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Phosphorus Sorption in Some Great Soil Groups of Iraqi Kurdistan Region

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Abstract

Phosphorus (P) sorption in soils is a key process governing its availability for crops. There is scanty information on the P sorption characteristics of calcareous soils of Kurdistan region of Iraq. P sorption characteristics were determined in seven soil samples belonging to four agricultural soil great groups located in Sulaimani province. (Xerorthents, Haploxererts, Haploxerolls and Calcixerolls). Total equivalent $CaCO_3$ contents ranged from (33.80 to 350.65 g kg^{-1}). Active $CaCO_3$ contents ranged from (20.00 to 150.00 g kg^{-1}). The amount of available P contents ranged from (4.49 to 6.92 mg P kg^{-1} soil). Langmuir and Freundlich models were applied on seven different textured calcareous soils, in order to characterize the P adsorption isotherm for these soils. Langmuir and Freundlich parameters (K_L, b, K_f and 1/n) values were (130.00 to 800.00 L mg^{-1} , 28.57 to 76.92 mg kg^{-1}, 42.27 to 121.06 mg kg^{-1} and 0.656 to 0.974) respectively. High values of (K_L) for all investigated soil samples indicate a strong attraction between sorbed P and sorbent surface.

Key words: Phosphorus, adsorption, precipitation, Langmuir and Freundlich isotherms, calcareous soils.

I. Introduction:

Phosphorus (P) is the most important nutrient element (after nitrogen) limiting agricultural production in most regions of the world. It is an extremely chemically reactive mineral. In all its natural forms, including the organic state, P is very stable or insoluble, and only a very small portion exists in the soil solution at any time [1]. The availability of phosphorus (P) to plants is very low in calcareous soils. This had been attributed to adsorption and/ or precipitation reactions that occur between P and soil constituents [2]. The reaction chemistry of phosphorus is very complex and it is very difficult to manage the behavior of P in arid and semi arid soils [3]. Understanding of P adsorption and desorption by soils is important for fertilizer management. Little is known about the P sorption characteristics of calcareous soils [4]. The relation between the amounts of P that a soil will adsorb from a phosphate solution and the concentration of the P left in the solution known as the *sorption isotherm* [5]. [6] stated that adsorption-desorption is the dominant inorganic process influencing soil solution P concentration. Soil components such as clay content, various pools of iron oxides [7, 8, 9], soil carbonates [10, 11, 12] and organic matter [9] play very important role in the adsorption chemistry of P in calcareous soil. The mechanism of the adsorption of phosphate to $CaCO_3$ has been previously studied [13, 14, and 15]. Earlier studies suggested that the initial uptake of phosphate on calcite occurs by chemisorptions, followed by a slow transformation of amorphous calcium phosphate to crystalline apatite. [16] reported that the available P significantly decreased with an increase of soil pH and increased with an increase of organic carbon, cation exchange capacity (CEC) and clay content. [11] reported that below an initial concentration of 0.5 m*M* the adsorption processes were predominant while above this level precipitation became predominant in calcareous soils.

The objectives of this study are 1) to investigate sorption characteristics of surface of four great groups of calcareous soils, 2) Identify soil properties related to sorption and precipitation of applied phosphate in calcareous soils, 3) demarcate between adsorption and precipitation processes based on Freundlich K_f value.

II. Materials and Methods:

Seven soil samples belonging to agriculturally important soil series were taken from agricultural regions in Sulaimani governorate in Kurdistan region, Iraq .

Soil samples were taken from surface (0-30 cm) layer of calcareous agricultural soils in the Iraqi Kurdistan region Shown in Table(I). The soil samples were air dried and ground to pass through a 2 mm- sieve prior to analysis.

A. Soil analysis

Soil particle size distribution was determined by the pipette method [17]. Organic matter (O.M.) was determined by dichromate oxidation (Walkley and Black procedure) as described by [18]. Electrical conductivity (EC) and pH were measured for the soil saturation extract with EC-meter, model (WTW 82362 Weilheim, Germany) and a pH-meter, model (Microprocessor pH meter, Hanna pH 211) respectively. Cation exchange capacity (CEC) was obtained by saturation with 1*M* ammonium acetate (NH_4OAc) at pH 8.1 as an extraction solution [19]. Total calcium carbonate ($CaCO_3$) in the soil, expressed as the equivalent calcium carbonate (ECC) was determined by a rapid titration method [20]. The active lime or active equivalent $CaCO_3$ (AECC), which is a fine particle-size calcite, was determined by the 0.5 *M* NH4-oxalate method [21]. Extractable P from the soil samples was determined by extracting the samples with 0.5 *M* $NaHCO_3$ [22], studied soils were classified according to USDA (United State Department of agriculture) Soil Taxonomy [23] as shown in Table(I).

Table. I: Some physical and chemical properties of investigated soils.

Locations	Great-group	PSD g kg^{-1}			Text. class	pH	EC_e dSm^{-1} at 25°C	CEC $Cmol_c$ kg-1	available P(mg kg-1)	O.M.	equivalent $CaCO_3$	
											Total	Active
		Sand	Silt	Clay						g kg^{-1}		
Qlyasan	Haploxererts	93.55	506.7	399.75	SiCL	7.78	0.44	50.50	6.92	34.70	156.25	70
Kanypanka	Haploxerolls	34.15	528.35	437.5	SiC	8.18	0.38	51.56	5.60	30.50	33.8	20
Arbat	Xerorthents	65.0	521.25	413.75	SiC	8.07	0.31	52.46	4.56	23.10	89.65	52.5
Bakrajow	Haploxererts	65.25	501.5	433.25	SiC	7.61	0.54	47.7	5.55	24.30	327.25	117.5
Bazyan	Xerorthents	61.35	565.9	372.75	SiCL	7.44	0.46	45.28	4.49	25.85	206.1	82.5
Serwan	Haploxerolls	12.21	448.2	539.55	SiC	7.74	0.31	52.98	5.58	18.40	350.65	150
Said Sadiq	Calcixerolls	135.4	411.9	452.7	SiC	7.90	0.52	50.25	5.70	33.7	150.0	65

B. *Phosphate sorption*

P-sorption isotherms of soils were determined by equilibrating 2.000 g soil with 50 ml of [10, 25, 50, 75, 100, 150, 200, 250 and 300 mg P (as KH_2PO_4) L^{-1}] solution prepared in 0.01*M* $CaCl_2$ solution the suspensions were shaken for 24 hours at 25 ± 2 ^oC. After equilibration, the samples were centrifuged for 10 minutes and filtered through a Whatman No.42 filter paper and P in supernatant solution was determined calorimetrically at 882 nm wavelength [24]. The amount of P adsorption/precipitation converted from mg P L^{-1} to mg kg^{-1} by using the formula [25] as:

$X/m=[(C_o–C)*V]/W_s$ ……………….(1)

Where:

X/m is adsorption/precipitation of P at equilibrium (mg P kg^{-1})

C_o is the initial concentration of P added (mg P L^{-1})

C is the concentration of P in solution after 24-hours equilibrium (mg P L^{-1})

V is the volume of P solution added (L)

W_s is the oven dry weight of soil (kg)

The experiment was run in triplicate, means of which were used for further calculation. The data so collected were computed according to the Linear, Langmuir and Frendlich equations.

Langmuir Model $x/m=[(K_LbC)/(1+K_LC)]$………………..(2)

Frendlich Model $x/m=K_fC^{1/n}$ ………….. (3)

Where:

C = Concentration of P in soil solution at equilibrium (EPC) (mg L^{-1}).

x/m = Amount of P adsorbed/ precipitated (mg P kg^{-1} soil).

1/b = Slop of the line, when [C/(x/m)] vs. C was plotted.

b = Maximum Adsorption (mg P kg^{-1} soil = Reciprocal of the slop.

$1/K_Lb$ = Y-intercept of the Langmuir model, when [C/(x/m)] vs. C was plotted.

K_Lb = Reciprocal of Y- intercept.

K_L = Bonding energy constant (mg P L^{-1}) = K_Lb/b.

K_f = Proportionality constant for the Frendlich model (mg kg^{-1}),

1/n = Slop of the curve, when log(x/m) vs. log(C) was plotted.

III. Results and Discussion:

A. *Phosphorus Sorption isotherm*

Figure (1) shows the trend of P-sorption with different rates of P application. Among the investigated soils sorbed P tends to increase with increasing rate of phosphate application. Phosphorus adsorption and equilibrium concentration of phosphate values for investigated soils are presented in Table (II).

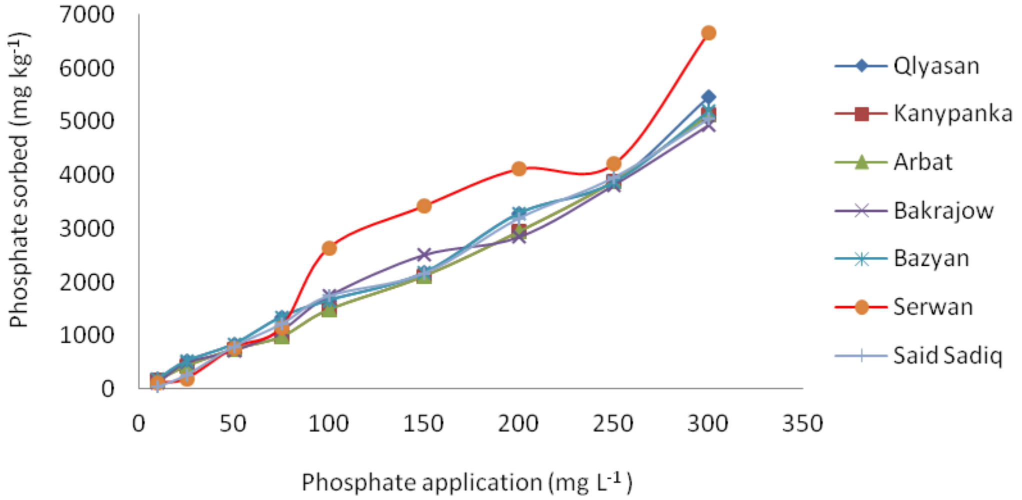

Fig.(1) Trend of phosphate sorption in different investigated soils with different rates of P application.

Table.II: The relation between concentration of P in soil solution at equilibrium C (mg L^{-1}) and amount of P adsorbed/ precipitated (mg P kg^{-1} soil) for investigated soils.

Locations													
Qlyasan		Kanypanka		Arbat		Bakrajow		Bazyan		Serwan		Said Sadiq	
C(mg/L)	x/m(mg/kg)	C(mg/L)	x/m(mg/kg)	C(mg/L)	x/m(mg/kg)	C(mg/L)	x/m(mg/kg)	C(mg/L)	x/m(mg/kg)	C(mg/L)	x/m(mg/kg)	C(mg/L)	x/m(mg/kg)
2.80	180	4.0	156.0	3.87	155.5	2.0	126.0	2.80	179.88	2.3	115.04	1.50	42.50
4.27	518	8.0	422.0	8.12	421.9	5.0	502.0	4.27	518.35	7.6	193.42	13.22	262.85
16.48	838	20.0	742.0	20.33	741.7	21.0	724.0	16.48	838.05	16.0	770.68	19.68	793.84
21.17	1346	36.0	973.0	36.08	973.0	31.0	1104.0	21.17	1345.7	29.1	1146.63	40.89	1214.75
33.67	1658	41.0	1481.0	40.77	1480.7	30.0	1745.0	33.67	1658.2	47.6	2637.93	76.14	1742.18
63.12	2172	66.0	2108.0	65.67	2108.1	50.0	2510.0	63.12	2172.1	84.0	3417.45	126.89	2159.98
68.61	3285	82.0	2943.0	82.30	2942.5	86.0	2845.0	68.61	3284.8	219.6	4109.98	287.78	3192.65
95.13	3872	95.0	3887.0	94.54	3886.5	97.0	3815.0	95.13	3871.8	410.2	4204.63	429.2	3956.6
198.15	5460	95.0	5130.0	94.81	5129.6	103.0	4936.0	198.15	5205.0	1623.0	6662.88	645.72	5057.0

Phosphate adsorption and equilibrium concentration tend to increase with increasing levels of added P in all soil samples. The values of amounts of P sorbed by soil differ among various soil great groups the high amount from Serwan location was(6662.88 mg P kg^{-1}) while the lowest from Bakrajow location was (4936 mgP kg^{-1}) and P adsorbed for other locations were between these two values. This can be attributed to physico-chemical properties of soils such as clay content, total $CaCO_3$, and CEC (Table I). The higher value of the P sorption tendency for the soil of Serwan location this may be related to high $CaCO_3$, clay contents and CEC. Our results are agreed with [26, 3].

B. P Sorption Indices:

1- Langmuir Model

Phosphorous adsorption data were plotted according to the Langmuir (plotted 1/Xm vs. 1/C) equation for all soils the data show a satisfactory agreement with Langmuir equation table (III). The values of adsorption maximum (b) and bonding energy constant (K_L) are given in table (III) which are ranged from (28.57 to 76.92 mg kg^{-1} soil) and (130 to 800 L mg^{-1} P) respectively. And all investigated soil samples give high K_L values, which indicate a strong attraction between sorbed P and sorbent surface. The magnitude of specific adsorption which is characterized by high bonding energy (K_L) for most species depends on pH.

Table.III: Adsorption parameters of the Langmuir model for investigated soils.

Locations	Langmuir parameters					
	Slop=(1/b)	b (mg kg^{-1})	Y-intercept= (1/K_Lb)	K_Lb (mg kg^{-1})	K_L(L mg^{-1})= (K_Lb/b)	R^2
Qlyasan	0.013	76.92	0.0001	10000.0	130.0	0.903
Kanypanka	0.024	41.67	0.00003	33333.0	800.0	0.977
Arbat	0.024	41.67	0.00005	20000.0	480.0	0.982
Bakrajow	0.015	66.67	0.0001	10000.0	150.0	0.964
Bazyan	0.013	76.92	0.0001	10000.0	130.0	0.903
Serwan	0.021	47.62	0.0003	33333.0	700.0	0.926
Said Sadiq	0.035	28.57	0.0002	5000.0	175.0	0.997
mean	0.021	54.29	0.00013	17381.0	366.0	0.950

2- *Freundlich Model***.**

From the data plotted according to the linear form of the Freundlich model, almost an analogous linear relationship was observed. Values of the exponent (1/n) were ranged from (0.656 to 0.974 with mean 0.812). Freundilch model is empirical in nature and implies that sorption decreases exponentially with increasing saturation of exchange sites with P. Slop of Freundlich model is measure of the heterogenetiy system. A more homogeneous system will have (1/n) value approaching unity and more heterogeneous system will have 1/n value approaching zero [27]. It is obvious from Table (IV) that soil of Serwan location had minimum (1/n) value, i.e. 0.656 while soil of Kanypank location had maximum (1/n) value, i. e. 0.974 approaching unity. Therefore, soil of Kanypanka location will be more homogeneous while soil of Serwan will be more heterogeneous system (Table IV).

Freundlich K_f was divided by a value taking the antilog of the Freundlich slop [K_f/antilog(1/n)= SEPC], solution P concentration equilibrium (SEPC) with adsorbed P was calculated. These values were indicated in Table (IV). [28] stated that K_f is the amount of sorbed P that would sustain a unit P concentration in equilibrium solution. [29] described that K_f is dependent upon the solution concentration. [4] called it adsorption capacity while according to [30] it is extent of adsorption (mg kg^{-1}). [4] stated that low Freundlich K_f values indicate low P adsorption capacities at low P concentration ($\leq$1 mg P L^{-1}). Moreover, even a large amount of P may be retained by precipitation at high P concentration. Our results agree with [31].

Table. IV: adsorption parameters of the Freundlich model for investigated soils.

Location	Freundlich parameters					
	Y-intercept= logK$_{f)}$	K$_f$ (mg kg^{-1})	Slop=1/n	Antilog 1/n	SEPC	R^2
Qlyasan	2.077	119.40	0.745	5.56	21.47	0.957
Kanypanka	1.626	42.27	0.974	9.42	4.49	0.963
Arbat	1.630	42.66	0.972	9.38	4.55	0.963
Bakrajow	1.930	85.11	0.828	6.73	12.65	0.945
Bazyan	2.083	121.06	0.739	5.48	22.09	0.955
Serwan	2.004	100.93	0.656	4.53	22.28	0.870
Said Sadiq	1.674	47.21	0.767	5.85	8.07	0.950
mean	1.860	79.81	0.812	6.707	10.63	0.953

IV. Conclusions:

Phosphorus added to calcareous soils was removed from soil solution by the combination of adsorption and precipitation processes. The P adsorption data was described by Langmuir and Freunblich isotherms. The linear forms of the Langmuir and Freunblich equations were used to calculate the parameters of the equations. High values of Bonding energy constant (K$_L$) (mg P L^{-1}) for all investigated soil samples indicated strong attraction between sorbed P and sorbent surface. In soil with high P sorption capacities and strong P binding energy (like our soils), added to soils a less soluble P source that releases P to soil solution in smaller concentrations spread over a longer period and slow down the P fixation reaction in soil.

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