

# Use of modified clays for retention and supply of water and nutrients

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Clay minerals are natural materials well known for their role in retention and persistence of organic and inorganic compounds in soil. Clay minerals are being modified through different processes to alter their charge and surface properties tailored for specific purposes. Modified clays in general include pillared layered clays, organoclays, nanocomposites, acid and salt-induced and thermally and mechanically induced modified clays. Pillared organoclays and nanocomposites constitute a novel class of materials, mainly one kind of modification of expanding 2:1 clay minerals. Acid and salt treatments lead to modification of the catalytic properties of clays. Clay mineral-polymer nanocomposites are the hybrids which exhibit a change in composition and structure on a scale of nanometres. Modified clay imparts slow-release property to fertilizers and enhances the water-holding capacity of soil. Therefore, understanding the methods of clay modification and properties of modified clays may facilitate development of agricultural management systems that ensure long-term sustainability of soil resources.

**Keywords:** Clay minerals, modified clay, nanocomposites, slow-release fertilizers.

THE modification of cationic characteristics of soil clays for soil reclamation purposes is an ancient practice that is still in use today<sup>1</sup>. However, there has been steady progress in clay materials technology through modification of the properties of natural clays, for example, changing from hydrophilic to hydrophobic, or forming clays with an interlayer characterized by selective pore sizes<sup>2</sup>. Recent work has shown that the preparation of clay mineral-polymer nanocomposites and superabsorbents, which are hybrids, leads to changes in composition and structure of the mineral over a nanometre scale<sup>3</sup>. There are works which show that the preparation of clay-polymer composites by the hybridization of inorganic clay minerals with organic superabsorbent polymer, leads to changes in composition and structure of the product which impart higher water-holding capacity, swelling rate and slow-release property. Superabsorbents are loosely crosslinked

hydrophilic polymers (CPs) that can absorb and retain aqueous fluids up to thousand times their own weight. In the hybridized clay-polymer composite, CPs get fixed between the clay structure which imparts more stability to clay composite and improves the slow-release property of the product. Like natural clay, modified clay also imparts slow-release property to a fertilizer and enhances water-holding capacity of the soil. Preparation and evaluation of superabsorbent polymers with slow-release phosphate fertilizer (SAPSRPF) by Zhan *et al.*<sup>4</sup> have found to influence water absorbancy and phosphorus release property. Incorporation of a small amount of pure montmorillonite into the copolymeric gel was reported to increase water absorbency<sup>5</sup>. Slow-release fertilizer with superabsorbent and moisture preservation (SRFSMP) property showed good retention and release of water and nutrient<sup>6</sup>. Studies with pillared clay-modified phosphate fertilizers reported decreased fixation and increased bioavailability of soil phosphorus<sup>7</sup>. In this review a general picture will be provided on the modified clay materials and their mechanisms of interaction with water and fertilizer nutrient which will play a significant role in improving water retention and nutrient use efficiency in soil.

## Methods of clay modification

Clay minerals are natural materials well known for their effect on retention and persistence of organic and inorganic compounds in soil. Modification of clay minerals like organoclay and organo-modified clay is the new avenue of clay mineral research. Actually these organic and inorganic hybrids are produced by exposing the purified clay to Na<sup>+</sup> and H<sub>2</sub>O, leading to separation of individual platelets; and on treatment with the polymer, it gets fixed between two platelets. The most important property regarding the improved water and nutrient retention capacity of modified clays is the barrier property. In general, barrier property refers to the hindrance of natural release of any material from clay structure. The organically modified clay creates a unique structure with the composite (termed as intercalated morphology) resulting into a complex microstructural diffusion pathway<sup>8</sup>. The intercalated morphology and tortuous pathway of this composite limit natural movement of water molecules as well

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nutrients, thereby increasing the holding time of water and nutrients inside. The ideal and widely used clay type for this kind of composite is montmorillonite layered silicate (MLS)<sup>9</sup>.

The polymer as such binds to the water molecule and nutrients and imparts slow-release property, but when the polymer get fixed between the interlayer structure of clay the stability of the polymer composite increases, which further improves the slow-release property of the product.

Modification of clay can be achieved in many ways and different types of modified clay are named according to the methods followed. Following is a short description of the different types of modified clay materials.

(a) Pillared layered clays: These clays constitute a novel class of materials created by propping apart the lamellae of 1:2 clays (e.g. smectites) with nanosized pillars of metal oxides or small organic cations. Some of the charge-balancing cations of the interlamellar space are exchanged with positively charged polymeric hydroxycations.

(b) Organoclays: These are produced by replacing the native exchangeable inorganic cations with organic cations. When the interlayer metal cations are replaced with an organic cation (e.g. alkylammonium), the surfaces of the clay are greatly modified and become organophilic.

(c) Nanocomposites: These include clay materials that exhibit a change in composition and structure over a nanometre scale. For true nanocomposites, the clay nanolayer must be dispersed uniformly (exfoliated) in the polymer matrix<sup>10</sup>.

(d) Acid and salt-induced modifications: Another procedure for clay modification, used mainly for improving the catalytic properties of minerals, is the acid treatment. Since the adsorptive and catalytic behaviour of the clay minerals is determined by the nature of their surface, an acid treatment will lead to the modification of original active sites.

(e) Thermally and mechanically induced modifications: The clays can be modified thermally, leading to a change in their mineralogical and chemical composition. Progressive heating of clays leads to the removal of free, adsorbed and structural water. Irreversible dehydration occurs at temperatures greater than 400°C.

#### *Clays and their modification: nanoclay polymer composite formation*

Clays are naturally occurring minerals with variability in chemical constitution depending on their groups and sources. The clay platelets are truly nanoparticulate. Clays often have very high surface areas, up to hundreds of square metres per gram of clay, and cation exchange capacities. Nanoclays are prepared from the smectite group of clays (2:1 phyllosilicates), the most common being montmorillonite, where the octahedral site is isomorphically substituted. Other smectite groups of clay are beidillite, nontronite and saponite in which the tetrahedral

site is isomorphically substituted. The crystal lattice of smectite group clay consists of two-dimensional, 1 nm thick layers which are made up of two tetrahedral sheets of silica (SiO<sub>2</sub>) fused to an edge-shaped octahedral sheet of alumina. The lateral dimensions of these layers vary from 30 nm to several micrometres depending on the particular silicate. Isomorphous substitution within the layer by Mg<sup>2+</sup>, Fe<sup>3+</sup>/Fe<sup>2+</sup> or Al<sup>3+</sup> generates negative charges that are normally counterbalanced by hydrated alkali or alkaline earth cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>++</sup>, etc.) residing in the interlayer. Because of the relatively weak Van der Waals forces existing between the layers, intercalation of various molecules, and even the polymer, is feasible<sup>11,12</sup>. Clays are inexpensive materials which can be modified by ion exchange, metal-metal complex impregnation, pillaring and acid treatment to develop catalysts with the desired functionality<sup>13,14</sup>. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species. Nanoclays are extensively used today for preparation of polymer nanocomposites, paints, inks, greases and cosmetics formulations, as drug-delivery vehicles and in wastewater treatment<sup>15</sup>. There are three kinds of nanocomposites categorized according to whether the filled particles have one, two or three dimensions in the nanometer scale<sup>3</sup>.

#### *Superabsorbent polymeric montmorillonite nanocomposites*

The chemicals used for the preparation of superabsorbent polymeric montmorillonite nanocomposites are acrylic acid (AA) purified by vacuum distillation, *N,N*-methylenebisacrylamide (NMBA), sodium hydroxide, (3-acrylamidopropyl) trimethylammonium chloride (TMAACl) and sorbitan monostearate (Span 60). Here, NMBA is used as a crosslinking agent, TMAACl, as an initiator and Span 60 as a stabilizer.

The NaA (sodium acrylate) monomer solution is purified according to standard procedure<sup>16</sup>. Na-MMT is prepared by making a suspension MMT in NaCl solution. The suspension is centrifuged and washed with water to get pure sodium montmorillonite (Na-MMT). Then a suspension is prepared by mixing Na-MMT and TMAACl in water. The crosslinking agent, NMBA, and the appropriate amount of Na-MMT or TMAACl-MMT are introduced into NaA monomer solution. After polymerization the suspension is allowed to cool, washing is done with water-methanol mixture and the content dried in a vacuum oven at 100°C (ref. 5).

#### *Slow-release and superabsorbent nitrogen fertilizer*

AA and maleic anhydride (MA) are mainly used for the synthesis of slow-release and superabsorbent nitrogen fertilizer (SSNF). Along with the above two compounds,

sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) and ammonium persulphate ( $\text{NH}_4\text{S}_2\text{O}_8$ ) are used as redox initiator, N-methylene bis-acrylamide (NNMBA) as crosslinker, trihydroxymethyl propane glycidol ether (6360) as surface crosslinker and urea ( $\text{NH}_2\text{CONH}_2$ ) as nitrogen fertilizer.

A series of samples with different amounts of cross-linker, initiator, urea, MA and AA with different degrees of neutralization is prepared using the standard procedure<sup>17</sup>. Typically, MA and AA are dissolved in distilled water and then neutralized. The required amount of NNMBA aqueous solution as crosslinker is added to the solution. A mixture of  $\text{NH}_4\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{SO}_3$  aqueous solution as initiator is introduced to the mixed solution. To improve the slow-release and water-retention properties, the product is surface crosslinked using trihydroxymethyl propane glycidol ether (6360).

#### *Modification of phosphatic fertilizer with pillared clay*

Different types of modified pillared montmorillonite are used as additives along with phosphatic fertilizers to obtain several high-efficiency phosphate fertilizers (HEPFs). Generally three types of modified pillared montmorillonite are available – organic pillared montmorillonite (OrPM), organic–inorganic pillared montmorillonite (OIPM) and inorganic pillared montmorillonite (IPM) based on the type of material used for modification.

The processing of IPM, OrPM, OIPM and HEPFs is as follows:

(1) IPM: The purified montmorillonite is dried, and pulverized to pass through a 75  $\mu\text{m}$  mesh sieve to prepare IPM<sup>18</sup>. Montmorillonite is modified to Na-montmorillonite to obtain grains less than 2  $\mu\text{m}$ . Then  $\text{AlCl}_3$  and  $\text{Na}_2\text{CO}_3$  solutions are mixed slowly, until a final OH/Al ratio of 2.4 is reached to get the pillared reagent. The pillared reagent is slowly introduced into Na-montmorillonite. The resulting IPM is centrifuged, washed and dried at 80°C.

(2) OrPM: Montmorillonite is modified to Na-montmorillonite. Then humic acid solution is slowly added into Na-montmorillonite. Then the same procedure is followed as in the case of IPM preparation.

(3) OIPM: This is prepared by humic acid and IPM.

(4) HEPFs: For preparing HEPFs OrPM is mixed with phosphate rock, reacted with concentrated sulphuric acid and air-dried. HEPFs can also be prepared by treating superphosphate with or without additives following the same procedure<sup>19</sup>.

#### *Modified bitumen emulsion for control release fertilizers*

Bitumen is a cheap coating material which can be used to produce slow and/or controlled release fertilizers (CRFs). A complex fertilizer 20:20:20 is prepared by coating with a modified bitumen emulsion (50% active

material) containing 20% of each N,  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$ . The cationic emulsifier tri-ethanol ammonium hydroxide, bentonitic clay and the emulsified polymer (50% active material) polyvinyl acetate butyl acrylate (PVAcBuA) are used for this purpose.

The bentonitic clay (5% by weight) and the emulsifier (2% by weight) are added in warm water (70°C). This is followed by stirring and warming of the bitumen (135°C). Stirring is continued until the emulsion became completely homogenous. The emulsified polymer PVAcBuA is added to the emulsified bitumen just before using in the coating process, taking into consideration that the bitumen polymer ratio is 9:1. The prepared coating material is sprayed on the fertilizer using a modified horizontal rotary drum with pan granulator<sup>20–22</sup>.

#### *Surfactant-modified zeolite as a slow-release fertilizer for phosphorus*

Zeolite-A (zeolite acrylate) is modified using hexadecyltrimethylammonium bromide, a cationic surfactant, to modify its surface and increase its capacity to retain anion, namely phosphate ( $\text{PO}_4^{3-}$ ). Research is going on to study feasibility of using surfactant-modified zeolite (SMZ) as a carrier for fertilizer and for slow-release of phosphorus.

#### *Modern techniques for characterization of nanoclays and nanocomposites*

Nanotechnology attempts to understand the composition and properties of soil constituents on a single-particle basis (micro or nanoscale) in order to know their role in the soil system. Electron microscopy can be used successfully for the study of organoclay nanocomposites<sup>23</sup> and nutrient release pattern from clay minerals<sup>24</sup>. Scanning probe microscopy is used to study the fundamental processes of molecular soil chemistry, characterization of micro topography on soil colloids<sup>25</sup>, study of ultrafine particles (UFPs)<sup>26</sup>, etc.

#### *Study of ultrafine particles using high-resolution transmission electron microscopy*

Chen *et al.*<sup>27</sup> conducted a study to observe the microstructure of UFPs. These are defined as particles having diameter less than 100 nm. The rutile particles have been found to be rod-shaped and lime particles were spongy in structure.

#### *Study of organoclay nanocomposites using high-resolution transmission electron microscopy*

By incorporation of organic guest species in the interlayer space of layered clay minerals organo–inorganic nanocomposites are formed. There is a large increase in specific surface area, adsorption capacity and ion

exchangeability. Such properties can be used to control retention, transport and persistence of toxic chemicals in the geosystem<sup>26</sup>.

#### *Change in structure of humic substances with variation in moisture content as studied by scanning electron microscope*

Redwood *et al.*<sup>28</sup> studied the microstructure of humic aggregates as a function of humidity. On hydration the structure becomes bulky, while it shrinks on dehydration. The study was noteworthy as humic substances are potentially important in the retention and bioavailability of trace metals as well as pollutants in soil<sup>28</sup>.

With the help of the scanning tunnelling microscope (STM) we can study the interaction of small organic molecules with silica surfaces at atomic level. STM can also be employed to study the chemical binding of organic molecules on the clay surface, or to obtain the image of constitutional Cr impurities on the goethite surface.

#### **Utility of modified clay**

##### *Modified clay and water retention*

Superabsorbent polymeric materials in combination with clay minerals play a significant role in improving the water-holding capacity<sup>29</sup>. Currently, reinforcing polymer with small amounts of smectite clays has attracted increasing interest because these materials exhibit high stability.

##### *Effect of Na-MMT content on water absorbency in deionized water*

According to Flory's theory<sup>30</sup>, the water absorbency of a gel is dependent on ionic osmotic pressure, crosslinking density and the affinity of the gel for water. Buchanan *et al.*<sup>31</sup> suggested that the swelling kinetic for the absorbent is significantly influenced by swelling capacity, size distribution of the powder particles, specific surface area, and apparent density of the polymer. The water absorbency in deionized water is measured by suction filtration and the tea-bag method as a function of the content of Na-MMT in the copolymeric gels (series of gel). The swelling ratio depends on the affinity of the gels for water. The hydrophilicity of the Na-MMT series of gels is increased at low Na-MMT content, and this enhances the hydrophilicity of the gels. It also indicates that the tendency of the initial absorption rate is in the order NB2 > NB4 > NB6 > IB2 = IB4 = IB6 [NaA/montmorillonite xerogels (NB series) obtained from inverse suspension (IB series) and water solution polymerization (SB series)]<sup>5</sup>.

##### *Water retention of superabsorbent and moisture retentive fertilizer*

A slow-release NP compound fertilizer with superabsorbent and moisture preservation (SRFSMP) is prepared by carboxyl methyl starch, AA, ammonia, urea and diammonium phosphate.

The water transpiration rate and content of the soil are greatly influenced by SRFSMP. The experimental results have shown that the water content of the soil with SRFSMP is obviously higher than that of the soil without SRFSMP; the water content of the soil without SRFSMP was only 3% on the 30th day, while that of the soil with SRFSMP was 14.5%, about 12% higher than the former<sup>32</sup>. An experiment conducted on the water retention of SAPSRPF, showed that the water evaporation rate decreased after the addition of SAPSRPF to the soil<sup>4</sup>. This is because SAPSRPF has excellent water absorbency and hence the water evaporation rate decreased.

In general, the addition of hydrogel increases the moisture content at field capacity of both sandy loam and loam soils. It is found that the application of hydrogel slows down the rate of soil moisture loss that causes a delay in wilting of seedlings grown in both sandy and loamy soils<sup>33</sup>.

##### *Modified clay and nutrient release studies*

Slow-release property of any fertilized product is important with respect to increase in the nutrient-use efficiency, which is significant in terms of increased agricultural production and environmental safety.

##### *Slow-release nitrogen fertilizer*

The nitrogen release rate of the urea/superabsorbent mixture is less compared to urea, in agreement with the results of Smith and Harrison<sup>34</sup>. The nitrogen in SSNF and SSNF without surface crosslinking both possessed slow-release properties, but the slow-release behaviours were different<sup>6</sup>. The nitrogen in SSNF released 9.8%, 53.8% and 78.2% within 24 h (1 day), 72 h (3 days) and 672 h (28 days) respectively, whereas the nitrogen in SSNF without surface crosslinking released 20.3%, 57.8% and 82.0% respectively. The release behaviours of nitrogen in SSNF and SSNF without surface crosslinking were the same as those of other conventional slow-release urea fertilizers, whose release characteristics were fast initially and slowed down gradually<sup>35</sup>.

The slow-release behaviours of N and P in SRFSMP are greatly influenced by water absorbency. The urea and  $(\text{NH}_4)_2\text{HPO}_4$  dissolved in the network of three-dimensional crosslinking polymers would slowly diffuse into the solution through dynamic exchange. So the aperture size of the swollen network would determine the release rate of urea and  $(\text{NH}_4)_2\text{HPO}_4$  (refs 36, 37).

In a laboratory experiment, Iza *et al.*<sup>38</sup> reported that the presence of kaolin and poly(acrylic acid-co-acrylamide) content significantly affects the water absorbency and diffusion coefficient of urea released from poly-(AA-co-Am)/kaolin composite hydrogel. The physical filling of kaolin particle in the polymer decreases the amount of hydrophilic groups and consequently results in the reduction of water absorbency<sup>5</sup>. According to Liang and Liu<sup>39</sup>, the changes in the water absorbency of the product is due to existence of synergistic effect among the groups of  $-\text{COOH}$ ,  $-\text{COO}^-$ ,  $-\text{CONH}_2$  and  $-\text{OH}$  (on kaolin).

### *Slow-release phosphate fertilizers*

**Modified pillared clay:** A study has been conducted to determine the potted plant biomass and phosphorus absorption capacity of different phosphate fertilizer treatments. The superphosphate treated with additives was named as CK1 and the superphosphate treated without additives was named CK2. The treatments are: CK1 (superphosphate treated with additives), CK2 (superphosphate treated without additives), GX series comprising GX1 = OrPM + phosphate rock +  $\text{H}_2\text{SO}_4$ ; GX2 = rock phosphate with OIPM and GX3 = rock phosphate with IPM. The results have shown that CK2 has 9.22% biomass increase than CK1. These data indicate that phosphorus in the three fertilizers has high bioavailability, among which GX2 is the best. The treatment GX2 has the highest phosphorus content and phosphorus absorption capacity which corresponds to its highest biomass. On the contrary, treatment CK1, has the lowest phosphorus content and phosphorus absorption capacity<sup>40</sup>.

**Surfactant-modified zeolite:** SMZ has a great potential as the fertilizer carrier for slow-release of P. The results show that the P supply from fertilizer-loaded SMZ is available even after 1080 h of continuous percolation, whereas P from  $\text{KH}_2\text{PO}_4$  is exhausted within 264 h. The results indicate that SMZ is a good sorbent for  $\text{PO}_4^{3-}$  and a slow-release of P is achievable<sup>41</sup>.

### *Modified bitumen for controlled release of N, P and K fertilizers*

The modification of bitumen-coated complex N, P and K fertilizer (method of preparation already described) is evaluated for its slow-release property. Determination of N, P and K is carried out using the methods described by Bremner and Mulvaney<sup>42</sup> for nitrogen, and Cottenie *et al.*<sup>43</sup> for the other two nutrients. A considerable amount of the uncoated fertilizer is found to be released in the first day, which reached more than 75% of the fertilizer and its nutrients. On the other hand, coated granules released their nutrients much more slowly. The higher the coating fertilizer ratio, i.e. the thicker the coating, the slower is

the release of the fertilizer nutrients<sup>44</sup> and the longer is the period of release, referring to the possibility of long duration of the fertilizer in the soil.

The coated fertilizers are reported to have higher crop use efficiency than that obtained from regular fertilizers. On comparing regular and coated fertilizers, researchers have demonstrated how coatings improve crop uptake efficiency and have reported that poly-olefin or lignin-coated N fertilizers are particularly effective in minimizing N losses and enhancing N use efficiency in sandy soils<sup>45</sup>. In the case of P, coating of fertilizer reduces the contact between the fertilizer P and soil, reduces fixation of P and increases the time for plant absorption. It has been observed that P recovery rates are three to five times higher with polyolefin-coated double superphosphate and multi-superphosphate than with uncoated ones<sup>46</sup>.

### *Zeoplant*

Zeoplant is an effective water-retaining soil amendment, consisting of fully natural clay mineral treated with a special natural organic component. The major functions of zeoplant are: (i) It can retain high amount of irrigation water. (ii) It reduces the percolation rate of the irrigation water in the soil. (iii) It reduces the usage of NPK fertilizers drastically by preventing its leaching.

### *Components of zeoplant*

- (i) Rhyolitic tuff active volcanic glass and clinoptilolite ( $\text{Na,K,Ca}$ )  $2-3\text{Al}_3(\text{Al, Si})_2 \text{Si}_{13}\text{O}_{36} \cdot 12 \text{H}_2\text{O}$ .
- (ii) Natural phyllosilicate clay minerals: illite and montmorillonite ( $\text{Na,Ca}$ )(Al,Mg)6( $\text{Si}_4\text{O}_{10}$ )3(OH)  $6-n\text{H}_2\text{O}$ .
- (iii) Component: natural fibre material cellulose which is also used as a food additive.

The irrigation water cannot 'rush' through anymore due to the strongly decreased percolation time. The zeoplant particles bind the nutrition elements on their active surface and avoid their washing away by the irrigation water.

### *Clay-organic-microbe interactions in relation to retention and supply of nutrients*

Minerals, organics and microbes profoundly affect the physical, chemical and biological properties of soils. The interactions affect sorption and desorption of elements in soil and thus alter nutrient availability. Humic and other organic acids are found to compete with sulphate and phosphate ions for adsorption sites<sup>47</sup>, whereas humin-clay interaction is the most important for phosphorus adsorption in Andisols<sup>48</sup>. Clay type and surface properties are reported to be the major factors determining the extent of carbon sequestration in the soil<sup>49</sup>. Siderophores, the microbial secretions, even when bound to clay,

increase the availability of iron to plants<sup>50</sup>. Organisms and humic substances play a significant role in maintaining the structure and water-retention properties of the soil<sup>51</sup>.

Combination of atomic/molecular structural data and energy derivatives opens up new insights into binding sites and transport forms between biological and/or xenobiotic substances and soil organic matter<sup>52</sup>.

Mandal and Datta<sup>53</sup> studied the effect of rhizosphere, which is a site of intense microbial activity, on clay–organic complexation and mineral transformation. Fitting of XRD profile showed that in the rhizosphere sample organic molecules entered the interlayer space and increased the basal spacing to 28 Å. A portion of smectite is also transformed to randomly interstratified smectite–kaolinite minerals. Differential X-ray diffraction showed that clay–organic complex formed in the rhizosphere sample of Vertisol seemed to be more stable than that of Alfisol.

The humus adsorbed on clay plays an important role in preventing clay dissolution by organic acids. X-ray diffraction analysis showed that micaceous mineral is partially dissolved and vermiculite is completely dissolved when humus is partially removed from the clay before extraction<sup>54</sup>. Particle size, crystallinity of the minerals and nature of the mica particles play an important role in governing the potassium release from clays<sup>55</sup>. Extensive studies have been made to develop simulation models to characterize soils with respect to potential phosphorus and potassium supply capacity<sup>56,57</sup>.

Carbohydrates, heterocyclic-N and alkylaromatics in nanocomposites are released at higher temperatures than the temperature at which the same compound is released from clay fraction. This indicates that these components of organic matter are held more strongly in the nanocomposite fraction through preferential interaction with the inorganic components<sup>58</sup>.

## Conclusion

Modification of clay with polymers, particularly surface crosslinking polymers, increases the barrier property of the clay composites, and fertilizer treated with the clay composites leads to slow-release property. The surface crosslinking polymer gel can get fixed between the interlayers of the expanding clay and becomes more stable than the other polymer. This characteristics imparts better slow release property of modified clay. The surface crosslinked product not only shows good slow-release property, but also excellent soil moisture preservation capacity, which could effectively improve the utilization of fertilizers and water resources simultaneously. Clay polymer-coated N-fertilizers are found to be particularly effective in minimizing N losses and enhancing N use efficiency in sandy soils, whereas clay polymer-coated P-fertilizers are effective in calcareous soil. Studies should be directed towards development of suitable polymer

composites for *in situ* modification of soil clays. Till date, most of the research in this direction is done under laboratory conditions or in pot culture experiments. Therefore, future studies should be carried out under field conditions using different clay and clay composites to develop N and P fertilizers with high-use efficiency.

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