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Solubility of Glauconite Nano-Particle in Root Exudates

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A B S T R A C T

It is well established that glauconite has potassium (K) content but issue of discussion is that whether it has ability to release its content or not when it comes under the action of plant's exudates or secretions. Plant's exudates generally contain mild organic acids. So in this experiment, organic acids with same concentration as in maize root exudates were taken as solubilising medium to solubilise glauconite nano-particle. There are a number of mild organic acids present in maize root exudates but organic acids with high concentration and impact were taken as solubilising medium and they are viz., oxalic acid, acetic acid, malic acid and citric acid. Along with these four mild organic acids, water was also taken as control solubilising medium. All the four organic acids were with different concentration but similar to maize root exudates' concentration and the experiment led to result that different acids had different solubilising effect on glauconite nano-particle and the solubilising order of different acids on release of potassium from glauconite nano-particle is oxalic acid> malic acid> citric acid> acetic acid. Among all oxalic acid showed maximum solubilising effect on glauconite nano-particle while water's solubilising effect was least.

Introduction

The primary soil factors viz. soil pH, cation and anion exchange capacities e.g. surface charge, texture, soil type and soil organic matter strongly affect the bioavailability of nano particles. Thus soil type mainly determines the fate and behavior of nano particles and their bioavailability is influenced at the root-soil interface given the biochemical changes induced by plants in the rhizosphere. Root exudation and associated microbial activities significantly influences the characteristics of the rhizosphere soil than the bulk soil. Both the properties of the soil and the nature of nano particles determine the transformation and fate of nano particles in soil. The effectiveness of glauconite nano particles is influenced by particle size and generally increased with decreasing particle size. After application of glauconite nano particles to soil, the fate of nano particles was governed by mainly two phenomena viz. direct uptake by crop by nano particles piercing through the root epidermal cell or by conversion to soluble phosphate ion by soil microorganisms or by plant root exudates and soil acidity.

The nutrient availability from nano particles is closely related to the solubilization processes that occur in the soil. Once plants take up only those elements that are available to them in the soil solution, the equilibrium between solution and solid phase, as well as its reaction kinetics, should be considered when the nutrient elements phyto-availability is predicted. Therefore, nutrient element mobilization from solid phase due to the formation of soluble complexes could play an important role on their phyto-availability. Organic ligands present in the rhizosphere, such as mild organic acids which have low molecular weight and amino acids, are considered solubilization agents of metals linked to some mineral fractions of soils, because they form stable soluble complexes with metallic ions. There is not a consensus about organic acids composition in the rhizosphere. It is considered to be that citric acid is the most abundant (Li *et al.*, 1997) in rhizosphere. Lauherte *et al.*, (1990) determined the presence of citric, malic, fumaric, gluconic, lactic and succinic acids in the rhizosphere of different species. Studying the corn rhizosphere, Mench *et al.*, (1988) found the following concentration sequence: succinic > citric > lactic > malic. Koo (2001) studied the rhizosphere of different species and observed that acetic, butyric, lactic and oxalic acids together represented 72 to 88% of the low molecular weight organic acids collected. For these reasons, the study of organic acids composition in the rhizosphere of maize crop and of the connection between these organic acids and trace elements up taken by plants is of great interest and may represent a step forward concerning the phyto-availability issue.

Materials and Methods

Different mild organic acid solution viz., oxalic acid, acetic acid, citric acid, malic acid and water (control) of concentration same as released in rhizosphere of maize (Table 1) was prepared and 20 mg/kg K_2O concentration solution was also prepared from glauconite nano-particles (NPs). Then 3 parts of organic acid solution and 1 part of glauconite solution was added to make volume 100 mL. Then kept for 3 months as shown in figure 1 and then taken reading for K-content released from glauconite NP in Flame-photometer (Elico, CL-378).

Results and Discussion

Solubility experiment showed that different organic acids like acetic acid, malic acid, oxalic acid, citric acid solubilized glauconite NPs at different rate. Amongst the organic acids used in these incubation experiment, oxalic acid is strongest depending on the pK value and about 93% glauconite NP dissolved to produce K^+ ions while the least dissolving power of water (10%) was recorded during a period of 90 days (Table 2) and depicted in figure 2.

Acid dissociation constant

Strength of an acid in a solution is quantitatively measured by acid dissociation constant. It is symbolically represented as K_a. It has synonyms such as acidity constant or acid-ionization constant. In the type of acid-base reaction such as dissociation (a chemical reaction), it is called as equilibrium constant. In aqueous solution, acid dissociation reaction occurs and reaches to the equilibrium, which symbolically can be depicted as:

$$HA + H_2O\ A^- + H_3O^+ \rightleftharpoons \qquad (1)$$

Where HA is a generic acid that dissociates into its conjugate base A^-. Along with its conjugate base it also generates hydrogen ion which reacts with abundantly present water molecule and produce hydronium ion.

Fig.1 Solubilty study of glauconite nano-particle in organic acids

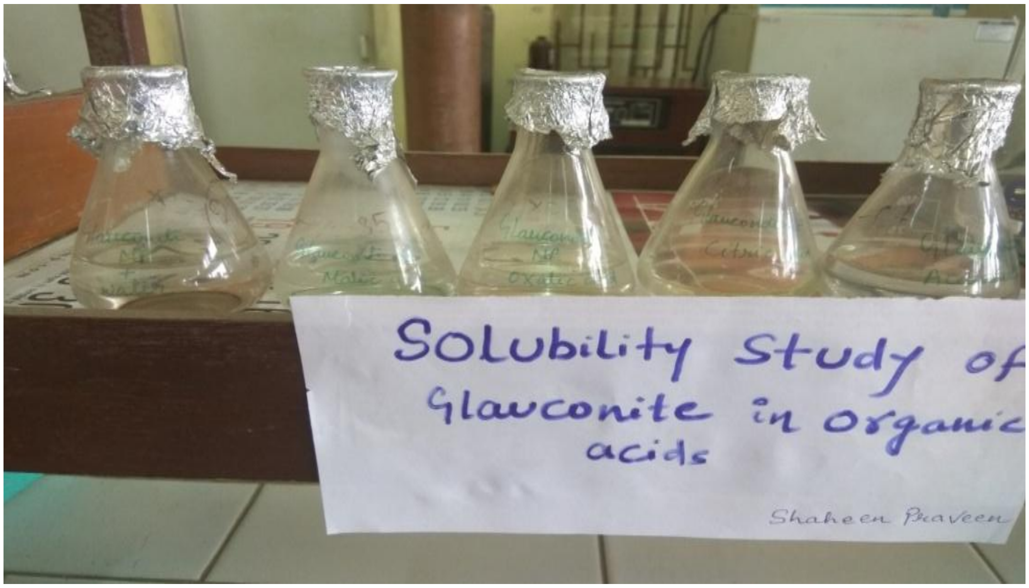

Fig.2 Solubility test of glauconite NP in different organic acids in 3 months period. Values are means with standard error

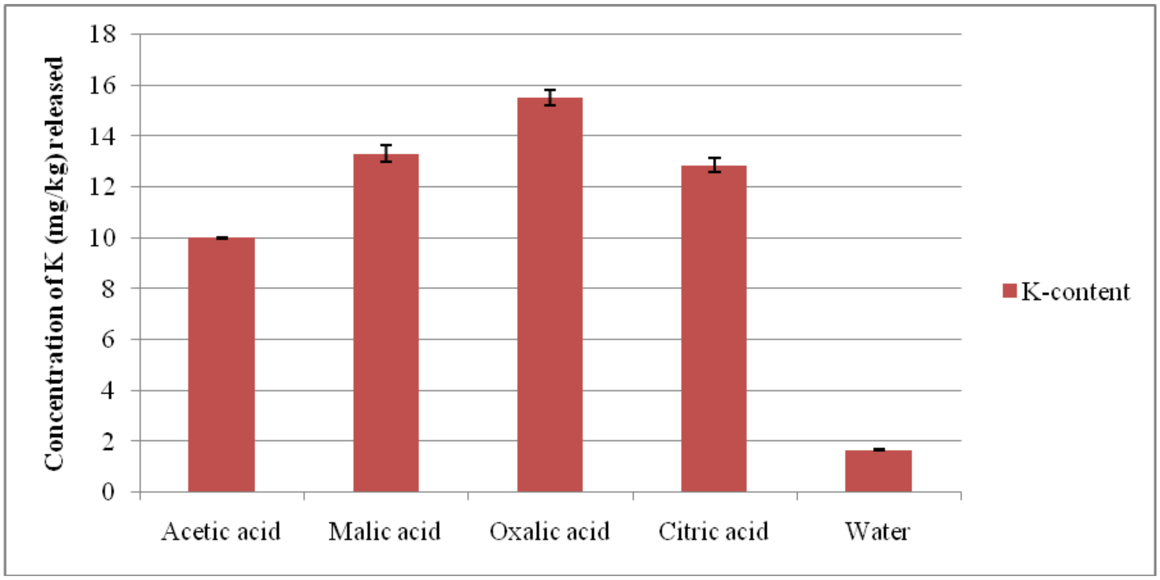

Table.1 Concentration of different organic acids released in maize rhizosphere

Treatments/ organic acids	Concentration (mg/kg)
Oxalic acid	15
Citric acid	40
Malic acid	60
Acetic acid	30
Water (Control)	-

Table.2 Solubility study of glauconite NP in different organic acids in 3 months period

Sl. No.	Organic acids	K (mg/L)
1	Acetic Acid	10.02 (60)
2	Malic Acid	13.33 (80)
3	Oxalic acid	15.53 (93)
4	Citric acid	12.86 (77)
5	Water	1.67 (10)

*20 mg/L K_2O; Source: Glauconite nano-particles; % release given in parenthesis

Table.3 Dissociation constant (pK) of different organic acids

Sl. No.	Organic acids	pKa value
1	Acetic Acid	4.76
2	Malic Acid	3.40
3	Oxalic acid	1.23
4	Citric acid	3.14
5	Water	15.74

In the example mentioned above, HA is representing acetic acid, and A^- is representing the conjugate base, acetate ion. When a chemical reaction reaches to equilibrium, concentration of reacting chemical species and also of products also becomes constant and hence concentration of HA, A^- and H_3O^+ does not change with time. Quotient of the equilibrium concentrations (in mol/L), as written as [HA], [A^-] and [H_3O^+] defines the dissociation constant. In the chemical reaction occurring in aqueous solution, concentration of water is very much abundant so its concentration remained unchanged after reaction and that's why it can be ignored. This definition is in common use. For practical purposes, logarithmic constant, pK_a is much conveniently used. For any given pH, value of pK_a has inverse relationship with acidity strength of acid and dissociation of acid i.e., the more positive the pK_a value, the weaker the acid. The range of pK_a value for weak acid lies in between -2 and 12 in aqueous solution. Strong acids have pK_a value less than -2; the stronger the acid is the more effectively it dissociate into its components with very few remaining of undissociated part to be measured and present in pK_a values. Theoretical mean is another way of measuring pK_a values for strong acids (Table 3).

It is the presence and strength of mild organic acids which are released in rhizosphere in the form of root exudates and also by the metabolic activity of micro-organisms which make utilization of applied fertilizers and manures possible and to release its contents and to make able to be in available form for nutrient uptake by the plants. As the experiment was done to know the effect of root exudates on the solubility of glauconite nano-particles to release its K content in plant available form, it resulted into significant positive results and also got the understanding and knowledge of different efficiency effect of various organic acids on the solubility of glauconite nano-particles.

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