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International Journal of Current Research
Vol. 8, Issue, 03, pp. 27231-27237, March, 2016

INTERNATIONAL JOURNAL
OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

FACTORS AFFECTING RESIN-P ADSORPTION UNDER ARID ENVIRONMENT

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ARTICLE INFO

Article History:
Received 18th December, 2015
Received in revised form
20th January, 2016
Accepted 28th February, 2016

Key words:

Aridisol,
P adsorption, Resin bag,
Soil environment.

ABSTRACT

A number of laboratory studies were conducted to know the condition favorable for resin-P adsorption under arid environment. Several type of ion exchange resins were used for the study. The results clearly demonstrated more P accumulation by resin bag at pH 7.8. Resin bag adsorbed maximum P when soil EC was 2 dSm^{-1}. In low organic matter soil chelating resin was more efficient; while with increase in organic matter level strongly basic anion exchange resin was found to be most effective in trapping P. Saturated moisture level in the soil demonstrated best P trapping by resin bag. Clay content in the soil had a positive influence on more P adsorption into the resin bag. The resin P accumulation was more at 30°C and a drastic fall was noticed with increase in soil temperature from 30 to 40°C. The result clearly demonstrated that pH, EC, temperature, moisture, and organic matter content in the soil had affected much on P adsorption by the resin bag under arid environment.

Citation: Rathor Indira and Tarafdar, J.C. 2016. "Factors affecting resin-P adsorption under arid environment", *International Journal of Current Research,* 8, (03), 27231-27237

INTRODUCTION

Ion exchange resins are highly ionic, covalently cross-linked, insoluble polyelectrolyte's supplied as beads. The beads have either a dense internal structure with no discrete pores (gel resins) or a porous, multichannel structure (macro porous resins). They are commonly prepared from styrene and various levels of cross-linking agent divinyl benzene, which controls the porosity of the particles. Porous beads can be made also by adding homopolystrene, which is soluble in the monomer mixture, and leaching it out later with, toluene, for instance. Acrylic based, ion-exchange resins are also available. These ionic polymers contain two types of ions, those which are bound within the structure and the oppositely charged counter ions which are free. The property of ion exchange is a consequence of Donnan exclusion – when the resins is immersed in a medium in which it is insoluble, the counter ions are mobile and can be exchanged for other counter ions from the surrounding medium; ions of the same type of charge as the bound ions do not have free movement into and out of the polymer. Ion exchange resins have been classified based on the charge on the exchangeable counter ion (cation exchanger or anion exchanger) and the ionic strength of the bound ion (strong exchanger or weak exchanger).

Ion exchange resins are a sensitive biologically meaningful tool to study the behavior of inorganic and organic ions in the soil environment. The ability to use ion exchange resins as dynamic exchangers or sinks under relatively undisturbed conditions in the laboratory or field opens up a number of possibilities for future research. Soil analysis method in which ion-exchange resins are inserted into the soil without subsequent mixing or stirring action provide a reliable index of nutrient bio-availability. Ion adsorption by the resin is affected by competition, both biologically and chemically when resin is placed in soils. Competition from nutrient conversion by microorganism will affect supply available to the resin for adsorption (Giblin *et al.*, 1994., Subler *et al.*, 1995). Fixed bed removal of equimolar metal ions (CO^{2+}, Ni^{2+}, Mn^{2+}, Sr^{2+}) from aqueous solutions using a strong-acid ion exchange resin was examined by Rueyshin *et al.* (2003).The solution contained a water soluble complexing agent including ethylenediamine tetra acetic acid, citric acid and nitrilotriacetic acid. It was showed from batch studies that the equilibrium exchange of metals and resin mainly depended on solution pH, and partly on the type of complexing agent used. The ion exchange process has been increasingly used by Al-Enezi *et al.* (2004) for the removal of heavy metals from sludge or the recovery of precious metals. The exchange potential of an ion exchange resin is influenced by a number of factors, the most important being molecular size, valency and concentration (BDH chemical Ltd., 1971). Zhiming *et al.* (2003) suggest that Anion

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exchange membrane-P is a more reliable indicator of labile P than M_3P (Mehlich III extractable P). Mamo *et al* (2004) used ion exchange resin for *in situ* nutrient monitoring. Millar *et al*. (2006) used ion exchange resin bags to measure nutrient bioavailability. The present paper deals with the factors which affect the adsorption of P by ion exchange resin under arid environment.

MATERIALS AND METHODS

Construction of Resin bags

Rectangular resin bags of size 3.5 × 4.0 cm were constructed from terylene net in a manner similar to Sibbesen (1978). The terylene has a mesh size of 0.3 mm, sufficient to retain the resin without loss and allow through movement of moisture. The bags were sewn with non-rotting polyester thread. 0.4 g ion-exchange resin was placed in each bag and then the bags were heat sealed.

Preparation of Resin bags for analysis

Each resin bag put in a glass beaker containing 50 mL $NaHCO_3$ (0.5M, pH 8.5) and shake for 1 h by repeated stirring. Now repeat it with fresh 50 mL $NaHCO_3$ and yellow by 2 washing with distilled water. Store these conditioning resin bags in 0.5M HCl for use of estimation of Labile P.

Labile P estimation

For labile P estimation, 1 g soil was taken in plastic bottle and 40 mL deionized water was added. A resin bag was kept in each bottle and placed on shaker and shaken for 6 hours at 150 rpm at room temperature. The resin bag was then removed and gently washed under tap water and then with distilled water. After washing, the resin bag was kept in a 50 mL beaker, 20 mL of 0.5N HCl was added and was shaken for 1 h. The extract in the 0.5N HCl was then used for estimation of phosphorus by Molybdenum blue method (Jackson, 1967).

Effect of moisture on P adsorption by resin bag

To study the effect of soil moisture on resin P, we collected soil samples from Central Research Farm, Central Arid Zone Research Institute, Jodhpur, Rajasthan, India. The soil samples (Aridisol) were sieved (< 2mm) and then filled in pot of 10 kg soil capacity (30 cm height and 20 cm diameter). There were six treatments i.e. without addition of any water (0), 20, 40, 60, 80 and 100% moisture level. Each treatment was replicated thrice. The pots were covered with black polythene sheets to prevent the evaporation of excess moisture from soil. The resin bag was placed at 15-18 cm depth of each pot before start of the experiment. After one week all bags were taken out from pots, gently washed by de-ionized water. They were then extracted by 0.5N HCl and removed from the beaker. Extract of all the pots used for estimation of labile P.

Effect of soil pH on P adsorption in resin bag

To understand the effect of pH on resin P accumulation, buffer solutions each of eight different pH (3, 4, 5, 6,7,8,9,10) were prepared and three different types of soils were selected (high organic matter <2.5%, medium organic matter 1-2.5%, low organic matter >1%) for the study. The effect on three different soil textural class of the soil was also study. One gram of soil in triplicate was taken for each treatment and 40 mL buffer solution of different pH was added to it after that resin/labile P estimation method was followed.

Effect of soil EC on resin P adsorption

To understand the effect of EC on P accumulation of resin bag, six level of EC (1,2,3,4,5,6,7,8,9,10) was prepared with the salt solutions. Two types of resins (weakly basic anion exchange resin in freebase and chelating resin in sodium form) was used for the study with three different types of soils having wide range of organic matter i.e. low organic matter 0.5%, medium organic matter 1.3% and high organic matter 3%. One gram soil in triplicate was taken for each treatment and 40 mL of salt solution as different EC was added to it followed by resin P estimation method.

Effect of temperature on P accumulation in resin bag

To know the effect of temperature on P accumulation of native phosphorus by the ion exchange resin, five different temperatures were used (25°, 30°, 35°, 40° and 45°C) after taking two different types of resin bag. Three different soils having wide range of organic matter (low 0.5%, medium 1.3%, high organic matter3%) were used for the study. Temperature was maintained on the water bath shaker.

Effect of clay

To find out the effect of clay on accumulation of P from native sources, thirty different soils from Uttarakhand and Rajasthan having wide variation of clay content (4.1 to 50.6%) was collected. The ion exchange resin from Assess Chemicals was used for extraction of native phosphorus.

Effect on organic matter on resin-P accumulation

To find out the organic matter effect on the accumulation of P by the resin from native sources seventy eight soils from different places having wide variation of organic matter (0.15 to 4.16%) was collected and analyzed for accumulation of phosphorus from native sources after using ion exchange resin from Assess Chemicals. According to organic matter status, the soils were grouped under three different levels low organic matter (< 1%), medium organic matter (1-2.5%) and high organic matter (> 2.5%).

Statistical Analysis

The data obtained were subjected to statistical analysis by the analysis of variance method (Sokal and Rohlf, 1981). The significance of different sources of variance was carried out. The least significant difference was calculated (p=0.05) for appropriate degree of freedom using t method.

RESULTS

Effect of moisture

To determine the effect of soil moisture on resin-P accumulation, a pot experiment was conducted in Aridisol at 0 (air dry soil), 20, 40, 60, 80 and 100% moisture level with the application of two different resins namely Weekly basic anion exchange resin and ion exchange resin (Assess Chemicals). The results (Fig. 1) clearly showed a gradual increase in P accumulation by the ion exchange resin, which was more in weekly basic anion exchange resin and maximum accumulation at 100% moisture level. In general, 5 to 7 fold increase in the accumulation of phosphorus by the ion exchange resin was observed at the saturation point (100% moisture level) of the Aridisol, as compared to dry soil.

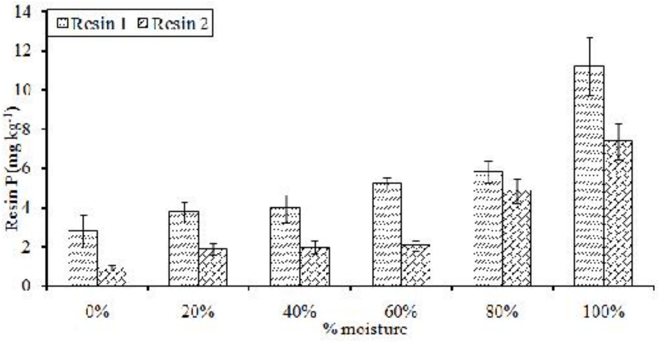

Fig. 1. Effect of moisture on resin P extraction. Vertical bars represents the standard errors of the mean . Resin 1: Weekly basic anion exchange resin in free base, Resin 2: Ion exchange resin (assess chemicals), 0%-dry soil

Effect of soil pH on resin P accumulation

The accumulation of phosphorus by ion exchange resin clearly depends on soil pH (Fig. 2). In general more accumulation was observed around pH 8, irrespective of organic matter present in the soil. Although the accumulation was higher at high organic matter soil but the trend of accumulation at different soil pH was almost similar. The pH 3 showed least accumulation of P, irrespective of organic matter present in soil as compared to the soils having higher pH level. In general, 4 to 9 fold variation in P accumulation was observed when different organic matter soil was exposed to different soil reaction. The more P accumulation by ion exchange resin was noticed between pH 7 and 9 in low organic matter soil, between pH 6 and 8 in medium organic matter soil and between pH 5 and 8 in high organic matter soil. Although the accumulation started at a higher note at pH 3.0 in the entire organic matter level but thereafter a gradual decline was noticed till pH near 6 and further enhanced accumulation was observed upto pH 8.0. At high organic matter soil there was not much decline in P accumulation between pH 9 and 10 but for low and medium organic matter soil a sharp decline in resin-P accumulation was noticed after increase in pH from 9.0 till 10.0. The differences in soil textual classes (Fig 3) showed more P accumulation by resin bag at sandy loam soil followed by clay and sandy clay loam soil. The textural class of the soil found to be a major role to play in accumulation of P from the native sources. Irrespective of textural classes the more accumulation of P in ion exchange resin was observed around pH 8.0. An interesting result among the textural classes was observed at pH 5.0 when sandy loam soil results a small peak of accumulation while sandy clay loam soil showed least accumulation of resin-P, whereas clay soil showed a slight improvement in accumulation than that in lower pH.

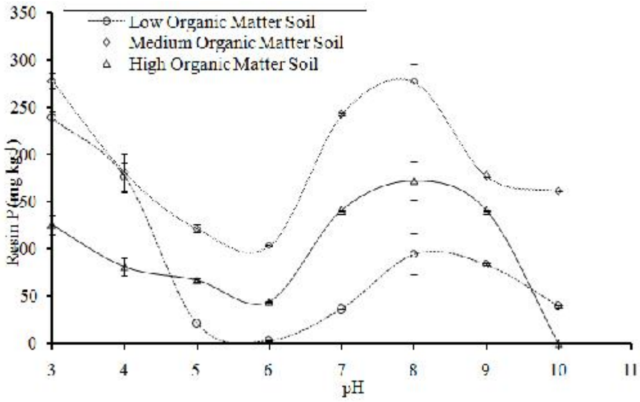

Fig. 2. Effect of organic matter on labile phosphorus content under different pH level. Vertical bar represents the standard errors of mean

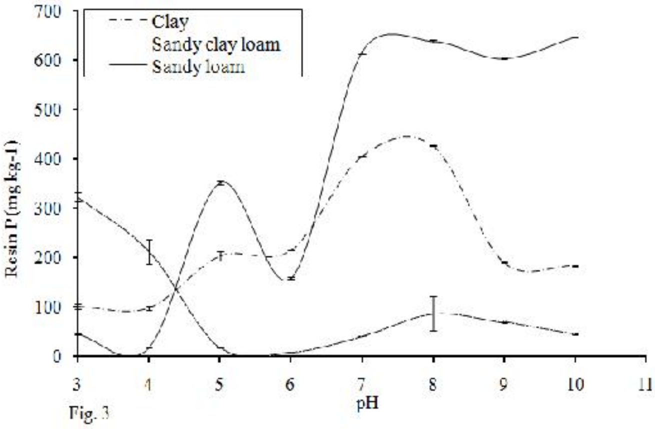

Fig. 3. Variation in labile P extraction by ion exchange resin in different textural classes of soil types. Vertical represents the standard errors of mean

Effect of EC

Effect of electrical conductivity on labile-P content estimated three different types of soils having low 0.5%, medium 1.3% and high 3% organic matter. The results (Table 1) clearly show that the labile-P content increases with increase in electrical conductivity from 1 dSm^{-1} to 2 dSm^{-1}, and decrease between 4 to 8 dSm^{-1} which was further increases at 10 dSm^{-1} EC level. The highest labile-P observed at 2 dSm^{-1} EC levels, while least labile P observed at 4 EC dSm^{-1} level with weekly basic anion exchange resin and 6 dSm-1 EC level at chelating resin in sodium form (Fig 4). Under low and high organic matter soil condition chelating resin was more efficient compare to basic anion exchange resin for labile P extraction.

Resin P extracted from entire soil types under different EC level represented more variation in resin-P at 10 dSm^{-1} EC while least per cent variation was observed at 6 dSm^{-1} EC. The per cent variation at 1 and 2 dSm^{-1} EC was almost same.

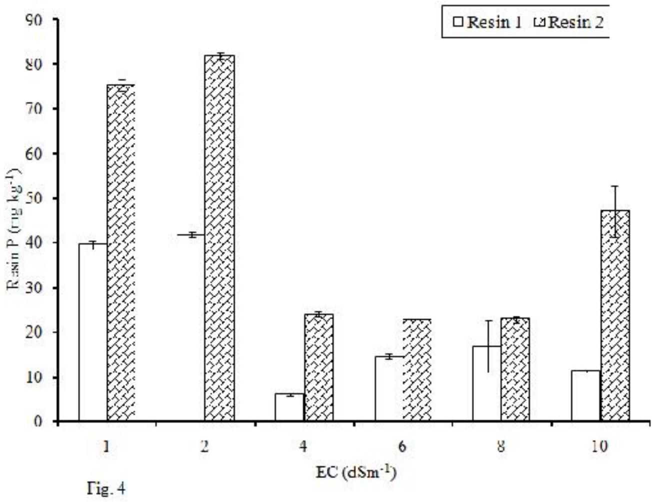

Fig. 4. Resin P extraction from different salinity level (Resin 1: weekly basic anion exchange resin in Cl^- form, Resin 2: chelating resin in Na^+ form)

Effect of temperature

To know the effect of temperature on P accumulation of native phosphorus by the ion exchange resin, five different temperatures were used (25°, 30°, 35°, 40° and 45°C) after taking two different types of resin bag. The results (Fig. 5) showed the maximum accumulation of P at 30°C by both the resins. But after increase in temperature, above 30°C, a drastic fall in native P accumulation was observed till 40°C, thereafter, the change in P accumulation was not altered much. In general, strongly basic anion exchange resin was found to be much superior to ion exchange resin from assess chemical till 40°C temperatures. No difference in accumulation of native P by both the resins was observed at 40°C and thereafter.

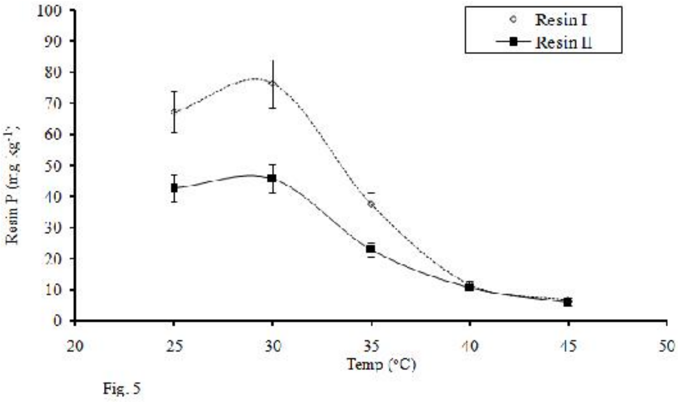

Fig. 5. Pattern of release of resin P by soil at different temperatures (Resin 1: strongly basic anion exchange resin: Resin 2 anion exchange resin from Assesss chemicals), vertical bars represent s the standard errors of the mean at each temperature

Effect of clay

The results (Table 2) showed a wide variation in clay content as well as resin P accumulation (5.8 to 848.0), which fulfills our aim to collect the soils having wide variation in their characteristics to accumulate native P. Although, in general, a correlation between clay content and P accumulation by ion exchange resin ($r = 0.3611$, $p < 0.05$) was observed but soils from some of the locations does not have proportionate accumulation of native phosphorus with the respective clay content present in it. From the regression equation (Fig. 6) it may be suggested that for every unit increase in clay percentage there was 6.12 mg kg^{-1} increase in accumulation of P from native sources by ion exchange resin, provided the clay content in the soil is more than 1.9%.

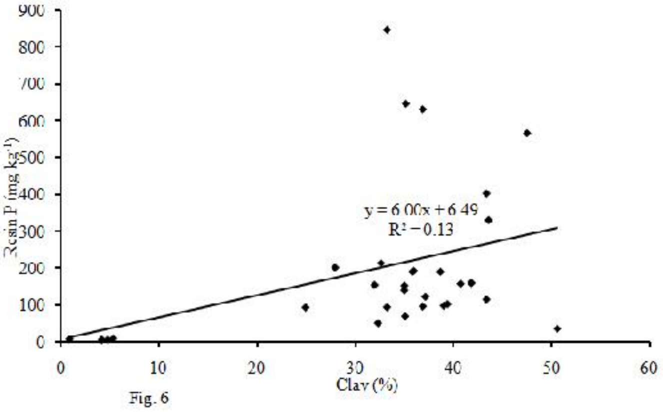

Fig. 6. Regression equation between clay content and resin P accumulation

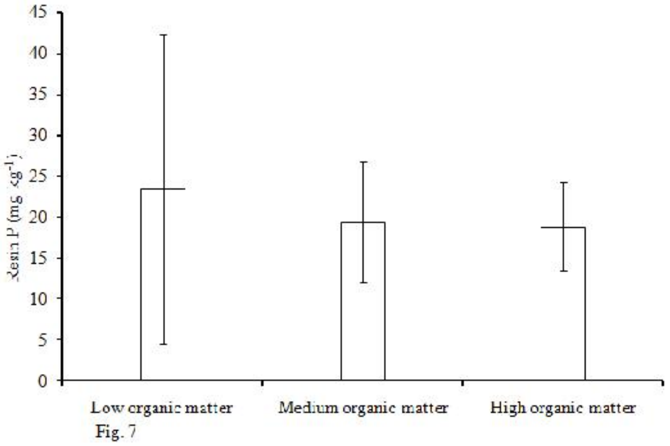

Fig. 7. Variation of P accumulation under different organic matter, vertical bars represnts the standard errors of the mean

Effect on organic matter on resin-P accumulation

To find out the organic matter effect on the accumulation of P by the resin from native sources seventy eight soils from different places having wide variation of organic matter (0.15 to 4.16%) was collected and analyzed for accumulation of phosphorus from native sources after using ion exchange resin from Assess Chemicals. According to organic matter status, the soils were grouped under three different levels low organic matter (< 1%), medium organic matter (1-2.5%) and high organic matter (> 2.5%). The results clearly demonstrated that there was wide variation in accumulation of phosphorus from native sources by the resin. Although, no significant differences was observed due to variation in organic matter level of the soils analyzed but in general soils having lower organic matter accumulated more phosphorus than higher organic matter. The least resin-P was extracted from higher organic matter soil and more from low organic matter soil tested (Fig 7). The statistical analysis showed a significant negative correlation ($r = -0.288$, $p < 0.05$, $n = 78$) between the release of resin-P from ion exchange resin and the soil organic matter level.

Table 1. Effect of electrical conductivity on labile P extraction (mg kg^{-1}) by different ion exchange resins in three different types of soils

EC (dSm^{-1})	Low organic matter (0.5%)		Medium organic matter (1.3%)		High organic matter (3%)	
	Resin I*	Resin II*	Resin I	Resin II	Resin I	Resin II
1.0	39.1	118.9	62.6	29.8	17.6	77.4
2.0	46.9	114.7	58.9	40.5	19.9	90.2
4.0	7.7	20.4	6.2	31.3	4.4	15.6
6.0	12.6	13.2	20.4	37.4	10.6	17.2
8.0	15.4	33.9	7.6	21.2	10.7	13.5
10.0	15.4	45.6	7.7	52.1	10.6	25.7
LSD (p = 0.05)	0.82	0.80	0.64	0.82	0.50	1.01

* Weakly basic anion exchange resin in free base

** Chelating resin in sodium form

Table 2. Effect of clay content on resin P accumulation

S.No.	Soil source	Clay Content (%)	Labile P Content (mg kg^{-1})
1	Prafullagao; Kuthal gate	32.66	214.15
2	Kulu khetra	40.77	157.97
3	Hathi pao	41.87	160.27
4	Bhalta gao	27.98	202.14
5	Town	35.03	139.91
6	Bikasnagar kalsi forest area	24.99	93.66
7	Bikasnagar nagar	32.36	51.27
8	Bikasnagar haripur	50.62	35.92
9	Dehradun forest area	35.11	69.85
10	Daiwala forest	43.4	115.48
11	Kabul forest area	47.55	567.16
12	Chamoli Narayan nagar	39.44	102.85
13	Rajaji national park rishikesh	43.4	403.45
14	Narayan nagar	35.84	190.66
15	Laxmanjhula, malita	33.28	848.03
16	Vyashi,uttranchal	33.28	94.49
17	Rani pukuri,Rishikesh	36.91	631.79
18	Rajaji national park	35.19	647.25
19	Rani pukuri,uttranchal	37.19	123.00
20	Crop field Dehradun	32.00	154.53
21	Crop field Rishikesh	36.02	192.85
22	Fallow after crop harvesting, Dehradun	39.04	98.25
23	Joli Grant uttranchal	36.91	96.58
24	Kardevi uttranchal	35.04	153.28
25	Dehradun airport area	38.71	190.76
26	Dehradun forest area	43.62	330.67
27	CAZRI Farm	5.4	9.46
28	NATP Farm	4.2	6.12
29	National Fellow Farm	4.8	5.84
30	Fallow land soil	0.9	7.83

DISCUSSION

Ion exchange resin was found to be a great tool to measure P availability in arid soils (Rathore and Tarafdar, 2008; Rathore and Tarafdar, 2012). Soil moisture and temperature are important factors affecting ion supply to and adsorption on/in the resin. The present study showed that saturated moisture level and 30°C was best to accumulate maximum P in the resin bags. A study conducted by Qian and Schoenau (1996) showed the amount of nitrate-N, phosphate-P, potassium and sulfate-S removed from two Chernozeinc soils by buried resin membrane decreased significantly with decreasing moisture content in the soil. The decrease in ion supply rate with decreasing soil moisture content reflects the diffusive flux of nutrient ions. As the soil becomes drier, the diffusion path becomes longer, as the large pores are no longer filled with soil solution. This is the same limitation on diffusive flux that plant roots encounter in the field as the soil dries out. Similar results were obtained by Schaff and Skogley (1982) in a study of the moisture effects on diffusion of K, Ca and Mg to the resin in bead form. Moisture contents in the field are highly variable and most nutrient uptake occurs when the plants is actively growing under moist soil conditions. The present result clearly demonstrated that moisture variations can be a significant source of variation in ion supply rates measured with resins. Tremendous effect of temperature to ion diffusion to resins was also observed in the present study. Increase in temperature does lead to a significantly increase in P accumulation till 30°C. The higher accumulation at that temperature may results from microbial conversions as well as through altered dynamics of nutrient movement towards resin (Yang *et al.*, 1991). Temperature effects were specific and depending on whether microbial conversions are involved or whether the influence was due to the rate of nutrient diffusion to the resin. At higher temperature drastic fall of P adsorption to resin may be due to least microbial conversion as microorganisms were less active above 35°C. A wide variation of resin-P accumulation was observed due to changes in clay content. The P adsorption was increased with increase in clay content. It has been shown that the clay content affects the increase in extractable, P when P is added to soil. In an incubation study, Johnson *et al.* (1991) used clay content to predict the P fertilizer required to raise the soil test value. Our result showed clay content is a good indicator for P adsorption by resin bag. The P adsorption on the resin bag was more at pH 7.8 and least at 5.8. The adsorption was more in non-saline soil. Ion-exchange resins behave in a similar manner to a plants root in their ion uptake capacity (Sibbesen, 1978; Smith, 1979). Anion exchange resin extracted phosphate levels and cation-exchange extracted potassium levels have been shown to have as good correlations with plant growth as have conventional soil extracted level (Smith, 1979). Because of this, and the *in-situ* nature of the resin bag method proposed here the levels of ions eluted are considered to be a measure of soil nutrient supply. This is in contrast to a potential nutrient supply of a soil expressed by conventional methods. Skogley (1994) shown resin methodology has great potential as an innovative approach of soil testing.

Organic matter and enzyme activities had positive influence on resin-P adsorption. Sui *et al.* (1999) hypothesized that the labile and moderately resistant fractions of P were significantly correlated with soil organic matter. The enzymes are important components involved in the dynamics of soil nutrient cycling. A wide variation of resin-P accumulation was observed due to changes in clay content. The P adsorption was increased with increase in clay content. It has been shown that the clay content affects the increase in extractable, P when P is added to soil. In an incubation study, Johnson *et al.* (1991) used clay content to predict the P fertilizer required to raise the soil test value. Clay content also has been shown to be as good as the buffering capacity or surface area in improving P recommendations in kaolinite and oxidic soils (Lins and Cox, 1989). Enzyme activities in the soil environments are considered to be a major factor contributing to overall soil microbial activity and to soil quality. The evidence available (Tarafdar *et al.*, 2001; Tarafdar and Claassen, 2005) indicates that, under suitable conditions enzymes readily attached different P compounds. The rate of P mineralization depends on microbial activity (Tarafdar *et al.*, 1988) and on the activity of free phosphatases (Dalal, 1978), which is controlled by the solution P concentration (Yadav and Tarafdar, 2001).

Conclusion

The results clearly showed that under saturated soil condition resin P accumulation was more as compared to the other moisture condition of the soil. Phosphorus accumulation by resin bag was more at 30°C and a drastic fall was noticed with further increase in the temperature. Present result demonstrated that for every unit increase in clay percentage of the soil above 1.9%, there was 6.12 mg kg^{-1} more accumulation of P by the resin bag. In general, at lower organic matter level the resin-P accumulation in the bag was more than at higher organic matter. Soils having organic matter between 1 and 2.5% had more accumulation of resin P than other organic matter level. The highest accumulation of resin P was observed ≅ pH 7.8 and least at pH 5.8. Resin-P accumulation was more at 2 dSm^{-1} than other EC levels. The results clearly demonstrated affect the resin-P adsorption by the soil and showed the estimation of resin-P is an important tool to know the plant P availability and available soil P status for plant nutrition.

Acknowledgment

The authors are grateful to ICAR and UGC for funding the projects under which present work carried out.

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