

PHOSPHORUS ADSORPTION ISOTHERM IN SOIL UNDER ORGANIC FARMING USING PATCH AND FLOW METHODS

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ABSTRACT

A substantial amount of effort has been put into understanding soil P availability for soils under long-term organic farming. Soils of two organic farms were collected to evaluate phosphorus (P) adsorption isotherm. S1 and S2 were Sicum farm soils (loamy sand soils) with 23 years and 12 years organic farming, respectively. F1 and F2 were Faium farm soils (sandy clay loam soils) with 10 years and 2 years organic farming, respectively. Organic matter percentage for S1, S2, F1, and F2 were 10.4, 6.1, 22.9, and 16.8g/kg, respectively. P-adsorption isotherm was studied using two different methods, namely the standard patch method and a new flow method. In the new method, soil column were placed in glass column and continuous flow was induced by controlled suction. Solution, 10 times the weight of the soil, was applied and recycled until apparent equilibrium concentrations were observed. P adsorption was evaluated on the basis P partition coefficients (Kd) calculated from Freundlich isotherm equations. Amount of phosphorus adsorbed, at equilibrium, and Kd was higher for soils with lower organic matter, for both farms and both methods. Flow method show more phosphorus adsorption at equilibrium and higher Kd than batch method, for the two farms. Flow method provides a way to obtain adsorption-isotherm data under more realistic conditions.

Keywords: Adsorption, Freundlich isotherms, organic farming, phosphorous, flow method, patch method.

INTRODUCTION

Organic farming refers to agricultural production systems used to produce food and fiber organically. It has developed into one of the most dynamic agricultural sectors in European Union and United State. Nowadays there is a transition to organic farming in Egypt, where it covers about 15,000 Fd, and it is going to expand. Organic farming means sustainable agricultural systems which depend on maintaining adequate amounts of plant nutrients, including P, without unduly increasing either nutrient load or loss.

Many studies have shown an increase in soil P, usually documented as soil test P, with continual land application of manure (Sharpley *et al.*, 1993). Under continual long-term (>10 yr) manure applications, results revealed a relative increase in inorganic P forms compared with organic P in soils to which manure had been applied, where in untreated soils, 43 to 74% of the total P was inorganic, compared with 49 to 80% in manured soils (Sharpley *et al.*, 2004).

In arable soils, the phosphorus (P) concentration in the soil solution is controlled by plants (uptake) and additionally by two groups of processes i.e. dissolution/precipitation and adsorption/desorption processes (Nash and Halliwell, 1999). Adsorption may be considered as a process leading to net accumulation of nutrients in the soil solid phase, whereas precipitation should be treated as a formation of a "new solid soil phase". Both processes may

result in nutrient depletion from soil solution (Sanyal and De Datta, 1991). Lin *et al.* (1983) reported that P adsorption dominates in soils characterized by low P content and precipitation may occur when solution concentration of P is very high.

Phosphate anions undergo specific and nonspecific sorption in soils. Nonspecific sorption is phosphate retention by protonated hydroxyl groups ($-\text{OH}_2^+$) at the surface of soil particle. This type of retention depends on columbic forces and is rather weak and hence nonspecific adsorption is totally reversible. Specific P sorption is attributed to ligand exchange between hydroxyl groups (OH^-) and phosphate anions forming inner-sphere complexes. This process proceeds irrespectively of the value of surface charge and decreases quantitatively with increasing soil pH. Phosphate anions can be adsorbed by aluminum and iron hydroxyls even when the resultant charge is negative (Mengel, 1985).

Practically sorption of P by soils is frequently characterized by isotherms established by the use of Langmuir and Freundlich equations (Del Bubba *et al.*, 2003). According to Langmuir's theory, maximal adsorption is attained at full monolayer saturation. On the other hand Freundlich assumes that the full saturation of all sorption sites in soils is never reached (Piwowarowa and Ginzburg, 1981).

Solute transport models often use batch-generated adsorption isotherms to partition solute between the aqueous and adsorbed phases, but the relationship at equilibrium between aqueous and adsorbed solute concentrations may be different in closed (batch) and open (flow) systems. Batch-generated anion adsorption isotherms are likely to underestimate the extent of adsorption in the corresponding flow system, particularly at relatively low aqueous phase sorbate concentrations.

The saturated-flow technique was designed to yield data analogous to conventional adsorption-isotherm experiments in the following manner: (I) the solution was allowed to equilibrate with the soil by recycling through the soil core, (II) the procedure was replicated on different cores using different initial solute concentrations to give varying final equilibrium concentrations.

The aim of the present work was to illustrate methods of measuring P-adsorption isotherms using flow and patch techniques for soils with different periods of organic farming.

MATERIALS AND METHODS

Soil used for these laboratory experiments was collected from Sicum and Fauim organic farms. S1 and S2 were Sicum farm soils (loamy sand soils) with 23 years and 12 years organic farming, respectively. F1 and F2 were Faium farm soils (sandy clay loam soils) with 10 years and 2 years organic farming, respectively. Organic matter percentage for S1, S2, F1, and F2 were 1.04, 0.61, 2.29, and 1.68% respectively.

All soils were air dried, crushed, sieved (2-mm sieve), and thoroughly mixed for homogeneity. The particle size distribution was determined by pipette method (Day, 1965). Organic matter percentage was measured as

describe by Walkely-Black method (Nelson and Sommers, 1982). P was assayed by the molybdate blue method as modified by Olsen and Dean (1965).

Batch Method. (Graetz and Nair, 2000).

5.0 g dry mass of soil was shaken continuously for two hours in a plastic cup with 50 ml of P-solution, after which mixtures were left to equilibrate for 24 hours, followed by centrifugation and determination of P concentration. Initial P-solutions concentrations were 0.5, 1.0, 2.5, 5.0, 10.0, 20.0, and 40.0 mg/kg, with 0.01 M CaCl₂ as background electrolyte. Two cups per initial concentration were used. Adsorption isotherms were established after equilibrium.

- The amount of P (mg P kg⁻¹ soil) adsorbed was calculated as:

$$P_{\text{adsorbed}} = (P_{\text{initial solution}} - P_{\text{final solution}}) \times \text{solution volume/soil wt.}$$

Flow Method. (Communar *et al.*, 2004).

Soil columns with 5.0 cm length were fitted in glass columns (2.5 cm i.d.) with glass wool underneath, to receive continuous flow of P-solution (Figure 1).

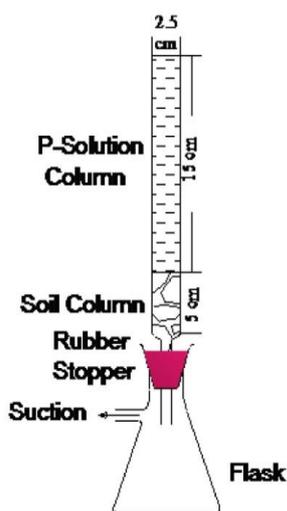


Fig. 1. Schematic diagram of flow method apparatus.

Adsorption isotherms were established by equilibrating soil columns with four P concentrations (1, 5, 20, and 40 mg/kg) with 0.01 M CaCl₂ as background electrolyte. Volume of the solutions was 10 times the weight of the soils.

Continuous flow was induced by controlled suction. After the initial solution was completely exhausted, the collected effluent from each column was recycled and the process repeated until the P concentration of the effluent appeared to reach a steady state and the effluent concentration was approximated as the influent concentration. Samples were taken periodically. This required only two cycles.

Phosphorus adsorbed by soils was evaluated using both Langmuir and Freundlich methods. The obtained data was best fitted to Freundlich model:

$$q = K_d C^{1/n}, \tag{1}$$

Where:

q : The amount of adsorption (adsorbate per unit mass of adsorbent) in mg kg^{-1} ,

C : Is the equilibrium concentration of the adsorptive (mg/l).

K_d : Partition coefficient.

N : Correction factor.

By plotting the linear form of Eq. (1), $\log q = 1/n \log C + \log K_d$, the slope is the value of $1/n$ and the intercept is equal to $\log K_d$.

RESULTS AND DISCUSSION

Patch Method.

The shapes of P-adsorption isotherms under patch method were similar (Fig. 2a and 2b). P adsorption isotherm curves (Fig. 2) for soils with low organic matter content (S2 and F2) display upper curves of soils with high organic matter content (S1 and F1).

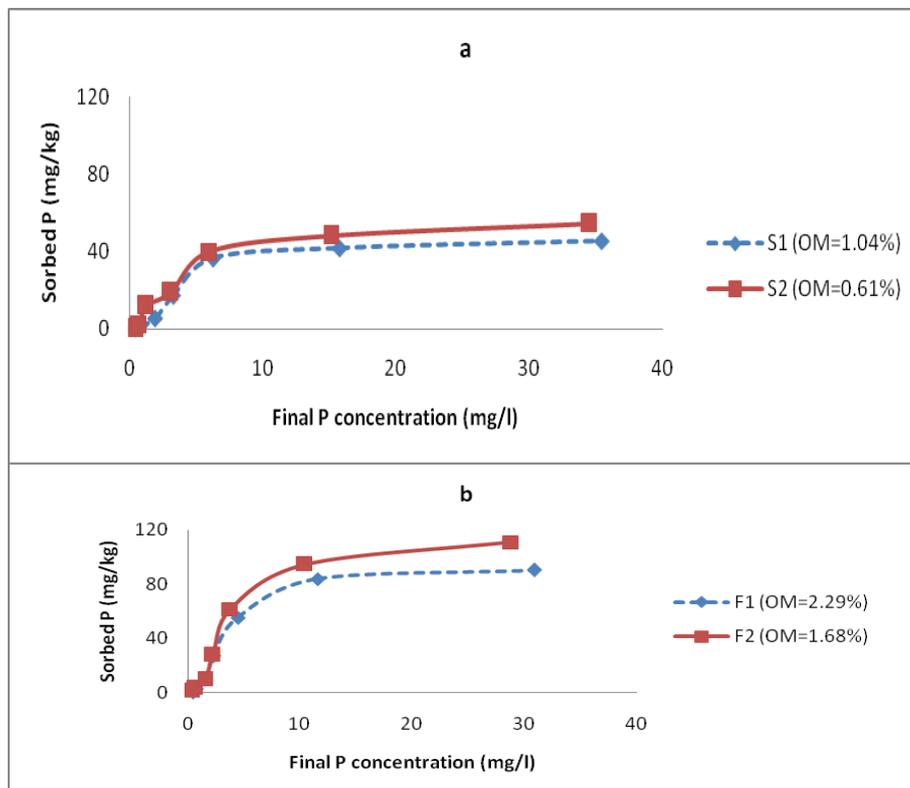


Fig. (2): Phosphorus adsorption isotherm for (a) Sicum farm and (b) Faium farm, under patch method.

P-adsorption isotherms for all soils under both farms (Fig. 3) were highly represented by Freundlich equation, ($R^2 = 0.818$ and 0.807 for Sicum and Faium soils, respectively). Aslam *et al.* (2000) stated that P-adsorption by rice soils was best explained by Freundlich equation. Slope value of the linear regression was correlated to clay content while the intercept can be considered an equilibrium-P available for plant uptake.

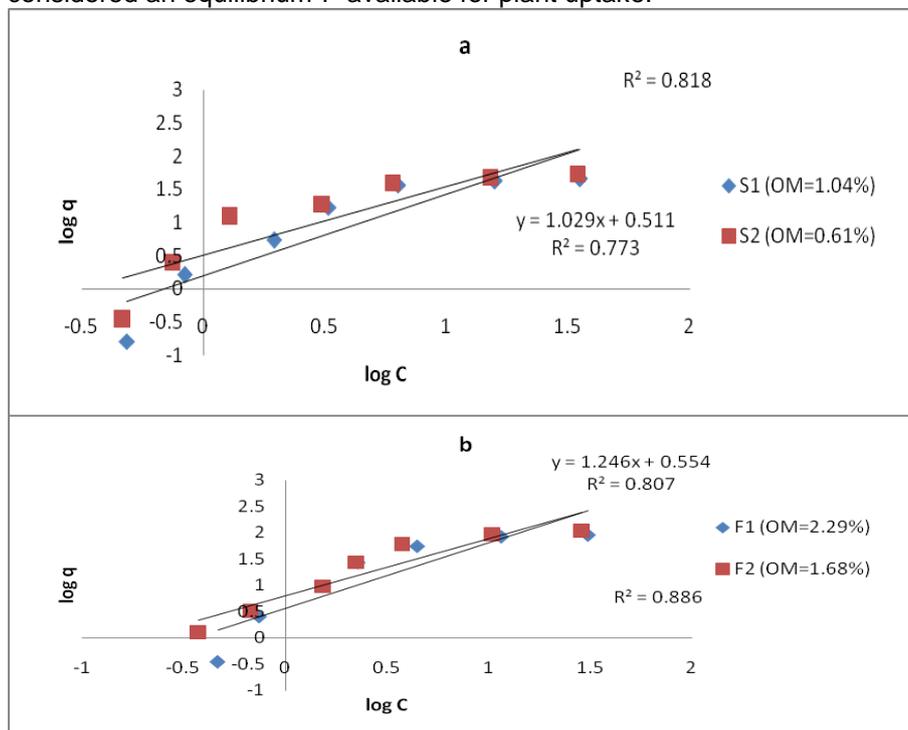


Fig. (3): Linear Freundlich P-adsorption isotherm for (a) Sicum and (b) Faium farms, under patch method.

Flow Method.

The shapes of P-adsorption isotherms were similar for both S1 and S2 (Fig. 4a), with S2 curve, which represent lower organic matter percentage, display upper S1 curve. The same result was obtained under Faium farm between F1 and F2 (Fig. 4b), where F2 curve, which represent lower organic matter percentage, display upper F1 curve.

P-adsorption isotherms for all soils under both farms were highly represented by Freundlich equation, where it gives high R^2 with Freundlich linear forms equations (Fig. 5).

Results from two methods (Patch and Flow) showed that in both farms soils with lower organic matter adsorbed more P, at the same initial P-concentration, than soils with higher organic matter. Kafkafi *et al.*, (1988) showed that several anions of organic acids have been found to prevent P fixation and are able to replace P bound to the soil resulting in greater concentrations of available P.

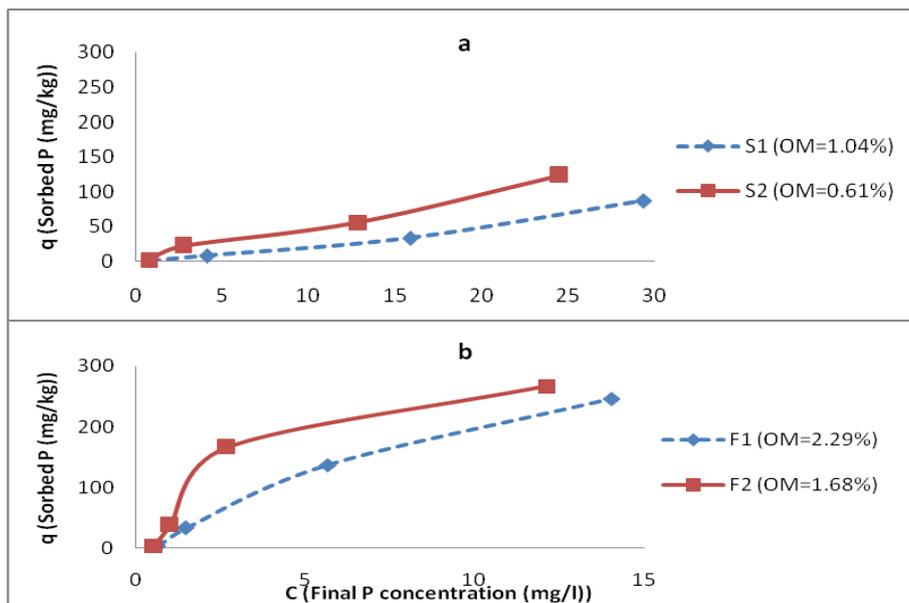


Fig. (4): Phosphorus adsorption isotherm for (A) Sicum farm and (B) Faium farm, under flow method.

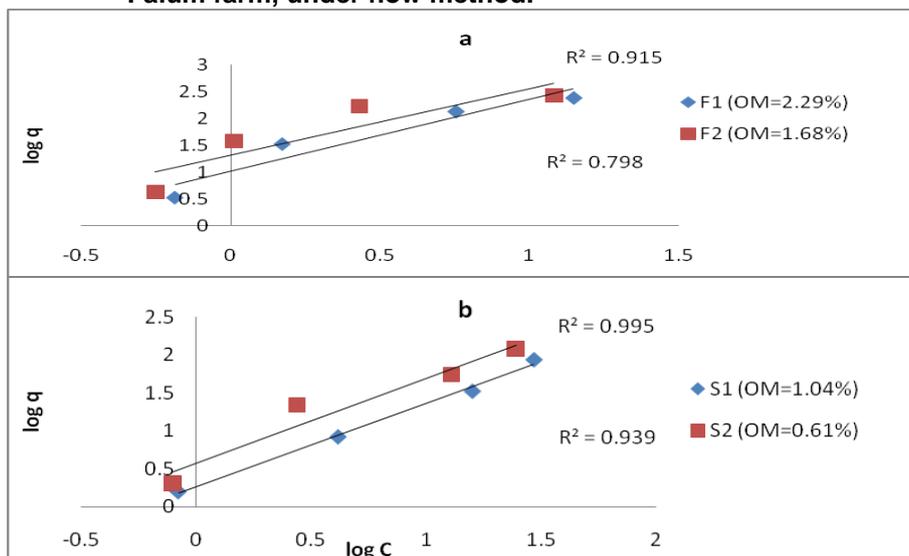


Fig. (5): Linear Freundlich P-adsorption isotherm for (a) Sicum and (b) Faium farms, under flow method.

Siddique and Robinson (2003) suggested that soluble organic compounds of low molecular weight form complexes with Al, Fe, and Ca that decrease soil P sorption capacity. Struthers and Sieling (1950) discovered that at any pH found in agricultural soils, there were organic anions that could effectively prevent P sorption to Fe and Al and they were the same anions of

organic acids that are produced in great quantity by microbial degradation of organic matter. Hue (1991) theorized that complex organic acids (containing phenolic rings) added to soil were more effective in increasing lettuce (*Lactuca sativa* L.) yield than short-chained aliphatic acids because the complex organic acids were more resistant to degradation and remained in the soil longer at concentrations that were effective in reducing P sorption.

Holford *et al.*, (1997) reported that application of organic fertilizers may result in a limitation of P sorption throughout complexation of iron compounds by organic matter. Cations occurring in plant rhizosphere, and they constituting specific bridges between sorbents and phosphates, those cations can be bound during chelating processes, with organic acids, resulting in a direct increase of phosphate activity (Breeuwsma *et al.*, 1993). According to this hypothesis, organic acids modulate the amounts of plant available P by reducing P adsorption and simultaneously increasing phosphate in the soil solution.

Potarzycki *et al.* (2004) stated that 50-60% of maximum adsorption can be considered a specifically retained-P, irrespective of the type of applied fertilizer. The significance of organic matter in the process of P-adsorption is thought to modify sorptive capacity of active P-sorbent such as free iron oxides.

Patch vs. Flow methods.

The amount of P adsorbed by soils was obviously higher under flow method compared with patch method. Results in Table (1) showed that Kds calculated from continuous flow P-adsorption isotherm were higher with respect to those calculated from patch method. Flow method increases the opportunity of P in solutions to be adsorbed by soil, by percolating through all soil layers.

Table (1): Freundlich constants for Patch and Flow methods.

Experiment	Sicum				Faïum			
	S1 (OM 1.04%)		S2 (OM 0.61%)		F1 (OM 2.29%)		F2 (OM 1.68%)	
	Patch	Flow	Patch	Flow	Patch	Flow	Patch	Flow
n	0.94	0.91	0.97	0.69	0.75	0.74	0.93	0.81
Kd	1.55	1.85	3.24	3.80	3.58	10.30	6.32	20.84

Miller *et al.* (1989) found that the shapes of the isotherms generated by the two methods were very similar in all cases, although the flow-generated isotherms were displaced slightly upward relative to the batch isotherms. All systems containing phosphate, flow-generated distribution coefficients were greater than the corresponding batch-generated values, particularly at low surface coverage. They concluded that that provided transport processes do not keep the flow system far from chemical equilibrium, batch-generated anion adsorption isotherms are likely to underestimate the extent of adsorption in the corresponding flow system, particularly at relatively low aqueous phase sorbate concentrations. This appears to be due; in part that prolonged, continuous, one-way flow removes ions that may compete with the sorbate. In batch systems, these leached products are retained within the system, but in more dilute state.

Conclusion

Organic farming enhance the building of soil organic matter, one of the most important source for P, and which play an important role in soil P availability for plants.

Batch adsorption isotherms are likely to underestimate the extent of adsorption in the corresponding flow system .Flow method provides a way to obtain adsorption-isotherm data under more realistic conditions.

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الادمصاص الايزوثيرمي للفسفور في اراضي تحت الزراعة العضوية باستخدام طريقتي الاستخلاص و التدفق

محمد عبد الرحيم داود عمر ، رضا رجب شاهين و حسن أحمد خاطر
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جمعت التربة من مزرعتين عضويتين من اجل دراسة ادمصاص الفسفور. S1 و S2 و هي التربة الممتلئة لمزرعة سيكم (Sicum , loamy sand soil)، ٢٣ و ١٢ سنة تحت الزراعة العضوية، على التوالي. كما ان F1 و F2 و هي التربة الممتلئة لمزرعة الفيوم (Faium, sandy clay loam soil)، ١٠ و ٢ سنة تحت الزراعة العضوية، على التوالي. نسبة المادة العضوية لكل من S1، S2، F1، F2، كانت ١٠، ٤، ٦، ١، ٢٢، ٩، ١٦، ٨ جرام/كيلو جرام، على التوالي. تم دراسة ادمصاص الفسفور باستخدام طريقتين مختلفتين، هما طريقة الاستخلاص التقليدية (Patch method) وطريقة التدفق (low method) و هي طريقة جديدة، حيث وضعت التربة في عامود زجاجي ليتم غسلها بتدفق مستمر من محلول الفسفور و الذي كان يستحث بنظام تفرغ ثابت. و كان حجم المحلول المستخدم عشر اضعاف وزن عامود التربة، و الذي تم اعادة استخدامه لأكثر من مرة حتى ثبت تركيز الفسفور في المحلول المستخلص من العامود. وجرى تقييم ادمصاص الفسفور على أساس معامل التوزيع (Kd) المحسوب من معادلة Freundlich للادمصاص. و تبين بعد نهاية التجربة ان كمية الفوسفور المدمص و معامل التوزيع (Kd)، عند مرحلة الاتزان، أعلى بالنسبة للتربة ذات المادة العضوية الأقل، لكلا المزارعتين و الطريقتين. و لقد تبين ان كمية الفسفور المدمص و معامل التوزيع اعطت قيما اعلى باستخدام طريقة التدفق عما هو عليه الحال باستخدام طريقة الاستخلاص التقليدية، و ذلك لجميع الترب. و لقد وجد ان استخدام طريقة التدفق في دراسة ادمصاص الفسفور يعتبر الاكثر واقعية و قدرة على تمثيل ما يحدث في الحقل.