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Adsorption and desorption of P from abou-tartour phosphate rock as affected by partial acidulation with triple super phosphate and particle diameter

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The main objective of the current work is to study the effect of partial acidulation with Triple super phosphate (TSP) on the adsorption, desorption and fixation of phosphate ions and the factors affecting it (diameter of phosphate rock (PR) partially acidulated at the range and rate of application). Comparing the amounts of adsorbed P, results indicated that adsorbed phosphate increased gradually with increasing the rate of application. The relative increase for the P rates were 44.38, 70.34, 67.48, 59.18 and 40.96% for the rates of 100, 200, 300, 400 and 500 mg P kg⁻¹, respectively. Concerning the effect of acidulation by increasing the rate of TSP application, results showed decreasing the values of adsorbed P and increasing the values of desorbed P. This effect was true for all rates of P applications (100, 200, 300, 400 and 500 mg P kg⁻¹). Regarding the effect of particle diameter of Abou-Tartour PR, results revealed that using the rates of 100, 200 and 300 mg P kg⁻¹, the values of adsorbed P increased and also, the desorbed P slightly increased. In addition, decreasing the particle diameter from 500 µm to <100 nano, caused a relative decrease in fixed P at the rates of applied P (400 and 500 mg kg⁻¹). The values of the desorbed of the previously adsorbed P decreased with increasing rate of application. Phosphate adsorption efficiency (PAE %) and P desorption efficiency (PDE%) were clearly affected by acidulation with TSP and particle diameter of investigated Abou-Tartour PR.

Keywords: Phosphate rock, P adsorption and desorption, x-ray of P-rock, scanning electron microscopy, Nano particles.

INTRODUCTION

Phosphorus (P) is one of the nutrients added as fertilizers. Rock phosphate is the basic raw material for manufacturing soluble phosphate fertilizers and can be a source of P in acid soils or when given with phosphate dissolving bacteria or other P-dissolvers (Lottollahi et al., 2001). Despite it is insoluble in neutral and alkaline soils, it is rather sparingly soluble when finely ground and may be applied to acid soils, as well as neutral soils with high organic matter contents (Rao, 1993).

Rock phosphate can be chemically reactive

and may be substituted for ordinary soluble phosphate fertilizers if given in finely ground forms for soluble P fertilizers (El-Sayed et al., 2009 and Saied, 2016). The decrease in the particle size of the phosphate rock is associated with an increase in its solubility (Watkinson, 1994; Otero et al., 2013; Saied, 2016). According to Hore-Lacy (2012) Phosphate rock contains 79 to 175 g P kg⁻¹, the main mineral being apatite, and most commonly, fluorapatite Ca₅(PO₄)₃F or Ca₁₀(PO₄)₆(F,OH)₂; such P is insoluble but the material may be used as a fertilizer. When phosphate rock is processed with sulfuric acid it produces the

chemical fertilizer of ordinary superphosphate (OSP) which contains 68 to 87 g soluble P kg⁻¹. To obtain phosphate fertilizers of greater soluble P, treatment with phosphoric acid is done giving fertilizers such as double superphosphate (DSP) or triple super phosphate (TSP) which may contain 192 to 219 g soluble P kg⁻¹.

Mechanisms of phosphate sorption (adsorption)/ desorption between the soils or sediments and their water suspension is very important (Otero et al., 2013). The adsorption reaction is considered as the first step in the mechanism of P fixation (Bear, 1969).

In determining the sediment's role as either a trap or a source of phosphorus, sediment phosphate adsorption is recognized as one of the most important components of phosphate retention mechanisms (Wang and Li, 2010). Long-term estimates of sediment phosphate adsorption are important in determining phosphate pollution and suitable restoration techniques in lakes (Watkinson, 1994).

The study of the sorption of phosphorus on soils can give relevant information for understanding the P-distribution in systems (Wang and Li, 2010) for soils, Otero et al., (2013) reported a kinetic constant ranging between 0.007 and 0.017 µg P h⁻¹.

The current study aims at assessing the effect of acidulating phosphate rock by mixing with TSP at different ratios and the resultant adsorption/desorption of the systems to give clear and useful indications on the possibility of using a suitable ratio for agriculture use.

MATERIALS AND METHODS

A laboratory experiment was carried out to study the effect of partial acidulation with TSP and particles diameter of Abou-Tartour PR on adsorption and desorption of phosphorous.

Materials

Phosphorous fertilizers used in the study were (1) Phosphate Rock from (Abou-Tartour) and Triple super phosphate (TSP)

The soil used in the study was collected from the farm of Faculty of Agriculture, Zagazig University Egypt. The soil was characterized by a light clay texture, pH value of 8.1, total soluble salts of 0.465 dS m⁻¹, organic matter of 6.8 g P kg⁻¹, CaCO₃ of 20 g kg⁻¹, total P of 0.23 g P kg⁻¹ and available P of 21 mg P kg⁻¹ (Olsen *et al.*, 1956). Tables 1, 2 and 3 show main properties of Abou-Tartour phosphate rock.

Materials Preparation

Phosphate rock and Triple super phosphate fertilizer were crushed to pass a set of sieves with the following diameters 500, 212, 75 and <45 µm. Another part was crushed to the nanometer size (43.6 nm).

The soil was air dried, crushed, sieved through 2mm screen, and stored for analysis and experimental work.

Classification and identification

Portions of 20 g of light clay soil were mixed with TSP at different rates (100, 200, 300, 400 and 500 mg P kg⁻¹) and suspended in distilled water. The suspensions were shaken for one hour and left for 48 hours to equilibrate. The soil suspensions were filtered through Whatman 42 filter paper (Chapman and Pratt, 1961). Phosphorous adsorption on the soil was re-extracted through slow leaching with 100ml of 10% sodium chloride solution.

Water-Soluble P

Portions of 20 g was extracted by 100 ml distilled water, shaking for one hour then filtration through Whatman 42 filter paper (Chapman and Pratt, 1961).

Total P

0.5g was digested with concentrated H₂SO₄ + 5 ml HClO₄ on a heater (Jackson, 1967). Phosphorus was determined in the extracts using the colorimetric method of the ascorbic acid (Murphy and Riley, 1977)

Acidulation ratio

Partial acidulation was performed by adding two combined sources PR and TSP at different ratios :0, 25, 50, 75 and 100 TSP and 100, 75, 50, 25 and 0 PR.

Calculation of fixed or released P, Phosphorous adsorption efficiency and phosphorous desorption efficiency

Fixed or released P was calculated from the equation:

Fixed or released P = (adsorbed P mg kg⁻¹ – desorbed P mg kg⁻¹). Phosphorous adsorption efficiency (PAE%)

= (adsorbed P ÷ rate of P added) × 100

Phosphorous desorption efficiency (PDE %)

$$= \frac{\text{desorbed P mg kg}^{-1}}{\text{added P mg kg}^{-1}} \times 100$$

Table 1; Content of Total (P) in Abou-Tartour Phosphate Rock of as affected by particles diameter

Particle diameter	g P kg ⁻¹
500(μm)	129.48
212(μm)	133.68
75(μm)	135.78
<45(μm)	137.88
43.6(nm)	171.48

Table 2; Content of total and extractable P (g kg⁻¹) in PR Abu Tartour and ranking grades (according to Diamond 1979) for sustainable agriculture

Water-soluble	Available*	Citric acid soluble	Ranking
0.28	14.15	40.22	High

* Olsen

Table 3; Mineral composition of (Abou Tartour) as given by X-ray diffraction

Mineral name	Compound name	Chemical formula
Hydroxy apatite	calcium phosphate hydroxide	Ca ₅ (PO ₄) ₆ OH
Quartz	silicon oxide	SiO ₂
Calcite	calcium carbonate	CaCO ₃
Brushite	Calcium hydrogen phosphate hydrate	Ca HPO ₄ .(H ₂ O) ₂

RESULTS

Obtained results will be discussed under the following heading.

Classification and Identification of P in the PR Source

X-ray diffraction (XRD) analysis

The X-ray diffraction was carried out by scanning a powdered sample of PR source (Fig. 1). The diffraction pattern revealed that P in Abu Tartour PR exists in the form of calcium phosphate hydroxide "Ca₅(PO₄)₆ OH. The other crystalline phase was in the form of silicon oxide SiO₂, calcium carbonate CaCO₃ and calcium hydrogen phosphate hydrate CaHPO₄.(H₂O)₂

Plate 2 shows that the apatite grain size 25.76 nm in the ball mill ground sample phosphate rock of Abou –Tartour.

Adsorption and desorption of Phosphate ions were studied under the following factors i.e., P-rate and the degree of acidulation and PR particle diameter.

The obtained results recorded in Tables 4, 5, 6, 7 and 8 and Fig. 2 will be discussed under the following headings:

Acidulation ratio

effect was true for all rates of P application. On the other hand, values of desorbed P were increased. the relative decrease in adsorbed P and relative increases in desorbed P were pronounced by increasing the rate of P application from 100 to 500 mg P kg⁻¹ Regardless of particle diameter, the mean values of adsorbed P for different ratios of TSP and PR were 52.20, 50.03, 47.74, 41.72 and 30.19, respectively while the mean values of desorbed P were 51.58, 51.27, 51.39, 51.91 and 51.76, respectively. From the results, it can be indicated the changes in desorbed P was slightly concerning the values of fixed or released P as shown in Table 4. Results showed that increasing the ratios of TSP increased the released P using the rate of 100 mg P kg⁻¹, then the fixed P was decreased. On the other hand, increasing the rate of P applied up to 200 mg P kg⁻¹ increased the values of adsorbed, desorbed and fixed P more than the first rate of (100 mg P kg⁻¹) as shown in Table 5.

Rate of P application

The results recorded in Tables 4, 5, 6, 7 and 8 and illustrated in Fig. 2 present the effect of P concentration on the adsorption and desorption of P.

Phosphorous adsorption efficiency (PAE%)

On the assumption that PAE equal (adsorbed P ÷ rate of P added)×100

Results revealed that PAE was highly increased from the first rate (100 mg P kg⁻¹ soil) to the second rate (200 mg P kg⁻¹ soil). After wards, slight increases were recorded for the subsequent rates. The PAE percentage for the general mean equals 44.38, 70.34, 67.48, 59.18 and 70.91 for the rates of application 100, 200, 300, 400 and 500 mg P kg⁻¹ soil, respectively.

Phosphorous desorption efficiency (PDE)%

The item PDE% computed by the efficiency equation:

$$PDE = \frac{\text{desorbed P mg kg}^{-1}}{\text{added P mg kg}^{-1}} \times 100$$

From the results it can be recognized that PDE (%) was clearly increased from the first rate to the second rate and then indicated a drop in values. The PDE (%) are 51.64, 70.34, 23.77, 20.68 and 17.88 respectively for the 100, 200, 300, 400 and 500 mg P kg⁻¹ added. It can be concluded that desorption of P not a complete reversible process. This result accommodate with that recorded by Bear (1969).

As it is well established that when the desorbed P was higher than that adsorbed for the applied rate, this can be explained as a result of release and dissolution. In this study the ratios of desorbed to adsorbed were 116.36, 43.69, 35.24, 34.94 and 24.96% for the 100, 200, 300, 400 and 500 mg P kg rates, respectively. This means that

the first rate of 100 mg P kg⁻¹ resulted in P released and dissolution of initial P compounds more than the others.

With regard to the desorption of the adsorbed P, the results showed slight changes under all the rates of acidulation except the first rate. It is of interest to mention that most of the desorbed P may be slowly dissolved from precipitates.

The release of sorbed P into soil solution or desorbed is not completely reversible. This hysteresis effect is the result of precipitation, occlusion, solid- state diffusion and bidentate or binuclear bonding with colloid surface. Several studies have reported that P desorption during a short time is a low activation energy process (Sharpley et al., 1981).

Carter and Tarrent (1995) working on phosphate availability in calcareous soils and found that the relative contribution of adsorption and precipitation processes to P fixation in calcareous soil seems to depend on P application rate.

PR particle diameter

Concerning the effect of particle diameter of Abou-Tartour phosphate rock using 200 mg P kg⁻¹ Table 5, the mean values of adsorbed P increased from 137.82 to 143.15 mg P kg⁻¹. Also, the mean values of desorbed P slightly increased from 52.22 to 65.77 mg P kg⁻¹. On the other hand, the mean values of fixed P slightly decreased from 80.60 to 77.37 mg P kg⁻¹. The same trend was observed using the rate of applied P 300 mg kg⁻¹ (Table 6).



Plate 1; Scanning electron microscope SEM with EDX unit

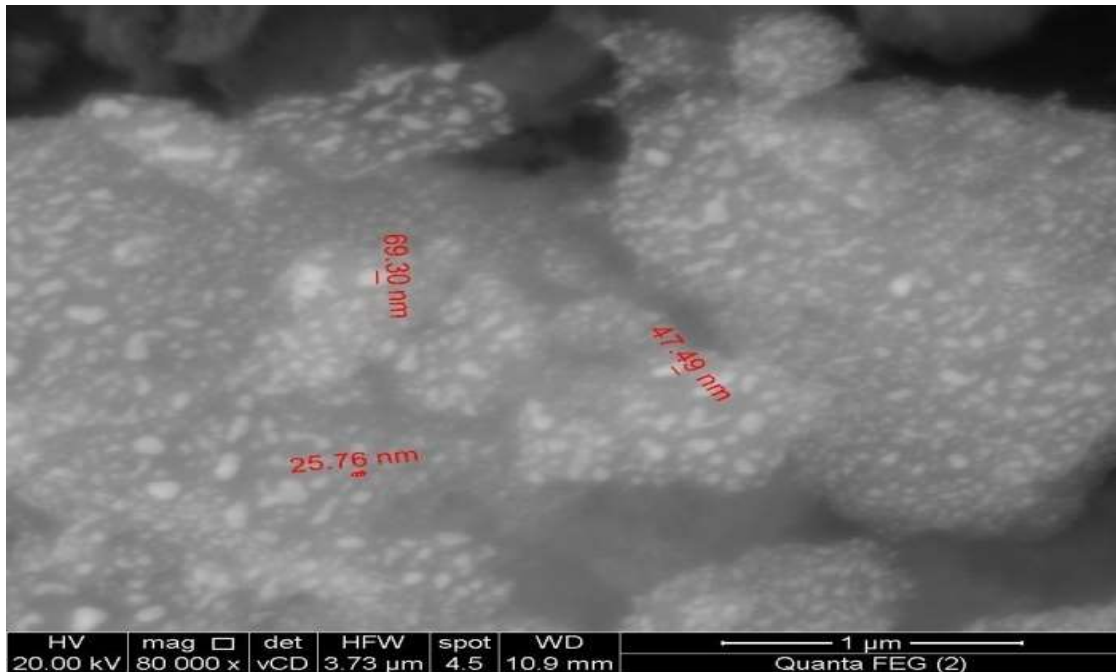


Plate 2; Abou-Tartour phosphate rock SEM analysis showing apatite grain size of 25.76 nm

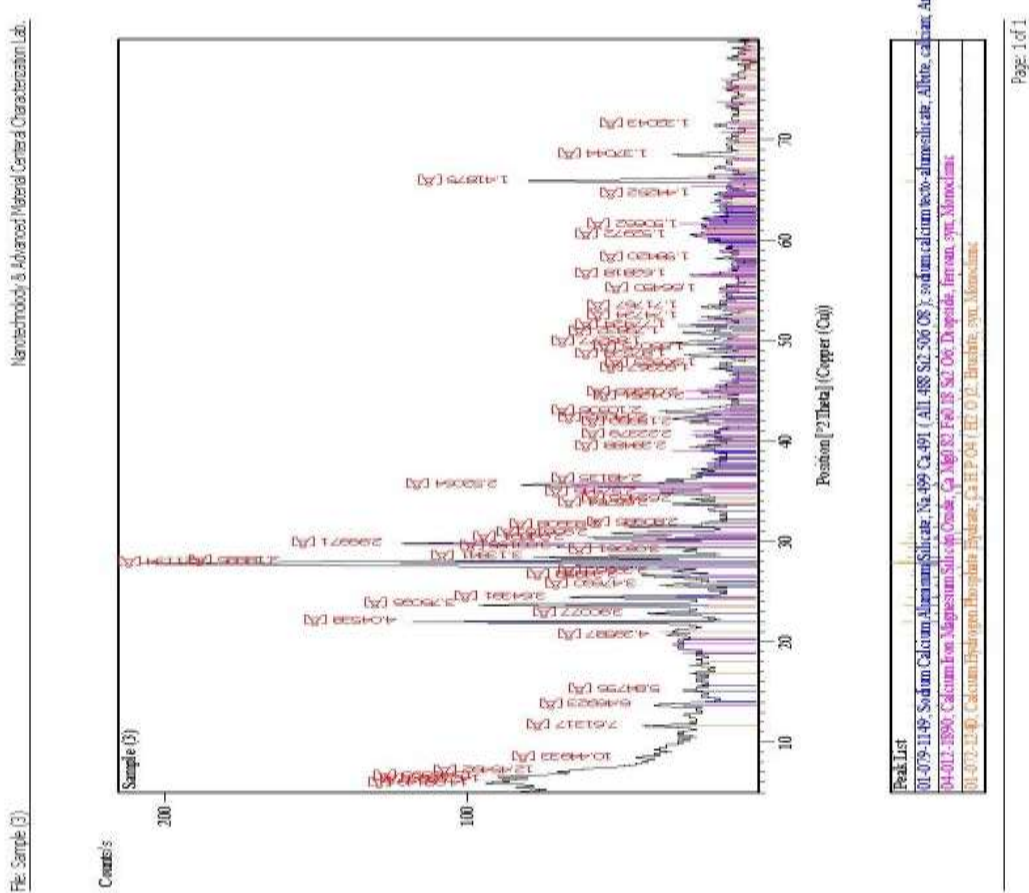


Figure 1; X-ray diffraction for Abou -Tartour PR

Table 4; Adsorption and desorption P (mg kg⁻¹) from Abou-Tartour phosphate rock as affected by particle diameter and partial acidulation with (TSP) in light clay soil at P rate of 100 mg kg⁻¹

Mixing ratio	TSP	0	25	50	75	100	Mean
	PR	100	75	50	25	0	
Particle diameter							
Adsorbed							
500(μm)	52.70	48.67	47.12	36.58	31.31	43.27	
212(μm)	51.77	50.53	48.36	43.4	31.00	45.01	
75(μm)	51.15	48.98	47.43	42.78	29.76	44.02	
<45(μm)	52.39	49.60	47.43	42.47	29.45	44.26	
43.6(nm)	53.01	52.39	48.36	43.40	29.45	45.32	
Mean	52.20	50.03	47.74	41.72	30.19		
Desorbed							
500(μm)	48.60	49.84	50.46	52.13	52.01	50.92	
212(μm)	50.15	50.77	51.08	52.01	51.70	51.14	
75(μm)	51.70	51.08	51.39	52.01	51.70	51.58	
<45(μm)	53.25	51.39	51.08	50.77	51.70	51.64	
43.6(nm)	54.18	53.25	52.94	52.63	51.70	52.94	
Mean	51.58	51.27	51.39	51.91	51.76		
Fixed or released							
500(μm)	4.10	-1.17	-3.34	-15.43	-20.39	-7.25	
212(μm)	1.62	-0.24	-2.72	-8.61	-20.70	-6.13	
75(μm)	-0.55	-2.10	-3.96	-9.23	-21.94	-7.55	
<45(μm)	-0.86	-1.79	-3.65	-8.30	-22.25	-7.37	
43.6(nm)	-1.17	-0.86	-4.58	-9.23	-22.25	-7.61	
Mean	0.63	-1.23	-3.65	-10.16	-21.50		

(-) means released and (+) means fixed

(nm) Nanometer diameter

Table 5; Adsorption and desorption P (mg kg⁻¹) from Abou-Tartour phosphate rock as affected by particle diameter and partial acidulation with (TSP) in light clay soil at P rate of 200 mg kg⁻¹

Mixing ratio	TSP	0	25	50	75	100	Mean
	PR	100	75	50	25	0	
Particle diameter							
Adsorbed							
500(μm)	151.15	146.50	137.20	129.45	124.8	137.82	
212(μm)	151.77	146.81	138.75	134.10	127.59	139.80	
75(μm)	152.08	147.43	140.30	135.65	128.83	140.85	
<45(μm)	152.39	148.05	141.85	137.20	129.45	141.78	
43.6(nm)	153.01	149.60	143.40	140.30	129.45	143.15	
Mean	152.08	147.67	140.30	135.34	128.02		
Desorbed							
500(μm)	47.98	48.91	54.80	60.38	74.02	57.22	
212(μm)	50.46	51.70	56.97	63.48	74.02	59.33	
75(μm)	53.25	54.80	57.59	69.37	73.40	61.68	
<45(μm)	54.80	57.90	60.38	70.30	73.40	63.36	
43.6(nm)	59.45	61.00	61.62	73.40	73.40	65.77	
Mean	53.19	54.86	58.27	67.39	73.65		
Fixed or released							
500(μm)	103.17	97.59	82.40	69.07	50.78	80.60	
212(μm)	101.31	95.11	81.78	70.62	53.57	80.47	
75(μm)	98.83	92.63	82.71	66.28	55.43	79.17	
<45(μm)	97.59	90.15	81.47	66.90	56.05	78.42	
43.6(nm)	93.56	88.60	81.78	66.90	56.05	77.37	
Mean	98.89	92.81	82.02	67.95	54.37		

See foot note Table 4.

Table 6; Adsorption and desorption P (mg kg⁻¹) from Abou-Tartour phosphate rock as affected by particle diameter and partial acidulation with (TSP) in light clay soil at P rate of 300 mg kg⁻¹

Mixing ratio	TSP	0	25	50	75	100	Mean
	PR	100	75	50	25	0	
Particle diameter							
Adsorbed							
500(μm)	240.10	236.07	218.40	168.49	146.48	201.91	
212(μm)	241.34	238.55	196.70	168.18	147.61	198.48	
75(μm)	242.58	235.45	203.83	168.80	147.61	199.65	
<45(μm)	243.20	237.00	209.41	180.73	147.61	203.59	
43.6(nm)	243.51	237.31	223.98	190.62	147.61	208.61	
Mean	242.15	236.88	210.46	175.36	147.38		
Desorbed							
500(μm)	57.48	58.40	64.30	69.88	83.52	68.51	
212(μm)	59.96	61.20	66.47	72.98	83.52	68.82	
75(μm)	62.75	64.30	67.09	78.87	82.90	71.18	
<45(μm)	64.30	67.40	69.88	79.80	82.90	72.85	
43.6(nm)	68.95	70.50	71.12	82.90	82.90	75.27	
Mean	62.68	64.36	67.77	76.88	83.15		
Fixed or released							
500(μm)	182.62	177.66	154.10	98.61	62.96	135.19	
212(μm)	181.38	177.35	130.23	95.20	64.09	129.65	
75(μm)	179.83	171.15	136.74	89.93	64.71	128.47	
<45(μm)	178.90	169.60	139.53	100.93	64.71	130.73	
43.6(nm)	174.56	166.81	152.86	107.72	64.71	133.33	
Mean	179.46	172.51	142.69	98.48	64.24		

See foot note Table 4.

Table 7; Adsorption and desorption P (mg kg⁻¹) from Abou-Tartour phosphate rock as affected by particles diameter and partial acidulation with (TSP) in light clay soil at P rate of 400 mg kg⁻¹

Mixing ratio	TSP	0	25	50	75	100	Mean
	PR	100	75	50	25	0	
Particle diameter							
Adsorbed							
500(μm)	339.17	321.50	270.35	253.30	219.20	280.70	
212(μm)	337.93	318.40	268.80	250.20	214.55	277.98	
75(μm)	242.58	235.45	203.83	168.80	213.00	212.73	
<45(μm)	243.20	237.00	209.41	180.73	147.61	203.59	
43.6(nm)	243.51	237.31	223.98	190.62	147.61	208.61	
Mean	281.28	269.93	235.27	208.73	188.39		
Desorbed							
500(μm)	76.39	75.85	74.30	75.85	83.60	77.20	
212(μm)	76.70	74.50	79.80	80.56	84.56	79.22	
75(μm)	79.70	79.80	82.90	82.20	84.56	81.83	
<45(μm)	84.45	82.90	81.56	92.20	84.56	85.13	
43.6(nm)	84.60	95.30	93.75	92.20	84.56	90.08	
Mean	80.37	81.67	82.46	84.60	84.37		
Fixed or released							
500(μm)	264.87	245.65	196.05	177.45	135.60	203.92	
212(μm)	258.13	233.84	190.86	173.81	138.70	199.07	
75(μm)	254.10	235.5	187.45	170.40	142.50	197.99	
<45(μm)	249.45	233.95	189.00	175.05	138.78	197.25	
43.6(nm)	243.25	230.85	181.25	176.60	133.20	193.03	
Mean	253.96	235.96	188.92	174.66	137.76		

See foot note Table 4.

Table 8; Adsorption and desorption P (mg kg⁻¹) from Abou-Tartour phosphate rock as affected by particle diameter and partial acidulation with (TSP) in light clay soil at P rate of 500 mg kg⁻¹

Mixing ratio	TSP	0	25	50	75	100	Mean
	PR	100	75	50	25	0	
Particle diameter							
Adsorbed							
500(µm)	438.45	415.82	341.42	328.40	274.15	359.65	
212(µm)	432.56	401.56	350.10	326.85	260.20	354.25	
75(µm)	435.04	409.31	325.30	271.67	259.27	340.12	
<45(µm)	435.04	411.48	354.75	299.88	271.67	354.56	
43.6(nm)	435.35	420.78	373.04	304.53	287.48	364.24	
Mean	435.29	411.79	348.92	306.27	270.55		
Desorbed							
500(µm)	75.85	76.16	77.40	85.15	86.39	80.19	
212(µm)	80.50	89.80	88.56	87.94	86.39	86.64	
75(µm)	93.60	92.90	91.35	89.80	86.70	90.87	
<45(µm)	94.55	92.00	94.00	92.90	86.70	92.03	
43.6(nm)	95.45	95.30	93.75	92.20	86.80	92.70	
Mean	87.99	89.23	89.01	89.60	86.60		
Fixed or released							
500(µm)	361.05	330.67	255.03	273.40	189.55	281.94	
212(µm)	344.00	313.62	263.71	251.00	184.04	271.27	
75(µm)	343.69	319.51	238.60	191.17	169.47	252.49	
<45(µm)	343.04	318.58	268.05	206.28	178.77	262.94	
43.6(nm)	341.60	328.58	280.84	217.73	192.93	272.34	
Mean	346.68	322.19	261.25	227.92	182.95		

See foot note Table 4.

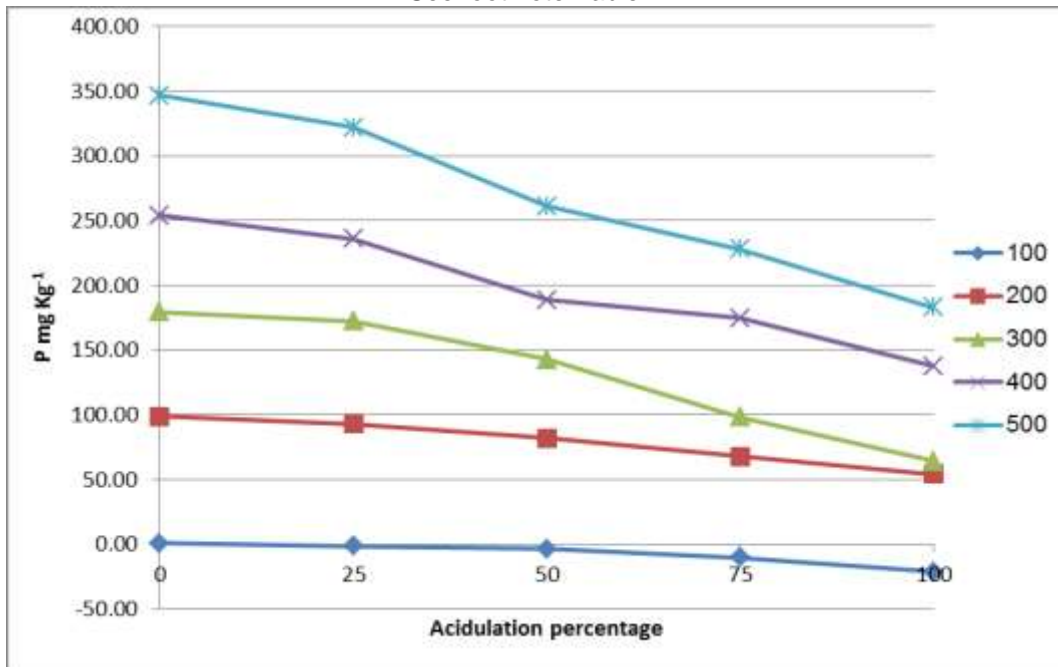


Figure 2; Mean of fixed and released P from Abou-Tartour PR under different rates of added P.

Regarding the effect of applied P of PR at rates of 400 and 500 mg P kg⁻¹ (Tables 7 and 8), opposite direction was noticed, while the mean values of adsorbed P was decreased from 280.70 to 208.61 mg P kg⁻¹ (400 mg P kg⁻¹) and from 359.65 to 354.24 mg P kg⁻¹ for <45(μm) 500 mg P kg⁻¹). The results showed gradual decrease in adsorbed P by increasing TSP application. This PR ratio: 100, 75, 50, 25 and 0%, respectively. 500 μm to nano caused a relative decrease in fixed P at the rates of applied P of 400 and 500 mg P kg⁻¹.

With regard to the adsorbed amounts of added P, it can be recognized that the higher the diameter the higher the desorbed P. the highest of desorbed P was recorded for the nano particles. The obtained data confirm that found by Chien and Hammond (1978) who found that the solubility of PR granules decreased drastically as the granules size increased from the average diameter of 0.05 mm to 1.00 mm.

CONCLUSION

In general, the values of P adsorption, desorption and fixed or released were clearly affected as a result of acidulation of PR with TSP and particle diameter under different P-addition rates. It can be concluded that desorption of P not a complete reversible process.

CONFLICT OF INTEREST

The authors declared that present study was performed in absence of any conflict of interest.

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AUTHOR CONTRIBUTIONS

A. E. designed and leading the experimental design and also wrote the manuscript. A.H and S.D facilitating the research equipment with data analysis and H. S performed treatments, setting up the experiment and data collection. All authors read and approved the final version.

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