Plant Archives Vol. 19, Supplement 2, 2019 pp. 147-151 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

ADSORPTION OF PHOSPHOROUS ON TOTAL FREE IRON OXIDES SURFACES IN TWO GYPSIFEROUS SOILS

Basim Shakir Obaid AL –Obaidi and Adnan Mhaimeed Hawas Al jabori
Department of Soil and Water Resources, College of Agriculture, University of Tikrit, Iraq
Corresponding Author: Basim Shakir Obaid AL–Obaidi, Email: basimalobaidy@tu.edu.iq

Abstract

This study was conducted to determine the nature of phosphorus adsorption in some Gypsiferous soils in Saladin Governorate and the effect of agricultural cultivation on iron oxides. Two sites were selected in Saladin governorate depending on the agricultural cultivation. The sites included Baiji and Dour districts, Two Pedons were selected for each site, the first pedon is a soil used for wheat crop, it is irrigated by surface irrigation with well water and the second pedon was uncultivated soil. Langmuir Equation is used to describe the relationship between adsorbed phosphorus on soil and phosphorus in equilibrium solution, the results of the adsorption experiment showed that Exceeding Rise the maximum adsorption of soil with the oxides compared to soil which the oxides were removed. It is due to the fact that iron oxides have provided effective surfaces for adsorption of phosphorus as well as the high surface area of non-crystalline iron oxides. This explains why greater adsorption of soil samples containing oxides has increased compared to the soil which the oxides were removed, the soil of Dour gave the highest value of phosphorus adsorption, which reached 12.13 mg kg^{-1} at level 40 mg kg^{-1} compared with the rest of the studied soils, while the uncultivated soil of Baiji gave the lowest value of phosphorus adsorption which reached 1.55 mg kg^{-1} at level 40 mg kg^{-1}. Showed that the phosphorus absorbed by the oxides at the low concentrations was relatively high in the studied soils, which explains why free iron oxides may play a large role in the rapid fixation of phosphorus (Rapid phosphate sorption), which occurs at low concentrations.

Key words**:** Adsorption, Phosphorous, Iron oxides, Gypsiferous soils.

Introduction

Many researchers have studied phosphorus fixation in soil. In its various aspects, most of them confirmed the absorption and precipitation processes, indicating thermodynamic and kinetic relationship. Klibanski *et al.* (2007), showed the process of adsorption of phosphorus on the surfaces of oxides is by holding ions strongly on the surfaces of iron oxides because of the penetration to the surfaces of these oxides, Iron oxides are linked with phosphate adsorption on their surfaces by OH and OH_2 groups. Havlin *et al.*, (2005) noted that adsorption is a chemical process that occurs between phosphates ions, hydroxyl ion and water molecule on the surface of iron oxides. Rhoton *et al.* (2005) found that non-crystalline iron oxides (amorphous) Is more effective compared to the other forms of iron oxides in adsorption of phosphates in soil because of its large surface area and the small particles sizes and the nature of its composition. The charges on iron oxide surfaces are pH-dependent charge and that these charges are equivalent with either negatively or positively charged ions on the surfaces and outside of the electric doubled layer (Havlin *et al.*, 2005). Studies have shown that maximum adsorption values of different ions on surfaces of iron oxides such as phosphates changing according to the pH. For example, when pH between 4-5, the maximum adsorption of ions on the surfaces of the oxides is30-300 gmmole^{-1} (Wang, 2013).

Materials and Methods

Two sites were selected of Gypsiferous soils from the governorate of Salah Al-Din depending on agricultural cultivation, these sites were Beiji and Dour districts, two pedons were dug for each site, the first one refer to soil which cultivate with wheat crop and irrigated by the surface irrigation and the second pedon for uncultivated soil.

Particle size distribution

The distribution of soil particle size was estimated using the method described by Hesse (1976) (Table 1).

Chemical Analysis

The soil reaction (pH), electrical conductivity, total carbonate minerals and cations and anions were estimated according to the methods described in Handbook 60 USDA (1954). (Table 2)

Cation Exchange Capacity (CEC)

Cation Exchange Capacity were estimated in soil according to Savant (1994) by treating samples with (Na_2CO_3) 1% and back titration with Methylene blue 4%. (Table 2)

Iron Oxides Remove

Iron Oxides was extracted Citrate-Bicarbonate-Dithionite (CBD), according to Mehra and Jackson, 1960. Total free iron oxides were estimated by Atomic absorption spectrophotometer and were estimated at the College of Agriculture / University of Tikrit.

Adsorption Experiment

To study the adsorption of phosphorus in soil with oxides and without oxides, 5 g of soil and 50 mL of KH_2PO_4 was added with the following concentrations: 40, 30, 20, 10, 0 mg P ml^{-1}. samples were shaked for 24 hours after adding two drops of toluene to soil suspensions in order to inhibit microorganisms activity. And then samples were lifted for another 24 hours for equilibrium, the samples were filtered to obtain soil solution. The phosphorus was estimated in according to Murphy and Riley (1962), the amount of phosphorus adsorbed was calculated by the difference between P in extracted solution and initial add P, The Langmuir Equation was used to describe the relationship between adsorbed phosphorus and phosphorus in equilibrium solution. After plotting the relationship between the absorbed quantity and the concentration in the solution and from the regression equation, the Xm values and the intercept are obtained as shown below:

$$\mathrm{Xm} = \frac{1}{\mathrm{Inclination}} \quad \mathrm{Intercept} = \frac{1}{\mathrm{K.Xm}}$$

Table 1 : Particle size distribution of soils

Sand	Silt	Clay	Depth	horizon	pedon code	Site	Pedon number
gm Kg^{-1}							
581	300	125	0-11	A	P3	Beiji (Cultivated)	1
596	300	100	11-27	By			
559	295	150	27-56	C1y			
631	294	140	56-79	C2y			
586	225	102	79-105^{+}	C3y			
502	312	128	0-10	A	P4	Beiji (uncultivated)	2
555	310	131	10-29	C1y			
550	369	158	29-51	C2y			
524	290	181	51-75	C3y			
558	294	210	75-100^{+}	C4y			
519	320	224	0-12	A	P7	Dour (Cultivated)	3
496	256	231	12-28	By			
497	256	231	28-50	C1y			
466	270	222	50-68	C2y			
516	290	193	68-105^{+}	C3y			
521	266	212	0-12	A	P8	Dour (uncultivated)	4
531	273	195	12-29	C1y			
515	282	201	29-58	C2y			
456	317	225	58-82	C3y			
860	286	253	82-105^{+}	C4y			

Table 2 : The chemical properties of the studied soils

Sites	Horizon	Depth (cm)	pH	EC ds.m^{-1}	CEC Cmol.c. kg^{-1}	O.M	Gypsum	Total carbonates
						gm.kg^{-1}		
Cultivated Baiji	P3A	0-11	7.38	2.68	16.8	11	55	250.9
	P3By	11-27	7.80	3.64	14.5	4	100	365.7
	P3Cy1	27-56	7.68	3.67	13.2	2	250	370.2
	P3Cy2	56-79	7.85	3.59	10.2	0.09	326	396.6
	P3Cy3	79-105^{+}	7.91	2.73	9.6	Nil	413	321.5
uncultivated Baiji	P4A	0-10	7.84	1.68	13.7	5	109	370.1
	P4Cy1	10-29	7.91	2.38	13.8	2	178	261.9
	P4Cy2	29-51	7.70	2.43	12.2	0.4	269	282.8
	P4Cy3	51-75	7.49	2.41	10.1	0.08	412	289.5
	P4Cy4	75-100^{+}	7.40	2.36	8.9	Nil	607	297.5
Cultivated Dour	P7A	0-12	7.55	3.27	12.8	10	112	289.8
	P7By	12-28	7.23	3.06	12.8	3	243	265.6
	P7Cy1	28-50	7.45	3.54	11.3	1	410	271.8
	P7Cy2	50-68	7.38	3.42	10.2	0.02	556	294.1
	P7Cy3	68-105^{+}	7.38	3.51	9.3	Nil	618	300.2
Uncultivated Dour	P8A	0-12	7.38	2.28	10.9	4	123	307.4
	P8Cy1	12-29	7.25	3.61	10.5	2	267	320.9
	P8Cy2	29-58	7.70	2.76	9.2	0.5	498	312.8
	P8Cy3	58-82	7.36	2.80	8.2	0.02	576	293.8
	P8Cy4	82-105^{+}	7.30	3.51	7.8	Nil	719	297.1

Results and Discussion

Total free iron oxides (Fe$_t$)

The results of Table (3) showed that there is variety in the values of total Fe$_t$ for studied soil. This may be due to the nature of iron-containing soil components as a result of variation of the soil texture and the different clay content, as well as the lack of rainfall and vegetation cover, which in turn affects the c on tent of these soils from organic matter, especially with regard to the cultivated soil, which leads to differences in distribution of iron within soil pedon. Rudramurthy and Dasog 2001 found a decrease in total Fe$_t$ in the soil was the result of reduced content In the crystalline structures of the primary minerals, and the high percentage in the soil due to the increase in the presence of iron in the origin rocks. The results of Table (3) show that there is superiority in the total oxides value.

The increase in the values of the oxides in the surface horizons compared to the subsurface precipitation may be due to the fact that these soils do not receive large amounts of rain water enough to transport the parts associated with the oxides such a clays from surface to sub-surface horizons Moreover, the period of agricultural cultivation and irrigation has a major role in this process and these results are agreed with (Pronk *et al*., 2011).

In general, we conclude from the data in Table (3) that the soil content of iron oxides was low and this may return to the nature of the origin of these soil, or the pedogenic process, as these oxides originate from the parent material and weathering processes of iron oxides in soil.

Adsorption Experiment

The results of Table (4) indicate that Langmuir equation schussed in the mathematical description of phosphorus adsorption in studied soil. We obtained a high R^2 ranging from 0.984 to 0.977 for the soil with oxides, whereas the soil which the oxides were removed gave R^2 ranging from 0.996 - 0.953.

The results of Table (4) showed that the maximum adsorption values of the samples differed according to soil content of total iron oxides. The maximum adsorption values with oxides in general were higher than the samples without oxides, the highest value of the maximum adsorption of the soil with oxides was 384.61mg P kg^{-1}which belong to cultivated of our soil, while the soil with oxides recorded less value 142.85 mg P kg^{-1}, which belong to the cultivated Baiji soil, while the soil with the removed oxides has recorded the highest value 222.22 mg Pkg^{-1}, which belongs to uncultivated Dour soil. Whereas The lowest value was recorded in cultivated Baiji soil 108.69 mg P kg^{-1}.

Table 4 shows that the maximum adsorption values of the soil with the oxides are higher than the oxides, which removed oxides from them and which may be due to the fact that iron oxides have provided effective surfaces for adsorption of phosphorus as well as the high surface area of non-crystalline iron oxides. This explains why increased adsorption of soils containing oxides than in oxides has been removed this indicates the importance of iron oxides in the process of adsorption and precipitation reactions of ions, especially phosphorus in soils, and have an effect on the phosphorus availability of the phosphorus reaction with the effective surfaces of iron oxides and convert them from available to unavailable form made and these results are compatible with Nur *et al.* (2014) contributed to increase the values of adsorption, which may be attributed to the effectively of iron oxides deposited on the surface of these menials or at equilibrium Caused an increase in the number of adsorption sites. While the bonding energy behaved differently than the maximum adsorption values, as it decreased in soils containing iron oxides while the bonding energy values increased when removing the oxides from the studied soils. There is an inverse relationship between the bonding and adsorption capacity.

We notice from the table (4) the studied soils (with oxides) has high adsorption values mainly for carbonate and calcium sulphate and low bonding capacity due to the low quantity iron oxides and aluminum in it (Arco-Lázaro *et al.*, 2016), confirming that phosphorus adsorbed in Iraqi soils situation is still available for processing. However, as we have seen from this study, increasing iron oxides caused by soil management processes that add to fertilizers or by adding organic fertilizer will play a significant role in increasing phosphorous bonding energy.

The content of iron oxides and their relation to phosphorus adsorption in equilibrium solution

It is noted from the data in Table (5) that there is a correlation between the amount of absorbed phosphorus and the content of the studied soils of total iron oxides, as well as the increase in adsorbed phosphorus on Oxides with the increasing of added phosphorus to the soil at all levels, these results were agreed with Wang *et al.* (2013) who showed that adsorbed phosphorus by soil increased with the increasing of the added phosphorus to the soil. It is noted from the table that there is a positive relations.

Relationship between phosphorus adsorbed by the total free iron oxides and the added levels of phosphorus. As is known, the surface area quantity of iron oxides for ranging from (500, 100) m^2. Therefore, this large surface area allows increased adsorption of phosphate ions when the amount of phosphorus added to the soil increases (Zeng *et al.*, 2004). Table (5) and Figure (1) show a variation in the phosphorus adsorbed by oxides. Dour soils gave the highest value of phosphorus adsorption, which was 12.13 Mg kg^{-1} at level 40 ppm compared with the rest of the studied soils. The cultivated dour soil recorded the lowest value of phosphorus adsorption Which were 3.98 Mg kg^{-1} at level 40 mg PL^{-1}, while the other soils remaining between them, these results were consistent with the amount of clay content of studied soils (Table 1), as is well known, the iron oxide minerals, which are crystalline and non-crystalline, are found associated with clay and represented the high activity of total iron oxides (Zeng *et al.*, 2004). As shown in Table 5, Figure 1 phosphorus adsorbed by oxides at low concentrations were relatively high in the studied soils. This explains why free iron oxides may play a large role in Rapid phosphate sorption which occurs at low concentration especially at the second level 10 mgP L^{-1} as well as at the third level 20 mg PL^{-1}. Therefore, the presence of total iron oxides Even if it is in small quantities, it fixed or adsorbed high quantities of phosphorus from soil solution or when the addition of fertilizer, especially if iron oxides occurrence in high quantities in crystallized form, as they have a large role in the rapid fixation of phosphorus and thus converted to unavailable form in studied soils, these results agreed with what Wang *et al.* (2013) showed that the process of adsorption of phosphates at low concentrations is significant due to the amount of active surfaces in the crystallized iron oxides in the adsorption process.

Table 3 : Total free iron oxides in the studied soils

Pedon	Site	Horizon	Fe_t	$Fe_{t(C)}$	$Fe_{t(Si)}$	$Fe_{t(S)}$
			gm.kg^{-1}			
1	Cultivation Baiji	Surface	3.800	3.016	0.712	0.007
		Sub surface	2.465	1.840	0.630	0.0140
2	Uncultivation Baiji	Surface	4.114	3.220	0.890	0.003
		Subsurface	5.431	3.971	1.450	0.0019
3	Cultivation Dour	Surface	5.132	3.702	1.420	0.001
		Sub surface	4.342	3.308	0.964	0.079
4	Uncultivation Dour	Surface	5.543	3.880	1.598	0.065
		Sub surface	4.470	3.128	1.300	0.042

Table 4 : R^2 and maximum adsorption and bonding energy of Langmuir equation

Pedon		With oxides			Without oxides		
	Sites	**R^2**	**K**	**Xm mg P kg^{-1}**	**R^2**	**K**	**Xm mg P kg^{-1}**
1	Cultivated Baiji	0.977	0.0030	142.85	0.953	0.0054	108.69
2	uncultivated Baiji	0.981	0.0020	204.08	0.968	0.0038	144.92
3	Cultivated Dour	0.984	0.00082	384.61	0.942	0.0064	111.1
4	uncultivated Dour	0.979	0.0015	250	0.996	0.0024	222.22

Xm =Maximum adsorption K = Bonding energy

Table 5 : Addition levels of phosphorus and its concentrations in studied soils

Pedon.	Sites	Added level mg P L^{-1}	With oxides	Without oxides	Adsorbed
			Absorbed quantity mg kg $^{-1}$	**Absorbed quantity mg kg $^{-1}$**	**From oxides mg kg $^{-1}$**
3	Cultivated Baiji	0	0	0	0
		10	7.098	6.985	0.113
		20	16.03	14.86	1.17
		30	22.03	19.01	3.02
		40	31.23	27.25	3.98
4	uncultivated Baiji	0	0	0	0
		10	7.829	7.398	0.431
		20	16.23	13.23	3
		30	22.73	20.65	2.08
		40	30.83	26.38	4.45
7	Cultivated Dour	0	0	0	0
		10	7.798	7.105	0.693
		20	17.76	9.012	8.748
		30	26.56	22.65	3.91
		40	35.98	28.96	7.02
8	uncultivated Dour	0	0	0	0
		10	7.227	5.521	1.706
		20	14.23	11.69	2.54
		30	22.36	19.28	3.08
		40	37.71	25.58	12.13

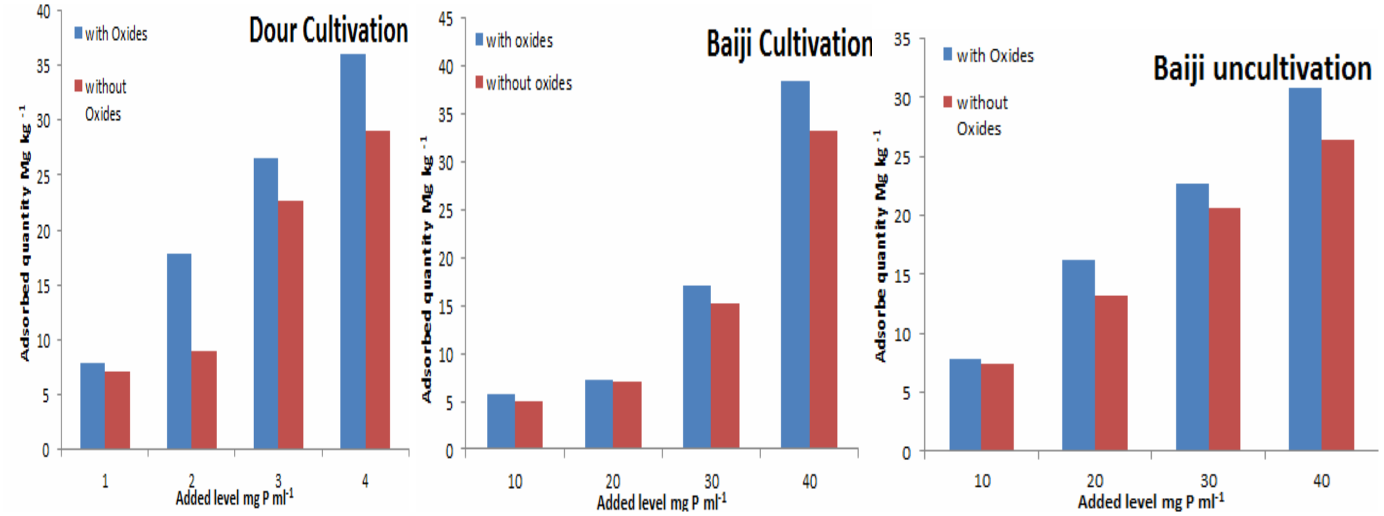

Fig. 1 : Quantities of phosphorus adsorbed from the additive (mg kg^{-1}) with and without iron oxides

References

Arco-Lázaro, E.; Agudo, I.; Clemente, R. and Bernal, M.P. (2016). Arsenic (V) adsorption-desorption in agricultural and mine soils: effects of organic matter addition and phosphate competition. Environmental pollution, 216: 71-79

Havlin, J.L.; Beaton, J.D.; Tisdale, S.L. and Nelson, W.L. (2005). Soil Fertility and Fertilizers (7ed.). ISBN: 0-13-027824-6 Pearson Education Limited USA.

Hesse, P.R. (1971). A text book of soil chemical analysis. John murray. LTD. London, British.

Klibanski, S.; Litaor, M.I. and Shenker, M. (2007). Overestimation of phosphorus adsorption capacity in reduced soils : An artifact of Typical batch adsorption experiments. Soil Sci. Soc. Amer. J., 71: 1128-1136.

Mehra, O.P. and Jackson, M.L. (1960). Iron oxide removal from soil and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clay and clay minerals 7: 317-327.

Murphy, J.A.M.E.S. and Riley, J.P. (1962). A modified single solution method for the determination of phosphate in natural waters. Analyticachimicaacta, 27: 31-36.

Nur, T.; Johir, M.A.H.; Loganathan, P.; Nguyen, T.; Vigneswaran, S. and Kandasamy, J. (2014). Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. Journal of Industrial and Engineering Chemistry, 20(4): 1301-1307.

Pronk, G.J.; Heister, K. and Kögel-Knabner, I. (2011). Iron oxides as major available interface component in loamy arable topsoils. Soil Science Society of America Journal, 75(6): 2158-2168.

Rhoton, F.E. and Bigham, J.M. (2005). Phosphate adsorption by Ferrihydrite – amended soils. Environ Qual. J., 34 : 890-896.

Rudramurthy, H.V. and Dasog, G.S. (2001). Studies on associated red and black soils of North Karnataka. Journal of the Indian Society of Soil Science, 49(2): 301-309.

Savant, N.K. (1994). Simplified methylene blue method for rapid determination of cation exchange capacity of mineral soils. Communications in soil science and plant analysis, 25(19-20): 3357-3364.

Staff, U.S.D.A. (1954). Diagnostic and improvement of saline and Alkali soils. (USDA Handbook-60). Washington, D.C).

Wang, X.; Liu, F.; Tan, W.; Li, W.; Feng, X. and Sparks, D.L. (2013). Characteristics of phosphate adsorption-desorption onto ferrihydrite: comparison with well-crystalline Fe (hydr) oxides. Soil Science, 178(1): 1-11.

Wang, X.; Liu, F.; Tan, W.; Li, W.; Feng, X. and Sparks, D.L. (2013). Characteristics of phosphate adsorption-desorption onto ferrihydrite: comparison with well-crystalline Fe (hydr) oxides. Soil Science, 178(1): 1-11.

Zeng, L., Li, X. and Liu, J. (2004). Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. Water research, 38(5): 1318-1326.