Research Paper

An Investigation into the Effect of Calcium and Sodium Ions on pH Dependent Retention of Phosphate by Some Soil Samples and Correlating It to the Soil Properties: a Study Done at Visakhapatnam City

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Abstract- *In the present study the adsorption of phosphate was investigated in presence of alkali and alkaline earth metals by the soil samples collected from a heterogeneous industrial zone. The study was carried out at varying pH medium at two different concentrations of phosphate ions. Sample no.5 (Table No. 2 and 3) which was collected near a petrochemical industry showed the highest amount of adsorption. It is assumed that the ionized phosphate species undergoes complexation with metal ions present in the sample.CEC and organic carbon was found to be highest for Sample no. 5. Sample no.3 (Table No. 2 and 3) which was collected in the vicinity of a fertilizer industry has shown to have lower adsorption of phosphorus as compared to other samples. The correlation coefficient between organic matter and P adsorption was found to be fairly good (r = 0.94) in calcium chloride medium. The equation was found to be y =18.16x. CEC of the soil samples could be satisfactorily related to phosphorus adsorption. The variation of adsorption of phosphates with CEC of soil samples at pH 5 at higher concentration of phosphate has been shown in the Figure No. the equation was found to be y=2.546x and R² = 0.80. The maximum adsorption of phosphate was observed at pH 5. Adsorption of phosphate was found to be fairly correlated with pH in calcium chloride medium. The equation was found to be $y = 0.745x^2-11.40x +113.7$ with R² = 0.750.*

Keywords: Soil Properties, Calcium, Sodium, heterogeneous industrial zone, Visakhapatnam City.

Introduction

Phosphorus is an essential element that poses a detrimental effect and hazard to the quality of water at high concentration. Phosphorus may be lost from soils and transport to the nearby streams and lakes [1]. Phosphorus in soil is associated with soil particles. The association of phosphorus to the soil particles depends upon soil physicochemical properties like pH, minerals, organic carbon etc.[2] two types of inorganic reaction control the concentration of phosphate ions in solution these are precipitation, dissolution and sorption desorption process. Adsorption and precipitation are known to regulate the concentration of nutrients in soil solutions. The buffering capacity of a soil for adsorption-desorption processes usually affects quantity, intensity and kinetic parameters, which determine the capacity of the soil to supply plant nutrients. The phosphate ion can occur in three states of phosphorus at pH value normally found in soil (4.5-6.2) viz. $H_2PO_4^-$ and HPO_4^{2-} Binuclear or bridging complexes may be formed between HPO_4 ions and metal oxide surfaces. The precise nature of these reactions depends upon pH. In the present study the adsorption of phosphate was investigated in presence of alkali and alkaline earth metals by the soil samples collected from a heterogeneous industrial zone. The study was carried out at varying pH medium at two different concentrations of phosphate ions .Ca^{2+} and Na^+, which is nutrient elements required for the plant growth, may have antagonistic and synergistic effect on the availability of other nutrient anions by complexation.

Material and Methods

The soil samples were collected at a depth of 15 cm from the industrial area of Visakhapatnam. The randomly collected samples, at different distances from around the industry, were then air dried, homogenized and sieved to get 2mm fractions. The soil samples were analyzed for selected physicochemical parameters like CEC, available phosphate, organic carbon using the standard methods reported in the literature. Soil pH was determined electrometrically using a pH meter in a soil solution ratio of 1:2.5.[3] The CEC was

determined using the ammonium acetate saturation method as described by Hesse.[4] Organic carbon was determined using Walkley-Black (1934) method.[5] Phosphorus (P) content determination was done using the colorimeter method using sodium hydrogen carbonate extraction.[6]

Weighed amount of KH_2PO_4 was dissolved to get 15 ppm and a 30 ppm of PO_4^{3-} ions respectively in the solution .A Batch adsorption study was carried out using a solid solution ratio of 1:50.pH of the solution was varied from 5 to 9 using appropriate acid or base. To this solution required amount of calcium chloride and sodium chloride were added to get .01 moles of calcium and sodium ions respectively. The solution was equilibrated for 48hrs and the amount of phosphate remaining in the solution was determined using the standard method of ammonium molybadate.

Results and Discussion

The adsorption of the phosphate was found to be the maximum at pH 5 for all the samples. The probable reason is the ionization of the species as $H_2PO_4^-$ and HPO_4^{2-} sample no.5 which was collected near a petrochemical industry showed the highest amount of adsorption. It is assumed that the ionized phosphate species undergoes complexation with metal ions present in the sample. CEC and organic carbon was found to be highest for sample no.5

The amount of adsorption was found to be less at pH 7 as compared to the other pH. The possibility of precipitation along with sorption can not be ruled out at higher pH value. This is likely attributed to the fact that a higher pH value causes the surface to carry more negative charges and thus would more significantly repulse the negatively charged species in solution. Therefore, the lower adsorption of phosphate at higher pH values resulted from an increased repulsion between the more negatively charged PO_4^{3-} species and negatively charged surface sites.[7] Figure 3 (WHICH ONE) shows a significant relationship between pH and P-fixation. The equation was found to be $y = 0.745x^2 - 11.40x + 113.7$ with $R^2 = 0.750$ (from the graph). The lower the pH, the more available are the metallic ions, especially Mn, Fe and Al. These elements then combine with soluble P and form insoluble compounds. Similar results have been reported by Kanwar and Grewal .[8] Naidu et al explained the increase in P- fixation with decrease in pH through interactions between added P, negative charge and the electrostatic potential in the plain of sorption.[9]

The sorption capacity of the soil is the sum of the phosphorus initially adsorbed which account for the sorption sites already occupied and phosphorus adsorbed after equilibration in the solid solution .If phosphorus adsorbed initially is high the amount of phosphorus adsorbed after equilibration will be less. Sample no.3which was collected in the vicinity of a fertilizer industry has shown to have lower adsorption of phosphorus as compared to other samples. at pH 5 the higher adsorption of phosphorus was shown by sample no. 5 (Table 2 and 3).(Figure 5 the probable reason could be the highest C.E.C. of the sample among all the five samples. The variation of adsorption of phosphates with CEC of soil samples at pH 5 at higher concentration of phosphate has been shown in the Figure 1

the equation was found to be $y = 2.546x$ and $R^2 = 0.800$. CEC of the soil samples could be satisfactorily related to phosphorus adsorption.

The amount of phosphorus adsorbed was less in presence of Ca^{2+} ions as compared to Na^+. The probable reason could be the formation of complexes with Ca^{2+} ions.[10,11]

Soil organic matter (Total carbon) has very high impact on the sorption capacity of phosphorus. Knowledge of these relationships is therefore helpful in predicting P-availability for plants and/or for transfer from the terrestrial to aquatic environment where it causes eutrophication.[12]

The correlation coefficient between organic matter and P adsorption was found to be fairly good (r = 0.94) in calcium chloride medium (Figure 5). The equation was found to be $y = 18.16x$.This may be due to the formation of phosphohumic compounds.[13] However other workers[14] have found that addition of organic matter to soils increases the availability of the element[15]. The results show that P-fixation is quite a complex phenomenon depending upon many interacting factors.

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Table 1: Some Physico-Chemical Characteristics of Soil Samples

S. No.	Sampling Site (vicinity)	pH	Conductivity (Millimhos)	%Organic Carbon	C.E.C. (meq/g)	PO$_4$ mg/g	Ca^{2+} mg/g	Na$^+$ mg/g
1	Hindustan Zinc Limited	6.7	0.057	6.6	35.65	0.0055	23.03	0.41
2	Himadri Chemicals	7.42	0.155	7.8	39.13	0.0095	23.02	0.45
3	Coromandel Fertilizers	7.46	0.085	9.3	45.21	0.105	32.03	0.52
4	Hindustan Petrochemicals Limited	7.47	0.09	4.8	53.41	0.009	59.05	0.62
5	Andhra Petrochemicals Limited	6.71	1.08	11.4	92.17	0.009	25.02	1.06

Table 2: Percentage Adsorption of Phosphate with varying pH in Different Electrolytic Medium
Initial Concentration of Phosphate Solution: 30 ppm

S. No.	Sampling Site (vicinity)	C.E.C (meq/g)	Organic Carbon	%adsorption of phosphate in CaCl$_2$					% adsorption of phosphate in NaCl				
				pH					pH				
				5	6	7	8	9	5	6	7	8	9
1	Hindustan Zinc Limited	35.65	6.6	74.59	73.94	69.05	70.03	71.66	91.20	86.64	75.57	78.82	77.19
2	Himadri Chemicals	39.13	7.8	79.19	77.19	58.63	65.79	59.28	96.09	94.46	87.29	86.31	86.31
3	Coromandel Fertilizers	45.21	9.3	78.17	75.57	55.70	60.26	56.35	86.064	66.67	65.14	65.79	66.77
4	Hindustan Petrochemicals Limited	53.41	4.8	85.66	78.50	83.06	84.38	81.75	47.71	95.43	91.20	94.46	91.83
5	Andhra Petrochemicals Limited	92.17	11.4	98.69	95.43	67.42	78.17	68.40	99.34	76.54	72.31	74.59	72.9

Table 3: Percentage Adsorption of Phosphate with varying pH in Different Electrolytic Medium
Initial Concentration of Phosphate Solution: 15 ppm

S. No.	Sampling Site (vicinity)	C.E.C. (meq/g)	Organic Carbon	%adsorption of phosphate in $CaCl_2$					% adsorption of phosphate in NaCl				
				pH					pH				
				5	6	7	8	9	5	6	7	8	9
1	Hindustan Zinc Limited	35.65	6.6	82.4	40.06	18.56	62.86	36.15	90.22	65.79	43.07	86.97	56.65
2	Himadri Chemicals	39.13	7.8	71.98	18.56	10.74	29.64	19.86	77.19	56.35	43.32	54.39	69.38
3	Coromandel Fertilizers	45.21	9.3	69.38	11.40	3.58	10.74	6.84	73.94	56.34	31.59	49.83	34.85
4	Hindustan Petrochemicals Limited	53.41	4.8	70.68	66.12	29.64	56.63	60.91	85.66	78.50	73.06	69.38	81.75
5	Andhra Petrochemicals Limited	92.17	11.4	73.94	54.39	44.62	59.60	51.14	94.78	85.01	50.48	62.86	60.91

Fig.1.Variation of the %Adsorption of the Phosphates with CEC at Higher Concentration of Phosphates

$y = 2.636x$
$R^2 = -0.51$

NaCl medium at pH5

Fig.2.Variation of the %Adsorption of the Phosphates with CEC at Higher Concentration of Phosphates

$y = 2.546x$
$R^2 = 0.800$

CaCl2 medium ...

Fig.3.Variation of Phosphorus Adsorption with pH at Higher Concentration of Phosphate in CaCl2 Medium

$y = 0.745x^2 - 11.40x + 113.7$
$R^2 = 0.750$

Fig.4.Variation of Phosphorus Adsorption with pH at Higher Concentration of Phosphate in NaCl Medium

$y = -3.584x + 106.9$
$R^2 = 0.710$

Series1
Linear (Series1)
Linear (Series1)

Fig.5.Variation of the %Adsorption of the Phosphates with Soil Organic Carbon at Higher Concentration of Phosphates

$y = 18.16x$
$R^2 = -0.94$

CaCl2 medium at pH 5

Fig.6.Variation of the %Adsorption of the Phosphates with Soil Organic Carbon at Higher Concentration of Phosphates

$y = 16.36x$
$R^2 = 0.691$

NaCl Medium at pH 5

Fig.7.Variation of the % Adsorption of Phosphates with pH in Calcium Chloride Medium at Higher Concentration of Phosphate

Fig.8.Variation of % Adsorption of Phosphate with pH in Calcium Chloride Medium at Lower Concentration of Phospate

Fig.9.Variation of % Adsorption of Phosphate with pH in Sodium Chloride Medium At Higher Concentration of Phosphate

Fig.10.Variation of % Reduction of Phosphate with pH in Sodium Chloride Medium at Lower Concentration of Phosphate