



Leaching mechanism of alkaline soil under phosphate application; a kinetic approach

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ABSTRACT

The kinetics of leaching of phosphate has been studied on undistributed columns of alkaline soil (pH =8) of Kota region of Rajasthan India. Na₂HPO₄ has been taken as source of added phosphate. Initial leaching rates (LR_{obs}) have been calculated using Latshaw method and linear power from equation (LR_{obs} = k [PO₄³⁻]_i^{1.3}) has been derived for dependence of LR_{obs} on leachable concentration of phosphate present initially in the column during leaching. Various extractions viz. sodium bicarbonate, sodium oxalate, sodium citrate and water have been used to study leaching. Detailed kinetics has been followed with 0.5 M NaHCO₃ as extractant. Change in water filled porosity, θ, cm³ cm⁻³ of the column has not affected LR_{obs}. An increase in temperature in the range 25-50°C increased LR_{obs}. Experimental data on fitting on various kinetic models showed zero and first order kinetic models to be most suited while parabolic diffusion and elovich equations were rejected. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Phosphates;
Adsorption;
Desorption;
Leaching kinetics;
Water filled porosity;
Total leachable phosphate;
Kinetic models.

INTRODUCTION

Leaching, one of the most important physical processes responsible for migration of soil nutrients and pollutants, occurs either by active transport or passive permeation accompanied by diffusion of energy and matter through soil matrix. The leaching rates of salts are basically the relative mobility or fluidity of water along with salt movement as diffusion of salt is not possible without diffusion of water in saturated soils. One of the worst consequence of leaching from polluted sites as well as from over fertilized agricultural fields during irrigation, rain events and water percolation is contamination of subsurface and ground water^[1]. Leaching may depend on macro porosity in soil^[2] as well as laminar

flow of water in cracks and channels found in soils^[3]. It is also reported to further depend on soil quality, applied water quality, ion exchange^[4], salt solubility, initial water content of soil^[5], pH^[6] and temperature etc. in various types of soils.

To meet the ever-increasing demand of the food supply, application of chemical fertilizers has become eminent for higher yield and better quality in the present agricultural system adopted all over the world. Application of fertilizers in excess to the crop demand becomes a curse for the ground water eventually in almost all types of agricultural soils. Transport of phosphate from over fertilized soil has also been reported to cause eutrophication of lakes and estuaries because even a little amount of 20-30 mg/l of phosphate in surface

runoff can stimulate phytoplankton growth^[7,8]. Inorganic phosphates such as mono and diammonium hydrogen phosphate, tri-calcium phosphate, super phosphate, calcium metaphosphate etc. are widely applied as fertilizers and overfertilise most of the agricultural land in developed countries^[9,1]. Besides that inorganic phosphate also occur naturally in soil as rock phosphate from disintegration of rocks and minerals. However, in agricultural fields only a portion of inorganic phosphate remains in the legand exchangeable form while the rest may be released by dissolution^[10]. Organic anions capable of forming stable complexes^[11] with Al and Fe and on mineral surfaces^[12] are reported to reduce sorption and release of phosphate for leaching from sorbed and insoluble phosphate pool. The solubilisation of inorganic phosphate occurs due to microbial production of organic and inorganic acids which effectively dissolve inorganic phosphate and render its availability to the plants. In soil water, many soil microorganism produce lactic, glycolic, citric, formic and acetic acids which can solubilize insoluble inorganic phosphate such as tricalcium phosphate^[13]. Number of other organic acids including 2-ketogluconic acid which are found in soil and act as effective chelating agent capable of complexing with Ca, Cu, Ni, Mn, Fe and Al salts of phosphate resulting in solubilisation of phosphate.

Many previous studies related desorption of phosphate from soil to availability of plant roots and phosphate desorption to soil properties^[14-17]. Sharpley et al.^[17] has related phosphate leaching to soil chemical and mineralogical properties, soil phosphate levels, agriculture management^[18], landscape position^[19], climate^[20] and pH^[6] has shown that an increase in soil pH may decrease phosphate retention in soil there by increasing phosphate leaching.

From the point of view of environmental quality, it is important to understand the kinetics and dilution effects of phosphate release from soils of overland flow and runoff waters. In earlier studies, kinetics has been applied as an effective tool to study heterogeneous soil liquid reactions accompanied by transport processes such as displacement of solute and sorbate in the liquid phase, solid phase and at the interphase^[21,22]. To study the kinetics of adsorption and desorption of phosphate in soil, different techniques such as miscible displacement^[23], pressure jump relaxation^[24], mixed batch^[25]

and flow method^[26] have been used.

In the present investigation, a new and simple method has been found out to generate linear power form equation to represent leaching kinetics of three different phosphate salts viz. Na_2HPO_4 , KH_2PO_4 and $\text{Mg}_3(\text{PO}_4)_2$ in alkaline soil of pH 8. Initial leaching rates have been determined using plain mirror method^[27] during column studies. Effects of water filled porosity, temperature, concentration of leachable salts and extractants have been studied in details. The suitable expressions have been derived to represent leaching kinetics. In addition various kinetic models were also applied to justify our experimental results.

MATERIAL AND METHOD

The clay loam soil collected from Kota, an industrial city of Rajasthan, India, was dried and sieved for uniform particle size ($53 \geq r$). Three different phosphate salts viz. Na_2HPO_4 , KH_2PO_4 and $\text{Mg}_3(\text{PO}_4)_2$ were taken for leaching studies. Phosphate was analyzed spectrophotometrically^[28] at 675 nm. The concentration terms determined in mg/l in leachates were converted into mg/kg in soil during kinetic work. All the solutions were prepared in deionised water.

Procedure for leaching studies

Glass columns of $20 \times 3 \text{ cm}^3$. Surrounded by glass jacket of continuously flowing thermostated water, were used to study phosphate leaching. 60 g soil of pH 8.0 and of particle size ($53 > r$) was gently packed at water filled porosity $0.42 \text{ cm}^3 \text{ cm}^{-3}$. The leachate pore volume was determined using equation (1).

$$Pv = qt/\theta v \quad (1)$$

Where q = volume of the effluent collected per unit time, i.e. flow rate, θ = water filled porosity $\text{cm}^3 \text{ cm}^{-3}$, v = total volume of the soil column

A fixed volume of aqueous salt solution (slug) with desired anion concentration was added at the top of the soil column and allowed to get adsorbed uniformly for 24 hrs, after which the columns were continuously leached with deionised water or with other extractants as per requirement of the study. The flow rate was maintained to $2 \pm 0.5 \text{ ml/10min}$. The leaching was carried out till the soluble anions were completely removed. Then the soil of the column was transferred into the

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beaker in a known volume of extractants and stirred for 2 hrs. The ion concentration was further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column. The total leached concentration was taken equal to the total leachable concentration present initially during leaching (i.e. concentration at $t = 0$) during each kinetic run. The concentration of anions were determined in leachates collected periodically at an interval of 10 minutes.. Initial leaching rates were calculated and the results were also applied on various kinetic models to establish the nature of leaching kinetics of water-soluble Na, K and Mg salts of phosphate ions. The concentration terms used for presenting the analytical results are:

- $[\text{PO}_4^{3-}]_i$ = Total leachable concentration in mg/kg present initially
 $[\text{PO}_4^{3-}]_t$ = Leached concentration in mg/kg at time t
 $[\text{PO}_4^{3-}]_l$ = $[\text{PO}_4^{3-}]_i - [\text{PO}_4^{3-}]_t$
 = Leachable concentration in mg/kg remaining at time t
 $[\text{PO}_4^{3-}]_{ad}$ = Concentration introduced / added in the soil column
 $[\text{PO}_4^{3-}]_s$ = Leachable phosphate present naturally in column soil is = 0.6mg/Kg

TABLE 1: Change in maximum leachable content, $[\text{PO}_4^{3-}]_l$ with change in NaHCO_3 Conc. in extractant water at 30°C in unadded columns, soil = 60g

S. no.	NaHCO_3 g mol/ l	$[\text{PO}_4^{3-}]_l$ mg/kg
1	0.00	1.57
2	0.01	7.57
3	0.50	9.86
4	1.00	9.46
5	2.00	9.21

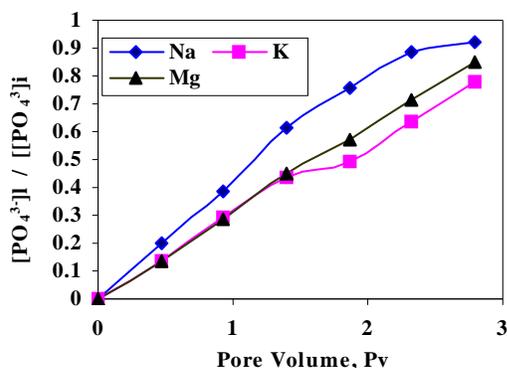


Figure 1 : Variation in $[\text{PO}_4^{3-}]_t / [\text{PO}_4^{3-}]_i$ with no. of pore volume of effluent on soil column at 30°C ; Soil = 30 g; $q = 0.86 \text{ cm}^3 \text{ cm}^{-3}$

Breakthrough curves of leaching

Breakthrough curves obtained in this study supports previous views^[29] (Dalal 1974) that in undisturbed naturally structured soil only partial displacement of resident water and solute by incoming water and solute occurs. Figure 1 gives change in $[\text{PO}_4^{3-}]_t / [\text{PO}_4^{3-}]_i$ with number of pore volume which estimate change in the volume of soil water with time participating in solute transport.

Barrow^[15] has reported that the pore volume of the effluent depends on the flow velocity and initial wetness θ of the soil column, but in the present case, a variation of θ from 0.36 to 0.63 $\text{cm}^3 \text{ cm}^{-3}$ showed no significant change in $[\text{PO}_4^{3-}]_i$ and LRob. This is probably due to comparatively higher adsorption of phosphate in soil column then leaching at various added phosphate concentration. Jardine et al.^[30] has also studied the effect of θ on Mg leaching and showed that leaching of salt is accompanied by diffusion of adsorbed/ desorbed salt in to the extractants volume present in the macroscopic pores of the soil column. Higher is the adsorption, lesser will be the effect of θ on leaching rates as shown in figure 1.

RESULTS AND DISCUSSION

Alkaline soil has high adsorption capacity for different phosphate salts. Hence to extract phosphorus various extractants such as NaOH ^[31], Na_2CO_3 ^[32], H_2SO_4 ^[33], oxalate, formate and citrate^[10] and bicarbonate^[16] were used previously. In this study, NaHCO_3 was used to study the leaching kinetics of phosphate. The values of maximum leachable content $[\text{PO}_4^{3-}]_l$ by different concentrations of NaHCO_3 in extractant solution in 60g soil at 30°C are given in TABLE 1.

The leaching kinetics was followed using 0.05M NaHCO_3 as extractant, because this concentration was found to leach maximum $[\text{PO}_4^{3-}]_l$. Higher desorption of phosphate by HCO_3^- ions in alkaline soil may occur either due to direct dissolution of phosphate with HCO_3^- ions or due to production of OH^- ion by hydrolysis of HCO_3^- ions following equation(2).



OH^- ions replace phosphate ions from Ca and Mg salts dominantly present in the experimental soil.

Initial leaching rate

Initial rate of leaching, LR_{obs} represent the rate of change in leachable concentration, [PO₄³⁻]_i with time t. The LR_{obs} is calculated for various added phosphate concentrations in the range 10-80 mg/kg for all three salts. The initial rate plots are straight lines. From the slope of straight lines LR_{obs} were calculated. The dependence of LR_{obs} on [PO₄³⁻]_i shows that the LR_{obs} values increase with increase in [PO₄³⁻]_i. The log-log plots of [PO₄³⁻]_i and LR_{obs} indicated a fractional order (>1) in [PO₄³⁻]_i. The leaching rates were found to fit at following rate law-

$$LR_{obs} = [PO_4^{3-}]_i^n$$

The values of k, n, r² and SEE for the three phosphate salts are given in TABLE 2.

Effect of extractants

Low mol. wt. organic acids such as sodium oxalate (di-carboxylic) and sodium citrate (tri-carboxylic) were found to affect phosphate dissolution. Results are given in TABLE 3, which shows that oxalate and citrate were found to have low release of phosphate ions than NaHCO₃ but higher than water. TABLE 3 Change in [PO₄³⁻]_i and LR_{obs} for various Our results are in accordance with the studies of Kuo et al.^[26] and Kuo and Lotse^[34] who reported that the rate of phosphate desorption is affected by low mol. wt. organic anions and found to be faster in EDTA than formate and citrate. Most of the phosphate in alkaline soils is associated with Ca and Mg metals to which formate and citrate

TABLE 2 : The values of rate constant (k), order (n) and correlation parameters (r² and SEE) for different phosphate salts

Salts ---> parameters	Na ₂ HPO ₄	KH ₂ PO ₄	Mg ₃ (PO ₄) ₂
10 ⁴ k	5.2	12.3	8.4
n	1.3	1.2	1.2
r ²	0.902	0.998	0.980
SEE	0.0013	0.0009	0.0015

*Unit of k is mg¹⁻ⁿ kgⁿ⁻¹s⁻¹

TABLE 3 : Change in [PO₄³⁻]_i and LR_{obs} for various extractants

Extractants	Blank [PO ₄ ³⁻] _i mg kg ⁻¹	10 ³ LR _{obs} mg kg ⁻¹ s ⁻¹	Na ₂ HPO ₄ [PO ₄ ³⁻] _i mg kg ⁻¹	10 ³ LR _{obs} mg kg ⁻¹ s ⁻¹	KH ₂ PO ₄ [PO ₄ ³⁻] _i mg kg ⁻¹	10 ³ LR _{obs} mg kg ⁻¹ s ⁻¹	Mg ₃ (PO ₄) ₂ [PO ₄ ³⁻] _i mg kg ⁻¹	10 ³ LR _{obs} mg kg ⁻¹ s ⁻¹
H ₂ O	2.15	2.5	4.17	3.9	3.78	4.6	2.92	2.6
Sodium citrate	6.84	6.9	5.61	6.8	4.26	2.1	3.62	3.1
Sodium oxalate	5.09	4.6	7.93	9.3	12.63	4.2	6.5	4.2
Sodium bicarbonate	7.53	25	9.97	19.6	16.9	4.8	8.6	5.3

can effectively chelate and hence increase phosphate leaching.

Temperature dependence

The effect of temperature on [PO₄³⁻]_i and LR_{obs} was studied in the range 25°C – 50°C at fixed [PO₄³⁻]_{ad} of 200 mg/kg. Results shows that with increase in temperature, adsorption of added phosphate is reduced and solubility and leaching is increased. Barrow^[15] has also given three effects of temperature on the reaction between inorganic phosphate and soil in which phosphate was present (a) in solution, (b) adsorbed in equilibrium with solution and (c) firmly held. When neither adsorption nor desorption occurred the phosphate concentration in solution increased with temperature (5-38°C).

In our experimental conditions, as the desorbed phosphate was continuously removed from the macroporic water through leaching, increase in temperature has increased solubility of firmly held or surfacial adsorbed phosphate remarkably, increasing equilibrium phosphate concentration in soil water which resulted in higher LR_{obs} and [PO₄³⁻]_i values for all three phosphate salts. Thus the phosphate leaching in our soil conditions can be attributed mainly to the formation of soluble complexes rather than to the true ion exchange within the soil matrix.

The effect of temperature on Na₂HPO₄ leaching was examined in detail by applying the Arrhenius equation i.e. k = Ae^{-Ea/RT} on the rate constant data. A plot of log k vs 1/T yielded a straight line from the slope of which activation energy Ea was calculated to be 22.052 Kj/mol [SEE= 1.032].

Effect of co-cation

The size of co-cation attached to the phosphate ion has influenced its leaching. Figure 4 depicts the relation between LR_{obs} and radii of the co-cation.

LR_{obs} values depends upon the radii of hydrated

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TABLE 4: Average values of r^2 , SEE, and slope for different kinetic modals applied on Na_2HPO_4 , KH_2PO_4 and $\text{Mg}_3(\text{PO}_4)_2$ leaching data at different $[\text{PO}_4^{3-}]_i$ at 30°C

Salts	Na_2HPO_4			KH_2PO_4			$\text{Mg}_3(\text{PO}_4)_2$		
	Kinetic Models	r^2	Slope	SEE	r^2	Slope	SEE	r^2	Slope
Zero order	0.992	-0.002	0.276	0.979	-0.003	0.427	0.993	-0.003	0.263
First order	0.962	0.00045	0.131	0.959	-0.00024	0.076	0.975	-0.00027	0.066
Elovich equation	0.944	3.941	0.701	0.935	4.204	0.811	0.932	4.073	0.807
Parabolic diffusion	0.921	0.147	0.967	0.921	0.159	1.06	0.916	0.152	1.032

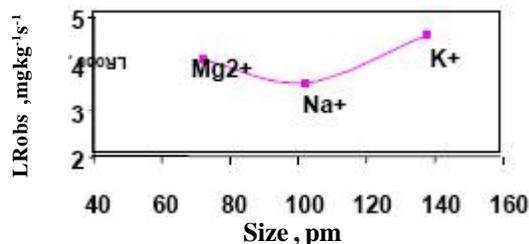


Figure 4 : Change in LRobS with size of cation at a fixed $[\text{PO}_4^{3-}]_i = 16 \text{ mg/kg}$ at 30°C

ion, smaller is the size of the cation, larger will be the radius of its hydrated ion and lesser will be its mobility. The size of the cation is in the order $\text{K}^+ > \text{Na}^+ > \text{Mg}^{+2}$ and the radii of hydrated ion $\text{K}^+ < \text{Na}^+ < \text{Mg}^{+2}$. Hence the LRobS for salts should follow the order same as that of radii of cation but it is in the order $\text{KH}_2\text{PO}_4 > \text{Mg}_3(\text{PO}_4)_2 > \text{Na}_2\text{HPO}_4$. As the alkaline soil was rich in Ca and Mg, unavailability of Mg adsorption sites on the soil surface resulted in higher desorption rate of $\text{Mg}_3(\text{PO}_4)_2$ than Na_2HPO_4 . Leaching rate of KH_2PO_4 was found highest because of smallest size of hydrated K^+ ion.

Application to the kinetic models

Most of the earlier studies on kinetics of phosphate desorption from soil found that release of phosphate deviate from first order kinetic reaction and described better by a high order reaction^[34]. Barrow^[16] used the framework of Freundlich equation and developed kinetic model for desorption incorporating power form equation. He explained that parameters of the models depended upon the length of the incubation period allowed addition of phosphate to soil and the start of desorption further. Chien and Clayton^[35] described desorption of phosphate by modified form of Elovich equation. Sharpley^[17] presented a very simple model for the release of phosphate to water

$$P_d = KP_0 \alpha W^\beta$$

Where P_d = amount of phosphate desorbed in time t at a water

soil ratio, W , with P_0 the initial amount of desorbable phosphate present in the soil and K , α and β are constants for a given soil. Linear power form equation used by us is different in the manner that it include initial leaching rates but not the initial amount of desorbable phosphate.

This equation is more suited to our soil conditions. Besides experimental results were also fitted to the previously explained conventional kinetic models. Average values of slope, r^2 and SEE are given in TABLE 4 for different concentrations of $[\text{PO}_4^{3-}]_i$ for the three phosphate salts. It is clear from the TABLE that leaching followed zero and first order kinetics.

The first order kinetic model was used to describe release and sorption of phosphate in soil by Chien and Clayton^[35](1980). For the slow release of phosphate as induced by anion exchange resin, a parabolic diffusion equation^[14](Cooke 1966) and a two constant rate equation^[29] (Dalal 1974) were found to describe reaction rates satisfactorily. Onken and Matheson^[36](1982) evaluated eight kinetic models for dissolution rate of EDTA extractable phosphate from the soil and in which two constant rate equation, elovich equation and differential rate equation were rejected, whereas zero order, first order, second order, third order and parabolic diffusion equations gave relatively higher values of r^2 and low values of SEE. These results indicate that several kinetic models might be used to describe the dissolution of phosphate from soils and any one model can not be fitted to describe the phenomenon of phosphate dissolution for different soils.

CONCLUSION

This paper demonstrates a new method of studying leaching of phosphate in water saturated soil conditions. In this study phosphate leaching was studied using extractants such as NaHCO_3 , sodium citrate and sodium oxalate. Carbonate and bicarbonate ions are present in the rain water, ground water and in irrigation

water. The results explain the effect of HCO_3^- ions on release of phosphate in soil and its downward transportation to subsurface and ground water.

This study suggests the applicability of initial rate method and development of linear power form equations to represent the leaching kinetics of phosphate in alkaline soils. It also shows that unleachable phosphate salts present in soil may also start leaching with increase in soil temperature. The rate of leaching is affected by relative movements of ions and size of the attached cation.

Our method can be applied in the agricultural fields as well as on other phosphate enriched sites for calculating the rate of leaching at any point of time. The findings of the present research study are of vital agro-environmental significance in understanding migration of salts in water saturated soils and in related environments. This work has also developed an analytical approach minimizing the theoretical calculations described in many previous models for phosphate transport in soil.

REFERENCES

- [1] J.P.Carefoot, J.K.Whalen; *Can.J.Soil Sci.*, **83**, 203-212 (2003).
- [2] W.L.Jonge de, P.Moldrup, G.Rubaek, K.Hschede, J.Djurhuus; *Soil Sci.Soc.Am.J.*, **3**, 462-470 (2004).
- [3] W.Willfried, T.Manfred, P.Uwe; ISSN 1673-1581 (2006).
- [4] J.D.Oster, L.S.Willardson, G.J.Hoffman; *Transactions of American Society Agriculture Engineers*, **15**, 115 (1972).
- [5] S.K.Verma, R.K.Gupta; *J.Ind.Soc.Soil Sci.*, **37**, 803-808 (1989).
- [6] P.R.Ernani, O.R.A.Fingueiredo, V.Becegato, J.A.Aloneido; *J.Soil Sci.*, **20(1)**, 159-162 (1996).
- [7] T.C.Danid, A.N.Sharpley, J.L.Lemunyon; *J. Environ. Qual.*, **27**, 251-257 (1998).
- [8] D.F.Broesch, R.B.Brins Field, R.E.Magnien; *J. Environ. Qual.*, **30**, 303-320 (2001).
- [9] E.Barberies, F.A.Marson, R.Scalenghe, A.Lammers, U.Schwermann, A.C Edwards, R.Manguire, M.J.Wilson, A.Delgado, J.Torrent; *Fertilizer research*, **45(3)**, 199-207 (1996).
- [10] T.R.Fox, N.B.Comerford, W.W.McFee; *Soil Sci. Soc.Am.J.*, **54**, 1763-1767 (1990).
- [11] P.M.Huang, Schnitzerl; 'Interaction of Soil Minerals with Natural Organics and Microbes', SSSA Spec.Publ.17, SSSA Madison WI, (1996).
- [12] U.B.Kaf-kafi, Bar-Yosef, R.Rosenberg, G.Sposito; *Soil Sci.Soc.Am.J.*, **52**, 1585-1589 (1988).
- [13] R.J.Swaby, J.I.Sperber, E.G.Hallsworth; 'Nutrition of Legumes, London', Batterworth's Scientific Publ., 289 (1958).
- [14] I.J.Cooke; *J.Soil Sci.*, **17**, 56-64 (1966).
- [15] N.J.Barrow; *J.Soil Sci.*, **30**, 259-270 (1979).
- [16] R.B.Singh, S.K.Das, K.L.Sharma, B.R.Prasada, K.Srinivas, M.Narayana Reddy; *J.Ind.Soc.Soil Sci.*, **44**, 381-386 (1996).
- [17] A.N.Sharpley, D.Curtin, J.K.Syers; *Soil Sci.Soc.Am.J.*, **52**, 637-640 (1988).
- [18] L.L.McDowell, J.D.Schreiber, H.B.Pionke; *Agr. Conservation Res.Dept.*, **26**, 509-533 (1980).
- [19] B.A.Miller, T.C.Daniel; *Trans.ASAE*, **24**, 375-381,390 (1981).
- [20] J.T.Sims, R.R.Simard, B.C.Joern; *J. Environ. Qual.*, **27**, 277-293 (1998).
- [21] R.A.Ogwada, D.L.Sparks; *Soil Sci.Soc.Am.J.*, **50**, 1158-1162 (1986b).
- [22] D.L.Sparks; 'Kinetics of Soil Chemical Processes', Academic Press, San Diego, C.A, (1989).
- [23] S.C.Hodge, G.Johnson; *Soil Sci.Soc.Am.J.*, **51**, 323-331 (1987).
- [24] P.C.Zhang, D.L.Sparks; *Soil Sci.Soc.Am.J.*, **54**, 1266-1273 (1990).
- [25] S.Saha, A.Dutta, S.K.Sanyal; *J.Ind.Soc.Soil Sci.*, **47**, 34-39 (1999).
- [26] S.Kuo, E.J.Jellum, W.L.Pan; *Soil Sci.Soc.Am.J.*, **52**, 974-979 (1988).
- [27] M.Latshaw; *J.Am.Chem.Soc.*, **47**, 793-794 (1925).
- [28] Olsen et al.; U.S.Dept., Agr.Circ., Washington D.C. in ref., **4**, 939 (1954).
- [29] R.C.Dalal; *Comm.Soil Sci.Plant Anal.*, **5**, 531-538 (1974).
- [30] P.M.Jardine, G.V.Wilson, R.J.Luxmoore; *Soil Sci. Soc.Am.J.*, **52**, 1252-1259 (1988).
- [31] J.D.H.Williamsons, J.K.Syers, R.F.Harris, D.E.Armstrong; *Soil Sci.Soc.Am.Proc.*, **35**, 250-255 (1971).
- [32] Kanehiro, Yoslinori, G.D.Sherman, C.A.Black; *Am.Soc.of Agron.Madison. Wis*, **9**, 952-958 (1965).
- [33] D.Kundsen; *Bull No.499.N.D.Agric.Exp.Stn.*, North Dakota State Univ.Fargo, N.Dak, 16-19 (1975).
- [34] S.Kuo, E.G.Lotse; *Soil Sci.Soc.Am.Proc.*, **38**, 50-54 (1974).
- [35] S.H.Chien, W.R.Clayton; *Soil Sci.Soc.Am.J.*, **44**, 264-268 (1980).
- [36] A.B.Onken, R.L.Matheson; *Soil Sci.Soc.Am.J.*, **46**, 276-279 (1982).