Cation Exchange

Soil Chemistry (Soil 503)

Instructor
Dr. A. K. Sachan
Professor

Presented By
Ravindra Sachan
Teaching Associate

Department of Soil Science and Agricultural Chemistry C.S.A
UNIVERSITY OF AGRICULTURE AND TECHNOLOGY
KANPUR(U.P.) 208002

Cation Exchange

Adsorption of cations by soil colloids

- Since clay carry –ve charge, cations are attracted to the clay particles
- They held electro statistically on the surface of the clay
- Most of them are free to distribute themselves thro' the liquid phase by diffusion. The density of ion population is greatest at or near the surface. These cations are called adsorbed cations.
- Generally, ions with the smaller hydrated size are preferably adsorbed
- The following decreasing order of preference for adsorption of monovalent cations by clays has been reported :

  Cs > Rb > K > Na > Li

- Such series of ions of decreasing preferential adsorption is called a lyotropic series.

Cation exchange reactions

The adsorbed cations can be exchanged by other cations. The process of replacement is called cation exchange.

$$\text{Ca-Soil} + 2\text{NH}_4^+ \longrightarrow (\text{NH}_4)_2 - \text{Soil} + \text{Ca}^{2+}$$

Cation exchange capacity

- **The capacity of the soils to adsorb and exchange cations**
- **Usually expressed in milli equivalents per 100 g / cmol (p^+) kg $^{-1}$ of soil**

Exchanging power of cations

- Different cations may have different abilities to exchange adsorbed cations
- The amount of adsorbed cations is often not equivalent to the amount exchanged
- Divalent ions are usually held more strongly than monovalent ions. They will be exchanged with more difficulty.

Emperical equations of cation exchange

The Freundlich equation :

This is one method to express the ionic composition in the soil solution

$$x = kC^{1/n}$$

Where

x = amount of cations adsorbed per unit of adsorbent

C = equilibrium conc. of the added cation

k, n = constants

The Langmuir-Vageler equation

$$\frac{x}{x^0} = \frac{kC}{1+kC}$$

Where

x = amount of cations adsorbed per unit weight of exchanger

x^0 = total exchange capacity

C = conc. of added cations per litre

k = affinity co-efficient

Schofield’s Ratio law

$$\frac{[Na^{+}](\sqrt{Ca^{2+}})}{[\sqrt{Ca^{2+}}](Na^{+})} = k$$

The ratio of products of adsorbed cations and cations free in solution are constant.

[ ] Denotes adsorbed ions

( ) Denotes ions in solution

If the amount of cations adsorbed does not change significantly, or remains constant, the ratio of cations in solution is also constant. This is called Ratio law by Schofield(1947).

Fixation of cations

- Under some situations, the adsorbed cations are held so strongly by clays and they cannot be recovered by exchange reactions. These are called fixed cations.

- Fixation is normally occur in K^+ & NH_4^+ ions. Fixation is due to the entrapment of the ions in the intermicellar regions of the clays.

- Soil minerals in which fixation occurs are : micas, illites, montmorillonites and vermiculites.

Anion Exchange

Adsorption of anions by soil colloids – two types

1. **Negative adsorption**
2. **Positive adsorption**

Negative adsorption :

- **It occurs at colloidal surface possessing a –ve charge.**
- **Cations are attracted and concentrated at the colloidal surface**
- **Anions are expelled from the double layer formed on the negative charged surface. This exclusion of anions is called –ve adsorption**
- **-ve adsorption of anions is approximately 1-5 % of the CEC**

2. Positive adsorption

- It is the adsorption & conc. of anions on the +vely charges surfaces or edges of soil colloids
- Repulsion of cations by the +ve charges occurs
- Usually smaller than CEC
- It is dependent on changes in electrolyte levels and on soil pH

Phosphate fixation

- Phosphate anions can be attracted to soil constituents with such a bond that they become insoluble and difficultly available to plants. This is called Phosphate fixation or Phosphate retention
- Tisdale & Nelson 1975 are of opinion that ‘retention’ refers to that part of adsorbed phosphorus that can be extracted with dilute acids. This fraction is relatively available to plants
- The term ‘fixation’ refers to the soil phosphorus which is not extractable by dilute acids. This portion of phosphorus is not readily available to plants

Phosphate retention

- Acid soils usually contain significant amount of soluble and exchangeable Al $^{3+}$, Fe $^{3+}$ and Mn $^{2+}$ ions.

- The phosphate retained by these cations are available to plants.

- Such reaction can also take place with Ca-saturated clays. Evidence has been shown that Ca clay adsorb large of amounts of phosphate

$\boxed{\text{Clay}} - Ca - H_2PO_4$

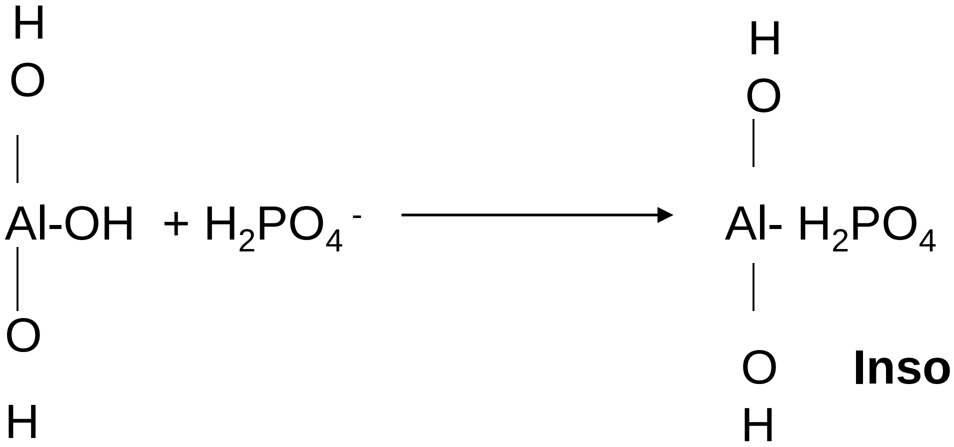
The phosphate ions can enter into chemical reaction with free metal ions :

$$Al^{3+} + 3H_2PO_4^{-} \longrightarrow Al(H_2PO_4)_3$$

- **The product formed is difficultly soluble in water and precipitates from solution. With the passage of time the Al phosphate precipitated become less soluble and less available to the plant.**
- **Lower the soil pH, the greater the concentration of soluble Al, Fe and Mn and the larger the amount of phosphorus retained.**

Phosphate fixation

- **Fixation renders phosphate insoluble in water and relatively non available to plants**
- **The fixation reaction can occur between phosphate and Al or Fe hydrous oxides or between phosphate and silicate minerals**
- **Many soils contain high amounts of Fe and Al hydrous oxides clays**
- **These clays react rapidly with phosphate forming a series of difficultly soluble hydroxy phosphates**



$$\underset{\substack{|\\ \text{O}\\ \text{H}}}{\overset{\substack{\text{H}\\ \text{O}\\ |}}{\text{Al}}}\text{-OH} + H_2PO_4^- \longrightarrow \underset{\substack{|\\ \text{O}\\ \text{H}}}{\overset{\substack{\text{H}\\ \text{O}\\ |}}{\text{Al}}}\text{-}H_2PO_4$$

Insoluble

- ✓ **Amorphous clays are also known to have considerable phosphate fixing capacities**

- ✓ **The product formed by both retention and fixation reactions are frequently not pure Al or pure Fe phosphates**

- ✓ **The ultimate product of the reaction between Al hydroxides and phosphates is called Variscite**

- ✓ **The ultimate product of the reaction between Fe hydroxides and phosphates is called Strengite**

Phosphate potential

- The amount of work that must be conducted to move reversible and isothermally an infinitesimally small amount of a phosphate ion from a pool of phosphates at a specified location at atmosphere pressure to the point under consideration

- Low PO_4 potential suggests high availability and vice versa

- Phosphate potential can be used to predict phosphate availability to plants.

- PO_4 potential $= -1/2 \log (Ca^{2+}) - \left[-\log (H_2PO_4^-) \right]$

Lime potential

- If the soil exchange complex is saturated with both H^+ and Ca^{2+} ions at equilibrium, Schofields ratio law says that,

$$(H^+)(\sqrt{Ca^{2+}}) = \text{constant}$$

- By taking –log, the ratio changes to,

$$-\log (H^+)(\sqrt{Ca^{2+}}) = \text{constant}$$

This equation is called the lime potential

- It characterizes the composition of the exchange complex with respect to its saturation by H^+ and Ca^{2+} ions

Quantity- Intensity Relationship

- **The proportion of nutrient in the soil reserve refers to quantity**
- **The strength of the nutrient in the soil solution referred as the conc. or activity of the ion in the solution is the intensity**
- **The quantitative estimation of the relationship between the two parameters is referred to as the Q/I technique**
- **This technique is purely based on thermodynamic principles and holds promise of being applicable to different soils and nutrient elements**

Importance of Q/I relationship for soil phosphorus

- **Provides a measure of immediately available phosphorus**
- **Information on phosphate buffering capacity of soil**
- **The probability of getting crop response to added phosphatic fertilizer based on equilibrium value of phosphate potential**