Iraqi Journal of Market Research and Consumer Protection
(2025) 17(1): 103-117
DOI:
Ghali & Shref

المجلة العراقية لبحوث السوق
وحماية المستهلك

STUDY OF THE EFFECT OF ZEOLITE AND AGRICULTURAL SULFUR ON THE PHOSPHORUS ADSORPTION AND RELEASE FROM ROCK PHOSPHATE IN CALCAREOUS SOIL

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Received 2/ 8/ 2023, Accepted 29/ 10/ 2023, Published 31/ 3/ 2025

ABSTRACT

Three experiments were conducted, an incubation experiment, to find out the effect of adding agricultural sulfur on the phosphorus release from rock phosphate and the amount of its adsorption on zeolite in a loamy calcareous soil taken from one of the fields affiliated with the College of Agricultural Engineering Sciences, University of Baghdad - Al-Jadriya, and zeolite was added to it at two levels (0.10) Mg.ha^{-1}. and agricultural sulfur at two levels (0.2) Mg.ha^{-1} and rock phosphate at two levels (0.80) kg P.ha^{-1} and mineral phosphorus were added in the form of Di Ammonium Phosphate (DAP) fertilizer at a level of (80) kg P.ha^{-1} as a control sample with three replicates 'according to the Randomized Complete Block Design (RCBD) for an incubation period of 60 days. Furthermore, the isothermal adsorption experiment of phosphorus using the parameters of the incubation experiment at its highest levels, which were treated with different concentrations of phosphorus (100, 200, 300, 400, and 500) µg P.ml^{-1}, and the phosphorus release experiment for the soil on which adsorption was conducted for one level of phosphorus (500) µg.g^{-1} soil, for the different treatments. The results of the incubation experiment showed a significant effect of the triple interaction between the treatments, as the highest value was (30.93) mg.kg^{-1}, compared to the control treatment, which amounted to (6.91) mg.kg^{-1}. Moreover, the adsorption experiment showed an increase in the adsorbed amount when zeolite was added to the soil, as the maximum adsorption values were Xm1428.57 and 2000 µg P.g^{-1} soil, and the bonding energy was 0.014 and 0.0114 µg P.ml^{-1} at the soil treatment and the soil treatment with zeolite respectively. The release amount of phosphorus increased when adding agricultural sulfur and zeolite with a ratio of 10.85, 56.11 and 63.31% for soil treatment with sulfur, soil treatment with zeolite, and soil treatment with zeolite and sulfur, respectively, compared to soil treatment only.

Keywords: Adsorption and release, Zeolites, Agricultural sulfur, Rock phosphate, Calcareous soils.

[*] **The article is taken from the master's thesis of the first researcher.**

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دراسة تأثير الزيولايت والكبريت الزراعي على امتزاز وتحرر الفسفور من الصخر الفوسفاتي في تربة كلسية

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الخلاصة

أجريت ثلاث تجارب وهي تجربة تحضين لمعرفة تاثير اضافة الكبريت الزراعي في تحرر الفسفور من الصخر الفوسفاتي ومقدار مايتم امتزازه على الزيولايت في تربة كلسية مزيجة أُخذت من احد الحقول التابعة لكلية علوم الهندسة الزراعية جامعة بغداد- الجادرية،وأُضيف لها الزيولايت بمستويين (10.0)ميكاغرام هـ$^{-1}$ والكبريت الزراعي بمستويين (2.0) ميكاغرام هـ$^{-1}$ والصخر الفوسفاتي بمستويين (80.0) كغمPهـ$^{-1}$ والفسفور المعدني اضيف بشكل سماد فوسفات ثنائي الامونيوم (DAP) بمستوى (80) كغم P هـ$^{-1}$ كعينة مقارنة وبثلاث مكررات، وفق تصميم القطاعات العشوائية الكاملة (RCBD) ولفترة تحضين 60 يوم ، وتجربة الامتزاز الايزوثيرمي للفسفور باستعمال معاملات تجربة التحضين بأعلى مستوياتها والتي عوملت بتراكيز مختلفة من الفسفور(100و200 و300 و400 و500) مايكروغرام P مل$^{-1}$ ، وتجربة الفسفور المتحرر للتربة التي اجري عليها الامتزاز ولمستوى واحد من الفسفور (500 مايكروغرام غم$^{-1}$ تربة) للمعاملات المختلفة.اظهرت نتائج تجربة التحضين التاثير المعنوي للتداخل الثلاثي بين المعاملات اذ بلغت اعلى قيمة 30.93 ملغم كغم$^{-1}$مقارنتاً بمعاملة المقارنة والتي بلغت 6.91 ملغم كغم$^{-1}$، وبينت تجربة الامتزازازدياد الكمية الممتزةعند اضافة الزيولايت الى التربة، إذ بلغت قيم الامتزاز الاعظم1428.57Xmو2000مايكروغرامP غم$^{-1}$ تربة ، وطاقة الربط K 0.014 و 0.0114 مايكروغرام P مل$^{-1}$ عند معاملة التربة و معاملة التربة مع الزيولايت بالتتابع، وازدياد الكمية المتحررة من الفسفور عند اضافة الكبريت الزراعي و الزيولايت وبنسبة 10.85 و 56.11 و 63.31 % لمعاملة التربة والكبريت ومعاملة التربة والزيولايت ومعاملة التربة والزيولايت والكبريت مجتمعة وبالتتابع، مقارنتاً بمعاملة التربة فقط .

الكلمات المفتاحية: الامتزاز والتحرر، الزيولايت ، الكبريت الزراعي، الصخرالفوسفاتي، الترب الكلسية.

INTRODUCTION

Phosphorous is one of the basic and necessary nutrients, and it is called the key to life for its direct role in most of the basic biological processes within the plant and other living organisms in general, which cannot take place without it (**Hussein & Al-Mamouri,2022)**. Phosphate fertilizers are exposed to loss from the soil, whether through various fixation processes, or loss from the soil surface by surface irrigation water or leaching. These processes constitute a phenomenon that reduces the rate of utilization of these fertilizers so that they become less available and utilized. The substance to which fixation occurs on the surface is called the Adsorbate, and the surface on which the adsorption takes place is called the Adsorbent **(Al-Hadidi, 2009; Naser *et al.*,2020)**. Phosphorous is an important and necessary nutrient for its direct role in most of the basic vital processes within the plant, which cannot take place without it, as it is included in energy compounds, coenzymes, and the formation of nucleic acids RNA and DNA **(Hussein & Al-Mamouri, 2022)**. The chemistry of phosphorous in the soil is a complex matter because the element phosphorus is linked to many different compounds through a group of energies or bonding strength, therefore when phosphate fertilizers are added to the soil, only a small amount of phosphorus is used immediately from the plant roots, and the remaining becomes retained by the soil components **(Johnston & Steen, 2013)**. Also, phosphorus added to calcareous soils undergoes a series of interactions with carbonate minerals and calcium ions dissolved or exchanged in the soil solution, including on the surface of carbonate minerals, forming different phosphate compounds in terms of their degree of solubility and crystallization **(Nasir & Shareef, 2018)**. The Iraqi soils suffer from high concentrations of calcium ions (Ca^{+2}) and magnesium (Mg^{+2}) and carbonate minerals are among the main factors that contribute to reducing the phosphorus availability in calcareous soils due to its exposure to adsorption processes on the active surfaces of the mineral calcite ($CaCo_3$), which is prevalent in most Iraqi soils **(Nasser,2016;Hussein & Al-Maamouri, 2021)**. Therefore, the studies indicated that most of the traditional methods for measuring the availability of phosphorous are no longer sufficient, and it is necessary to shift towards thermodynamic and kinetic concepts that can give a broad and comprehensive perception of the process of adsorption and release from soil **(Barrow, 1978)**, so it is necessary to use applied aspects such as soil properties that control its ability to absorb phosphorus. This adsorption in the soil can be expressed by summarizing the numerous data for the values of adsorption using factors called constants of the equations related to the adsorption properties of the soil and then reaching a better perception of the adsorption process **(Robbins *et al.*, 1999)**. The curves are based on some physical models to represent the adsorption of ionic solutions on charged surfaces **(Al-Hadidi, 2009)**. The Iraqi soils have a high adsorption capacity for phosphorus and a low bonding energy due to the high content of lime **(Al-Obaidi & Qabaa, 2003)**. Phosphate in saline calcareous soils is subjected to adsorption reactions with mineral soil components that lead to its lack of solubility and then precipitation, fixation, and reduced availability **(Nasir & Shareef, 2018)**. Therefore, the addition of agricultural sulfur is considered a reformer for calcareous soil by increasing its acidity and thus increasing the available phosphorus in it **(El-Fahdawi *et al.*, 2020)**. Zeolite is characterized by its high ability to exchange cations due to its high porosity, as it adsorbs nutrients, including phosphorus, and releases them slowly, so it is considered a long-term supply of nutrients (prolongation effect), meaning that it facilitates increasing the availability of nutrients for plants **(Shaker & Al-Bahrani, 2021)**.Since the most important thing that plant breeders need is productivity, which is achieved by increasing the cultivated area and providing appropriate environmental conditions, the most important of which is the planting date because it has adirect on the growth and stages of crop development **(Wahed & Al-Azawi 2023).** Maize is one of the crops stressing the soil and its fertilizer needs are great because it is a C4 plant which are highly responsive to added mineral fertilizers. Iraqi soils are characterized by their lack of organic matter and high pH, which reduces the availability of the essential nutrients, especially phosphorous, so various methods have been adopted to preserve soil fertility and supply nutrients without affecting environmental factors, and among these methods is the use of agricultural sulfur, which is considered a good conditioner for the physical and chemical properties of soil**(Al-Halfi & Al-Tamimi 2017; Abdulla *et al*.,2022)**.Therefore the research aims to conduct incubation, adsorption, and release experiments of phosphorus with soil, zeolite, and agricultural sulfur at its highest levels and to estimate the available phosphorus in the incubation experiment, the maximum adsorption capacity (Xm) and the bonding energy (K) using the equation of Langmuir in the adsorption experiment.

MATERIALS AND METHODS

Calcareous soil with a clay loam texture was taken from one of the fields of the College of Agricultural Engineering Sciences, University of Baghdad - Al-Jadriya, research station (A) during the agricultural season 2021-2022 at a depth of 0-30 cm, classified according to the modern American classification system Soil Survey Staff (2006) within the level of the Typic Torrifluvent. Table (1) shows some physical and chemical properties of this soil. The soil incubation experiment was conducted after taking the weight of 250 g air-dried soil, ground and sifted through a sieve with a diameter of 2 mm, and placed in plastic pots, and agricultural sulfur was added at two levels (0.2) µg.ha^{-1}, zeolite at two levels (0 . 10) µg.ha^{-1}, and Rock Phosphate (RP) at two levels (0.80) kg P.ha^{-1} and metallic phosphorus was added in the form of DAP contains 46% P_2O_5 at a level of 80 kg P.ha^{-1} as a control sample with three replicates so that the number of units become (27) experimental units according to the RCBD Watering was done with tap water containing several elements in different concentrations **(Hasan & Muhammad 2009)** for 60 days. Then the available phosphorus was extracted from the different treatments by the Olsen method (0.5M sodium bicarbonate solution) and estimated by spectrophotometer, The result were analyzed according to what was stated in **(Al-Sahuki & Wahib 1990)**.The differences between the arithmetic means were estimated using the least significant (LSD) with a significance level of(0.05) according to the Statistical Analysis System(2001).

The phosphorus adsorption experiment was carried out on the same previous treatments of the incubation experiment using soil, zeolite, and agricultural sulfur treatments at the highest levels. 5 g of incubated soil was placed in a 100 ml centrifuge tube made of polyethylene. Then phosphorous concentrations were added to it in increasing batches of a mono potassium phosphate solution (KH_2PO_4) in an amount of 45 ml at levels (100-200-300-400-500) µg P.ml^{-1}, the samples were shaken for 24 hours and left for 24 hours at the laboratory temperature. Then shaken for 15 minutes and placed in a centrifuge at 2500 rpm for 10 minutes to separate the clear solution from the soil. The samples were filtered to obtain the clear extract and the available phosphorus concentration was estimated from the different treatments by the Olsen method (0.5M sodium bicarbonate solution) and estimated by a spectrophotometer at two wavelengths. 882nm **(Page *et al.*, 1982)**. After that, the amount of adsorbed phosphorus was calculated by subtracting the concentration of phosphorus present in the filtrate from the added phosphorus, then the relationship between the adsorbed phosphorus and phosphorus in the equilibrium solution was described using the equation of Langmuir I, where the values of each of the bonding energy (K) and the maximum adsorption capacity (Xm) were calculated by using the following linear form of the Langmuir equation:

$$\frac{C}{X} = \frac{1}{kXm} + \frac{C}{Xm}$$

Since:

X: The concentration of adsorbed phosphorous, µg P.g^{-1} soil

C: Phosphorus concentration in the equilibrium solution µg P.ml^{-1}

k: bonding energy in ml^{-1}. µg P.

Xm: maximum adsorption µg P.g^{-1} soil.

By plotting the linear relationship C/X against C, and from the regression 1/Xm and the intercept 1/KXm, the constants Xm and K were extracted.

As for the phosphorous release experiment, it was carried out for the same soil in the adsorption experiment for the level (500 µg P.ml^{-1}) to find out the concentrations of the released phosphorus for each soil sample, successive extraction five times using calcium chloride solution (0.01M) 45 ml for each sample. The treatments were shaken mechanically for a quarter of an hour. Then a centrifugation process was performed on it at 2500 rpm for 5 minutes to separate the equilibrium solution from the soil, Then the solution was filtered to ensure obtaining a clear solution and the amount of phosphorus was measured by a spectrophotometer. This process was repeated for each soil sample five times to identify the concentrations of phosphorous released in each extraction process. The relationship between the amount of phosphorus released and the number of extraction times was plotted.

Table (1): physical and chemical properties of the study soil before planting.

Property		Value	Unit
Soil reaction pH $_{1:1}$		7.90	---
Electrical conductivity EC $_{1:1}$		2.40	$ds.m^{-1}$
Cation Exchange Capacity (CEC)		19.52	$Cmol.kg^{-1}$
Organic matter		8.73	$g.kg^{-1}$
Carbonate minerals		228.13	
Available nitrogen		27.41	$mg.kg^{-1}$soil
Available phosphorous		6.91	
Available Potassium		122.97	
Soil separates	Sand	24.5	(%)
	Clay	26.5	
	Silt	49.0	
Texture type		Clay Loam	

Table (2): chemical properties of the zeolite used in the study.

Property	Value	Unit
Soil reaction pH $_{1:1}$	7.7	
Electrical conductivity EC $_{1:1}$	1.39	$ds.m^{-1}$
Cation Exchange Capacity (CEC)	181.9	$Cmol.kg^{-1}$

RESULTS AND DISCUSSION

(Table, 3) shows the effect of each zeolite, agricultural sulfur, RP, and mineral fertilizer on the concentration of available phosphorus in the soil in the incubation experiment. The results showed a significant effect of zeolite on the concentration of available phosphorus in the soil. The concentration of available phosphorus increased significantly with the addition of zeolite mineral to the soil, as the values reached 17.42 and 23.21 $mg.kg^{-1}$ for treatments Z_0 and Z_1, respectively, with an increase of 33.24%. The high concentration of available phosphorus in the soil is attributed to the mineral zeolite because it has a high cationic exchange capacity that works on ion exchange, increasing moisture, and increasing the solubility and availability of most nutrients in the soil, including the phosphorus element **(Al-Zalimi, 2020).**

As for the effect of adding agricultural sulfur on the concentration of available phosphorus in the incubated soil, the results showed a significant effect of agricultural sulfur on the concentration of available phosphorus in the incubated soil, as the values reached 14.19 and 26.44 $mg.kg^{-1}$ for treatments S_0 and S_1, respectively, with an increase of 86.33%. This is because the process of biological sulfur oxidation reached its highest stage after 60 days of the incubation experiment, and the formation of sulfuric acid, which leads to an increase in the concentration of hydrogen ions in the soil solution, and thus a decrease in the degree of interaction of the incubated soil, leading to the dissolution of some unavailable phosphorus compounds in the soil then releasing the phosphorus, leading to an increase in the availability of phosphorus in the soil **(El-Fahdawi *et al*., 2020 ; Lisowska *et al.*, 2023 ; Jafaar& Abdulrasool, 2023)**.

The results of adding RP to the concentration of available phosphorus in the incubated soil indicated that there was a significant effect of RP on the concentration of available phosphorus, as the values reached 17.57 and 23.06 $mg.kg^{-1}$ for the treatments RP_0 and RP_1, respectively, with an increase of 31.25%. This increase in the concentration of available phosphorus in soil is attributed to the fact that mixing RP with soil increased the amount of phosphorus released from RP. This is consistent with **(Yunus, 2018)**, who indicated that mixing RP with soil led to an increase in the amount of phosphorus released from RP and measured in the soil extract compared to the treatment of RP alone. **(Habib, 2011)** showed that the addition of RP mixed with soil is prone to dissolution by 62%. In addition to the role of soil microorganisms in increasing the solubility of RP through the formation of organic and inorganic acids **(Al-Janabi & Al-Rubaie, 2017 ; Khoshru *et al*., 2023)**.

As for the interaction between zeolite and agricultural sulfur in the concentration of available phosphorus in the incubated soil, the results of the statistical analysis showed that there was no significant effect between zeolite and agricultural sulfur in the availability of phosphorus for the incubation experiment, as the values reached 10.27, 18.11, 24.55 and 28.32 $mg.kg^{-1}$ for treatments Z_0S_0 and Z_1S_0, Z_0S_1, and Z_1S_1, respectively. As for the interaction between zeolite and RP in the concentration of available phosphorus for the incubation experiment, the analysis results showed that there was a significant effect between zeolite and RP in the concentration of available phosphorus. The concentration of available phosphorus increased significantly at the treatments Z_0RP_1, Z_1RP_0 and Z_1RP_1, as the values reached 21.47, 21.77 and 24.65 $mg.kg^{-1}$, respectively, compared to the control treatment Z_0RP_0, which amounted to 13.36 $mg.kg^{-1}$, with an increase of 60.70% and 62.95%. 84.51% respectively. The results indicated that there was no significant difference between the two treatments Z_0RP_1 and Z_1RP_0. The reason for the rise is due to the mixing of zeolite with RP, considering zeolite as an ion exchanger loaded with monovalent ions such as H^+, Na^+, K^+, NH^{+4} as one of the factors that help in the dissolution of RP by isolating the calcium ions released from the RP, which leads to a conversion reaction of the rock dissolution towards an increase in the phosphorus release in soil. This is consistent with **(Yunus, 2018)** who confirmed in an incubation experiment that the amount of phosphorus released increased when mixing zeolite with RP.

As for the interaction between agricultural sulfur and RP in the availability of phosphorus in the incubation experiment, the statistical analysis results showed that there was a significant effect between agricultural sulfur and RP in the available phosphorus in the soil. The available phosphorous increased significantly in the treatments S_0RP_1, S_1RP_0, and S_1RP_1, as the values reached 16.00, 22.75, and 30.12 $mg.kg^{-1}$, respectively, compared to the control treatment S_0RP_0, which amounted to 12.38 $mg.kg^{-1}$, with an increase of 29.24%, 83.76%, and 143.29. % respectively. This is due to the role of agricultural sulfur in reducing the degree of interaction of soil pH. This is consistent with **(Lisowska *et al*., 2023)**. Therefore this decrease increased the concentration of available phosphorus in the soil from RP.

As for the effect of triple interaction in the concentration of available phosphorus in the incubated soil, the statistical analysis results showed that there was a significant effect of RP, agricultural sulfur and zeolite on the concentration of available phosphorus in the soil. The average values were 13.63, 17.84, 18.37, 19.80, 25.70, 29.30 and 30.93 $mg.kg^{-1}$ for the treatments $Z_0S_0RP_1$, $Z_1S_0RP_0$, $Z_1S_0RP_1$, $Z_0S_1RP_0$, $Z_1S_1RP_0$, $Z_0S_1RP_1$, and $Z_1S_1RP_1$, respectively, compared to the control treatment $Z_0S_0RP_0$, which amounted to 6.91 $mg.kg^{-1}$, with an increase of 97.25%, 158.17%, 165.84%, and 186.5%. 4%, 271.92%, 324.02%, and 347.61%, respectively. This increase is attributed to the role of agricultural sulfur in reducing the degree of soil reaction to the extent that increases the solubility of RP, thus increasing the phosphorus release, which adsorbs on the zeolite mineral, so it is preserved from loss and released gradually when needed. When comparing the treatment of mineral fertilizer P with the triple interaction of RP, agricultural sulfur and zeolite in concentration of available phosphorus in the soil, the statistical analysis results showed significant differences, as there was a clear increase in the values of the available phosphorus for the incubation experiment for the treatments $Z_1S_1RP_0$, $Z_0S_1RP_1$, and $Z_1S_1RP_1$, which amounted to 25.70, 29.30, and 30.93 $mg.kg^{-1}$, respectively, compared to the treatment of the mineral fertilizer P, which amounted to 24.30 $mg.kg^{-1}$, with an increase of 5.76%, 20.57%, and 27.28%, respectively. This is due to the fact that the availability of the available phosphorous decreases with the increase in the incubation period in calcareous soils because it is exposed to several processes, including fixation and sedimentation, so the concentration of available phosphorus in the soil decreases. This is consistent with **(Al-Dhalimi, & AL-Barakat 2021)** when they study phosphorus readiness in Calcareous soil.

Table (3): Concentration of available phosphorus in the soil for the incubation experiment (mg.kg).

Zeolite (Z)	**Agricultural sulfur (S)**	**Rock Phosphate (RP)**		**Z x S**
		RP_0	**RP_1**	
Z_0	S_0	6.91	13.63	10.27
	S_1	19.80	29.30	24.55
Z_1	S_0	17.84	18.37	18.11
	S_1	25.70	30.93	28.32
LSD_5%		0.63**		NS
Zeolite (Z)		Z x RP		Average Z
Z_0		13.36	21.47	17.42
Z_1		21.77	24.65	23.21
LSD_5%		0.44**		0.31**
Agricultural sulfur (S)		S x RP		Average S
S_0		12.38	16.00	14.19
S_1		22.75	30.12	26.44
LSD_5%		0.44**		0.31**
Average RP		17.57	23.06	
LSD_5%		0.31**		
Average comparison of P		24.30		
LSD_5%		0.62**		

The efficiency of zeolite mineral and agricultural sulfur in the adsorption and release of phosphorus was evaluated, as the equation of Langmuir I was applied to calculate the values of the bonding energy K and the maximum adsorption Xm for phosphorus added to the soil treated with zeolite and agricultural sulfur. The results shown in (Fig. 1) and (Table 5) showed the effect of zeolite and agricultural sulfur on the amount of adsorbed phosphorus in the soil, the effect was different according to the addition of zeolite and agricultural sulfur to the soil.

The added phosphorus led to an increase in the adsorbed phosphorus in the soil, and the relationship was positive with zeolite and inversely with agricultural sulfur.

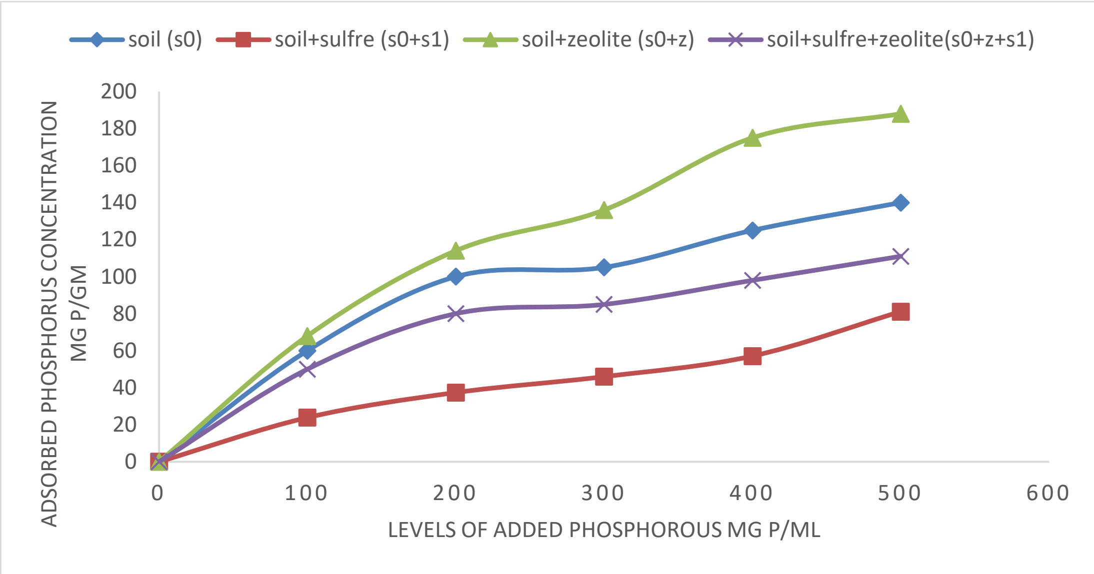

Figure (1) Effect of zeolites, agricultural sulfur, and phosphorus levels on the amount of phosphorus adsorbed in the soil.

(Table 4) and (Figures 2 and 3) show that when zeolite was added to the soil, the adsorbed amount of phosphorus increased in the soil, reaching 60 (µg P. gm^{-1} soil) at the control treatment S_0 to 68(µg P. gm^{-1} soil) at the soil treatment with zeolite 10 µg.ha^{-1} S_0 + Z, respectively for the level of phosphorus addition of 100 (µg P. ml^{-1}) (Table 5). The increases in the amount of adsorbed phosphorus continued with the increase in the levels of phosphorus added to the soil. Its quantity for the last level, 500(µg P. ml^{-1}), reached 140 and 188 (µg P. gm^{-1} soil) at S_0 and soil treatment with zeolite S_0 + Z, respectively. This was observed in the greatest adsorption capacity Xm and the bonding energy K in the phosphorus retention, as the values of Xm reached 1428.57 and 2000 µg P.gm^{-1} soil, with an increase of 40%, and the K values reached 0.014 and 0.0114 µg P.ml^{-1}, with a decrease of 18.57% at the soil treatment S_0 and the soil treatment with zeolite S_0 + Z, respectively. The reason for the increase in the amount of adsorbed phosphorus and the variation in the maximum adsorption values (Xm) and the bonding energy (K) is that the zeolite mineral has a high cationic exchange capacity as a result of the negative charge resulting from the symmetric substitution of cations in the mineral's crystal lattice, in addition to the cationic exchange capacity of the original soil, which increased the adsorbed amount of phosphorus. This was found by **(Yunus, 2018; Perumal *et al*., 2021 ; Deng *et al*., 2022 ; Marwa & Buthaina 2022)** when studying the effect of zeolite on the adsorption and release of phosphorus in the soil.

While (Figures 4 and 5) shows a decrease in the concentration of adsorbed phosphorus in the soil with the addition of agricultural sulfur 2 µg.ha^{-1} to the soil treatment S_0 and the soil treatment with zeolite S_0 + Z, which amounted to 23.87 and 50 (µg P. gm^{-1} soil), respectively, compared to the soil treatment only S_0, which amounted to 60 (µg P. gm^{-1} soil), and for the level of phosphorus addition 100 (µg P. ml^{-1}). The decrease in the amount of adsorbed phosphorus continued with the increase in the levels of phosphorus added to the soil, as its quantity for the last level reached 500 (µg P. ml^{-1}) 81.14, 111 and 140 (µg P. gm^{-1} soil)for soil treatment with agricultural sulfur S_0 + S_1 and the soil treatment with zeolite and agricultural sulfur S_0 + Z + S_1 and the soil treatment S_0 respectively. This was also observed in the maximum adsorption capacity Xm and the bonding energy K in phosphorus retention, as the values of Xm reached 1428.57, 833.33 and 1111.11 µg P.gm^{-1} soil, with a decrease of 41% and 22%, and the K values were 0.014, 0.0043, and 0.012, with a decrease of 69% and 14% for the soil treatment only S_0, the soil treatment with agricultural sulfur S_0 + S_1, and the soil treatment with zeolite and agricultural sulfur S_0 + Z + S_1, respectively. The reason for the decrease in the amount of adsorbed phosphorus and the average values of greatest adsorption and bonding energy when adding agricultural sulfur to the soil is attributed to the high ability of this compound to reduce the effect of carbonate minerals in the soil by reducing the pH and dissolving those compounds containing phosphorus or by maintaining the availability of phosphorus and decrease adsorption or precipitation on the surfaces of carbonate minerals **(El-Fahdawi *et al*., 2020)**.

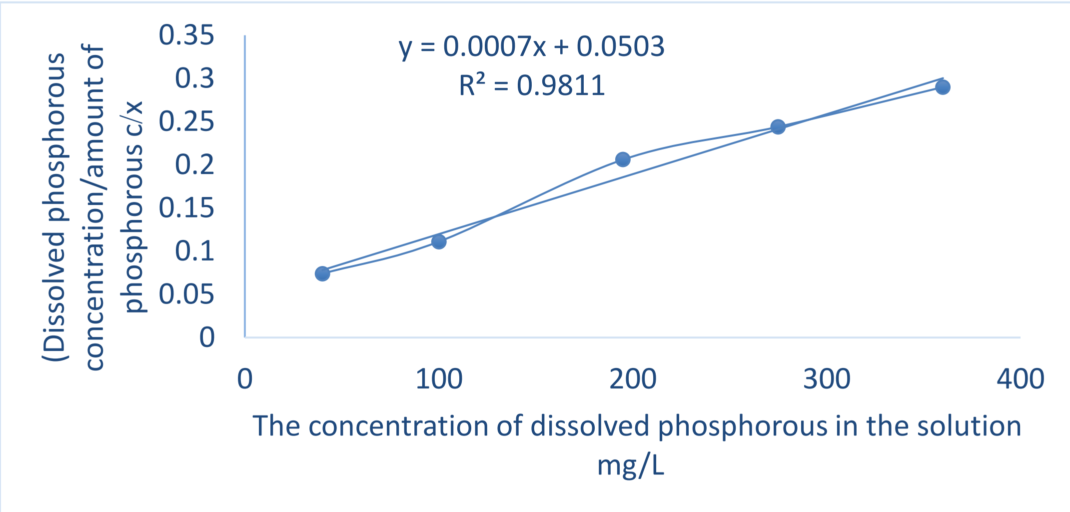

Figure (2): The relationship between the phosphorus concentration in the equilibrium solution (C) and the (C/X) values for the S_0 treatment.

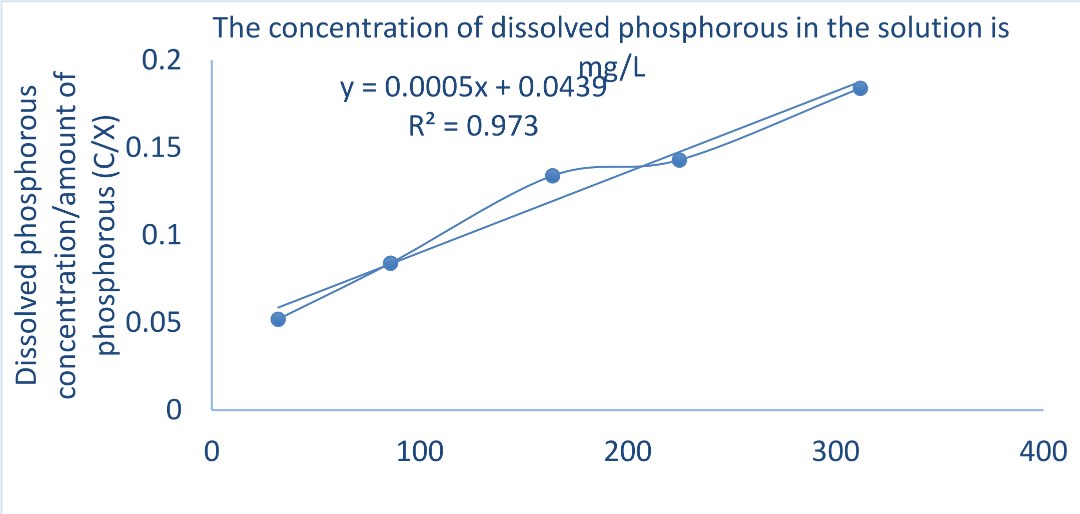

Figure (3): The relationship between the phosphorus concentration in the equilibrium solution (C) and the (C/X) values for the S_0+Z treatment.

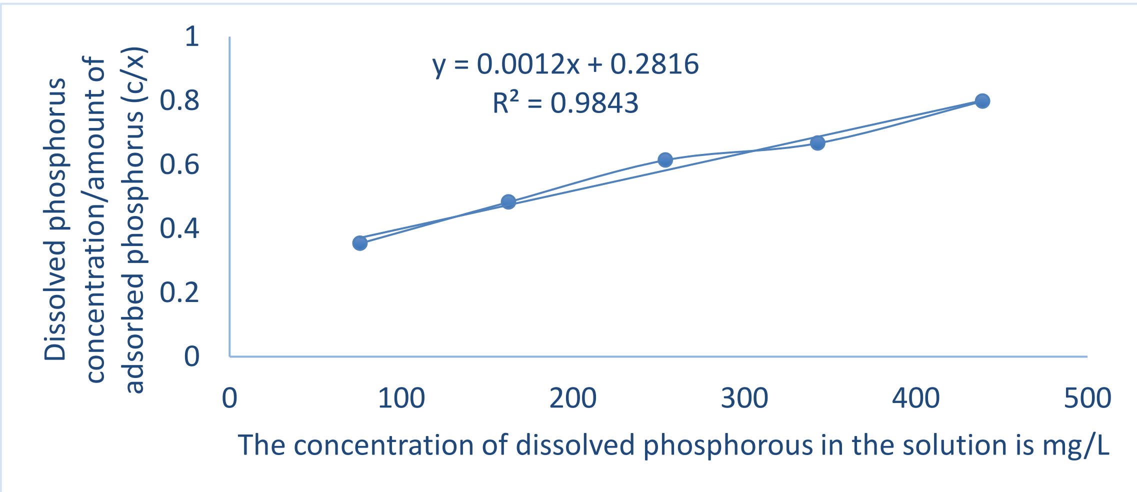

Figure (4): The relationship between the phosphorus concentration in the equilibrium solution (C) and the (C/X) values for S_0+S_1 treatment.

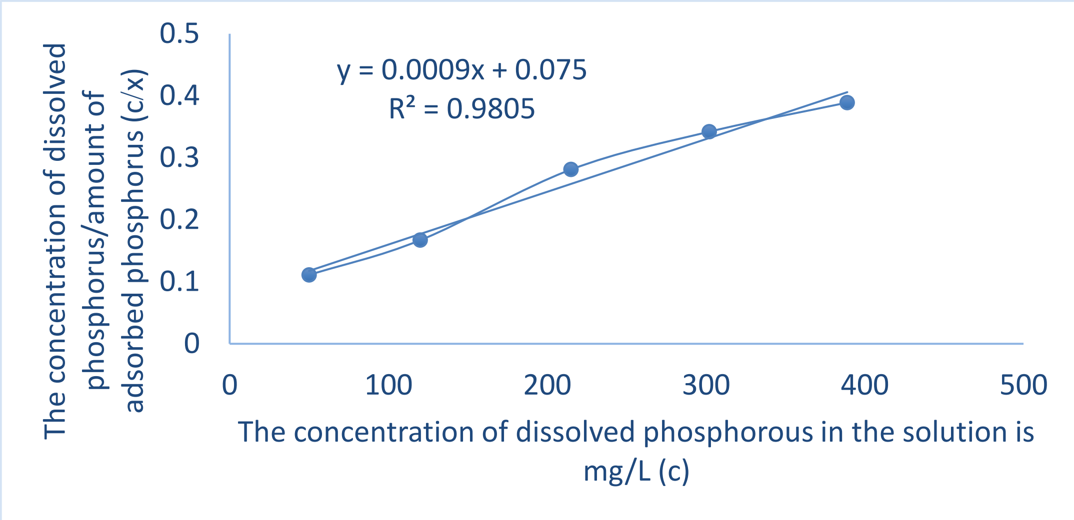

Figure (5): The relationship between the phosphorus concentration in the equilibrium solution (C) and the (C/X) values for the treatment S_0+Z+S_1.

Table (4): The effect of zeolite and agricultural sulfur on the values of bonding energy (K) and maximum adsorption (Xm).

Seq.	Treatment	Bonding energy (K) µg P.ml^{-1}	Max adsorption (Xm) µg P.gm^{-1} soil
1	Soil (S_0)	0.014	1428.57
2	Soil and sulfur (S_1+S_0)	0.0043	833.33
3	Soil and zeolites (S_0+Z)	0.0114	2000.00
4	(Soil, zeolite, and sulfur (S_0+Z+S_1)	0.012	1111.11

(Fig. 6) and (Table 6) also shows the effect of adding zeolite and agricultural sulfur on the amount of phosphorus released collectively. The results observed that the amount of released phosphorus increased when adding agricultural sulfur and zeolite mineral by 10.85, 56.11 and 63.31% for the soil and sulfur treatment S_0 + S_1 and the soil and zeolite treatment S_0 + Z and the soil, zeolite, and sulfur treatment S_0 + Z + S_1 respectively, compared to the soil treatment only S_0 (Not adding agricultural sulfur and zeolite mineral). It is noted that the released quantity was higher when treating the addition of agricultural sulfur and zeolite mineral combined S_0 + Z + S_1, followed by the treatment of zeolite mineral S_0 + Z and the agricultural sulfur treatment S_0 + S_1 and finally the soil treatment only S_0, as the released amount of five consecutive extractions was 105.27, 100.63 and 71. 46 and 64.46 µg P. gm^{-1} soil, respectively (Table 6). This is consistent with what was obtained from the values of bonding energy (K) and maximum adsorption (Xm) in the treatment of agricultural sulfur and soil S_0 + S and the treatment of agricultural sulfur, zeolite, and soil S_0 + Z + S_1 with the lowest value in bonding energy (K) and maximum adsorption (Xm) (Table 6). It is noted from (Figure 6) and (Table 6) the decrease in the cumulative released amount of soil and agricultural sulfur treatment S_0 + S_1, because the initial amount of adsorbed phosphorus is low and the dissolved phosphorus is high (Table 4). Consequently, the results showed a decrease in the cumulative released amount of phosphorus in the soil, and it is noted from (Figure 6) and (Table 6) the increase in the amount released for the two treatments $S_0 + Z + S_1$ and $S_0 + Z$ and the treatment $S_0 + Z + S_1$ by 4.61% over the treatment $S_0 + Z$ that has the highest adsorption capacity (Xm) (Table 4). The zeolite mineral has a High cation exchange capacity as a result of the negative charge resulting from the symmetric substitution of cations in the mineral's crystal lattice. This is consistent with **(Perumal *et al*., 2021; Deng *et al*., 2022; Marwa & Buthaina 2022)** when studying the effect of zeolite on the adsorption and release of phosphorus in the soil.

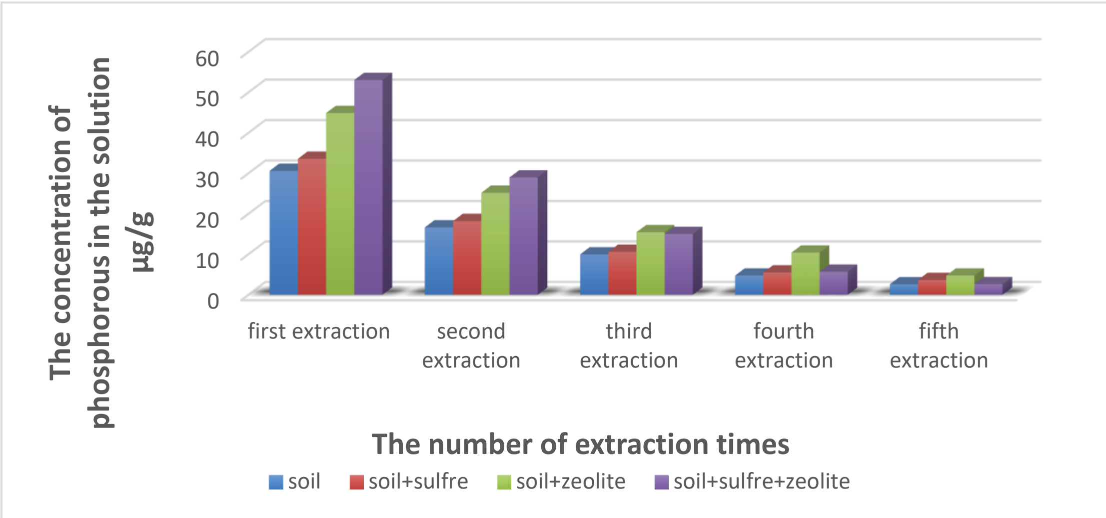

Figure (6): The effect of zeolite and agricultural sulfur on the release of phosphorus from the soil.

Table (5): Dissolved and adsorbed phosphorus in an adsorption experiment

Treatments		**Amount of added phosphorous (µg P.ml^{-1})**				
		$D_1$100	**$D_2$200**	**$D_3$300**	**$D_4$400**	**$D_5$500**
S_0	Dissolved phosphorus concentration	40.00	100.00	195.00	275.00	360.00
	Adsorbed phosphorus concentration	60.00	100.00	105.00	125.00	140.00
S_0+S_1	Dissolved phosphorus concentration	76.13	162.60	254.03	342.90	438.86
	Adsorbed phosphorus concentration	23.87	37.40	45.97	57.10	61.14
S_0+Z	Dissolved phosphorus concentration	32	86	164	225	312
	Adsorbed phosphorus concentration	68	114	136	175	188
S_0+Z+S_1	Dissolved phosphorus concentration	50	120	215	302	389
	Adsorbed phosphorus concentration	50	80	85	98	111

Table (6): The effect of adding agricultural sulfur and zeolite mineral on the released phosphorus (µg P. gm^{-1} soil).

Seq.	Treatments	Added phosphorous (µg $P.ml^{-1}$ soil)	Number of extraction times with calcium chloride ($CaCl_2$)					
			Released P (µg P. gm^{-1} soil)					
			First	Second	Third	Fourth	Fifth	Accumulative quantity
1	S_0	500	30.60	16.62	9.95	4.72	2.57	64.46
2	S_0+S_1	500	33.57	18.20	10.59	5.47	3.63	71.46
3	S_0+Z	500	44.88	25.19	15.45	10.39	4.72	100.63
4	S_0+Z+S_1	500	53.05	28.98	14.99	5.66	2.59	105.27

CONCLUSIONS

The addition of zeolite mineral to the soil led to an increase in the amount of adsorbed phosphorus and the variation in the values of maximum adsorption and bonding energy, as well as a decrease in the amount of adsorbed phosphorus and the average values of maximum adsorption and bonding energy when agricultural sulfur was added to the soil. As for the released phosphorus, its quantity increased with the addition of zeolite and agricultural sulfur to the soil, from which it can conclude the role of zeolite on the adsorption of released phosphorus from rock phosphate as a result of adding agricultural sulfur and reducing soil pH in the experiment of incubation, adsorption and release, and considering zeolite in the presence of agricultural sulfur and rock phosphate as a prepared fertilizer for phosphorus gradually for plants and an alternative to mineral fertilizer.

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