

**SYNTHESIS, CHARACTERIZATION AND CONTROLLED RELEASE STUDY OF ZN FROM ZINCATED NANOCLAY POLYMER COMPOSITES (ZNCPCs) IN RELATION TO EQUILIBRIUM WATER ABSORBENCY UNDER ZINC DEFICIENT TYPIC HAPLUSTEPT**

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**ABSTRACT**

*Zn deficiency is a widespread phenomenon globally. Conventional Zn fertilizers ( $ZnSO_4 \cdot 7 H_2O$ ), being highly soluble in water when applied to soils have very low use efficiency (1-5%) owing to its interaction with soil components. An attempt was made in formulating novel Zincated nanoclay polymer composites (ZNCPCs) with variable percentage of commercial bentonite and nanobentonite (8, 10 and 12 % of monomer for each case). Polyacrylic acid-Polyacrylamide copolymer was synthesized using N,N-Methylene bisacrylamide (NNMBA) as crosslinker and ammonium persulfate (APS) as initiator. Zinc was loaded as  $ZnSO_4 \cdot 7 H_2O$  during in-situ polymerization. Clays as well as ZNCPCs were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). TEM image of clays (bentonite) and nanoclay (nanobentonite) confirmed that fractionated bentonite (nanoclays) average diameter was <100 nm. It was confirmed that clays were completely dispersed inside the polymeric matrixes via exfoliation (disappearance of typical XRD peak of clays) and there were interactions among functional groups present in clays and polymers (Disappearance of -OH stretching vibration of clays and weakening of Si-O stretching vibration). ZNCPCs were evaluated in terms of controlled release of Zn in two Zn deficient soil (Typic Haplustept). It was found that formulations having 12 % nanoclay showed slowest release rate. Formulation containing 8 % clays showed highest equilibrium water absorbency.*

**Key words:** ZNCPCs, controlled release, equilibrium water absorbency, moisture characteristics

**INTRODUCTION**

Zinc deficiency is dominant micronutrient deficiency in Indian soils. Zinc availability in soil is controlled by various interactive factor namely, soil reaction, clays, presence of competitive cations ( $Fe^{+2}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ) and anions ( $CO_3^{2-}$ ,  $PO_4^{3-}$  etc. Zn fertilizers ( $ZnSO_4 \cdot 7H_2O$ ) when applied in soils, fertilizer use efficiency rarely exceeds 1-2% (Rattan *et al.* 2008). Not only, micronutrient content in soils but also limited amount of moisture availability results into lower availability of Zn to plant roots. Hence, there is need for developing fertilizer formulation which will be having controlled release behaviour in soil as well as moisture availability in soils increased. In recent times, attempt has been tried for developing nanoclay (having at least one dimension in 1-100 nm) direction has been tried to develop polymeric N, P formulation and there are reported to have controlled release property (Sarkar *et al.*, 2013). Keeping in view this background a novel nano clay polymer based fertilizer formulation was undertaken with objective to synthesize and characterize nano clay polymer composites based Zn fertilizer formulation and study controlled release behaviour of Zn in Zn deficient soils and moisture characteristics of ZNCPCs.

**MATERIALS AND METHODS**

**Separation of nanoclay from commercial bentonite**

Bentonite suspension was agitated in the mechanical shaker for forty minutes and then

fractionation of nanofraction was done by centrifugation method, time and speed of centrifugation was calculated based on Stokes' law. Centrifugation was done at 12000 rpm (equivalent to 17000 G) (Sarkar *et al.*, 2013) for 12 minutes to isolate < 80 nm clay particles. After centrifugation, the supernatant suspension was collected. The sediment in the centrifuging tubes was again brought into suspension and then centrifuging again for particular time and speed as specified earlier. This process was repeated to collect all nanoclay present in the suspension. Commercial bentonite and nanoclay was characterized in terms of specific surface area (SSA) (Jackson, 1973), crystallinity (X-ray diffractogram), Functional group analysis (FTIR spectra) (Sarkar *et al.*, 2013) and particle size (Transmission Electron Microscopy, TEM) (Sarkar *et al.*, 2013).

**Synthesis of Zincated nanoclay polymer composites (ZNCPCs)**

Synthesis of acrylic acid-acrylamide copolymer was done as per procedure outlined by Liang and Liu, (2007) with modifications as described hereunder: Acrylic acid (23.04 g) (AA) was neutralized with ammonia ( $NH_3$ ), neutralization degree being (60%) in a four necked reaction vessel (connected with condenser, thermometer and nitrogen line). Acrylamide (Am) (4.6 g) was added to the reaction vessel, after the neutralization reaction is over and there is no fume of ammonia present therein.

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Commercial bentonite and nanoclays were added as , 10% and 12% of total AA+Am , which were considered as treatment T1, T2, T3, T4 , T5 and T6 , respectively (Table 3). Zinc was added as Zinc sulphate ( $ZnSO_4 \cdot 7 H_2O$ ) and maximum amount (5 % of Zn of AA+AM+clay) of percentage of Zn loading was attempted. A crosslinking agent N, N Methylene bisacrylamide (NNMBA) was added (0.2308 g) which acted as a crosslinking agents. Ammonium persulfate (APS) (0.3204 g) was added as initiator. The reaction was carried out in a magnetic stirrer with hot plate and temperature gradually increased to 70°C. At the end of polymerization reaction, as the reaction was exothermic the heating was slowed down and the magnetic stirrer stopped moving as viscosity increased. After reaction was over, the synthesized polymer composites was washed with distilled water and collected in petriplates. NCPCs were dried in vacuum oven, under reduced pressure and at a temperature (60-70 °C). NCPCs were grinded in a mixer grinder and passed through 2 mm sieve for uniform particle size.

#### Estimation of Zn content in ZNCPCs

Tri acid ( $HNO_3$ :  $HClO_4$ :  $H_2SO_4$ :: 10:4:1) digestion procedure was followed (Paget *et al.*, 1982). At first 1 g sample (powdered and passed through 2 mm screen sieve) was taken in 250 ml conical flask and 5 ml con.  $HNO_3$  was added for pre-digestion and kept overnight. And then the remaining amount of tri-acid mixture was added and kept at hot plate at temperature of 200°C until the digestion is completed by appearance of dense white fumes. Digestion flasks were cooled down and then entire amount of digest was transferred quantitatively to 100 ml volumetric flask by washing with 6 N HCl. From this, 5 ml sample was taken for determination of Zn content by Atomic absorption spectrophotometer (AAS). Data was represented as % of Zn.

#### Controlled release study of Zn from different ZNCPCs

Controlled release study of Zn from NCPCs was carried out in specimen tube (60 ml capacity, Tarson make) taking two different Zn deficient soils. Field capacity moisture content was maintained. ZNCPCs was taken in nylon fiber packs (Amount taken which can provide 10 mg Zn  $kg^{-1}$ ) of soil. After incubation time intervals (0, 15, 30, 45 and 60 days ) soil was taken and DTPA extractable Zn (Lindsay and Norvell, 1978) and 0.5 M  $NaHCO_3$  extractable P was determined [Olsen *et al.* (1954); Watanabe and Olsen (1965)]. . Whole set of system was maintained in an incubator and under uniform temperature of 30°C.

#### Water absorbency experiment

Equilibrium water absorbency of ZNCPCs were determined by following procedure of Singh *et al.* (2011). A composite sample weighing 0.1 g (passed through 2 mm sieve) was immersed in the excess of distilled water (pH 7.0, EC 0.001 mhos/cm) in triplicate and kept room temperature (@ 25° C ) separately until equilibrium was attained. Free water was filtered through a nylon sieve (200 mesh size), gel allowed to drain on sieve for 10 min, and finally weighed. The water absorbency ( $Q_{H_2O}$ ) was calculated using the following equation:

$$Q_{H_2O} (g g^{-1}) = (w_2 - w_1) / w_1$$

where  $w_1$  is the weight of NCPCs and  $w_2$  is the weight of swollen gel.  $Q_{H_2O}$  was calculated as grams of water per gram of dry sample.

#### Specific surface area

Specific surface area of clay (commercial bentonite) and nano clay (fractionated bentonite) was determined by following standard procedure as outlined by Jackson *et al.* (1973). Cation exchange capacity (CEC) was also determined (Jackson *et al.* 1973).

#### X-ray Diffraction Analysis (XRD)

Original bentonite, fractionated nanoclay and ZNCPCs were subjected to XRD analysis by random powder diffraction method. Radiation type was  $CuK\alpha$ , (PHILIPS PW1710 diffractometer control equipped with PHILIPS PW1728 X-ray generator Phillip) Generator voltage 40 kV, Tube current 20 mA, Start angle ( $2\theta$ ) 3°, End angle ( $2\theta$ ) 40°, Scan step size 0.1, scan type : continuous, Scan speed ( $2\theta$   $Sec^{-1}$ ) 0.025.

#### Fourier Transform Infra-red spectrophotometer (FTIR)

Infrared spectroscopy of the powdered samples was carried out by using the Bruker: ALPHA, FTIR/ATR system (Typically 24 scans, Resolution-4 $cm^{-1}$ ). Samples were scanned in the region of 4000-400  $cm^{-1}$

#### Transmission Electron Microscopy (TEM)

TEM image of commercial bentonite and fractionated nanoclay were taken through a TEM made by JEOL, Japan (JEN 1011, 100 KV). Specific instrumental set-up was 80 kV HV with magnification 80000 X.

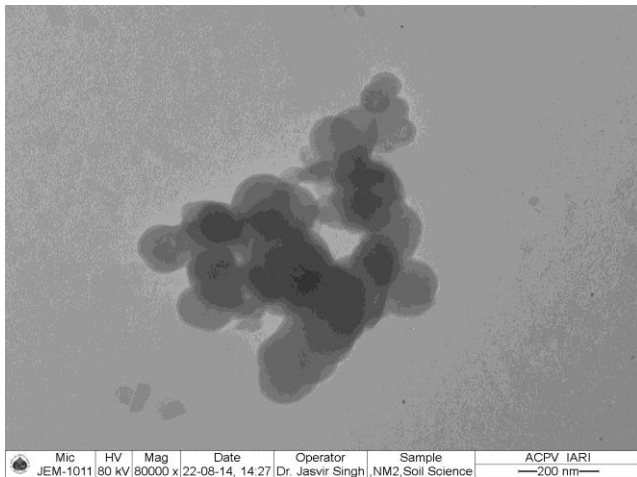
#### Soil characteristics

Two types of Zn deficient soils used for experimental condition, one from Haryana (Typic Haplustept I) and other from Gujrat (Anand, Typic Haplustept II) were collected from top soil layer following standard soil sampling procedure. Samples were dried in shed and ground and passed through 2 mm sieve. Collected soils samples were analyzed for

Table 1: Physico-chemical characteristics of experimental soils

Parameter	Typic Haplustept I	Typic Haplustept II
pH <sub>1:2</sub>	7.2	7.5
EC <sub>1:2</sub> (dS m <sup>-1</sup> )	0.26	0.30
Texture	Sandy loam	Sandy loam
Organic carbon (g kg <sup>-1</sup> )	3.0	4.5
Available N (kg ha <sup>-1</sup> )	120	130
Available P (kg ha <sup>-1</sup> )	10	15
Available K (kg ha <sup>-1</sup> )	129	150
Available S (mg kg <sup>-1</sup> )	7.2	10
Available Zn (mg kg <sup>-1</sup> )	0.45	0.50

different physico-chemical properties (Table 1). The soils were mildly alkaline, non-saline, low in organic C, 0.32 % KMnO<sub>4</sub> extractable N, 0.16 % CaCl<sub>2</sub> extractable S (Williams and Steinesbergs, 1959), 1 N NH<sub>4</sub>OAc extractable K and low 0.5 M NaHCO<sub>3</sub> extractable P and low in 0.05 M DTPA-extractable Zn (Lindsay and Norvell, 1978). The data generated were processed for analysis of variance as applicable



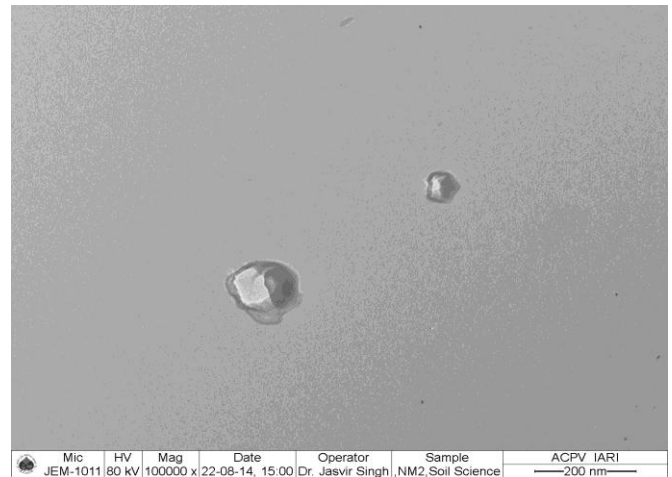
(a)

to completely randomized design to test differences among the treatment means as described by Gomez and Gomez (1984).

## RESULTS AND DISCUSSIONS

### Nanosize clay content and its properties

Continuous centrifugation revealed that the nanosize (1-100 nm) clay content in commercial bentonite used was 70 %. Fractionated bentonite was in nanosize (<100 nm), which was confirmed through TEM image (Fig. 1a and 1b). Specific surface area of commercial bentonite (referred to as clay) was 369.76 m<sup>2</sup> g<sup>-1</sup> whereas for fractionated nanoclay, it was 730.83 m<sup>2</sup> g<sup>-1</sup> (Table 2). Specific surface area of fractionated nanoclay was higher as compared to commercial bentonite. Cation exchange capacity (cmol (p+) kg<sup>-1</sup>) for commercial bentonite and fractionated nanoclay were 83.95 and 160.87 respectively. Cation exchange capacity was higher in case of nanoclay as compared with commercial bentonite.



(b)

Fig. 1: Transmission electron microscopy (TEM) image of clay (commercial bentonite) (a) and nanoclay (fractionated bentonite) (b)

### X ray diffraction (XRD) pattern of clay and nanoclay

Commercial bentonite and fractionated nanoclay were characterized through XRD by random powder diffraction method. The results showed that the presence of smectitic clay minerals ( $2\theta=6^\circ$ ) (Fig. 2) and other impurities such as quartz was present. However, the intensity of peak for fractionated nanoclay (containing 100 % clay in nanosized) was higher as compared to commercial bentonite.

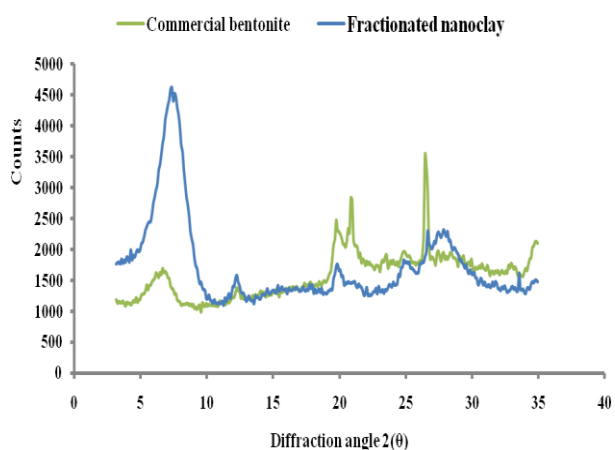


Fig. 2: XRD pattern of commercial bentonite and fractionated nanoclay

### XRD analysis of ZNCPCs

XRD analysis clearly shows that the typical montmorillonite peak ( $2\theta=6^\circ$ ) becomes absent in ZNCPCs (Fig 4a and 4b). Absence of typical montmorillonite peak clearly indicates that bentonite

clays completely disperse into the polymer matrixes which implies that the ZNCPCs prepared are exfoliated type of composites. Irrespective of types and % of clays exfoliation was observed. Sarkar *et al.* (2013) also observed similar types of observation.

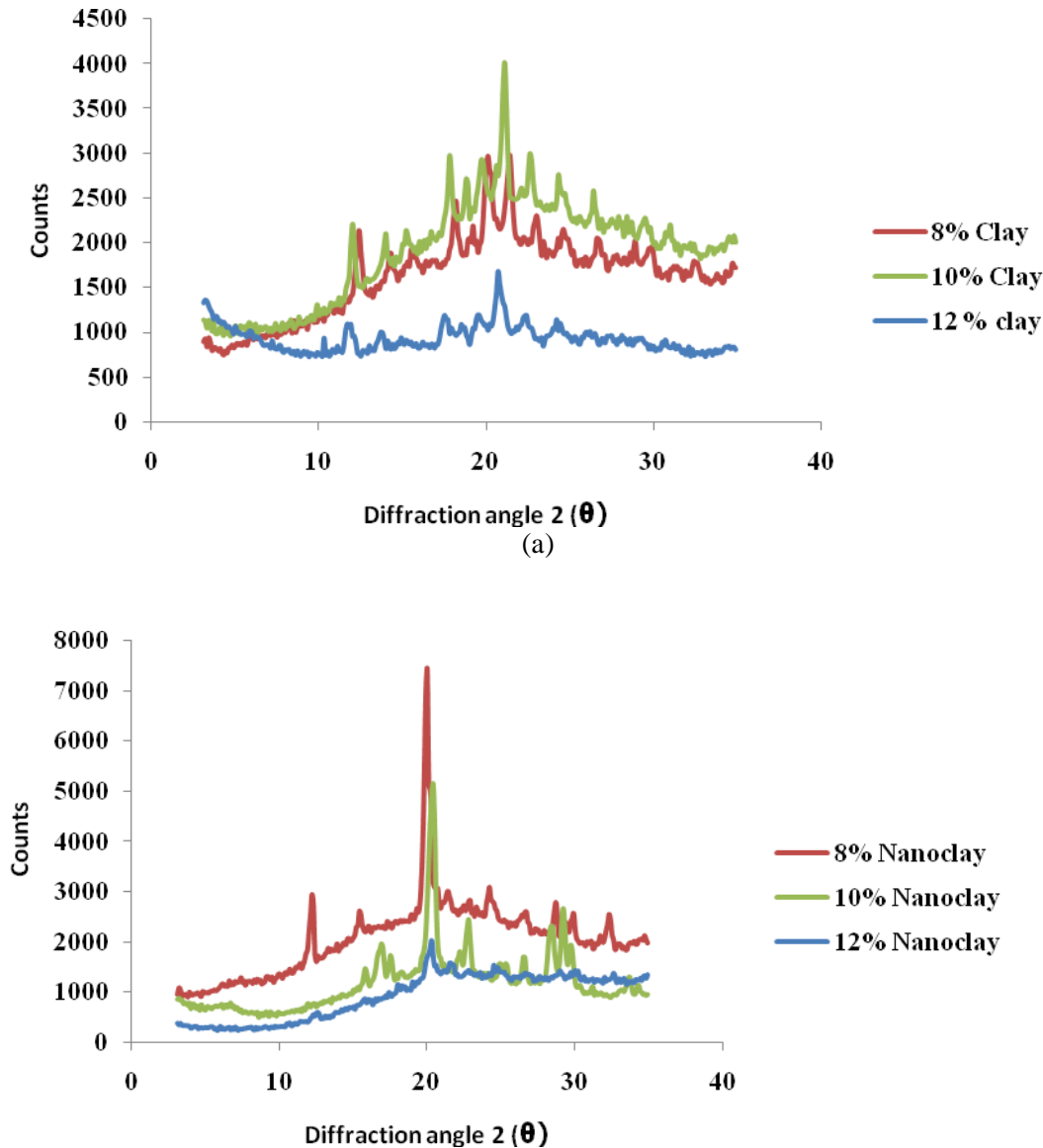
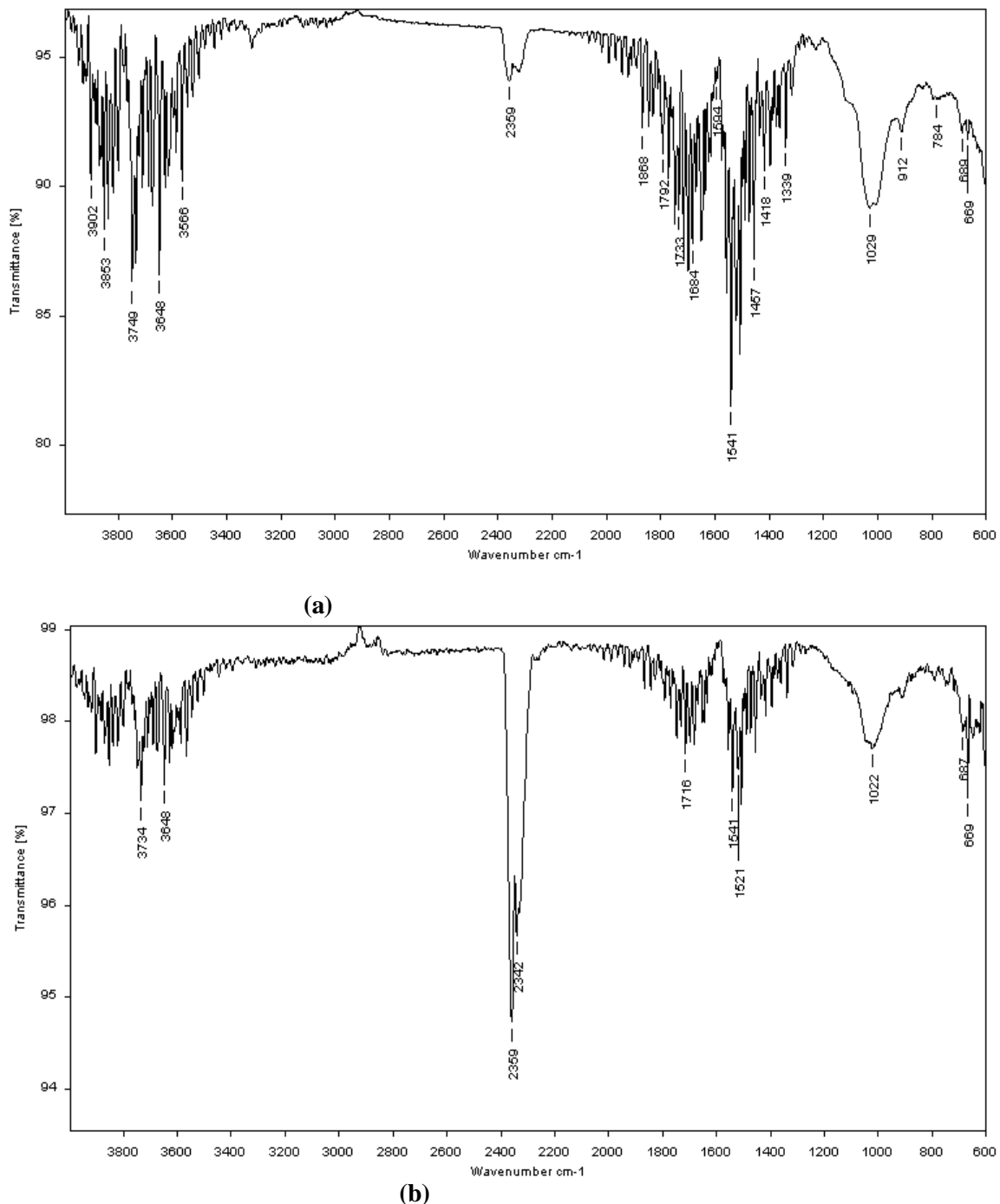


Fig. 4 XRD of ZNCPCs at various % of clay (a) and fractionated nanoclay (b)

### Fourier transform infrared spectroscopy (FTIR)

The strong band occurring around in the range of  $3400$  to  $3800\text{ cm}^{-1}$  is attributed to the stretching vibration of the Mg–OH, Al–OH or Fe–OH structural hydroxyls groups, typical of montmorillonite (Fig. 3a and b). The other vibrational modes characteristic of this clay mineral are the broad band at  $1020\text{ cm}^{-1}$  assigned to Si–O stretching

vibrations of the Si–O–Si tetrahedron, the band around  $500\text{--}700\text{ cm}^{-1}$  assigned to the angular deformation of Si–O–Al and the band centered at  $470\text{ cm}^{-1}$  assigned to the angular deformation of Si–O–Si. There was appearance of a small band at  $2359\text{ cm}^{-1}$  at FTIR spectra of commercial bentonite which was found to be more intensified for fractionated nanoclay (Fig. 3 a and 3 b)

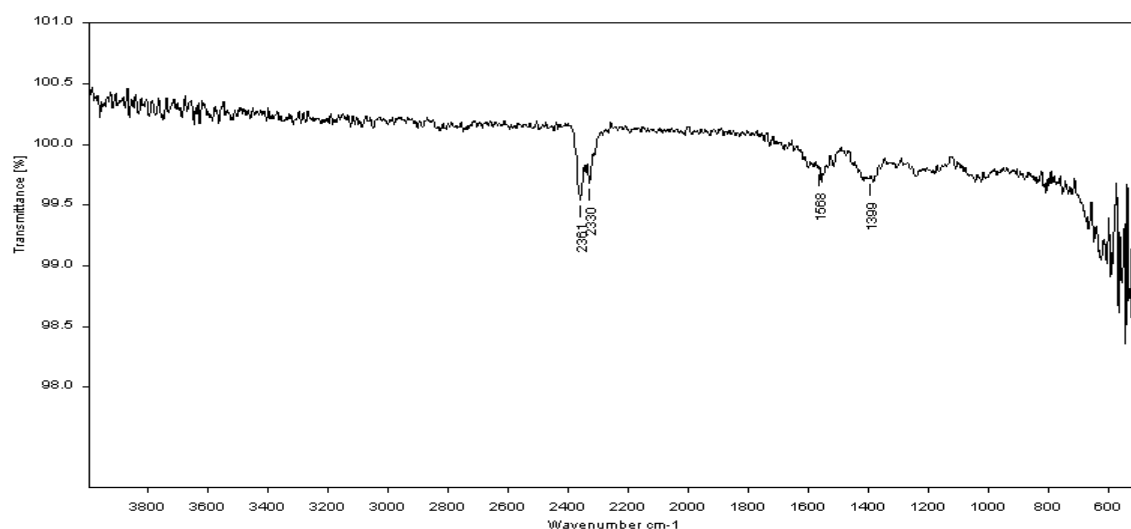


**Fig. 3:** FTIR spectra of commercial clay (a) and nanoclay (b)

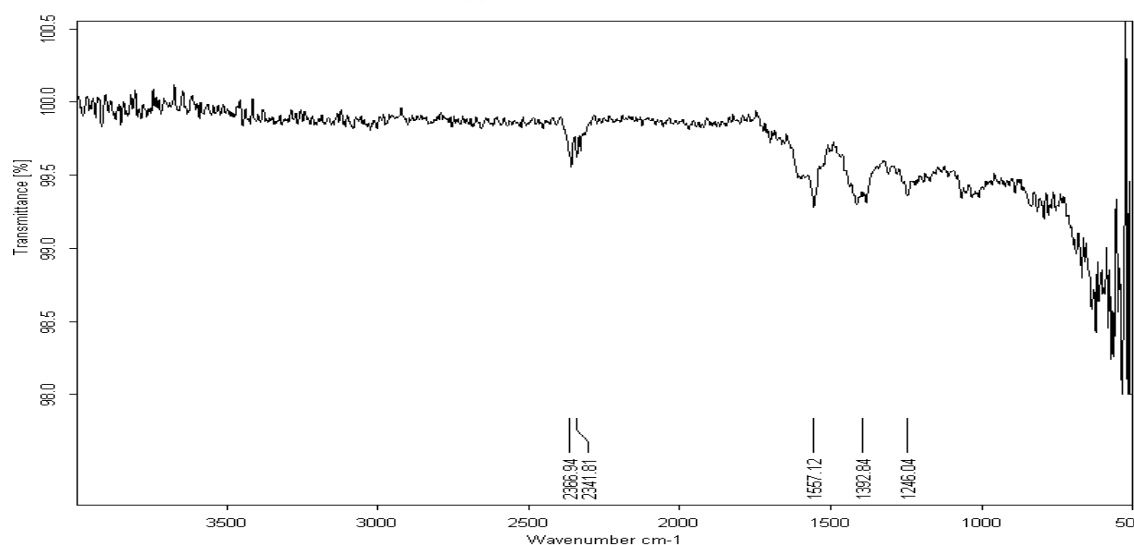
### FTIR spectra of ZNCPCs

The characteristics peak of  $-\text{OH}$  stretching vibration ( $3400 \text{ cm}^{-1}$  to  $3800 \text{ cm}^{-1}$ ) (Wolters and Emmerich, 2007) as observed in case of original and nanobentonites disappeared in case of ZNCPCs irrespective of clay types and % clay contents (Fig. 5a and b)). Absorption band at  $1030 \text{ cm}^{-1}$  (Si-O stretching) disappeared in ZCPNCs indicating the interaction of clays ( $-\text{OH}$ ) groups occur during

copolymerization reaction. The absorption band at  $1690 \text{ cm}^{-1}$ , ascribed to the  $-\text{CONH}_2$  of the pure polymer, shifted to  $1704$ , and  $1717 \text{ cm}^{-1}$  (Sarkar *et al.*, 2013) in the this indicated that the interaction between the clays and polymer had some influence on the chemical environment of  $-\text{CONH}_2$  and/or  $-\text{COO}-$  and might have had some influence on the physicochemical properties of the corresponding superabsorbent composites.



(a)



(b)

Fig. 5: FTIR spectra of ZNCPCs containing 10 % clay (a) and 10% nanoclay (b)

**Total Zn content in ZNCPC**

Total Zn content in ZNCPC ranged from 3.30

to 3.12 %. Highest Zn content was found in T5 followed by treatment T2 (Table 2).

Table 2: Treatment details along with Zn content (%) and equilibrium water absorbency of various ZNCPCs

Polymer notation	Polymer combination	Type of clay	Clay content (% of monomer)	Zn content (%)	Equilibrium water absorbency (g water g <sup>-1</sup> of ZNCPCs)
T <sub>1</sub>	Acrylic acid+Acrylamide	Bentonite	8	3.28	250
T <sub>2</sub>	Acrylic acid+Acrylamide	Bentonite	10	3.12	237
T <sub>3</sub>	Acrylic acid+Acrylamide	Bentonite	12	3.25	227
T <sub>4</sub>	Acrylic acid+Acrylamide	Nanobentonite	8	3.17	241
T <sub>5</sub>	Acrylic acid+Acrylamide	Nanobentonite	10	3.30	225
T <sub>6</sub>	Acrylic acid+Acrylamide	Nanobentonite	12	3.21	217
LSD (P=0.01)		-	-	-	4

**Effect of clay types and clay content on equilibrium water absorbency of ZNCPCs**

With increase in % clay (8, 10 and 12%) content, irrespective of clay types there were decrease in equilibrium water absorbency (g water g<sup>-1</sup> of

ZNCPCs). So far, clay type is concerned, nanoclay (irrespective of % clay) showed lower water absorbency. Water absorbency followed trend as: T1 < T4 < T2 < T5 < T3 < T6.

Highest equilibrium water absorbency was recorded for T1 (250 g water absorbed  $\text{g}^{-1}$  of ZNCPCs) and lowest water absorbency was found for T6 (217 g water absorbed  $\text{g}^{-1}$  of ZNCPCs).

#### Effect of clay types and % clay content on equilibrium water absorbency

Exfoliation of clay platelets into the polymeric matrixes increased with % increase in clay content and as compared with commercial bentonite, fractionated nanoclay has greater exfoliation. There was decrease in equilibrium water absorbency with increase in clay content as crosslinking density of polymeric matrixes increases with increases in clay content. These results are in conformity with previous worker (Sarkar *et al.*, 2013; Singh *et al.*, 2011). Nanoclay having more pronounced effect owing to higher cation exchange capacity and specific surface area occurred due to sufficient delamination of montmorillonite types of clay minerals (Hrachova *et al.*, 2008; Cataldo, 2007). Burnside and Giannelis, (2000) reported relationship between nanostructure and properties in polysiloxane layered silicate nanocomposites. Nanocomposites showed a significant decrease in swelling, even for very low filler loading (1% vol.) compared to conventional

composites. They also reported that strongly interacting filler reduces swelling owing to the formation of “bonds” in close proximity to the filler which is either physically or chemically sorbed and therefore restricted swelling

#### Effect of clay types and % clay content in controlled release of Zn in Typic Haplustept I and Typic Haplustept II during incubation time

#### Controlled release of Zn in soils Soil Typic Haplustept I

Clay content and clay type both has significant impact on release of Zn (DTPA extractable) in soil (Table 3). At same % of clay content, nanoclay recorded slower release rate as compared to clay throughout incubation time periods and across soil types. Contrasting result was observed for treatment T<sub>7</sub> ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), at initial periods of incubation there was higher DTPA extractable Zn content in soil, but as incubation progressed (15-60 days) content of DTPA extractable Zn decreased. At 60 days after incubation, maximum DTPA extractable Zn content was found for T<sub>1</sub> ( $4.5 \text{ mg kg}^{-1}$ ) whereas minimum was recorded for T<sub>7</sub> ( $2.5 \text{ mg kg}^{-1}$ ).

Table3: Release of DTPA extractable Zn ( $\text{mg kg}^{-1}$  soil) as affected by different polymer combination throughout incubation period in soil

Treatment	Typic Haplustept I				Typic Haplustept II			
	15 days	30 days	45 days	60 days	15 days	30 days	45 days	60 days
T <sub>1</sub>	3.20	3.82	4.23	4.5	3.11	2.68	3.02	3.65
T <sub>2</sub>	3.13	3.77	4.15	4.41	3.05	2.49	2.95	3.57
T <sub>3</sub>	3.03	3.6	4.1	4.39	2.97	2.26	2.92	3.49
T <sub>4</sub>	3.11	3.72	4.17	4.44	3.07	2.68	2.94	3.42
T <sub>5</sub>	3.02	3.62	4.07	4.37	2.98	2.42	2.75	3.37
T <sub>6</sub>	2.97	3.55	4.02	4.31	2.91	2.12	2.71	3.31
LSD (P=0.01)	5.12	3.26	2.97	2.5	5.01	2.03	2.82	2.43
T <sub>1</sub>	0.20	0.15	0.26	0.15	0.15	0.11	0.18	3.65

T1 : 8 % clay ;T 2: 10% clay; T3: 12 % clay T4 : 8 % nanoclay ;T 5: 10% nanoclay; T6: 12 % nano clay and T7: Conventional Zn sources ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ )

#### Controlled release of Zn in soils Soil Typic Haplustept I

Similar trend of result was observed for Typic Haplustept II also. Nanoclay was effective in slow release of Zn in soil as compared to clay at same percentage of clay. Zn sources as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , maintained higher DTPA extractable Zn at initial periods of incubation (15 days after incubation) but as incubation periods progressed, content of DTPA extractable Zn decreed. After 60 days of incubation maximum Zn content was recorded for T1 ( $3.65 \text{ mg kg}^{-1}$ ) whereas minimum was recorded for T7 ( $2.43 \text{ mg kg}^{-1}$ ) (Table 3).As compared with Typic

Haplustept II, Typic Haplustept I, maintained relatively higher content of DTPA extractable Zn throughout incubation periods and irrespective of treatment combinations. In soil II, there was no significant difference irrespective of clay types and % of clays regarding release of DTPA extractable Zn in soil at incubation time interval II (15 days after incubation Table 4).There was significant difference between different treatments and types of clays regarding controlled release of Zn at incubation time interval II (30 days after incubation).However, no significant difference was observed irrespective of either clay types or percentage of clays at incubation

time interval III. At incubation time IV (60 days after incubation) there was significant difference regarding types of clays and % content of clays. However, T2 and T4 differed do not differed significantly. Clay types and clay content have significant bearing on the controlled release behaviour of nutrients irrespective of soil types. Inorganic fillers (silicate clays) are believed to increase the barrier properties by creating a maze or “tortuous path” that retards the progress of gas molecules through the polymeric matrixes (Sinha Roy and Okomoto, 2003). The direct benefit of the formation of a path is clearly observed in all the prepared nanocomposites by dramatically improved barrier properties. With increase in clay content there were more controlled release pattern which can be substantiated by the fact that clay increases the crosslinking density of ZNCPCs owing to its exfoliation into the matrixes. This phenomenon can be explained by the fact that two particular characteristics of layered silicates that are generally considered for nanocomposites. The first is the ability of the silicate particles to disperse into individual layers which is technically called *exfoliation*. The second characteristic is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These two characteristics are, of course, interrelated since the degree of dispersion of layered silicate in a particular polymer matrix depends on the interlayer cation (Sinha Roy and Okomoto, 2003). In the present investigation, exfoliation of bentonitic types of minerals (as depicted by XRD) and interaction owing to interlayer cation (as evidenced by FTIR spectra) is

the reason for controlled release of Zn in both soil types.

There is also evidence that nano-sized clay restricts the molecular dynamics of the polymer chains surrounding the clay, thus retarding the relaxation of polymer chains. The retarded relaxation, in turn, reduces the diffusion of small molecules through nanocomposites (Sinha Roy and Okomoto, 2003). Osman and Atallah 2004 suggested that plate-like particles strongly reduce the permeability coefficients of the polymer and their effect depends on the aspect ratio, which in turn depend on degree of exfoliation. At constant clay content, the relative permeability coefficient decreases on increasing the length of clay (Yano *et al.*, 1997). ZNCPCs were effective in controlled release of Zn in soil as compared to conventional sources of Zn ( $ZnSO_4 \cdot 7H_2O$ ). ZNCPC at 12% nanoclay content (T<sub>6</sub>) showed slowest release rate across soil type. However, equilibrium water absorbency was higher in case of T<sub>1</sub> (Containing 8 % clay). ZNCPCs as controlled release Zn source seems to be promising owing to not only maintaining higher amount of DTPA extractable Zn for relatively prolonged periods but also maintaining moisture content simultaneously in soil. Efficacy of ZNCPCs under pot and field experimentation needs to be further investigated.

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