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Effect of Organic Compounds on Phosphate Sorption-Desorption of Some Pure Minerals

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PHOSPHORUS sorption-desorption in some pure systems, *i.e.*, goethite, kaolinite, and bentonite had been studied under different concentrations of phosphorus, pH values, constant time, wide solid: solution ratio. The effect of oxalate (OX) and or humic acid (HA), and the order of their addition on phosphorus sorption-desorption was also investgated.

The obtained P-adsorption isotherms for the tested minerals were of the high affinity type with maximum P-adsorption (b) in the order : goethite > kaolinite>bentonite. Adsorption energy of P on goethite surfaces was greater than that of clay surfaces. Amounts of P sorption on goethite and clay minerals decreased with increasing pH. Presence of OX and HA, of all systems, had no effect on P sorption by goethite or clay minerals under low P concentration . On the other hand, in the system with high P concentration organic acids reduced P sorption by goethite or clay minerals.The reduction on P sorption was dependent on the order of anions addition and pH value of the system. Organic acids drastically reduced P sorption either when added with P or especially when introduced before P. The higher the pH was, the lower the efficiency of organic acids in reducing P sorption was.

Amounts of desorbed P from goethite and clay minerals increased as the initial P concentration increased in all orders of addition. Percentages of desorbed P from goethite decreased as pH value increased from 5.5 to 7.5. On the other hand, percentages of desorbed P from clay minerals decreased as pH value was raised from 5.5 to 6.5 whereas raising pH to 7.5 resulted in an increase in the percentages of desorbed P for all treatments. Greater amounts of desorbed P have been recorded for the (P/OX) and (P/HA) orders of addition.

Keywords: Organic compound, Phosphate sorption-desorption, Puremineral.

Several factors influence the sorption of P by components of soils and sediments. These include the amount and nature of the soil components involved, other ions, pH of the system, time of reaction, concentrations of P, ionic strength of the background solution, solid: solution ratio, and organic compounds (McLaughlin *et al.*,1981; Borggaard,1983; Bolan *et al.*,1986; Barrow & Ellys,1986; Bar-Yossef *et al.*,1988; Syers & Curtien,1989; Khater, 1995 and He *et al.*, 1997).

The competitive sorption of some chelating acids usually present in the rhizosphere, and phosphate has received some attention because the supply of phosphate to plants should be strongly influenced by the presence of these ligands (Yuan, 1980; Lopez – Hernandez *et al.*, 1986; Kafkafi *et al.*, 1988; Violante & Huang 1989 and Violante *et al.*, 1991). Competition between organic matter and phosphate for adsorption sites on soils is thought to be due to the chelating ability of hydroxyl - carboxyl ligands found in soil organic matter (Parfitt, 1978 and Reddy *et al.*, 1980).

The competitive sorption of P and organic compounds was influenced by the initial organic / phosphate molar ratio, pH, order of anion addition, and nature of the adsorbent (Violante and Gianfreda, 1995). Fox and Comerford (1990) reported that the presence of large concentrations of oxalate may affect P availability in some selected forest soils of the Southeastern of USA. A study of Lopez-Hernandez *et al.* (1986) about the competition between organic anions (oxalate and malate) and phosphate for adsorption sites in tropical soils-indicated that, in the presence of organic anions, phosphate adsorption by soils is reduced. Humic acid competes strongly with phosphate for adsorption sites especially at the low pH values. It seems that the order of anion addition strongly influenced the adsorption of phosphate and organic acids or anions.Thus, the objective of this study was to evaluate effects of two naturally organic acids on phosphate sorption-desorption as influenced by type of adsorbent materials, phosphate concentration, pH, and order of anions addition.

Material and Methods

Goethite was prepared by addition of a 0.1 M NaOH solution to a 0.3 M $Fe(NO_3)_2$ solution until pH of the mixture of the suspension reached 7.0. The precipitate was washed thoroughly by a distilled water, dried at 50°C and stored (Hingeston *et al.*, 1972). Kaolinite (China clay, made in Germany) and bentonite (IRAQ clay) were used without any preliminary treatment.

Phosphate sorption isotherms

Fifty milliliters of a 0.02 M KCl solution containing various amounts of phosphorus as KH_2PO_4 were added to 125 mg of goethite, kaolinite, and bentonite. Initial concentrations of phosphorus solutions in case of goethite were 1.0, 2.5, 10.0, 20.0, 40.0, and 100.0 mg P/l, whereas, in case of kaolinite and bentonite clay minerals systems, the concentrations were 1.0, 2.5, 5.0, 10.0, and 20.0 mg P/l. The suspensions were shaken for 24 hr (based on data of the preliminary work) . pH values were readjusted to constant values of 5.5, 6.5, and 7.5 by adding 0.1 M HCl or KOH. The final suspensions were centrifuged at 5000 r.p.m. and filterated. Phosphorus concentrations were determined in the supernatants (Jackson, 1973). The amounts of P sorbed were calculated as mg P / kg from the difference between the initial and final concentrations of P in the solutions (Violante *et al.*, 1996).

Sorption-desorption experiments

Phosphate introduced before oxalate and humic acid

Phosphate was sorbed on 125 mg adsorbent agents of goethite, kaolinite and bentonite by shaking them with phosphorus solutions (KH_2PO_4 dissolved in 0.02 M KCl) containing 2.5, 10.0, 40.0, and 100.0 mg P/l in case of goethite and 1.0, 2.5, 5.0 and 10 mg P/l in case of kaolinite and bentonite for 24 hrs as described above. After phosphate sorption, the suspensions were equilibrated with a small volume of oxalate or humic acid solutions adjusted to pH values of 5.5, 6.5 and 7.5 and of suitable concentrations of $5x10^{-5}$, $5x10^{-3}$ and $5x10^{-2}$ M; 2.9, 11.6, and 29.0% (w/w), respectively. The suspensions were shaken for another period of 24 hr. pH of the suspensions were kept constant.

Phosphate introduced after oxalate and humic acid

Adsorbent agents (goethite, kaolinite and bentonite) were equilibrated in 0.02 M KCl solutions with oxalate or with humic acid solutions as previously mentioned. Various levels of P were added to the suspensions. Then, the suspensions were equilibrated for another 24 hr and their pH values were periodically adjusted at the initial values.

Phosphate introduced together either with oxalate or humic acid

Fifty milliliters of different solutions of 0.02 M KCl containing phosphorus and either oxalate or humic acid, whose pH values previously adjusted to 5.5. 6.5 and 7.5, were added to 125 mg adsorbent agents. The concentrations of phosphorus, oxalate and humic acid were the same as in the previous experiments. The suspensions were then equilibrated for 24 hr and the pH values were periodically adjusted to the initial values.

In all experiments, two drops of chloroform were initially added to inhibit microbial activity. At the end of the reaction period, the suspensions were centrifuged at 5000 r.p.m. for 15 min and filterated. Phosphorus was determined in the supernatant spectrophotometrically by the Troug and Meyer method (Jackson, 1973). The amounts of P sorbed were calculated as mg P/Kg from the difference between the initial and final concentrations of P in the solutions.

Sorbed phosphate on goethite, kaolinite, and bentonite was re-extracted from the precipitate using 25 ml of $5x10^{-5}$ M oxalate solution in case of oxalate treatments or 2.9 % (w/w) humic acid in case of humic acid treatments. Extraction of precipitates was carried out after adjusting the pH values of the extractants to 5.5, 6.5 and 7.5. The precipitates were shaked for 24 hr. After centrifugation, phosphorus was determined in the supernatants to calculate the amount of desorbed P. Humic acid had to be precipitated by the addition of 0.5 ml of a concentrated HCl to 10 ml of the supernatant liquid and separated by centrifugation to give a clear solution. Then, phosphorus was determined in the supernatants.

Results and Discussion

Phosphate sorption isotherms

Phosphate sorption isotherms on goethite, kaolinite, and bentonite at constant pH values of 5.5, 6.5 or 7.5 are shown in Fig. 1. The sorption curves were of the high affinity type, with phosphate being almost completely sorbed in dilute solutions in case of goethite.

The amounts of phosphate sorbed on goethite, kaolinite, and bentonite are listed in Table 1. On a basis of the used sorbent's weights, the amount of phosphate sorbed increased in the order: goethite > kaolinite > bentonite, at any P concentration or pH value.

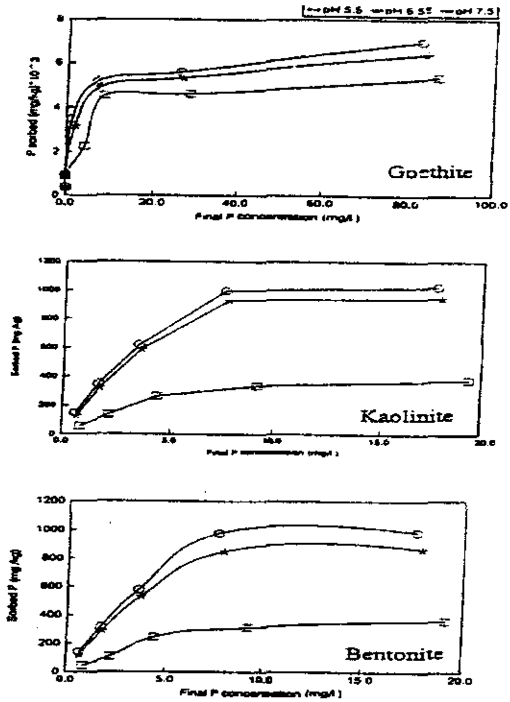

Fig. 1. Isotherms for the sorption of phosphare (P) by the studied adsorbents at pH 5.5, 6.5 and 7.5 final P concentrations.

TABLE 1. Amounts of phosphate sorbed (mgP/kg) on goethite, kaolinite and bentonite at constant pH values of 5.5, 6.5 and 7.5.

Initial P conc. (mg/l)	Adsorbent materials								
	Goethite			Kaolinite			Bentonite		
	pH values								
	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5
	Amounts of P sorbed (mg/kg)								
1.0	392	392	384	140	88	56	128	72	44
2.5	984	968	924	348	320	136	316	288	108
5.0				616	584	264	576	528	244
10.0	3472	3152	2232	996	928	336	976	848	312
20.0	5162	4912	4528	1024	944	376	984	864	360
40.0	5592	5328	4620						
100.0	6992	6428	5360						

The obtained data were plotted according to the linear form of the Langmuir equation (not shown) to achieve the maximum phosphate adsorption b and K constant values. Table 2 shows the Langmuir constants for the studied adsorbents. The K constants provide evidence that adsorbed phosphates on goethite surfaces have adsorption energy greater than those that bound phosphate on clay surfaces. The calculated b values indicated that the amounts of P adsorbed on the clay minerals (kaolinite and bentonite) are less than those of goethite. Therefore, goethite has a much large capacity to adsorb phosphate than the tested clay minerals. These could be attributed at least in part to the differences in affinity of phosphate for adsorbent materials with different surfaces and physicochemical properties.

TABLE 2. Langmuir constants and correlation coefficients (r) for P adsorption by the studied adsorbents at different pH values.

Minerals	pH	Maximum adsorption (b) (mg P/ kg)	Bonding energy (k)	r
Goethite	5.5	7081	0.408	0.997
	6.5	6537	0.392	0.998
	7.5	5545	0.278	0.997
Kaolinite	5.5	1323	0.230	0.964
	6.5	1034	0.221	0.962
	7.5	377	0.170	0.984
Bentonite	5.5	1270	0.231	0.965
	6.5	941	0.210	0.961
	7.5	366	0.140	0.982

The all r values are highly significant .

Effect of pH on phosphate sorption

Amounts of phosphate sorption on goethite and clay minerals decreased with increasing pH (Table 1). Similar results had been obtained by Violante *et al.* (1991) and He *et al.* (1997). The high capacity of goethite or clay minerals to sorb phosphate at the lower pH value (5.5) could be attributed to the higher positive charge and to the lesser competition of hydroxyl ions with phosphate at pH 5.5 than at either pH 6.5 or 7.5. At low pH, phosphate exchanged with protonated OH group but at high pH, phosphate exchanged with OH^- group. Phosphate is sorbed on the surface through ligand exchange and co-ordinate covalent bonding between metal ion of the solid and $H_2PO_4^-$. Thus, it appears that inner-sphere surface complexation of phosphate on Fe-oxide and clay minerals occur on the metal ion plane.

Effect of organic anions on phosphate sorption-desorption

Tables 3a and 3b show the amounts of phosphate sorbed on goethite, kaolinite, and bentonite as affected by pH value, P concentration, organic anions concentration, and order of P or organic anions addition. It has been shown that, in all systems, the presence of organic anions has no effect on phosphate sorption by goethite or clay minerals when phosphate was introduced in small concentrations up to 2.5 mgP/l for goethite and 1.0 mgP/l for clay minerals. When phosphate was present in the systems in high concentration, organic anions competed phosphate sorption. In this case, the only possible reaction, which consistent with the low amounts of phosphate, is chemisorption reaction at the surfaces (inner-sphere complexes). As the amounts of phosphate sorbed on the surfaces, at high concentration, increase to the degree of complete coverage of such surfaces, the reactions involved could be of physical type. Accordingly, it could be postulated that organic anions can exchange with phosphate at higher concentrations of the latter. It appears from Tables 3a and 3b that, the reduction on phosphate sorption is dependent on the concentration of the organic ligand, pH value of the system, and on the way in which phosphate or organic anions are added. The most effective concentration of organic ligand was $5x10^{-3}$ M (5m mol/l) for oxalate and 11.6% (w/w) for humic acid.

TABLE 3a. Amounts of sorbed P (mgP/kg) on goethite, kaolinite, and bentonite as affected by P and oxalate concentrations and mode of anions addition at different pH values.

Initial P conc (mg/L)	oxalate concentrations											
	0.0			[illegible]			[illegible]			[illegible]		
	pH values											
	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5
	Amounts of sorbed P (mg /kg goethite)											
	P alone			(P / OX) system								
2.5	984	968	924	984	968	924	982	968	924	976	948	912
10.0	3472	3152	2232	3440	3138	2232	3368	3085	2220	3326	2860	2140
40.0	5592	5328	4620	5408	5278	4608	5160	4976	4530	5082	4928	4398
100.0	6992	6428	5360	6600	6304	5327	5980	5904	5279	5496	5152	5044
	P alone			(P + OX) system								
2.5	984	968	924	928	928	924	920	912	908	905	908	900
10.0	3472	3152	2232	2976	2700	2176	2952	2620	2152	2868	2496	2216
40.0	5592	5328	4620	4194	4305	4472	3422	3776	4232	3256	3576	4056
100.0	6992	6428	5360	4968	5048	5183	3840	4472	4872	3656	4136	4604
	P alone			(OX / P) system								
2.5	984	968	924	938	928	912	934	912	912	950	888	886
10.0	3472	3152	2232	2840	2636	2152	2612	2432	2108	2552	2392	1976
40.0	5592	5328	4620	3976	4200	4435	3209	3380	4268	2936	3152	4028
100.0	6992	6428	5360	4868	4946	5024	3860	4056	4776	3568	3632	4582
	Amounts of sorbed P (mg /kg kaolinite)											
	P alone			(P / OX) system								
1.0	140	88	56	138	88	56	135	84	56	132	84	54
2.5	348	320	136	340	314	136	332	304	128	324	300	128
5.0	616	584	264	588	570	260	576	550	252	568	548	248
10.0	996	928	336	928	872	324	908	856	316	988	844	312
	P alone			(P + OX) system								
1.0	140	88	56	132	86	56	128	84	54	126	82	52
2.5	348	320	136	268	272	122	264	266	120	256	260	114
5.0	616	584	264	472	488	236	448	456	228	392	444	220
10.0	996	928	336	660	760	292	636	692	272	600	656	268
	P alone			(OX / P) system								
1.0	140	88	56	136	86	56	130	82	52	128	82	52
2.5	348	320	136	280	284	124	268	276	120	260	264	116
5.0	616	584	264	436	480	236	392	444	224	380	432	216
10.0	996	928	336	652	748	288	616	672	276	612	652	268
	Amounts of sorbed P (mg /kg bentonite)											
	P alone			(P / OX) system								
1.0	128	72	44	128	72	44	124	70	44	122	69	44
2.5	316	288	108	312	284	108	300	280	106	296	272	104
5.0	576	528	244	556	548	240	544	532	236	532	491	234
10.0	976	848	312	932	820	304	896	800	300	884	784	296
	P alone			(P + OX) system								
1.0	128	72	44	122	72	44	120	70	43	120	68	42
2.5	316	288	108	276	260	101	236	248	98	244	244	92
5.0	576	528	244	448	440	216	416	424	204	400	416	204
10.0	976	848	312	728	680	268	656	652	256	644	644	248
	P alone			(OX / P) system								
1.0	128	72	44	124	72	44	120	68	44	120	68	40
2.5	316	288	108	268	252	100	252	244	96	244	240	96
5.0	576	528	244	452	440	216	408	420	204	392	412	200
10.0	976	848	312	680	672	272	632	632	256	616	624	252

TABLE 3b. Amounts of sorbed P (mgP/kg) on goethite, kaolinite, and bentonite as affected by P and amounts of humic acid and mode of anions addition at different pH values.

different pH values.

Initial P conc. (mg/L)	Added humic acid % of sorbent material											
	0.0			[illegible]			[illegible]			[illegible]		
	pH values											
	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5
	Amounts of sorbed P (mg /kg goethite)											
	P alone			(P / HA) system								
2.5	984	968	924	980	968	924	976	968	924	960	958	920
10.0	3472	3152	2232	3344	3048	2232	3268	2996	2200	3128	2984	2152
40.0	5592	5328	4620	5334	5125	4548	5208	5176	4555	4796	5336	5472
100.0	6992	6428	5360	6120	5680	5248	6452	8104	5352	8588	8172	7728
	P alone			(P + HA) system								
2.5	984	968	924	972	956	920	940	932	902	932	930	896
10.0	3472	3152	2232	2940	2896	2144	2792	2808	2016	2672	2776	2008
40.0	5592	5328	4620	4708	4680	4160	4328	4480	3900	3868	4232	3917
100.0	6992	6428	5360	5504	5348	4680	5164	5032	4432	4648	4708	4432
	P alone			(HA / P) system								
2.5	984	968	924	972	956	924	946	936	898	940	930	892
10.0	3472	3152	2232	2916	2856	2096	2824	2776	2000	2504	2576	1928
40.0	5592	5328	4620	3856	3820	3782	3500	3584	3816	3180	3276	3631
100.0	6992	6428	5360	4640	4472	4376	4090	4134	4312	3732	3792	4044
	Amounts of sorbed P (mg /kg kaolinite)											
	P alone			(P / HA) system								
1.0	140	88	56	136	88	56	134	86	56	132	84	56
2.5	348	320	136	336	312	136	328	3.8	132	320	296	132
5.0	616	584	264	584	564	260	568	556	260	552	552	252
10.0	996	928	336	916	868	328	904	856	328	1012	936	340
	P alone			(P + HA) system								
1.0	140	88	56	132	85	56	132	84	54	132	84	54
2.5	348	320	136	320	296	130	292	288	128	284	276	124
5.0	616	584	264	508	520	252	472	488	244	464	480	236
10.0	996	928	336	760	772	316	716	732	304	692	712	292
	P alone			(HA / P) system								
1.0	140	88	56	136	86	56	132	84	54	128	84	54
2.5	348	320	136	312	304	128	296	292	124	288	280	120
5.0	616	584	264	500	516	248	472	488	236	456	476	228
10.0	996	928	336	756	776	316	696	712	296	676	696	284
	Amounts of sorbed P (mg /kg bentonite)											
	P alone			(P / HA) system								
1.0	128	72	44	126	72	44	124	70	44	123	72	44
2.5	316	288	108	308	280	108	300	276	108	296	276	104
5.0	576	528	244	552	513	244	532	504	240	524	540	268
10.0	976	848	312	908	800	304	896	784	296	984	912	352
	P alone			(P + HA) system								
1.0	128	72	44	124	72	44	124	72	44	118	72	44
2.5	316	288	108	284	268	104	272	268	104	260	264	100
5.0	576	528	244	496	474	232	452	454	224	448	442	224
10.0	976	848	312	772	728	296	724	692	280	704	676	286
	P alone			(HA / P) system								
1.0	128	72	44	124	72	44	120	72	44	120	68	44
2.5	316	288	108	288	268	104	276	264	100	268	256	100
5.0	576	528	244	488	468	228	456	450	220	444	435	216
10.0	976	848	312	764	728	288	728	676	276	700	664	268

In general and as shown from Tables 3a and 3b, organic anions drastically reduced phosphate sorption by goethite and clay minerals either when added with P or especially when introduced before P. The order of addition of the organic anions can influence the reaction and according to the results it seems that, organic anions are more efficiently adsorbed to the surfaces of the studied adsorbents than phosphate anions. Moreover, it can able to block some sites, which are responsible for binding phosphate ions. When phosphate was added before organic anions, the amounts of P sorbed were not greatly influenced except, at higher concentrations of phosphate and organic anions for each of the studied adsorbents. The only possible explanation of this finding is, when phosphate was sorbed before organic anions addition, the net surface charge of the goethite or clay minerals becomes more negative with a consequent lower affinity of oxalate to the surfaces.

In order to evaluate the ability of organic anions to depress phosphate sorption in the different systems, the percentage efficiency of organic anions was calculated according to the expression of Deb and Datta (1967):

$$\text{Efficiency of oxalate \%} = \left(1 - \frac{\text{P sorbed in the presence of oxalate}}{\text{P sorbed when applied alone}}\right) * 100$$

The data show that, organic anions efficiency was pH dependent for the studied adsorbents. The higher the pH was the lower the efficiency of organic anions in preventing phosphate sorption was. The efficiency of OX and HA was higher at pH 5.5 than that at pH 6.5 or 7.5. This may be refered to two factors: (i) at pH 7.5 all the organic anions were completely dissociated, while P prevailed as HPO^{2-}_{4}; and (ii) the charge on the goethite and clay edges becomes more negative at pH 7.5 as compared to pH 5.5. A similar trend was observed by Kafkafi *et al.* (1988). In general, the efficiency of OX in reducing phosphate sorption was greater than the efficiency of HA. The probable explanation responsible for this result could be refered to the amount of HA or OX used in the experiment and the chain length and / or carboxyl density of the two organic anions.

As shown in Table 4a and 4b, amounts of desorbed P from goethite increased as the initial P concentration increased in all orders of addition. On the other hand, amounts of desorbed P decreased as the pH value increased. Concerning clay minerals, the amounts of desorbed P had the same trend of that of goethite. Percentages of desorbed P decreased as pH value was raised from 5.5 to 6.5, whereas, raising pH to 7.5 resulted in an increase in the percentages of desorbed P for all treatments.

A greater amount of desorbed P has been recorded for the (P/OX) and (P/HA) order of addition. In case of (P+OX), (P+HA) and (OX/P), (HA/P) systems it was found that, there is a tendency to decrease in amounts of desorbed P especially in the treatments which previously contain high concentrations of oxalate ($5x10^{-3}$ and $5x10^{-2}$ M) or humic acid (11.6 and 29.0%).

From the abovementioned discussion, it could be concluded that organic ligands were more efficient in reducing P-sorption when introduced in the system before or with phosphate. In this study, it was shown that the sorption of phosphate by the studied adsorbents (goethite, and clay minerals) provided a realistic model for the sorption of phosphate by soils. Consequently, data obtained in the present study might be used to predict the likely importance of organic anions in affecting the mobility and availability of phosphate in soils.

TABLE 4a. Amounts of desorbed P (mg P/kg) extracted by a 5×10^{-5} M oxalate solution as affected by pH values.

Initial P conc (mg/L)	Oxalate concentrations (M)											
	0.0			5×10^{-5}			5×10^{-3}			5×10^{-2}		
	pH values											
	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5
	Amounts of desorbed P (mg /kg goethite)											
	P alone			(P / OX) system								
2.5	12	8	8	16	8	8	12	6	6	14	4	4
10.0	62	50	32	72	56	34	78	64	38	86	70	40
40.0	620	288	196	792	376	210	860	400	238	892	512	226
100.0	1050	686	362	1096	762	392	1142	814	372	1216	886	212
	P alone			(P + OX) system								
2.5	12	8	8	14	8	6	12	4	4	10	4	2
10.0	62	50	32	54	46	28	48	40	26	42	34	24
40.0	620	288	196	500	272	186	490	224	144	324	116	78
100.0	1050	686	362	920	666	198	800	556	166	500	222	136
	P alone			(OX / P) system								
2.5	12	8	8	12	6	6	12	4	4	10	2	2
10.0	62	50	32	54	42	26	44	36	26	40	34	22
40.0	620	288	196	556	362	188	520	272	152	370	152	102
100.0	1050	686	362	880	638	232	620	382	172	580	206	148
	Amounts of desorbed P (mg /kg kaolinite)											
	P alone			(P / OX) system								
1.0	16	12	10	16	10	10	14	10	8	10	8	6
2.5	64	48	34	48	36	26	38	32	22	24	20	16
5.0	188	122	98	182	108	82	176	92	64	112	86	58
10.0	368	255	142	308	210	122	298	168	108	192	158	96
	P alone			(P + OX) system								
1.0	18	12	10	14	10	8	12	8	6	8	6	6
2.5	64	48	34	42	32	18	28	26	16	22	20	14
5.0	188	122	98	144	96	76	142	84	64	98	78	60
10.0	368	255	142	275	178	92	256	146	84	162	108	72
	P alone			(OX / P) system								
1.0	18	12	10	12	10	8	10	8	6	8	6	2
2.5	64	48	34	32	26	18	24	22	16	20	18	14
5.0	188	122	98	136	88	64	128	82	60	92	72	60
10.0	368	255	142	268	160	88	234	134	72	148	98	62
	Amounts of desorbed P (mg /kg bentonite)											
	P alone			(P / OX) system								
1.0	16	10	8	14	10	8	12	8	8	10	6	6
2.5	56	40	30	42	30	24	36	32	22	22	18	12
5.0	164	108	90	164	96	76	168	84	62	108	80	64
10.0	324	228	126	266	196	102	272	156	102	186	116	90
	P alone			(P + OX) system								
1.0	16	10	8	12	10	8	10	8	6	10	6	4
2.5	56	40	30	38	26	18	26	20	14	18	14	10
5.0	164	108	90	126	90	68	110	82	60	92	68	54
10.0	324	228	126	232	148	94	214	138	86	154	106	70
	P alone			(OX / P) system								
1.0	16	10	8	12	10	8	10	8	6	8	6	4
2.5	56	40	30	32	24	18	22	18	12	16	12	10
5.0	164	108	90	122	86	62	102	82	56	94	68	50
10.0	324	228	126	214	140	88	202	134	82	152	100	58

Such observations could be taken as evidence of a delibrate strategy to improve phosphate nutrition for the grown plants.

TABLE 4b. Amounts of desorbed P (mg P/kg) extracted by a 2.9% (w/w) humic acid solution as affected by pH values.

Initial P conc. (mg/l)	Amounts of humic acid added of sorbent material %											
	0.0			2.9			11.6			29.0		
	pH values											
	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5	5.5	6.5	7.5
	Amounts of desorbed P (mg /kg goethite)											
	P alone			(P/HA) system								
2.5	32	8	8	14	14	8	10	20	12	10	12	10
10.0	156	42	30	48	44	38	44	40	42	32	50	40
40.0	542	212	202	444	306	208	452	226	216	416	214	212
100.0	656	632	356	610	424	368	610	374	364	668	336	382
	P alone			(P + HA) system								
2.5	32	8	8	14	12	10	14	12	10	12	10	10
10.0	156	42	30	58	40	28	38	44	34	36	44	30
40.0	542	212	202	406	260	226	386	236	200	316	216	166
100.0	656	632	356	678	462	362	642	404	296	642	384	204
	P alone			(HA / P) system								
2.5	32	8	8	14	12	8	14	12	10	14	12	10
10.0	156	42	30	32	26	22	34	40	34	36	40	30
40.0	542	212	202	347	246	188	306	200	134	306	162	102
100.0	656	632	356	604	370	224	610	352	166	428	302	138
	Amounts of desorbed P (mg /kg kaolinite)											
	P alone			(P/HA) system								
1.0	16	12	10	14	12	8	12	8	6	10	8	6
2.5	52	38	28	38	34	22	32	30	18	26	24	14
5.0	152	102	82	142	92	70	134	84	58	102	80	64
10.0	314	212	120	262	184	102	244	142	92	184	142	86
	P alone			(P + HA) system								
1.0	16	12	10	12	10	8	10	8	6	10	6	4
2.5	52	38	28	32	28	16	26	24	16	22	20	12
5.0	152	102	82	124	80	62	118	78	50	70	62	52
10.0	314	212	120	234	152	88	210	118	82	158	100	74
	P alone			(HA / P) system								
1.0	16	12	10	12	10	8	10	8	6	8	6	4
2.5	52	38	28	30	26	16	26	22	14	22	22	10
5.0	152	102	82	118	76	60	106	72	46	62	58	50
10.0	314	212	120	220	142	82	200	112	80	146	100	68
	Amounts of desorbed P (mg /kg bentonite)											
	P alone			(P/HA) system								
1.0	14	10	8	12	10	8	10	8	6	10	8	6
2.5	46	40	26	34	32	20	32	28	16	24	22	14
5.0	136	94	76	130	86	64	120	76	54	92	72	58
10.0	286	196	106	238	170	94	226	126	86	184	122	80
	P alone			(P + HA) system								
1.0	14	10	8	10	8	6	10	8	6	10	8	6
2.5	46	40	26	28	26	16	24	22	14	22	20	12
5.0	136	94	76	114	74	56	104	70	50	72	60	52
10.0	286	196	106	216	148	84	198	118	80	152	94	72
	P alone			(HA / P) system								
1.0	14	10	8	10	8	6	8	6	6	8	6	4
2.5	46	40	26	26	24	14	24	20	14	22	18	10
5.0	136	94	76	112	74	52	100	72	50	68	62	52
10.0	286	196	106	210	144	82	190	114	82	146	92	70

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تأثير المركبات العضوية على ادمصاص وانطلاق الفوسفور من بعض المعادن النقية

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تتناول هذه الدراسة ادمصاص وانطلاق الفوسفور فى نظم نقية من الجوثيت، الكاؤلينيت، البنتونيت. قدرت منحنيات ادمصاص الفوسفور تحت ظروف مختلفة تشتمل على تركيزات مختلفة من الفوسفور، وقيم الحموضة، زمن ثابت قدره ٢٤ ساعة ، نسبة واسعة من المادة الصلبة الى المحلول، اضافة انيونات عضوية مثل الاكسالات و الهيومات وكذلك ترتيب اضافة هذه الانيونات بالنسبة للفوسفور.

تظهر النتائج أن منحنيات ادمصاص الفوسفور على أى من المواد المدروسة من النوع العالى القابلية و قد انطبقت نتائج الأدمصاص على المعادلة الخطية للانجمير حيث كانت الكمية المحسوبة لاقصى ادمصاص الفوسفور متزايدة تبعا للترتيب التالى جوثيت > كاؤلينيت > بنتونيت و يدل معامل طاقة الارتباط k على ان الفوسفور المدمص على الجوثيت له طاقة أدمصاص اكبر من المدمص على سطوح معادن الطين . تتناقص الكمية المدمصة من الفوسفور على الجوثيت أو معادن الطين بزيادة رقم الحموضة – و لم يكن لوجود الاكسالات أو الهيوميك أى تأثير على ادمصاص الفوسفور عند تواجد الفوسفور بتركيز مخفف و لكن عند تواجد الفوسفور بتركيزات عالية ادت اضافة الأحماض العضوية الى نقص كمية الفوسفور المدمصة. وقد تبين أن اختزال كمية الفوسفور المدمص يتوقف على ترتيب اضافة الانيونات العضوية مع الفوسفور وعلى رقم حموضة الوسط . حيث أدت اضافة الايونات العضوية مع ايون الفوسفات و بدرجة خاص قبل اضافة الفوسفات الى تناقص حاد فى كمية الفوسفور المدمص على السطوح. وتتوقف درجة الكفاءة فى انقاص ادمصاص الفوسفور على رقم الحموضة حيث كانت اقل كفاءة عند رقم الحموضة المرتفع.

زادت كمية الفوسفور المنطلقة من الجوثيت ومعادن الطين بزيادة التركيز الأبتدائى للفوسفور فى كل طرق الأضافة – انخفضت النسبة المئوية للكمية المنطلقة من الفوسفور من معدن الجوثيت بارتفاع رقم الحموضة من ٥،٥ الى ٦،٥ فى حين ادى ارتفاع رقم الحموضة الى ٧،٥ الى زيادتها فى كل المعاملات . سجلت طريقة اضافة الفوسفور قبل الأنيونات العضوية اعلى قيم للكمية المنطلقة.