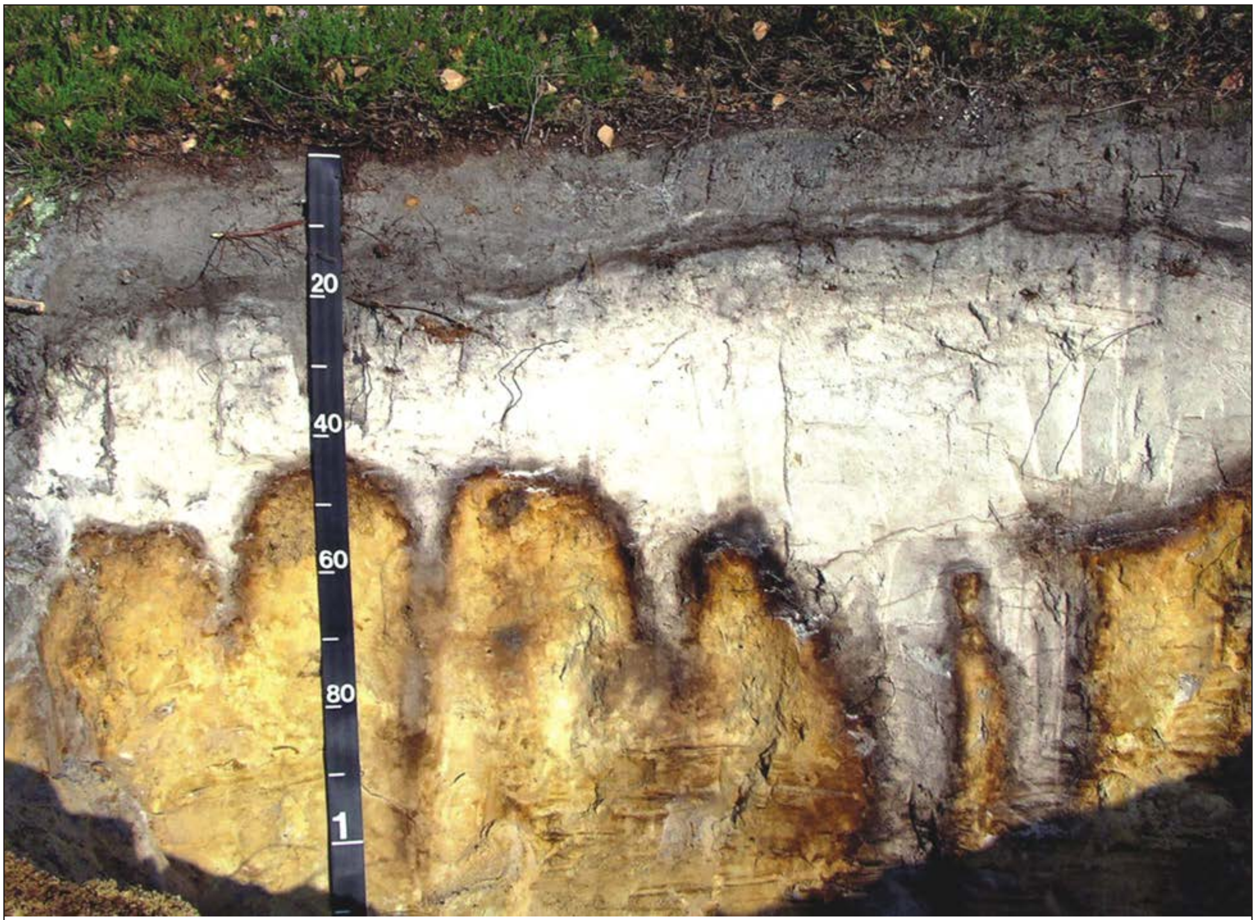

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Characterization and Impact of Newly Synthesized Superabsorbent Hydrogel Nanocomposite on Water Retention Characteristics of Sandy Soil and Grass Seedling Growth

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ABSTRACT

Superabsorbent polymers, a group of new water saving materials and soil conditioners that have been widely adopted in agriculture but little is known about their effects on soil physical and chemical properties. A novel Poly (acrylic acid-co-acrylamide) $AlZnFe_2O_4$/sodium humate superabsorbent Hydrogel Nanocomposite (PSHNC) was synthesized and its physical properties characterized using Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) and Fourier Transform Infrared (FTIR) spectroscopic techniques. Air dried sandy soil was amended with 0.0, 0.1, 0.2, 0.3 and 0.4% (w/w) of the prepared PSHNC to evaluate its soil moisture retention attributes. Additionally, the effect of PSHNC on pH, Electrical Conductivity (EC), Bulk Density (BD), Total Porosity (TP) and Hydraulic Conductivity (HC) of sandy soil was studied. Results revealed that, the soil amended with 0.1-0.4% (w/w) of PSHNC enhanced the moisture retention significantly at field capacity as compared to the untreated soil. Application of PSHNC from 0.1-0.4% (w/w) increased significantly the plant available water (from 10.94-19.22% (v/v)), field capacity (from 22.45-33.13% (v/v)) and wilting point (from 11.51-13.91% (v/v), respectively. Addition of PSHNC reduced soil BD while soil TP was increased. Soil pH was reduced significantly and it was 7.28, 7.19, 7.11 and 7.02 at concentration of 0.1, 0.2, 0.3 and 0.4%, respectively. Meanwhile, the soil EC was significantly increased with PSHNC application. In a separate experiment, seed germination and seedling growth of the Regular Seed Mixtures (RSM) grass was found to be notably improved with the application of PSHNC.

Key words: Superabsorbent hydrogel nanocomposite, water retention, hydraulic conductivity, grass growth

INTRODUCTION

Deficiency of irrigation water, drought, deforestation and soil erosion are one of the major problems of agriculture around the globe, particularly in sandy soils. Sandy soils are characterized by low water holding capacity and excessive drainage of rain and irrigation water below the root zone, leading to low water, poor water and fertilizer use efficiency by crops. Therefore, development of non-traditional new technologies to conserve water is becoming important for attaining a sustainable economic growth, especially in agriculture producing countries. Currently, cross-linked polymers with hydrophilic properties, known as Superabsorbent polymers (SAPs), have attracted much interest in this area as they can improve water and fertilizer retention in soil and thus increase plant growth. The SAPs can absorb significant amounts (up to 2,000 g/g) of water, therefore are considered very suitable for applications in agriculture (Zhang *et al*., 2006).

Most of the research in the area of development of polymers for soil water conservation involves the use of natural clays (kaolin, bentonite, montmorillonite, attapulgite and smectite) as nanocomposite materials to enhance only the physical properties of the superabsorbent hydrogels (SHCs) without considering the actual crop nutrient requirements (Wang and Gregg, 1990). However, there is much need to explore some specific and efficient of superabsorbent hydrogel nanocomposites to enhance not only the soil water retention capacity and porosity but also to simultaneously improve the crop yield and productivity (Bai *et al*., 2010; Dorraji *et al*., 2010).

Humic Substances (HS) not only improve absorption of plant biomass but also enhance photosynthesis, root development and soil structure (Zhang *et al.,* 2006; Zhang and Wang, 2007). It is widely accepted that these substances are an important potential sources of the humates used in agriculture (Yang *et al*., 2004). The Humic Acid (HA) products are usually available in the form of inexpensive soluble salts, referred to as sodium and potassium humates (Fong *et al*., 2007). This humates contains plenty of carboxylic and phenolic groups, provides favorable conditions for chemical reactions, biological activity and increase pH buffering which improves physical structure of soil and accelerates transport of nutrients to plants (Varga and Ducsay, 2003).

For the development of suitable polymers for soil water conservation, natural clays have been used as nanocomposite materials by several researchers to enhance the physical properties of superabsorbent hydrogels (Zhang and Wang, 2007; Bulut *et al*., 2009). However, some crop nutrients such as zinc (Zn) and iron (Fe) that enhance the crop yield and quality (Alloway, 2008) may be incorporated in the superabsorbent hydrogel to get larger nutrient surface areas, enhancing their availability to the plant roots (Seki *et al*., 2007; Shaver and Westfall, 2008). Moreover, sodium humate can be exfoliated to get further improvement in soil physical properties and biological activities and accelerate transport of nutrients to plants (Varga and Ducsay, 2003; Arbona *et al*., 2005).

The objectives of the present study were to synthesize a new superabsorbent hydrogel nanocomposite material (PSHNC), evaluate the morphological feature, chemical composition and water absorbency of the prepared PSHNC. Further, reported the effects of different levels of PSHNC on moisture retention characteristics of sandy soil, selected soil physicochemical properties and the growth attributes of Regular Seed Mixtures (RSM) grass grown in the amended soil.

MATERIALS AND METHODS

Soil: The experimental soil was collected from Potsdam-Golm (52° 24' 22.2" N and 12° 59' 14.9" E), Brandenburg, Germany. The soil sample (0-25 cm depth) was taken from a farmland cropped with corn (*Zea mays*), air dried, ground, homogenized, sieved through a 2 mm sieve and kept for the study. Some physical and chemical properties (Table 1) of soil were determined at the “Labor für Boden, Institut für Erd-und Umweltwissenschaften, Potsdam University, Germany”, by using international standard methods of soil analysis (Carter and Gregorich, 2007).

Chemicals: Acrylic Acid (AA) was distilled under a vacuum and after that it was stored at 10°C until required. Acrylamide (AAm), zinc sulphate, aluminum sulphate, sodium hydroxide, ferric chloride, diethylene glycol, triton X-100, methyl alcohol, ethanol and sodium humate were analytical reagent grade purchased from Alfa Aesar GmbH and Co.KG (St. Benz, Karlsruhe,

Table 1. Some physical and chemical properties of the studied soil

Particle size distribution (%)							
Sand	Silt	Clay	Texture class	BD (g cm^{-3})	TP (%)	OM (%)	pH
89.42	6.07	4.51	Sandy	1.51	43.02	1.63	7.32
	Soluble ions (meq L^{-1}) in 1:5 (soil: water) w/v						
ECe (dS m^{-1})	Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{-2}
0.77	4.34	1.22	0.52	1.62	3.11	1.62	3.00

BD, TP, OM and ECe denote Bulk density, total porosity, organic matter and electrical conductivity, respectively

Germany). While formaldehyde, potassium peroxydisulphate and potassium metabisulphite were purchased from Sigma-Aldrich Chemie GmbH (St. Ried, Steinheim, Germany).

Synthesis of nano-sized $AlZnFe_2O_4$: Nano-sized $AlZnFe_2O_4$ was prepared by the co-precipitation method (Shahid *et al*., 2012). The following solutions were prepared in deionized water: Solution A ($Al_2(SO_4)_3 \cdot 18\ H_2O$, 32.4 g/100 mL), Solution B ($ZnSO_4 \cdot H_2O$, 5.4 g/100 mL), Solution C ($FeCl_3\ 6H_2O$, 20.0 g/100 mL) and Solution D (NaOH, 22.0 g/200 mL). Solutions A, B, C were mixed and stirred for one hour and heated up to 65°C. Then solution D was added drop wise to the mixture with constant stirring. This process took two hours and reddish brown precipitates were formed. The resulting mixture was stirred continuously for half an hour and cooled to room temperature. The product thus obtained was washed and filtered repeatedly with deionized water until the chlorides were removed and the pH of the residual solution reached 7.0. The sample was then dried in an oven at 100°C for 4 h. The dried precipitate were ground with pestle and mortar to a fine powder and calcined at 600°C for 3 h in a muffle furnace to get nano-sized $AlZnFe_2O_4$ composite material.

Synthesis of poly(AA-co-AAm)/$AlZnFe_2O_4$/Na-H: The method of Liu and Rempel (1997) was followed with some modifications for the preparation of poly(AAm-co-AA)/$AlZnFe_2O_4$/Na-H superabsorbent hydrogel nanocomposite (PSHNC). Deionized water (450 mL) was placed in a flask fitted with a mechanical stirrer, condenser and thermometer. Acrylic acid (46 g) and acrylamide (4 g) were dissolved in the water. The nano sized $AlZnFe_2O_4$ (2.5 g), sodium humate (1.5 g), Triton X-100 (0.1 g) and diethylene glycol (5 g) were added also to the monomer solution and stirred for 30 min. Then potassium persulfate (0.2 g) and potassium metabisulfite (0.1 g) were added into the flask and heated to 65°C while stirring. Sodium hydroxide (1 M) solution was added to the reaction mixture to adjust the pH at 4.5. The temperature of the resulting solution was raised to 75°C and maintained for 2 h. Then the mixture solution was cooled down to 45°C and 37% formaldehyde (12.5 mL) was added and stirred for 30 min. Again the reaction mixture was heated to 75°C for 2 h and cooled to room temperature. The polymer thus formed was precipitated with methanol and washed with ethanol that dried at 80°C to constant weight and ground.

Physical and chemical characterization of nano-sized $AlZnFe_2O_4$ and PSHNC: The surface morphology and size of the $AlZnFe_2O_4$ nanoparticles and PSHNC superabsorbent were studied by scanning electron microscope (SEM, JEOL JSM 6510 SEM with tungsten hairpin filament, 15 kV). The chemical composition of either $AlZnFe_2O_4$ nanoparticles or PSHNC superabsorbent were determined by EDX-spectroscopy using an Oxford INCAx-act SN detector with a resolution of 135 eV at 5.9 keV. The dried PSHNC samples were characterized by FTIR spectroscopy using an equipment Tensor-27, Bruker Optics (Thermo Nicolet Nexus instrument, Germany) in the scanning range 4.000-500 cm^{-1}.

Measurements of the water absorbency of PSHNC superabsorbent: Water absorbency was determined using the procedure described by Zhang *et al.* (2005) and Bai *et al.* (2010). Swelling experiments were performed by immersing an accurately weighed sample (0.050±0.0001 g, average particle sizes between 180 and 380 µm) of the dry superabsorbent particles into 500 mL distilled water (EC = 0.007 dS m^{-1}), tap water (EC = 0.752 dS m^{-1}) and saline water (EC = 5.217 dS m^{-1} by NaCl aqueous solution) for 4 h to reach swelling equilibrium. The swollen PSHNC were filtered through a 100-mesh sieve for 30 min to remove unabsorbed water. The water absorbency capacity of the composite hydrogel (A) was calculated using the following equation:

$$A = \frac{W1 - W2}{W2} \qquad (1)$$

where, W1 and W2 are the weights of the water-swollen and dry sample, respectively. A is calculated in grams of water per gram of sample. The swollen samples of PSHNC were dried at 80°C in an oven. After complete drying, the same quantity of water was again added to the recovered PSHNC to get the swelling equilibrium for the 2nd and 3rd wetting-drying cycle.

Measurements of water-retention properties of soil: Effects of the synthesized superabsorbent (PSHNC) on soil water retention properties were determine using the procedure described by Akhter *et al.* (2004). Fine (180 and 380 µm) PSHNC was mixed uniformly with the soil at rates of 0.1, 0.2, 0.3 and 0.4% (w/w). The 200 g portions at different bulk density of each soil mixture were placed in 300 cm^3 plastic pots with a filter paper placed at the bottom with a small hole. Triplicate pots of each soil mixture were saturated with tap water by placing in containers for 24 h. The pots were raised to drain out the excess water gravimetrically. The pots were placed under laboratory condition (at temperature of 25°C with relative air humidity equal to 28%). The weights of the pots were recorded daily until no noticeable weight loss was observed and after that the soil water content (g/100 g) was measured up to 30 days.

Soil water content (θ): The completely moisture saturated samples were exposed to constant pressure levels of 0.01 and 1.5 MPa using the pressure chamber and membrane (soil moisture equipment) (Stakman, 1969). A series of metallic cores of 2.5 cm height and 5 cm diameter with two open ends was used for the experiment. One end was sealed by a filter paper supported by a filter tissue. Fifty grams of the dry soil or soil treated with 0.1, 0.2, 0.3 and 0.4% PSHNC was transferred to the core which immersed in distilled water to the half of its height and left for overnight equilibrium to be completely moisture saturated. The samples were then removed from water and left for few minutes to drain excess water. The saturated sample was weighed again to calculate the moisture content (g) at 0.0001 MPa pressure. The samples were then exposed to constant pressure levels of 0.01 and 1.5 MPa using the pressure chamber. At each pressure level, the wet sample was weighed. At the end, the samples were oven dried at 105°C for 48 h. The water percentage θ_v (%) at each pressure level was volumetrically calculated as well as the mass water percentage θ_m (%).

- The water content at 0.0001 MPa = $(\theta_m)_{0.0001}$ = Water Holding Capacity (WHC) of soil
- The water content at 0.01 MPa = $(\theta_m)_{0.01}$ = Field Capacity (FC) of soil
- The water content at 1.5 MPa = $(\theta m)_{1.5}$ = Wilting Point (WP) of soil
- The volume water percentage θ_v (%) at each pressure level was calculated

Saturated hydraulic conductivity (Ks): Saturated hydraulic conductivity (Ks) was calculated according to the Eq. 2 by using the constant head method as described by Klute and Direksen (1986):

$$\text{Ks}\,(\text{mm h}^{-1}) = \frac{\text{QL}}{\text{HAT}} \tag{2}$$

where, Ks (mm h^{-1}) is the saturated hydraulic conductivity, Q (mL) is the volume of the percolating water, L (cm) is the height of the soil column inside the core, H (cm) is the total head, A (cm^2) is the cross sectional area of the sample and T (h) is the time of collecting percolates (0.25 h).

Evaluation of seed germination and seedling growth: The PSHNC was mixed at the rate of 0.1, 0.2, 0.3 and 0.4% in air-dried soil. The 300 g portions of soil mixtures were filled in 400 cm^3 plastic pots with a filter paper placed at the bottom with a small hole. Five seeds each of RSM 7.2.1 grass (45% *Festuca ovina duriuscula*, 10% *Festuca rubra commutata*, 15% *Festuca rubra rubra*, 15% *Festuca rubra trichophylla* and 15% *Lolium perenne*) were sown in triplicate pots for each PSHNC level and control. The soil was saturated with tap water by placing the pots in trays containing water for 24 h. The pots were raised to drain out the excess water gravimetrically. Pots were placed in a growth chamber at 28±2°C. Pots were weighed on alternate days till no detectable weight loss was observed. Germination was recorded by counting the germinated seeds up to 2 weeks. Emergence of shoot was taken as an indicator of seed germination. No water was applied except the initial saturation of the pots. When the signs of wilting of seedlings appeared for the first time, the experiment was terminated. The plant shoots were harvested at ground level and shoot length and fresh weight were recorded. The plant material was dried at 70°C for 24 h and dry mass was determined.

Measurements of soil physicochemical properties: After plant harvest a soil sample from each pot was taken, dried, homogenized, sieved through a 2 mm sieve and kept to determine some soil physicochemical properties. Soil bulk density (BD, g cm^{-3}) was estimated according to the core methods described by Black (1982). Soil total porosity was calculated from the measured bulk density, assuming a particle density of sandy soil of 2.65 (g cm^{-3}) and by using the following Eq. 3:

$$\text{Total porosity}\,(\%) = \frac{\text{Particle density} - \text{bulk density}}{\text{Particle density}} \times 100 \tag{3}$$

Soil pH and Electrical Conductivity (EC, dS m^{-1}) were determined by the methods described by Carter and Gregorich (2007). The pH value was measured in soil, water suspension (1:2.5 w/v) while soil EC was measured in the soil extraction solution at 1:5 soils, distilled water (w/v) ratio.

Statistical analysis: Data were analyzed with a one-way analysis of variance (ANOVA) using the SPSS 11.5 software (SPSS Inc. 2002). The Duncan test was used to separate the means when the difference was significant ($p<0.05$).

RESULTS AND DISCUSSION

Characterization of $AlZnFe_2O_4$ nanoparticles and PSHNC superabsorbent

FTIR spectroscopy: Figure 1 shows the FTIR spectra for the synthesized poly(acrylic acid-co-acrylamide)/$AlZnFe_2O_4$/Na-H (PSHNC). Interpretation of the PSHNC spectra is based on numerous studies (Zhang *et al*., 2005; Zhang *et al*., 2006 and Shahid *et al*., 2012). The main absorbance bands noted were as described below. It is evident from the FTIR spectrum of the superabsorbent hydrogel that two N-H stretching bands appear at 3491 and 1115 cm^{-1}. There was a broad band between 3300 and 1750 cm^{-1} (H-bonded OH groups) with the highest O-H stretching band observed at 2932 cm^{-1}. The stretching of C = O is also observed at 1705 cm^{-1}, which may encompass the C = O of bonded conjugated ketones, carboxylic acids and esters. The peak at 1466 cm^{-1} is the stretching band of C-N and 802 cm^{-1} is another peak related to C-H stretch of aliphatic structures.

Scanning electron microscopic analysis and EDX spectroscopy: Figure 2 shows SEM micrographs of $AlZnFe_2O_4$ (Fig. 2a) nanoparticles and PSHNC superabsorbent (Fig. 2b) obtained from the fracture surface. The SEM analysis showed that nanoparticles have a mean diameter of 50 nm. The hydrogel (PSHNC) has a porous structure. It is postulated that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. Because of the crosslinking role of $AlZnFe_2O_4$ nanoparticles, the hydrogel composites have a structure with more pores but smaller in size, in comparison with the $AlZnFe_2O_4$ nanoparticles without any hydrogel.

The chemical composition of the synthesized nanoparticles was determined by Energy Dispersive X-ray analysis (EDX), which showed that $AlZnFe_2O_4$ nanoparticles contain only Fe, Zn, Al, Na and O with no traces of by-products (Fig. 3a). While the EDX of PSHNC hydrogel showed it consisted of Fe, Zn, Al, Na, K and O (Fig. 3b).

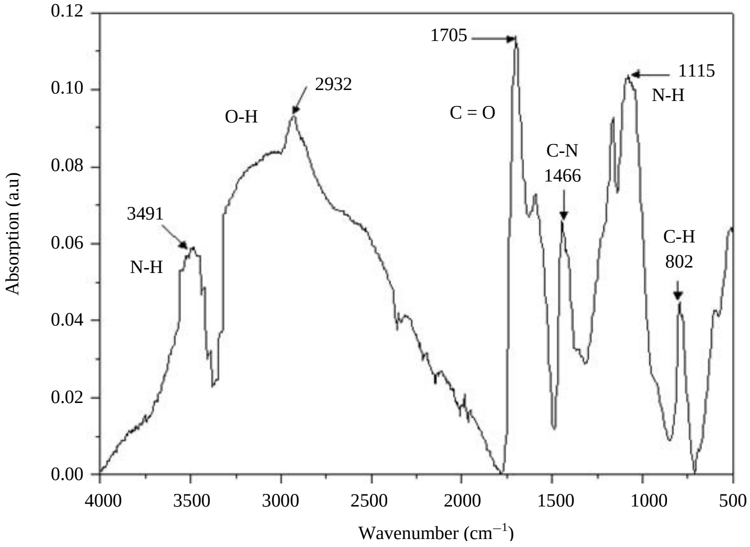


Fig. 1: FTIR spectrum of poly(acrylic acid-co-acrylamide)/$AlZnFe_2O_4$/Na-H

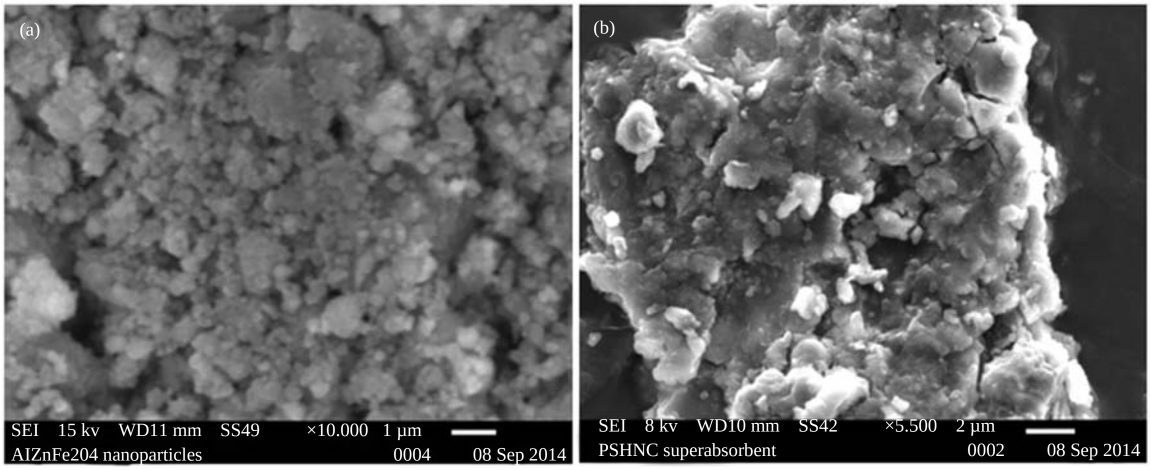
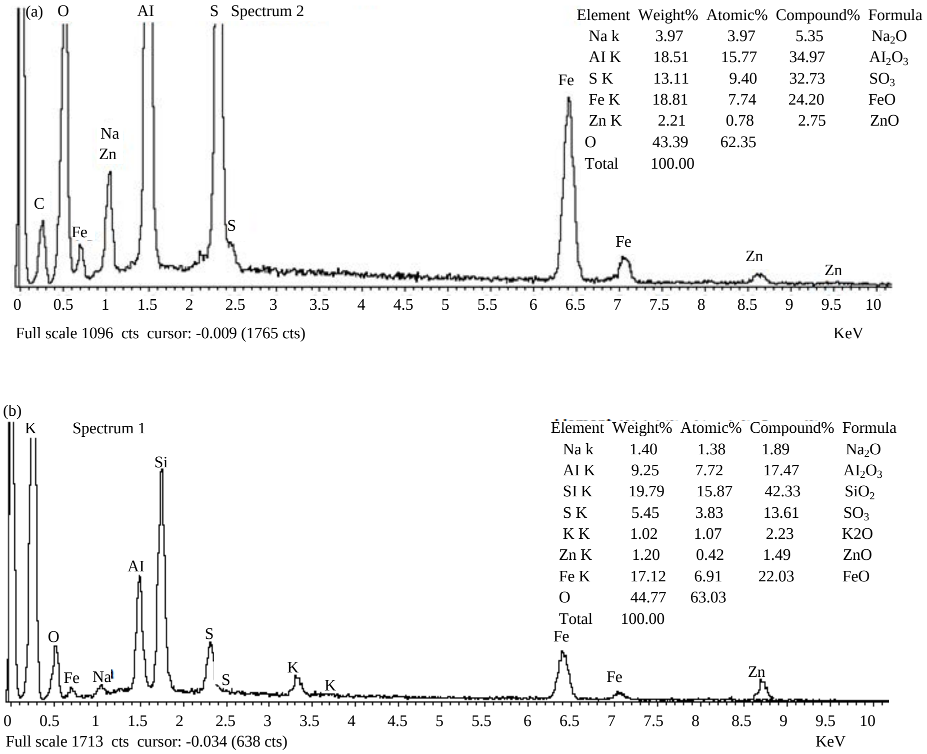


Fig. 2(a-b): Scanning electron microscope of (a) $AlZnFe_2O_4$ nanocomposite and (b) PSHNC superabsorbent



Element	Weight%	Atomic%	Compound%	Formula
Na k	3.97	3.97	5.35	Na_2O
Al K	18.51	15.77	34.97	Al_2O_3
S K	13.11	9.40	32.73	SO_3
Fe K	18.81	7.74	24.20	FeO
Zn K	2.21	0.78	2.75	ZnO
O	43.39	62.35		
Total	100.00			

Element	Weight%	Atomic%	Compound%	Formula
Na k	1.40	1.38	1.89	Na_2O
Al K	9.25	7.72	17.47	Al_2O_3
SI K	19.79	15.87	42.33	SiO_2
S K	5.45	3.83	13.61	SO_3
K K	1.02	1.07	2.23	K2O
Zn K	1.20	0.42	1.49	ZnO
Fe K	17.12	6.91	22.03	FeO
O	44.77	63.03		
Total	100.00			

Fig. 3(a-b): EDX spectrum of (a) $AlZnFe_2O_4$ nanocomposite and (b) PSHNC superabsorbent

Water absorption by PSHNC superabsorbent: Water absorption by PSHNC was rapid in distilled water and reached to the maximum in 4, 7 and 12 h in distilled, tap and saline water, respectively. Water absorption by PSHNC decreased with an increase in water salinity with maximum absorption in distilled water (796 g/g) followed by tap water (465 g/g) and saline water (325 g/g) during 1st hydration cycle (Fig. 4). The water absorption by PSHNC at three salinity levels decreased slightly but non-significantly in subsequent second and third hydration cycles (Fig. 4). Similar trends of water uptake by hydrogels synthesized from a mixture of poly (acrylic acid-co-acrylamide)/$AlZnFe_2O_4$/K-H was observed by Shahid *et al.* (2012). However, the maximum water uptake was 892 g/g in distilled water followed by 471 g/g by tap water and 390 g/g by saline water during the first hydration cycle.

The decrease in water absorbency during the 2nd and 3rd hydration cycle can be attributed to the fact that Ca^{+2}, Mg^{+2} and other ions (present in water) form insoluble salts with acrylic acid. These ions attach permanently to the carboxylic acid groups of acrylic acid blocking the active negative sites of the hydrogel and decreasing the absorbency of the hydrogel. The salts have poor ionization power thus reducing the water absorbing capacity of the polymer on rehydration after one soaking and drying cycle. This is also supported by the consistency of the behavior in distilled water. However, the enhanced water holding capacity of PSHNC might be linked to the presence of $AlZnFe_2O_4$ nanocomposite in the superabsorbent hydrogel polymeric network and can be attributed to the fact that the cations on the surface are ionized and dispersed in the super absorbent hydrogel and enhance the hydrophilicity of PSHNC (Bai *et al.*, 2010; Spagnol *et al.*, 2012).

Effect of PSHNC superabsorbent on soil water retention: The water retention by the amended sandy soil at field capacity (0.01 MPa pressure) is shown in Fig. 5, which indicates that the water retention of the soil depends on the quantity of the applied PSHNC superabsorbent. In general, the addition of PSHNC increased the moisture content at field capacity of sandy soil. The addition of 0.1, 0.2, 0.3 and 0.4% PSHNC increased field capacity by 28, 60, 92 and 130%, respectively, compared with untreated soil (Fig. 5). Similar effects on soil water holding properties of loamy soil were reported by Shahid *et al.* (2012), in sandy loam soil. This remarkable increase in soil water retention might be attributed to the hydrophilic polymer network and introduction of adequate amount of sodium humate in the superabsorbent hydrogel polymeric network which enhanced hydrophilicity of PSHNC. However, a gradual decrease in water contents of soil amended

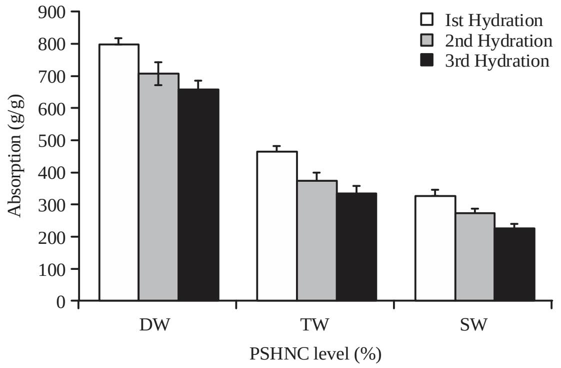


Fig. 4: Absorption of distilled water (DW, EC= 0.007 dS m^{-1}), tap water (TW, EC = 0.752 dS m^{-1}) and saline water (SW, EC = 5.217 dS m^{-1}) by PHNC during 1st, 2nd and 3rd wetting and drying cycle (Each leg of the error bar equals one the standard deviation of three replicates)

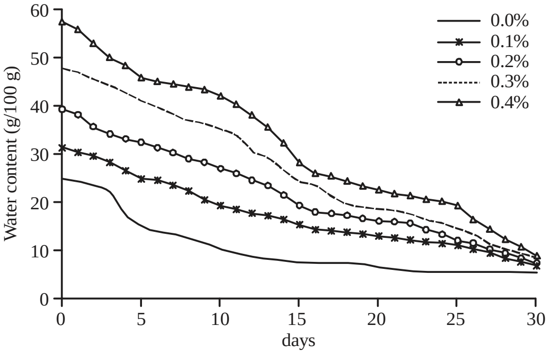


Fig. 5: Water retention by sandy soil amended with different levels of PSHNC superabsorbent at field capacity (0.01 Mpa)

Table 2: Water content and moisture characteristics for the studied different treatments

	Water content θ_v (v/v) (%)		
PSHNC level (%)	0.0001 MPa	0.01 MPa	1.5 MPa
Water content of soil treatments at increased pressure (MPa)			
0	39.55^e	18.87^e	9.22^e
0.1	45.65^d	22.45^d	11.51^d
0.2	52.23^c	26.21^c	12.79^c
0.3	59.76^b	29.04^b	13.23^b
0.4	66.11^a	33.13^a	13.91^a
LSD $_{0.05}$	3.23	0.37	0.19

	WHC (%)[a]	FC (%)[b]	PWP (%)[c]	AW (%)[d]
Relative increase in θ_m (%) of the moisture characteristics with respect to the control				
0.1	15.42	18.97	24.84	13.37
0.2	32.06	38.90	38.72	39.07
0.3	51.10	53.90	43.49	63.83
0.4	67.16	75.57	50.87	99.17

[a]Water holding capacity, [b]Field capacity , [c]wilting point and [d]available water, Mean of the same category followed by different letters are significantly different at 0.05 level of probability

with 0.1-0.4% (w/w) PSHNC was observed which finally approached 5-8 g/100 g after 30 days (Fig. 5). This gradual decrease in water contents can be linked to the water uptake by the plants, transpiration and some evaporation. The previous studies reported in the literature verify this phenomenon (Akhter *et al*., 2004; Dorraji *et al*., 2010).

Effect of PSHNC on soil water content and moisture characteristics: Mixing the sandy soil with the PSHNC showed high pronounced effect on its values of WHC, FC, WP and AW (Table 2). The values of these parameters in the PSHNC amended soils relative to the non amended control were listed in Table 2. Addition of PSHNC increased significantly soil water content (θ_v) under different pressure values (Table 2). The highest values of θ_v recorded to the 0.4% application rate of PSHNC and it were 66.11, 33.13 and 13.91% for 0.0001, 0.01 and 1.5 MPa pressure values respectively. While, untreated soil observed with the lowest values 39.55, 18.87 and 9.22% (v/v) of θ_v at different pressure values (0.0001, 0.01 and 1.5 MPa), respectively. With respect to the untreated soil, addition of PSHNC increased significantly water holding capacity (from 45.65-66.11% (v/v)), field capacity (from 22.45-33.11% (v/v)) and wilting point (from 11.51- 13.91% (v/v)) for 0.1 and 0.4% application rates of PSHNC respectively (Table 2). Also, the amount of plant available soil water (AW) increased significantly and linearly in soil with the addition of PSHNC compared with untreated soils (Table 2). The synthesized PSHNC enhanced the moisture retention of sandy soil and plant available water significantly, thereby slowing down the rate of moisture loss, due to which a delay of 20-25 days in wilting point was observed. Such a delay in wilting point reduces the water requirement of plants. These results are in agreement with those obtained by Akhter *et al.* (2004) and Dorraji *et al.* (2010).

Soil hydraulic conductivity: A significant decrease in hydraulic conductivity (Ks, mm h^{-1}) was observed with the increase in the concentration of PSHNC (Fig. 6). The high significant value of Ks was associated with control treatment (75.99 mm h^{-1}) while the lowest value (37.33 mm h^{-1}) recorded to 0.4% PSHNC treatment. Also, with respect to the control the addition of 0.1, 0.2, 0.3 and 0.4% of PSHNC reduced the soil Ks by 12, 29, 43 and 57%, respectively. The decrease in the Ks values of the soil-hydrogel mixture may be due to the decrease in the pore space between the soil particles and aggregates. The swelling of the hydrogel within the soil matrix was at the expense of some soil capillaries available for the water movement. Consequently, the volume of the water conducting pores decrease, the permeability of the matrix and thus the Ks decrease at low concentrations of the hydrogel (Dorraji *et al.*, 2010; Shahid *et al.*, 2012).

Effect of PSHNC on soil physical and chemical properties: Data in Table 3 indicate that BD of the soil mixed with PSHNC hydrogel was significantly reduced compared with the control treatment. The 0.4% PSHNC treatment exhibited a minimum significant value of BD (1.21 g cm^{-3}) and the untreated soil observed with the maximum significant value (1.51 g cm^{-3}) of BD (Table 3).

Table 3: Effect of different levels of PSHNC superabsorbent on soil physical and chemical properties

PSHNC level (%)	BD (g cm^{-3})^{a}	TP (%)^{b}	pH	EC (ds m^{-1})^{c}
0.00	1.51^{a}	43.02^{d}	7.37^{a}	0.77^{d}
0.10	1.48^{a}	44.15^{d}	7.28^{b}	0.84^{d}
0.20	1.39^{b}	47.55^{c}	7.19^{c}	0.94^{c}
0.30	1.32^{c}	50.19^{b}	7.11^{d}	1.12^{b}
0.40	1.21^{d}	54.34^{a}	7.02^{e}	1.26^{a}
LSD $_{0.05}$	0.05	2.02	0.06	0.09

Mean of the same category followed by different letters are significantly different at 0.05 level of probability, ^{a}Bulk density, ^{b}Total Porosity and^{c} Electrical conductivity

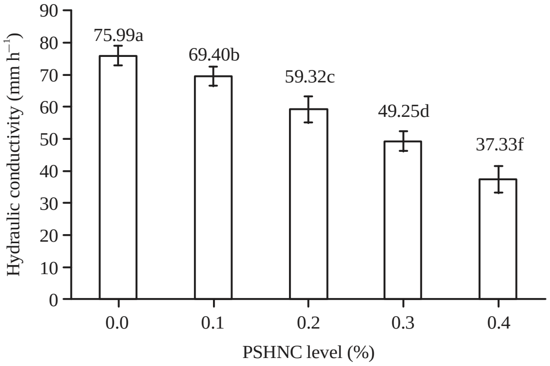


Fig. 6: Effect of PSHNC level on soil hydraulic conductivity (Each leg of the error bar equals one the standard deviation of three replicates). Mean of the same category followed by different letters are significantly different at 0.05 level of probability (LSD $_{0.05}$ = 3.44)

Table 4: Effect of different levels of PSHNC on seed germination and seedling growth (28 days) of RSM grass in sandy soil

PSHNC level (%)	Seed germination (%)	Shoot length (cm)	Shoot fresh weight (mg/pot)	Shoot dry weight (mg/pot)
0.00	80.00^{d}	15.40^{c}	70.53^{d}	13.22^{d}
0.10	86.66^{c}	18.17^{b}	81.83^{c}	19.54^{c}
0.20	93.33^{b}	19.90^{b}	101.90^{b}	23.65^{b}
0.30	100.00^{a}	25.53^{a}	116.57^{a}	25.31^{a}
0.40	100.00^{a}	26.40^{a}	119.47^{a}	26.22^{a}
$LSD_{0.05}$	3.57	2.33	9.71	1.55

Mean of the same category followed by different letters are significantly different at 0.05 level of probability

This trend was probably caused by the swelling of soil with the incorporated superabsorbent polymer embedded with sodium humate. The PSHNC hydrogel particles within the soil matrix absorb water and become larger in size. The soil particles are displaced and rearranged around the swollen particles of the hydrogel. So, the soil volume increases and hence the ratio of the dry mass of the soil to its volume decreases (Liu *et al*., 2007; Bai *et al*., 2010). In contrast soil Total Porosity (TP) increased relatively by 2.63, 10.53, 16.67 and 26.31% at PSHNC concentrations of 0.1, 0.2, 0.3 and 0.4%, respectively (Table 3). Addition of PSHNC increased significantly soil TP of 0.2, 0.3 and 0.4% PSHNC treatments while no significant increased occurred for the soil amended with 0.1% PSHNC. It may be due to the increase in the pore space between coarse sand particles reoriented around the swollen hydrogel particles. Easier displacement of larger sand particles by swollen hydrogel may create new pores (Bai *et al*., 2010).

The pH and EC varied with the application of PSHNC (Table 3). Soil pH was reduced significantly from 7.28-7.02 for PSHNC concentration of 0.1 and 0.4% respectively, compared with the control. Meanwhile, the Electrical Conductivity (EC) was significantly increased with PSHNC application (except at application rate of 0.1%). The application of 0.4% PSHNC recorded the highest value (1.26 dS m^{-1}) of EC followed by 0.3% (1.12 dS m^{-1}), 0.2% (0.94 dS m^{-1}), 0.1% (0.84 dS m^{-1}) and finally the control (0.77 dS m^{-1}). The decrease in pH of the soil might have enhanced the discharge of soil inorganic salts thereby increasing EC of the soil. Similar effect on the pH and EC of soils due to the chemical structure of the superabsorbent polymer and soil characteristics have previously been appraised by Liu *et al*. (2007) and Bai *et al*. (2010) while studying the characteristics of chitosan-graft-poly (acrylic acid)/sodium humate superabsorbent.

Effect of PSHNC on seed germination and seedling growth: The RSM seedling growth was enhanced by the addition of PSHNC. Seed germination was considerably higher in 0.1-0.4% PSHNC amended soils as compared to the control. Also, shoot length of RSM grass was significantly higher in 0.1-0.4% PSHNC compared with control (Table 4). The addition of PSHNC in sandy soil significantly increased the fresh and dry weights of grass shoots. Most of the studied seedling growth parameters of RSM grass were slightly higher (statistically insignificant) in 0.4% than in 0.3% treatment. However, seed germination of RSM was the same in 0.3 and 0.4% treatments (Table 4). This indicates that exchangeable acids and ions present in PSHNC can influence properties such as soil acidity and alkalinity, nutrient availability and microbial activity that all enhanced plant growth parameters. Also, this trend could be due to the prepared hydrogel improved the water storage and increased the field capacity of soil and thus the plant available water (Bulut *et al*., 2009; Bai *et al*., 2010; Shahid *et al*., 2012). Moreover, sodium humate of the locally prepared PSHNC hydrogel may be improving the bioavailability of micronutrients by complexion, which prevents early micronutrient deficiency (Varga and Ducsay, 2003; Fong *et al*., 2007).

CONCLUSIONS

Based upon the present study data, it could be concluded that novel poly(acrylamide-co-acrylic acid)/AlZnFe_2O_4/Na-H superabsorbent hydrogel nanocomposite had a respectable effect on the physical properties of sandy soil. The results of our studies showed that the locally prepared hydrogel had reasonably high water absorption capacity that was retained in subsequent wetting and drying cycles. The moisture retention and total porosity of sandy soil was remarkably increased with the application of 0.1-0.4% (w/w) PSHNC. The addition of PSHNC significantly reduced the hydraulic conductivity and soil bulk density relative to the control at concentrations 0.1-0.4% (w/w). The amount of plant available water significantly increased, leading to enhanced grass seed germination and seedling growth in the amended soil. The soil amendment with PSHNC practically ensured improvement of soil moisture retention for a longer time. These findings suggest that using PSHNC as soil amendment will be useful for increased soil available water and consequently plant establishment in drought prone environments. Moreover, the locally prepared PSHNC may enhance availability of nutrients and other environmental factors which may significantly improve grass yield.

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