



# Halloysite Nanoclay Polymer Composite: Synthesis, Characterization and Effect on Water Retention Behaviour of Soil

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## Authors' contributions

This work was carried out in collaboration between all the authors. Author ND designed the study and guided in discussion of results. Author PP and G ran the experiment, generated data, managed the literature searches and produced initial draft. All authors read and approved the final manuscript.

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## ABSTRACT

Going with the theme of *more crops per drop*, halloysite nanotube polymer composites superabsorbent is synthesized for promotion of rain fed agriculture. The synthesized composites were characterized by Fourier transformation infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Effect of graded percentage of halloysite nanoclay addition with respect to water sorption of composites has been studied along with its effect on water retention behaviour of soil. Peak of halloysite nano tube diminishes at 7.72 Å and broadens at 4.45Å after polymerization reaction indicating both internal and external surface of clay had been involved in polymerization reaction. Porous morphology of superabsorbent has been confirmed by SEM. Addition of halloysite nanoclay during polymerization reaction has increased water sorption capacity of polymer composites. Maximum water sorption was observed in composites with 7% clay loading. Polymer composite treated soil has 4% to 6% more available water and higher soil moisture regime as compared to control (untreated) soil.

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## 1. INTRODUCTION

India is an agriculture-based country. Nearly 70% of Indian population depends on agriculture directly or indirectly. About 2/3<sup>rd</sup> of arable land comes under rain fed agriculture, covering food crops like rice, pulses, oilseed, coarse cereal etc. contributing 44% to food basket and feeds nearly 40 % of Indian population. Rain fed agriculture is extremely challenging and warrants greater attention. Various technologies have been used for conserving water for promotion of rainfed agriculture, use of superabsorbent is one of it. Superabsorbent polymers are three-dimensional cross-linked hydrophilic materials that can absorb and retain large quantities of water or aqueous solution and displays a slow release rate [1]. Owing to their excellent properties, superabsorbent are widely used in many fields such as agriculture, bio-medicals, tissue engineering, waste-water treatment and other environmental & chemical engineering fields [2]. In the present study an attempt has been made to synthesize a halloysite nano clay based superabsorbent which can improve water retention behaviour of rhizosphere soil to maintain higher soil moisture regime and help plant to survive in water stress condition.

## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

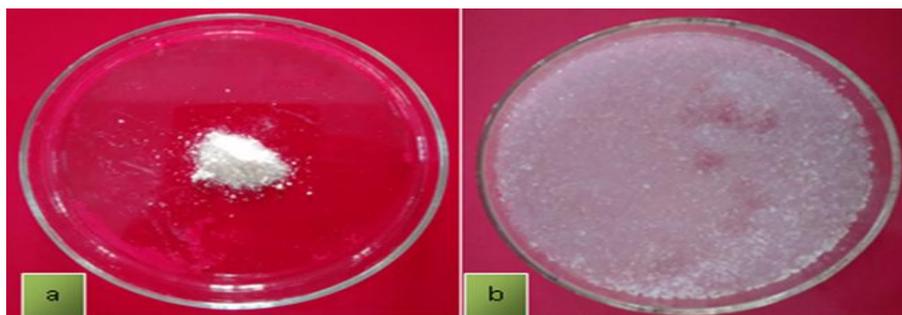
Acrylamide, Acrylic acid, Ammonium per sulphate, N, N' methyl bis acrylamide was procured from Hi-Media (India). Halloysite nanotube  $[Al_2Si_2O_5(OH)_4 \cdot 2H_2O]$  has been purchased from Sigma Aldrich, USA having tube diameter of 50 nm, surface area  $65 m^2 g^{-1}$ . Quartz distilled water was used for the preparation of

polymer composite. Organic solvents for synthesis, characterization and other essential chemicals were of analytical grade and procured from BDH, India.

### 2.2 Synthesis of Halloysite Nanotube Polymer Composite

Nano clay polymer composites were synthesized at Soil Physics laboratory, Department of Soil Science and Agricultural Chemistry, Institute of Agricultural Sciences, Banaras Hindu University, Varanasi. Nano clay polymer composites (NCPC) were synthesized by polymerization reaction following procedure of Ling and Liu [3], with 10% acrylic acid, acrylamide, 0.9% ammonium per sulphate as initiator, 0.12% N, N' methyl bis acrylate as cross linker loaded with (3%, 5%, 7%, 9% and 11%) halloysite nanotube. The composite formed was dried in oven at 70 °C, further crushed in a heavy wooden mortar and pastel into a fine powder and kept in air tight polyethylene bags. The polymer composite before and after absorption of water was depicted (Fig. 1).

Mechanism of reaction of various variables during polymerization reaction was shown in Fig. 2. Acrylic acid is firstly neutralized with liquid ammonia solution for getting a mixture of acrylic acid and ammonium acrylate. Acrylamide with sonicated clay was added to acrylic acid solution. After that reaction initiator and cross linker were added. The reaction was carried out in inert atmosphere of nitrogen with continuous stirring at 65°C. Once the polymerization reaction completed the product formed was called composite, which was then washed with water to remove unreacted residue of acrylamide if any, oven dried, grounded and kept in air free bags.



**Fig.1. Halloysite nanotube polymer composite (a) Dry (b) After absorbing water**

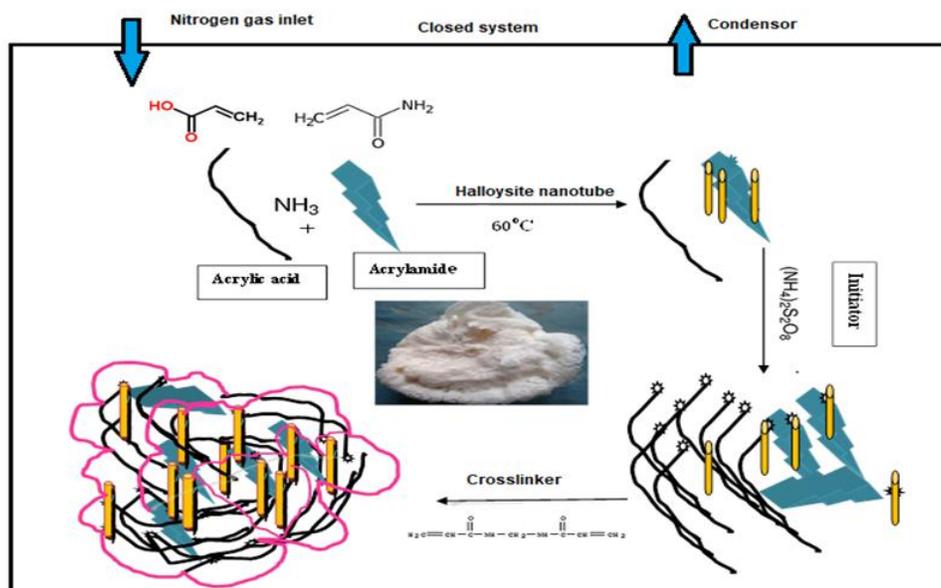


Fig. 2. Synthesis of Halloysite nanotube polymer composite

### 2.3 Water Absorption Behaviour in Water and Salt Solution Dip

0.5 g of finely grounded composite was taken in tea bags and dipped in tap water, distilled water and in 0.09% salt solution of NaCl,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  for estimating water sorption behaviour. After dipping for different time intervals tea bags were taken out and further weighed for analyzing maximum water absorption capacity of composite.

### 2.4 Characterization

Composite which has shown higher water sorption capacity was characterized by FTIR, XRD, SEM and taken for further study.

#### 2.4.1 FTIR analysis

Infrared spectroscopy of the powdered samples of clay and polymer composite was carried out by Perkin spectra 2 spectrophotometer. Clay samples and polymer composites were scanned in the region of  $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$  using KBr pellets. All the spectra were recorded and analysed to know the type and nature of the functional group attachment in clay and superabsorbent.

#### 2.4.2 XRD

XRD patterns of the clay and polymer composite were recorded by X-ray diffractometer (XRD,

Bruker D8 Advance Eco), USA using  $\text{CuK}\alpha$  radiation ( $k = 1.54 \text{ \AA}$ ) within 5 to 80, 2 theta range. XRD was obtained with X-ray tube having Cu-anode (Philips) running at 40 kV and 20 m A,  $\text{Cu-K}\alpha$ , scan step size-0.1, time per step (Sec). Sample holder, made up of aluminium, was cleaned with acetone solution and samples were filled in the space defined for specimen. The specimen holder was inserted in the X-ray diffractometer for the analysis of randomly oriented sample.

#### 2.4.3 SEM

Scanning electron micrographs (SEM) produced the morphological image of halloysite nanotube and polymer composite by an electron beam and was recorded on Zeiss EVO 18 (SEM) instrument. The accelerating voltage used was 15 kV and the applied magnification of the image was 2000 X. It provides information about the morphology of superabsorbent.

### 2.5 Effect on Water Retention Behaviour of Soil

Alluvial soil (Inceptisols) from agricultural research farm of Banaras Hindu University and red soil (Alfisols) from Rajiv Gandhi south campus, Barkachha, Mirzapur was taken. Properties of both soils were given in Table 1.

**Table 1. Physico-chemical properties of soil used**

Soil Properties	Alluvial soil, inceptisol (BHU, Varanasi)	Red soil, alfisol (RGSC, Mirzapur)
pH	7.67±0.27	5.87±0.35
EC (dSm <sup>-1</sup> )	0.34±0.74	0.19±0.41
Organic Carbon (%)	0.47±0.11	0.37±0.24
CEC [cmol (P <sup>+</sup> ) kg <sup>-1</sup> ]	13.8±0.62	8.30±0.51
Water holding capacity (%)	49.5 ±0.33	37.7±0.84

## 2.6 Effect of Composite on Water Holding Capacity of Soil

Red and alluvial soil were dried in oven at 105°C. Finely grinded nano clay polymer composites passed through 0.5 mm sieve was mixed with red and alluvial soil at rate of 5 mg /100 g of soil. The nano clay polymer composites mixed soil was filled in plastic pots with filter paper at bottom and kept in surface containing water for saturation for 24 hour. After the equilibration time pots were taken out and moisture content was measured gravimetrically [4]. The pots were kept under laboratory condition at 22°C in an incubator. The weight of pot was recorded periodically until constant weight was obtained. Moisture content of soil was calculated by equation:

$$\text{Moisture content (\%)} = (M-m)/m \times 100$$

Where, M denotes weight of wet sample (g) and m denotes weight of the oven-dried sample (g).

## 2.7 Effect of Composite on Water Retention Behaviour of Soil

Water retention study was done using pressure plate apparatus at different tensions: 0 pF, 2.4 pF, 2.7 pF, 3 pF, 3.7 pF and 4pF. Ceramic plates were kept overnight in water for saturation, amended soil filled in rubber rings arranged on bar plates and allowed to saturate overnight. Care was taken to ensure proper contact between the samples and ceramic plate surface. The saturated samples along with ceramic plates were placed in pressure chamber pertaining to different tensions. The pressure was applied and maintained until water stopped flowing out of the chamber. Samples were transferred to moisture boxes immediately and weighed. The moist samples were dried in a hot air oven at 105° C for 24 h, air cooled and reweighed [5]. The amount of water held at particular pressure was calculated using following equation:

$$\text{WC (\%)} \text{ by weight} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$$

Where, WC is the per cent water content of soil on weight basis,  $W_{\text{wet}}$  is the mass of wet soil at a particular tension, and  $W_{\text{dry}}$  is the weight of oven-dried soil.

## 2.8 Statistical Analysis

The data were subjected to the analysis of variance (ANOVA). The statistical analysis was done by standard process in SPSS version 20 software (SPSS, Inc., Chicago IL).

## 3. RESULTS AND DISCUSSION

### 3.1 Water Sorption Properties of Composites

Effect of graded dose of halloysite nano clay on water absorbency of composites was presented in Fig. 3. In distilled and tap water composite having 7% of clay loading absorbed more water i.e. 130 g/g and 112 g/g, respectively. On increasing clay content above 7%, water absorbing behaviour of composites has been decreased both in tap water and in distilled water. This phenomenon may be attributed to the fact that halloysite nano tube can act as an additional cross-linking point in the polymeric network to decrease the elasticity of polymers. Additionally, the excess of halloysite would also decrease the hydrophilicity as well as the osmotic pressure difference, resulting in shrinkage of the composite. This can be explained in the light of Flory's theory, according to which, water absorbency of a gel is dependent on ionic osmotic pressure, crosslinking density, and polymeric network. In low concentration (7%), the clay is easily ionized and dispersed into the polymeric gel, which enhances its hydrophilicity and makes it absorb more water [6,7]. In tap water absorbency of composites decreased by 15 % as compared to distilled water. It may be due to polyelectrolytic effect of tap water, the oppositely charged ion entered the polymeric network and neutralized the anions in polymeric complex. Result obtained was in agreement with [8,9].

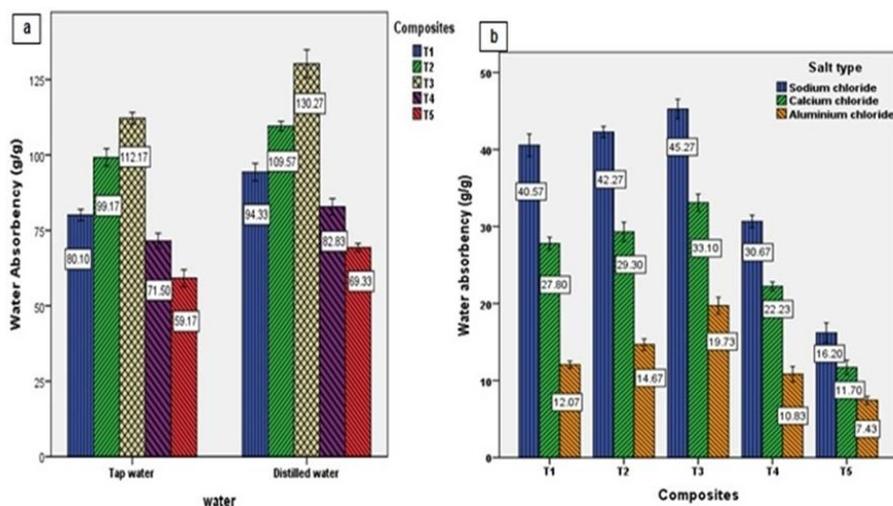


Fig. 3. Sorption behaviour of composites (a) Water (b) Salt solution

### 3.2 Water Sorption Behaviour of NCPC in Salt Solution

Nano clay polymer composites were swelled in 0.09 M sodium chloride, calcium chloride and aluminium chloride. In current study, the effects of electrolytes on the swelling behaviour of the composites were examined using NaCl, CaCl<sub>2</sub> and AlCl<sub>3</sub> salt solution and composite swelling behaviour was shown in Fig. 3. Absorbency of composites were decreased in order of NaCl > CaCl<sub>2</sub> > AlCl<sub>3</sub>. It was well known that swelling capacity of “anionic” hydrogels was significantly affected by the concentration, valence of external electrolytes and was result of “charge screening effect” of the additional cations. The charge screening effect increased with increasing the concentration of cations, it not only decreased the anion–anion electrostatic repulsion among graft polymer chains but the osmotic pressure between hydrogel networks and external aqueous solution, thus the swelling capacity was diminished. Composites have carboxylate groups in their structures and in salt solutions, the anion-anion repulsion of the carboxylate groups is prevented by the M<sup>n+</sup> cations that shield the carboxylate groups, so the swelling capacity is decreased. Multivalent cations drastically decrease the swelling capacity. The decrease was attributed to the complexing ability of carboxylate groups, inducing inter chain complex formation and consequent enhancement of the network crosslink density [10]. Thus water absorbency of the composite in the presence of

multivalent cation (Ca<sup>2+</sup> and Al<sup>3+</sup>) was lower than that in monovalent (Na<sup>+</sup>) ion in solution.

### 3.3 Soil Moisture Characteristic Curve Change after Addition of NCPC

The water absorbed and transported to the plant was powered by root pressure and the negative pressure of transpiration. Therefore, only the water absorbed in a certain negative pressure range is effective for plants, and not all water can be absorbed by plants. Fig. 5 displays the relationship between different pressure and the water retention by soil. Addition of halloysite nanotube polymer composite with 7% clay loading has improved water retention behaviour of soil at various soil moisture constant as depicted in Table 2. In Inceptisol, NCPC treated soil was found to have 13 % more moisture content at maximum water holding capacity (Θ<sub>s</sub>) compared to control while 14 % more moisture content was found in Alfisol treated with NCPC. Water content at field capacity (Θ<sub>FC</sub>) was ~7% more in NCPC treated Inceptisol and Alfisol. The observed higher soil moisture regime (3% more moisture) & AWC trigger a delayed attainment of temporary wilting point (Θ<sub>TWP</sub>) in NCPC treated Inceptisols and Alfisols compared to control i.e. untreated soil. The presence of water containing soil particles that were surrounded by the polymer composite may reduce the hydraulic gradient difference between soil particles and the swollen composites [10]. This, in turn, results in slower water evaporation rate from each component in the soil composite mixtures compared with untreated soil [11].

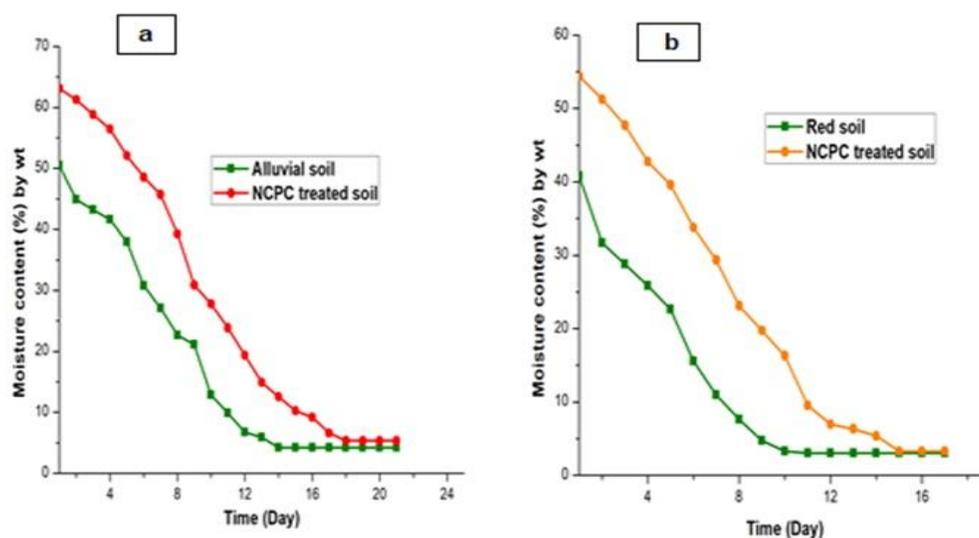


Fig. 4. Change in soil moisture regime in (a) Alluvial soil (b) Red soil

Table 2. Changes in Soil moisture constants after addition of NCPC in soil

Soil moisture constant	Inceptisol (%)		Alfisol (%)	
	No NCPC treated soil	NCPC treated soil	No NCPC treated soil	NCPC treated soil
Water holding capacity( $\Theta_s$ )	50.45	63.1	40.79	54.40
Field capacity( $\Theta_{FC}$ )	27.9	34.85	22.74	29.88
Permanent wilting point ( $\Theta_{PWP}$ )	5.86	6.6	4.7	5.36

NCPC treated alluvial soil have 4% more available moisture than untreated alluvial soil. In red soil advantage of 6% in available water content has been found. Polymer composite could absorb and store a large quantity of the water in soil, and allow the water absorbed in it to be released slowly with the decrease of the soil moisture [12]. This lets the water in soil evaporate more slowly so that it could be efficiently used by the plants and improved the utilization efficiency of water. Thus, it can prolong irrigation cycles and reduce irrigation frequencies, strengthening the ability of plants to survive in water stress condition.

### 3.4 FTIR Study

Composite with 7% clay loading performed better in terms of water retention behaviour of soil and was further characterized for spectral and morphological identification. The FTIR spectrum was in the range of 4000–400 $\text{cm}^{-1}$  wave number and shown in Fig. 6 (a, b). In the spectrum of halloysite, the absorption peaks at 3699

$\text{cm}^{-1}$  and 3627  $\text{cm}^{-1}$  were attributed to the stretching vibrations of hydroxyl groups at the surface of halloysite clay, peak at 1634  $\text{cm}^{-1}$  represented -OH deformation of water, perpendicular stretching of Si-O was visible at 1116  $\text{cm}^{-1}$ , 755  $\text{cm}^{-1}$  and 695  $\text{cm}^{-1}$  wave number [13]. Characteristic peaks of each component existed in the spectrum of the Halloysite nanotube-polymer composite.

The Al-OH stretching peaks at 3695  $\text{cm}^{-1}$  and 3624  $\text{cm}^{-1}$  wave number was disappeared in the spectrum because of the reaction between -C=C- in acrylic acid and hydroxyl group of halloysite nanotube. Peaks observed were at 3404.7  $\text{cm}^{-1}$  wavenumber corresponds to the N-H stretching of acrylamide unit, peak at 1460  $\text{cm}^{-1}$  indicated -CH<sub>2</sub>- group presence on the chain [13]. The characteristic band at 1572  $\text{cm}^{-1}$  was due to C=O asymmetric stretching in carboxylate anion that was reconfirmed by another peak at 1410  $\text{cm}^{-1}$ , which was related to the symmetric stretching mode of the carboxylate group [13]. However, the hydroxyl bending became wide and strong in

the frequency area of  $3427\text{ cm}^{-1}$  and was due to generation of hydrogen bonds between hydroxyl group of acrylic acid vibrating and silicate layers.

### 3.5 XRD

Halloysite nano tube showed two diffraction peaks one at  $11.17\ 2\theta^\circ$  and other at  $19.91\ 2\theta^\circ$

representing d spacing of  $7.72\ \text{A}^\circ$  and  $4.45\ \text{A}^\circ$ , respectively. The basal (d001) reflections were indication of fully hydrated ( $10\ \text{A}^\circ$ ), partially hydrated ( $7\text{--}10\ \text{A}^\circ$ ), and dehydrated ( $7\ \text{A}^\circ$ ) halloysite. The basal spacing reflections indicated a sharp peak at  $2\theta^\circ - 11.45$ , which translated to a basal spacing of  $7.72\ \text{A}^\circ$  [13].

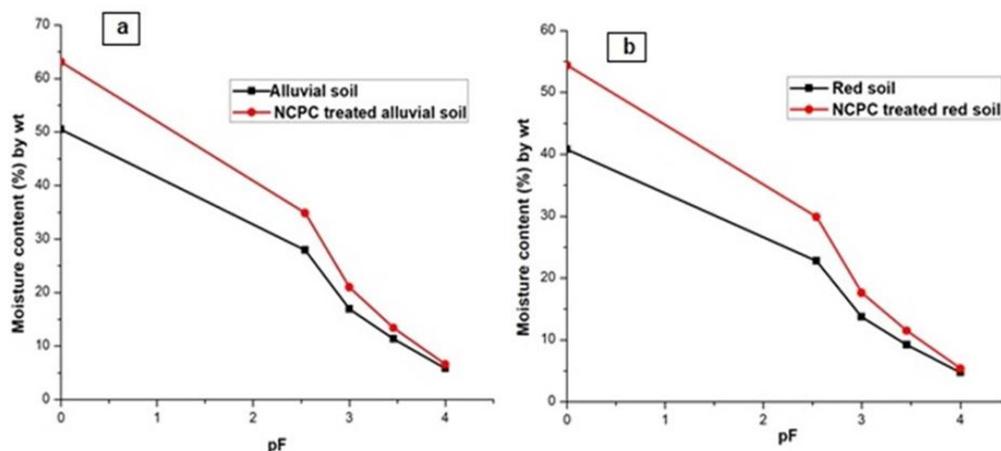


Fig. 5. Soil moisture characteristic curve after addition of NCPC in (a) Alluvial Soil (b) Red soil

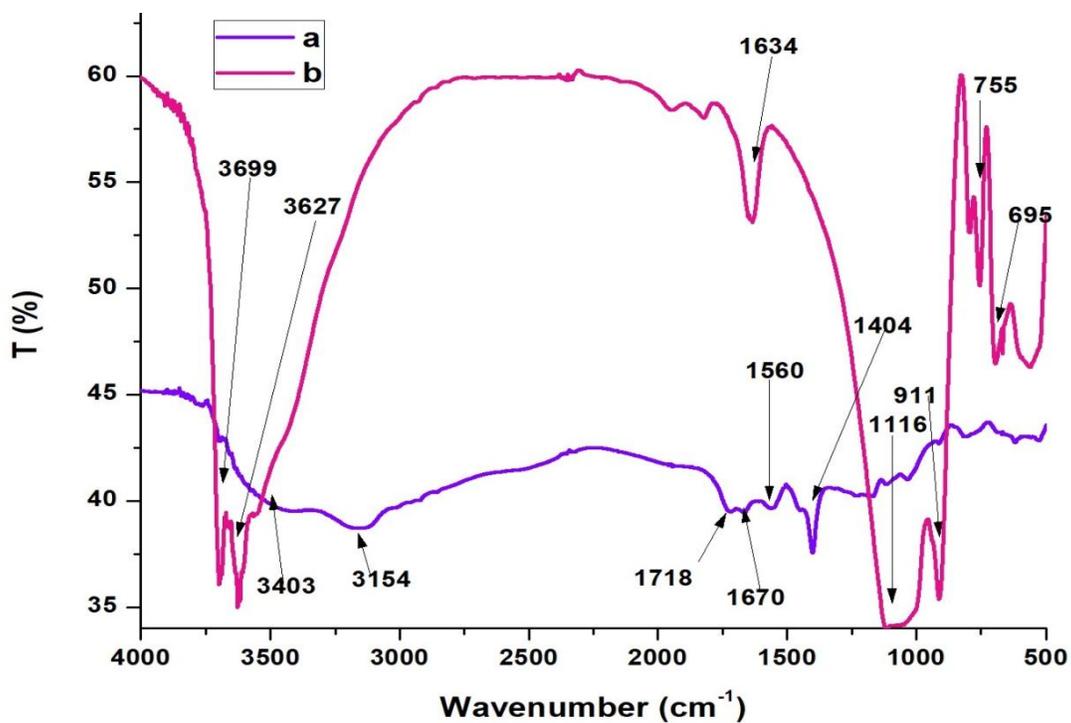


Fig. 6. FTIR spectra of (a) Halloysite nanotube polymer composite (b) Halloysite nanotube

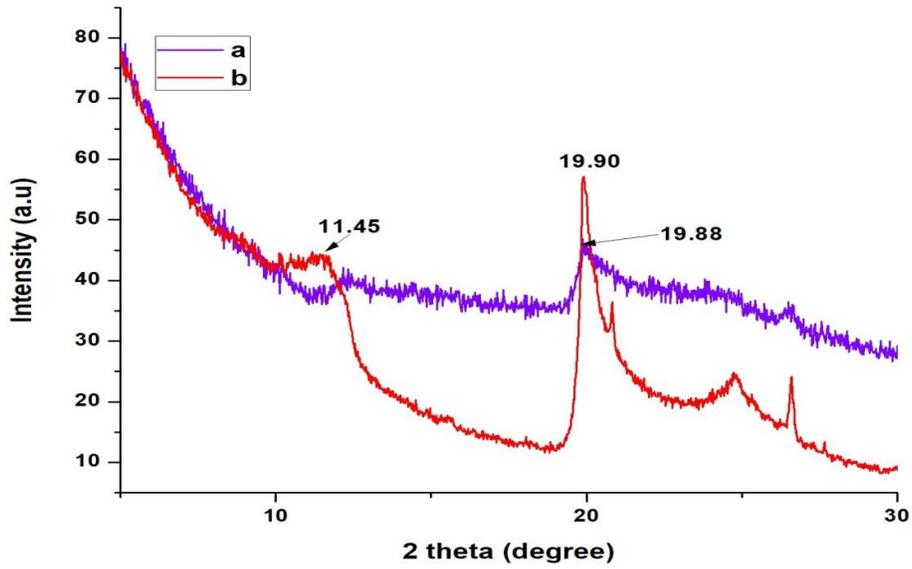


Fig. 7. X-ray diffraction (a) Halloysite nanotube polymer composite (7 % clay loading) (b) Halloysite nanotube

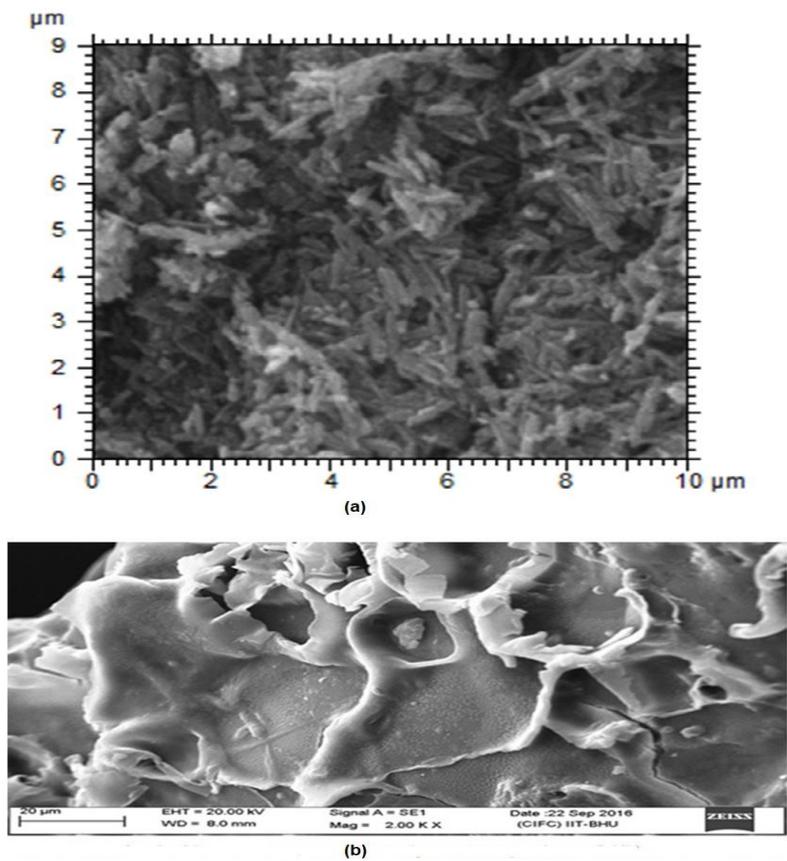
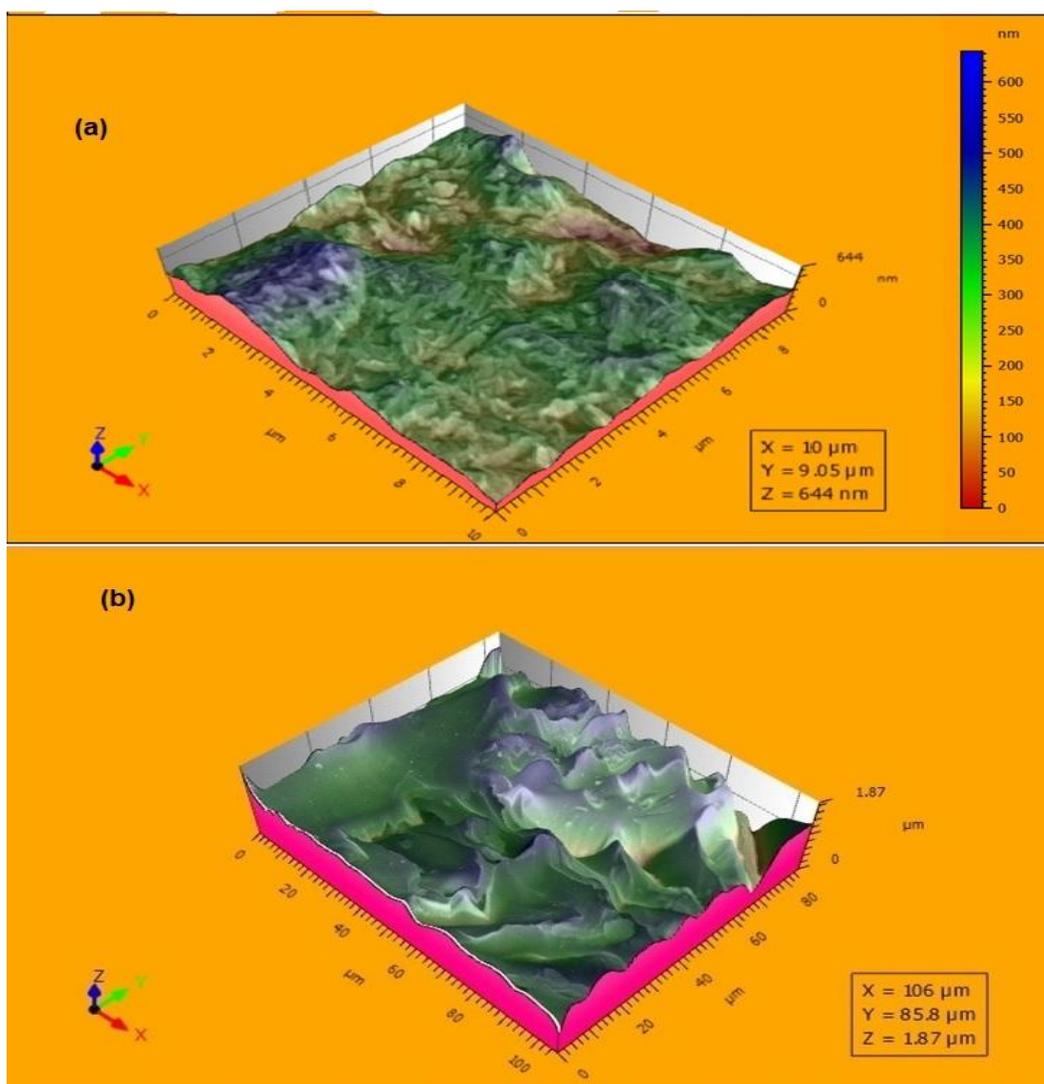


Fig. 8. SEM images of Halloysite nano tube (a) and Halloysite nanotube polymer composite (b)

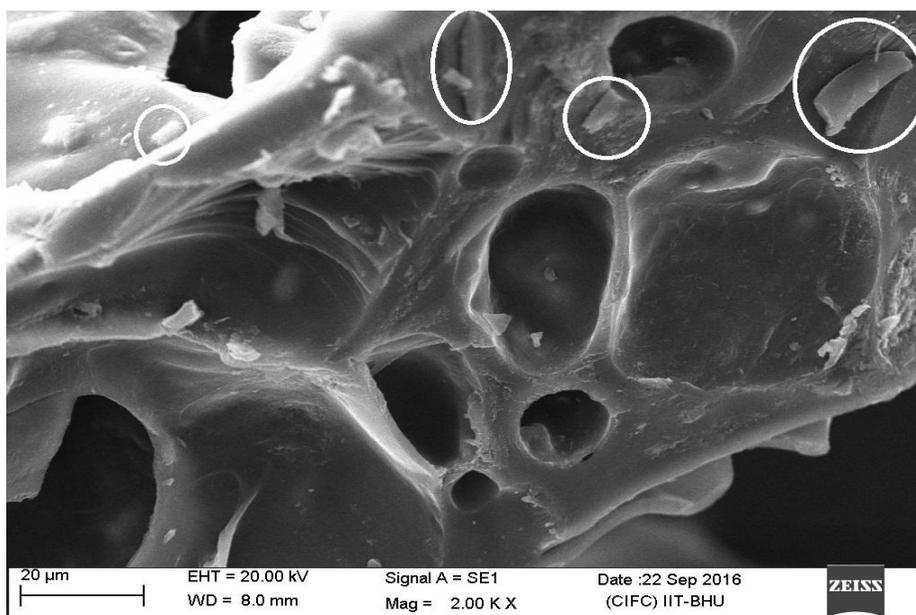


**Fig. 9. Three dimensional image of Halloysite nanotube (a) and Halloysite nanotube polymer composite (b)**

However, no peak was observed at  $2\theta=8.76$  indicating the absence of the  $10 \text{ \AA}$  form of halloysite nano tube. Halloysite used in this study was in partially hydrated state. In addition, the presence of the very intense reflection at  $\sim 4.45 \text{ \AA}$  was the diagnostic feature of common tubular morphology of halloysite. Results were in agreement with the result of [13,14]. Peak of halloysite after polymerization reaction diminished at  $7.72 \text{ \AA}$  and the peak at  $4.45 \text{ \AA}$  broadens indicating both internal and external surface of clay had been involved in polymerization reaction and clay was exfoliated in polymer matrix [15, 17, and 18].

### 3.6 SEM

Water absorbency and retention rate of polymer composite depend on its porous nature. The porous structure is favorable to water molecular diffusion and also provides sufficient space for potential adsorption of water molecules. Fig. 8 and Fig. 9 exhibits a magnified image, showing the fine surface structure of halloysite nano tube polymer composite. It was found that the halloysite nanotube could uniformly distribute in the composite. No aggregate of the HNTs can be found in any composites. The good dispersion of halloysite nanotube is attributed to the proper



**Fig. 10. Halloysite nanotube polymer composite with 7 % clay loading (The region in white circle represent the tube dispersed in polymer matrix)**

aspect ratio and relatively weak tube–tube interactions of halloysite. Results of present investigation corroborate with earlier findings of [13,16]. From the SEM Fig. 10, it can be seen that the outer walls of halloysite are less distinguished compared to that of raw halloysite, indicating the wrapping of tubes by the grafted polyacrylamide chains. This is attributed to the formation of hydrogen bond and charge interactions between halloysite and chains as illustrated by FTIR results discussed above which was in good agreement with literature [17].

#### 4. CONCLUSION

A novel halloysite clay-based polymer composite has been synthesized by free radical polymerization reaction. The prepared composite had a porous structure confirmed by SEM. Addition of clay (7%) in composite improved its water sorption property. Water retention behaviour of soil treated with nano clay polymer composite was also improved and showed higher moisture regime at saturation, field capacity and temporary wilting point. The developed soil moisture characteristics curve explained variation in water potential  $\psi$  and soil wetness  $\Theta$  values. The higher moisture regime and significantly higher available water content in soil moisture characteristic curve induces delayed attainment of temporary (after 4 days) and permanent wilting point to reach after 6 days as compared to

control soil, where no NCPC was added. The synthesized clay composite can help in supplementing moisture and dissolved nutrients in plants to mitigate water stress condition for a prolonged period of 4-6 days depending on evapotranspiration demand of crops.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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