and sampling periods during plant growth periods. The correlation coefficient was the best predictor of release phosphorous over time, Elovich equation achieved the highest correlation.

For many treatments compared to the first-order equation, as the treatment S_1P_2 achieved the highest correlation coefficient, which reached 0.9879, while the highest correlation coefficient in the equation of the first order for $Z_1S_2P_1$ of 0.7724. The lowest correlation coefficient of the two equation (Elovich and the first-order equations).

Table 2 : The effect of levels of zeolite, sulfur and phosphorous in availability phosphorous (mg. P kg⁻¹ soil) after 15 days of planting.

Zeolite	Phosphorus (Kg. ha ⁻¹)	Sulfur (Kg. ha ⁻¹)			Mean (Z×P)
		S ₀	S ₁	S ₂	
Z ₀	P ₀	20.7	19.9	19.8	20.1
	P ₁	31.1	34.0	30.1	31.7
	P ₂	34.4	47.5	49.7	43.9
Z ₁	P ₀	14.9	16.8	12.3	14.7
	P ₁	22.7	46.4	31.3	33.5
	P ₂	41.9	43.1	38.6	41.2
L.S.D _{0.05}	Z×P×S= 19.63				Z×P= 11.34
Zeolite	Sulfur (Kg. ha ⁻¹)				Mean (Z)
	S ₀	S ₁	S ₂	Mean (Z)	
Z ₀	28.7	33.8	33.2	31.9	
Z ₁	26.5	35.4	27.4	29.8	
L.S.D _{0.05}	Z × S = 11.34				Z = 6.54
Phosphorus	Sulfur (Kg. ha ⁻¹)			Mean (P)	
	S ₀	S ₁	S ₂		
P ₀	17.8	18.3	16.0	17.4	
P ₁	26.9	40.2	30.7	32.6	
P ₂	38.2	45.3	44.1	42.5	
L.S.D _{0.05}	P×S = 13.88				P = 8.02
Mean (S)	27.6	34.6	30.3		
L.S.D _{0.05}	S = 8.02				

Table 3 : The effect of levels of zeolite, sulfur and phosphorous in availability phosphorous (mg. P kg⁻¹ soil) after 30 days of planting.

Zeolite	Phosphorus (Kg. ha ⁻¹)	Sulfur (Kg. ha ⁻¹)			Mean (Z×P)
		S ₀	S ₁	S ₂	
Z ₀	P ₀	18.8	19.6	25.5	21.3
	P ₁	29.2	29.1	14.7	24.3
	P ₂	28.1	21.4	21.2	23.5
Z ₁	P ₀	18.4	21.2	21.9	20.5
	P ₁	21.7	23.5	4.71	20.0
	P ₂	33.4	30.1	36.8	33.5
L.S.D _{0.05}	Z×P×S= 14.51				Z×P= 8.38
Zeolite	Sulfur (Kg. ha ⁻¹)				Mean (Z)
	S ₀	S ₁	S ₂	Mean (Z)	
Z ₀	25.4	23.3	20.5	23.1	
Z ₁	24.5	25.0	21.1	23.5	
L.S.D _{0.05}	Z × S = 8.38				Z = 4.84
Phosphorus	Sulfur (Kg. ha ⁻¹)			Mean (P)	
	S ₀	S ₁	S ₂		
P ₀	18.6	20.4	23.7	20.9	
P ₁	25.4	26.3	9.71	23.8	
P ₂	30.7	25.8	29.0	28.5	
L.S.D _{0.05}	P×S = 10.26				P = 5.92
Mean (S)	24.9	24.2	24.1		
L.S.D _{0.05}	S = 5.92				

Table 4 : The effect of levels of zeolite, sulfur and phosphorous in availability phosphorous (mg. P kg⁻¹ soil) after 45 days of planting.

Zeolite	Phosphorus (Kg. ha ⁻¹)	Sulfur (Kg. ha ⁻¹)			Mean (Z×P)
		S ₀	S ₁	S ₂	
Z ₀	P ₀	16.1	17.7	20.6	18.1
	P ₁	25.6	22.8	21.3	23.2
	P ₂	36.6	35.4	34.1	35.4
Z ₁	P ₀	21.3	24.7	22.0	22.6
	P ₁	38.8	27.6	29.8	32.1
	P ₂	40.4	38.0	35.6	38.0
L.S.D _{0.05}	Z×P×S= 14.63				Z×P= 8.45
Zeolite	Sulfur (Kg. ha ⁻¹)				Mean (Z)
	S ₀	S ₁	S ₂	Mean (Z)	
Z ₀	26.1	25.3	25.3	25.6	
Z ₁	33.5	30.1	29.1	30.9	
L.S.D _{0.05}	Z × S = 8.45				Z = 4.88
Phosphorus	Sulfur (Kg. ha ⁻¹)			Mean (P)	
	S ₀	S ₁	S ₂		
P ₀	18.7	21.2	21.3	20.4	
P ₁	32.2	25.2	25.6	27.7	
P ₂	38.5	36.7	34.8	36.7	
L.S.D _{0.05}	P×S = 10.34				P = 5.97
Mean (S)	29.8	27.7	27.2		
L.S.D _{0.05}	S = 5.97				

Table 5 : The effect of levels of zeolite, sulfur and phosphorous in availability phosphorous (mg. P kg⁻¹ soil) after 60 days of planting.

Zeolite	Phosphorus (Kg. ha ⁻¹)	Sulfur (Kg. ha ⁻¹)			Mean (Z×P)
		S ₀	S ₁	S ₂	
Z ₀	P ₀	14.4	19.1	19.1	17.6
	P ₁	21.5	30.0	27.1	26.2
	P ₂	23.6	28.1	34.0	28.6
Z ₁	P ₀	15.3	22.0	23.9	20.4
	P ₁	29.7	36.8	24.6	30.4
	P ₂	37.0	30.8	34.5	34.1
L.S.D _{0.05}	Z×P×S= 20.29				Z×P= 11.71
Zeolite	Sulfur (Kg. ha ⁻¹)				Mean (Z)
	S ₀	S ₁	S ₂	Mean (Z)	
Z ₀	19.9	25.8	26.7	24.1	
Z ₁	27.4	26.5	24.3	26.1	
L.S.D _{0.05}	Z × S = 11.71				Z = 6.76
Phosphorus	Sulfur (Kg. ha ⁻¹)			Mean (P)	
	S ₀	S ₁	S ₂		
P ₀	14.9	15.5	16.5	15.6	
P ₁	25.6	33.4	25.9	28.3	
P ₂	30.3	29.5	34.3	31.3	
L.S.D _{0.05}	P×S = 14.35				P = 8.28
Mean (S)	23.6	26.1	25.5		
L.S.D _{0.05}	S = 8.28				

Table 6 : The effect of levels of zeolite, sulfur and phosphorous in availability phosphorous (mg. P kg⁻¹ soil) after 75 days of planting.

Zeolite	Phosphorus (Kg. ha ⁻¹)	Sulfur (Kg. ha ⁻¹)			Mean (Z×P)
		S ₀	S ₁	S ₂	
Z ₀	P ₀	10.6	13.1	11.9	11.9
	P ₁	29.6	17.6	19.1	22.1
	P ₂	25.9	27.3	23.3	25.5
Z ₁	P ₀	15.1	9.6	16.4	13.7
	P ₁	18.8	26.0	22.1	22.3
	P ₂	32.1	30.2	28.4	30.2
L.S.D _{0.05}	Z×P×S= 17.04				Z×P= 9.84
Zeolite	Sulfur (Kg. ha ⁻¹)				
	S ₀	S ₁	S ₂	Mean (Z)	
Z ₀	22.0	19.3	18.1	19.8	
Z ₁	22.0	21.9	22.3	22.1	
L.S.D _{0.05}	Z × S = 9.84				Z = 5.68
Phosphorus	Sulfur (Kg. ha ⁻¹)				
	S ₀	S ₁	S ₂	Mean (P)	
P ₀	12.8	11.3	14.1	12.8	
P ₁	24.2	21.8	20.6	22.2	
P ₂	29.0	28.7	25.8	27.9	
L.S.D _{0.05}	P×S = 12.05				P = 6.96
Mean (S)	22.0	20.6	20.2		
L.S.D _{0.05}	S = 6.96				

Table 7 : The effect of levels of zeolite, sulfur and phosphorous in availability phosphorous (mg. P kg⁻¹ soil) after 90 days of planting.

Zeolite	Phosphorus (Kg. ha ⁻¹)	Sulfur (Kg. ha ⁻¹)			Mean (Z×P)
		S ₀	S ₁	S ₂	
Z ₀	P ₀	11.58	8.27	9.90	9.92
	P ₁	29.19	33.92	12.69	25.27
	P ₂	15.70	17.14	24.97	19.27
Z ₁	P ₀	11.08	13.31	12.49	12.29
	P ₁	14.56	16.63	16.47	15.89
	P ₂	17.32	11.98	13.42	14.24
L.S.D _{0.05}	Z×P×S= 7.662				Z×P= 4.423
Zeolite	Sulfur (Kg. ha ⁻¹)				
	S ₀	S ₁	S ₂	Mean (Z)	
Z ₀	18.82	19.78	15.85	18.15	
Z ₁	14.32	13.97	14.13	14.14	
L.S.D _{0.05}	Z × S = 4.423				Z = 2.554
Phosphorus	Sulfur (Kg. ha ⁻¹)				
	S ₀	S ₁	S ₂	Mean (P)	
P ₀	11.33	10.79	11.19	11.10	
P ₁	21.88	25.27	14.58	20.58	
P ₂	16.51	14.56	19.20	16.76	
L.S.D _{0.05}	P×S = 5.418				P = 3.128
Mean (S)	22.0	20.6	20.2		
L.S.D _{0.05}	S = 3.128				

Table 8 : Amount of released phosphorus and extracted with citric acid during extraction periods (15-90 days).

T (day)	15	15	15	15	15	15
Tret.	mgP.kg ⁻¹					
0	1.61	1.75	0.85	0.39	0.18	0.13
S ₁	1.67	2.82	1.77	0.56	0.53	0.43
S ₂	2.21	2.69	2.48	0.65	0.59	0.57
P ₁	1.74	1.87	0.99	0.39	0.29	0.18
S ₁ P ₁	1.82	2.53	1.93	0.41	0.67	0.38
S ₂ P ₁	2.65	2.98	2.85	0.77	0.54	0.53
P ₂	1.97	2.14	1.77	0.57	0.32	0.29
S ₁ P ₂	1.94	2.93	1.33	0.59	0.89	0.37
S ₂ P ₂	2.63	3.00	2.74	0.81	0.69	0.35
Z ₁	1.73	1.89	1.47	0.35	0.32	0.23
Z ₁ S ₁	1.92	1.65	1.78	0.53	0.27	0.17
Z ₁ S ₂	1.95	2.14	2.22	0.58	0.32	0.19
Z ₁ P ₁	1.88	2.15	2.18	0.43	0.38	0.31
Z ₁ P ₁ S ₁	1.98	2.31	1.87	0.65	0.42	0.31
Z ₁ P ₁ S ₂	2.36	2.65	2.19	0.96	0.56	0.29
Z ₁ P ₂	2.18	2.97	1.98	0.62	0.51	0.34
Z ₁ P ₂ S ₁	2.33	2.89	1.95	0.99	0.46	0.39
Z ₁ P ₂ S ₂	2.34	2.87	2.38	0.64	0.31	0.25

Table 9 : Accumulation release phosphorus extracted with citric acid during extraction periods (15-90 days)

T (day)	15	30	45	60	75	90
Tret.	mgP.kg ⁻¹					
0	1.61	3.36	4.21	4.60	4.78	4.91
S ₁	1.67	4.49	6.26	6.82	7.35	7.78
S ₂	2.21	4.90	7.38	8.03	8.62	9.16
P ₁	1.74	3.61	4.60	4.99	5.28	5.46
S ₁ P ₁	1.82	4.35	6.28	6.69	7.36	7.74
S ₂ P ₁	2.65	5.63	8.48	9.25	9.79	10.32
P ₂	1.97	4.11	5.88	6.45	6.77	7.06
S ₁ P ₂	1.94	4.87	6.20	6.79	7.68	8.05
S ₂ P ₂	2.63	5.63	8.37	9.18	9.87	10.22
Z ₁	1.73	3.62	5.09	5.44	5.76	5.99
Z ₁ S ₁	1.92	3.57	5.35	5.88	6.15	6.32
Z ₁ S ₂	1.95	4.09	6.31	6.89	7.21	7.40
Z ₁ P ₁	1.88	4.03	6.21	6.64	7.02	7.33
Z ₁ P ₁ S ₁	1.98	4.29	6.16	6.81	7.23	7.54
Z ₁ P ₁ S ₂	2.36	5.01	7.20	8.16	8.72	9.01
Z ₁ P ₂	2.18	5.15	7.10	7.72	8.23	8.57
Z ₁ P ₂ S ₁	2.33	5.22	7.17	8.16	8.62	9.01
Z ₁ P ₂ S ₂	2.34	5.21	7.59	8.23	8.54	8.79

Table 10 : Kinematic equations for different parameters, release phosphorous speed coefficient (kd) and correlation coefficient (r) during the different plant growth period (15-90) days.

Treatment	first-order equation		Elovich equation	
	R ²	Kd	R ²	Kd
0	0.7083	0.0008	0.9657	0.1240
S ₁	0.7199	0.0011	0.9851	0.2285
S ₂	0.7649	0.0011	0.9818	0.2651
P ₁	0.7275	0.0008	0.9715	0.1395
P ₁ S ₁	0.745	0.0011	0.9826	0.2233
P ₁ S ₂	0.762	0.0010	0.9767	0.2950
P ₂	0.752	0.0010	0.9753	0.1956
P ₂ S ₁	0.7426	0.0010	0.9879	0.2254
P ₂ S ₂	0.7634	0.0010	0.9792	0.2942
Z ₁	0.739	0.0009	0.9757	0.1624
Z ₁ S ₁	0.7712	0.0009	0.9679	0.1736
Z ₁ S ₂	0.7475	0.0010	0.9634	0.2145
Z ₁ P ₁	0.7476	0.0010	0.967	0.2109
Z ₁ P ₁ S ₁	0.7564	0.0010	0.9854	0.2136
Z ₁ P ₁ S ₂	0.7724	0.0010	0.9845	0.2583
Z ₁ P ₂	0.7263	0.0010	0.9753	0.2417
Z ₁ P ₂ S ₁	0.756	0.0010	0.9853	0.2551
Z ₁ S ₂ P ₂	0.7214	0.0010	0.9654	0.2497

References

- Abdi, G.H.; Khui, M.K. and Eshghi, S. (2006). Effects on natural zeolite on growth and flowering on strawberry. *Int J Agric Res.*, 1: 384-389.
- Abdul-Hassan, S.N. (2018). The use of zeolite to improve the physical properties of soils of different textures and the growth of wheat plants. Master thesis, Faculty of Agriculture, Al-Muthanna University, Iraq.
- Abu Dahi, Y.M. and Al-Yunis, M.A. (1988). *Plant Nutrition Guide*, Ministry of Higher Education, University of Baghdad.
- Adhya, T.K.; Kumar, N.; Reddy, G.; Podile, A.R.; Bee, H. and Samantaray, B. (2015). Microbial mobilisation of soil phosphorus and sustainable P management in agricultural soils. *Current Science*, 108: 1280-1287.
- Al-Barakat, H.N.K. (2016). The effect of biological fertilization and addition of humic and fulvic acids on the readiness of iron and zinc in the soil and the yield of yellow corn. PhD thesis. Soil Department, University of Baghdad, College of Agriculture.
- Ali N.S. and Abdel Razzaq, S.A. (2016). Soil material and organic fertilization and their role in sustainable agriculture. Desertification Combat Section. faculty of Agriculture. Baghdad University. Ministry of Higher Education and Scientific Research.
- Al-Jubouri, A.L. (1999). The effect of sulfur and organic matter on phosphorous readiness in soil. Master thesis. faculty of Agriculture. Baghdad University.
- Awad, K.M. (1987). *Fertilization and soil fertility*. Directorate of Dar Al Kutub for Printing and Publishing. University of Al Mosul.
- Hassoun, S.N. (2010). The effect of levels of sulfur, magnesium, and phosphate rock on phosphorous release and growth of wheat yield. Master thesis, Soil Department, University of Baghdad, College of Agriculture, Iraq.
- Hussein, N.A. (2019). The effect of fine and coarse zeolites on soil properties, growth and yield of wheat. Master thesis, Faculty of Agriculture, Al-Muthanna University, Iraq.
- Imran, R.A.; Hussein, H.J. and Zahir, A.T. (2016). The effect of agricultural sulfur and concentrated superphosphate fertilizer on the readiness of phosphorous and its concentration in the leaves of the white corn crop (*Sorghum bicolor* L.) during its different stages of growth. *Dhi Qar University Journal*, 5(1): 217-221.
- Kavoosi, M. (2007). Effects of Zeolite Application on Rice Yield, Nitrogen Recovery, and Nitrogen Use Efficiency. *Communications in Soil Science and Plant Analysis*, 38(1-2): 69-76.
- Najafi-Ghiri, M. (2014). Effects of zeolite and vermicompost applications on potassium release from calcareous soils. *Soil and Water Research*, 9(1): 31-37.
- Page, A.L.; Miller, R.H. and Keeney, D.R. (1982). *Methods of soil analysis, Part2*, 2nd Ed. American Society of Agronomy: Madison, WI.
- Simard, R.R.; Zizka, J. and De Kimpe, C.R. (1992). Release of potassium and magnesium from soil fractions and its kinetics. *Soil Science Society of America Journal*, 56(5): 1421-1428.
- Simard, R.R.; Zizka, J. and Kimpe, C.D. (1989). The kinetics of nonexchangeable potassium and magnesium release from Quebec soils. *Canadian Journal of Soil Science*, 69(3): 663-675.
- Supapron, J.; Pitayakon, L.; Kamalapa, W. and Touchamon, P. (2002). Effect of zeolite and chemical fertilizer on the change of physical and chemical properties on Lat Ya soil series for sugar cane. 17th WCSS, 14-21 august 2002. Thailand. Symposium no. 57. Paper co. 1897.