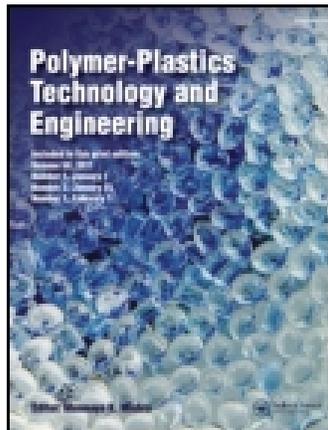


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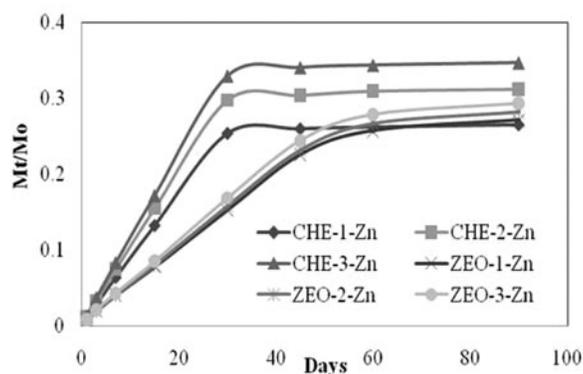
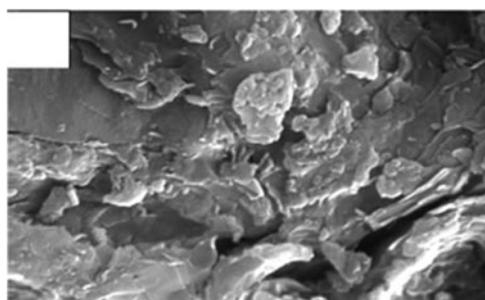
Synthesis and Characterization of Poly (CMC-g-cl-PAam/Zeolite) Superabsorbent Composites for Controlled Delivery of Zinc Micronutrient: Swelling and Release Behavior

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GRAPHICAL ABSTRACT



A series of novel superabsorbent hydrogel composites, poly(CMC-g-cl-PAam/Zeolite) (ZSAPC) were prepared by *in situ* graft polymerization using a cellulosic backbone, acrylamide and natural zeolite. The swelling and deswelling behavior of the prepared composites was evaluated and analyzed by different empirical models. The composite with optimum water absorption capacity were impregnated with $ZnSO_4$ *in situ* during polymerization reaction. Zincated composites showed less water absorption capacity as compared to non-zincated ones. Zinc release behavior of zincated test hydrogel composites was studied in water and soil. All the test compositions exhibited non-Fickian or anomalous transport ($0.43 < n < 0.84$) and behaved as slow release products.

Keywords Slow release; Superabsorbent composite; Swelling; Zeolite; Zinc

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INTRODUCTION

Water and micronutrients are critical inputs in realizing high agricultural productivity. Their low use efficiencies under limited water availability conditions is a cause of concern for agriculturists. Super absorbent polymer (SAPs), the cross-linked hydrogels finding lots of attention in this context due to their versatile fluid absorption- release characteristics and controlled release matrix properties. These polymers have been found useful in improving physical properties of soil such as water-holding capacity, permeability and infiltration rates, improve plant growth, particularly in drought prone areas^[1-6].

Their utility as carrier for controlled release of drug molecules and fertilizers has also been reported extensively^[7-10]. Superabsorbent composites have been receiving great attention in recent years because of their unusual and improve characteristics over conventional hydrogels^[11-12]. Hydrogel composites add a new dimension to the superabsorbent chemistry because of their cost effective and biocompatibility characteristics^[13]. Zinc deficiency in crops is one of the major micronutrient problems realized all over the world^[14]. Application rates of ZnSO₄ are very high, ~20–30 kg/hectare but use efficiency hardly exceeds 5% due to fixation problem in soil^[15,16]. Slow release nutrient approach holds tremendous potential in this context. Zeolites, the porous minerals with high cation exchange capacity and porosities are potential candidates for slow release of plant nutrients in soil. Present study reports synthesis of zeolite-based novel superabsorbent composites, their evaluation, swelling response and slow release nutrient potential in water and sandy loam soil as carrier of the micronutrient.

EXPERIMENTAL

Materials

Carboxy methyl cellulose (CMC) (viscosity range 500–700 cps), acrylamide (AM), N,N-methylene bisacrylamide (MBA), persulphate initiator, zinc sulphate heptahydrate (ZnSO₄·7H₂O) were procured from Merck Specialties Pvt. Ltd., Mumbai, India and used as received without further purification. Natural zeolite was procured from Neel kanth Minechem, Rajasthan, India. Zeolite was passed through sieve of 300 mesh size and was used as such without further modification.

Sandy loam soil was collected from a surface depth of 0–15 cm from the research farm of the Indian Agricultural Research Institute, New Delhi, India, dried in shade, ground to pass through a 2-mm sieve and stored in a polyethylene bag. The physicochemical characteristics of the soil, determined using standard analytical procedures were: pH 7.8 measured at 1:1.25 soil to water ratio (Elico pH meter); organic carbon 0.04% (Walkley and Black method), soil mechanical analysis: sand 78%, silt 10%, clay 12.4% (Bouycos hygrometer method), EC 5.6 dS /m (Elico Electrical conductivity meter).

Design and Synthesis of Zeolite Hydrogel Composites

poly(CMC-g-cl-PAam/Zeolite) composites (ZSAPC) were synthesized by *in situ* grafting of acrylamide (AM) on the cellulosic backbone in the presence of zeolite, cross-linker (MBA) and persulphate initiator by open air free radical solution polymerization reported previously^[17]. Briefly the procedure was as follows: Weighed quantities of monomer and cross-linker were dissolved in pre-standardized quantity of distilled water. A mixture of cellulosic backbone, initiator and zeolite was added to the solution with continuous stirring. The feed mass was kept at 60–70°C for 8 h. The gel mass formed was washed with excess water, dehydrated and oven dried at 70°C till constant weight. To optimize the concentration of various reactants namely monomer, cross-linker, backbone, initiator and zeolite, sequential design was adopted^[17].

Preparation of Zincated Hydrogel Composites

Two series of zincated composites, the zeolite free (CHE-1/2/3-Zn) and zeolite containing (ZEO-1/2/3-Zn) were prepared by *in situ* incorporation technique with varied amount of monomer in feed mass (1 g, 2 g and 3 g). Zinc sulphate (ZnSO₄·7H₂O) was added to the feed mixture along with monomer. The rest of the composite synthesis was kept same. After complete drying, the zincated composites were crushed in mixer grinder (Philips, Model No. HL 1606) and passed through 300 mesh size sieve (53 micron).

Characterization

The functional group characterization was done using Bruker Fourier transform infrared spectrophotometer (Model Alpha ATR-Bruker, PN-1010951, SN-200172, KBR palleting method). Wide-angle X-ray diffraction (XRD) measurements were performed using Philips PW1710 diffractometer control equipped with Philips PW1728 X-ray generator. The scanning range was 1–50° 2θ, with a scanning rate of 1.2° 2θ/min. Scanning electron microscopy images were obtained using ZEISS EVO MA10, 20kV and 10pa at two magnifications (3.48k and 30k) after 30 nm palladium coating. Zinc content was measured using ECIL atomic absorption spectrophotometer (Liquid samples were burnt in oxyacetylene flame under specific filter (213.9 nm).

Swelling Kinetics Measurement

Accurately weighed composite (0.1 g, particle size 100–240 mesh size) was taken in nylon bag and immersed in excess of distilled water (pH 7.0, EC 0.001 Mhos/cm) in triplicate and kept at room temperatures (40°C) until equilibrium was attained. The equilibrated swollen gel was allowed to drain for 10 min for removal of excess water from nylon bag. The bag was then weighed to determine the weight of the swollen gel. The water absorption capacity (Q_{H₂O}, g/g, dry weight basis) was calculated using the following equation:

$$Q_{H_2O} = (W_e - W_x)/W_x$$

Where W_x is the weight of xerogel or gel in glassy state and W_e is the weight of swollen gel at equilibration. Water absorbency of prepared composites was measured at different time intervals until equilibrium was reached.

Deswelling Kinetics Measurement

For deswelling study measurement, the nylon bag containing swollen material was immersed in 0.35 M aqueous NaCl solution^[18,19]. The periodic change in weight of the gel mass was measured gravimetrically. Water release from gel mass was calculated using the following equation:

$$\text{Released water} = (W_e - W_s)/W_e$$

where, W_e (g) is the weight of swollen gel at equilibrium and W_s (g) is the weight of deswelled gel mass at time t .

Water Retention Measurement in Sandy Loam Soil

An optimized poly(CMC-g-cl-PAam/Zeolite) superabsorbent composite (ZSAPC-1) was mixed with air dried soil at the rate of 0.25%, 0.5% and 0.75% (w/w). The amended soil samples (50 g each) were taken in preweighed plastic cups with perforated bases, fitted with filter papers. Each cup was immersed overnight in with water to allow its capillary rise. Water holding capacity (WHC) of the soil was calculated using following equation:

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

Where, W_{wet} denotes weight of wet sample and W_{dry} denotes weight of oven dry sample. WHC of amended soil

was calculated at different time periods to determine the water retention characteristics of amended sandy loam soil.

Analysis of Swelling and Release Mechanism

Different models used to determine the swelling/deswelling kinetics and release of zinc from of developed ZSAPCs are stated in Table 1. The best fit model in the present data was distinguished based on the coefficient of determination (R^2). The model with highest R^2 value is referred to as the best fit model.

Determination of Zinc Loading Efficiency of Zeolite Hydrogel Composites

The di-acid digestion method^[20] was used to estimate the amount of zinc loaded in the matrices of composites. Briefly, accurately weighed CHE-Zn/ZEO-Zn (0.1 g, particle size 100–240 mesh) taken in conical flasks was treated with 10 mL of concentrated nitric acid (HNO_3) and kept under fume hood for overnight. After 12 h, reaction mass was treated with di-acid mixture ($\text{HNO}_3:\text{HClO}_3$: 3:1, 12 mL) and further heated at 200°C for 4–6 h at 80°C until the brown color disappeared. The flask was washed with 6 N HCl, filtered and volume made up to 100 mL and finally analyzed in AAS.

Loading efficiency (%) of the zincation process was calculated as follows:

$$\text{Loading efficiency} = \frac{\text{Concentration of ZnSO}_4 \text{ detected in the formulation}}{\text{Concentration of ZnSO}_4 \text{ introduced in the feed mixture}} \times 100$$

TABLE 1
Mathematical models for analysis of swelling, deswelling and zinc release kinetics from ZSAPC

Sl. No.	Model	Equation	Mechanism	Reference
1.	Higuchi	$\frac{Mt}{M_\infty} = k_H t^{1/2}$ k_H - kinetic constant	Fickian diffusion	Higuchi, 1953 [21]
2.	Ritger–Peppas	$\frac{Mt}{M_\infty} = k_1 t^n$ k_1 - kinetic constant n -diffusion exponent	$n = 0.5$, Fickian diffusion $n = 1$, Case II transport $0.5 < n < 1$, anomalous transport	Ritger and Peppas, 1987 [22]
3.	Peppas–Sahlin	$\frac{Mt}{M_\infty} = k_1 t^m + k_2 t^{2m}$ k_1, k_2 - kinetic constant m -exponent	Fickian diffusion and Case II transport; first term represents the contribution of Fickian diffusion and the second term refers to the macromolecular relaxation contribution	Peppas and Shalin, 1989 [23]
4.	Zero-order	$\frac{Mt}{M_\infty} = kd t$ k_d - kinetic dissolution constant	Release rate independent of concentration	Serra <i>et al.</i> , 2006 [36]
5.	First-order	$\log\left(1 - \frac{Mt}{M_0}\right) = k_2 \frac{t}{2.303}$ K_2 - release rate constants	Rate is dependent of concentration of only one reactant	

* M_t is the amount absorbed or released at time t ; M_∞ , the initial amount at time 0.

Release Study of ZnSO₄ in Water

An accurately weighed quantity of zincated composite (0.1 g) was taken in nylon bag (3 cm × 3 cm; 200 mesh) in triplicate. Each bag was placed in distilled water (100 mL) in capped plastic containers. The containers were kept undisturbed in laboratory at room temperature (30 ± 2°C) and periodic sampling was done (1, 3, 7, 15, 30, 45, 60 and 90 days). On nth day water filtered and diluted to 100 mL and analyzed in AAS.

Release Study of ZnSO₄ in Soil

An accurately weighed quantity of zincated composite (0.1 g) was taken in nylon bag (3 cm × 3 cm; 200 mesh) in triplicate. Each bag was suspended in soil (15 g) in capped plastic containers. The containers were kept in laboratory at room temperature (30 ± 2°C). Soil moisture was maintained at field capacity throughout the study. Destructive sampling was done periodically (1, 3, 7, 15, 30, 45, 60 and 90 days). After removing bag soil were treated with EDTA extractant (soil: extractant ratio 1:2) and shaken for 2 hours. Supernatant solution was filtered through Whatman filter paper (No. 42), diluted to 100 mL and analyzed in AAS.

Analysis of the Release Data

Different types of models including Higuchi matrix^[21], Peppas–Korsmeyer^[22] and first-order equation have been reported previously to predict the release of an active agent from hydrogel composites as a function of time^[23]. The most widely accepted mechanism for describing solute release from hydrogels is the diffusion-controlled release^[23]. Zinc release data were fitted to these kinetic models and analyzed for understanding its release mechanism. The nutrient release data were analyzed using Sigma Plot software (Version 12.0, Systat Software, Inc).

RESULTS AND DISCUSSION

Effect of Synthesis Parameters on Water Absorbency of Zeolite Superabsorbent Composites

Synthesis parameters viz. cross-linker (N,N-methylene bisacrylamide) content, monomer (acrylamide) content, initiator (ammonium persulphate) content and filler (zeolite) content play important role influencing the water absorbency behavior of hydrophilic polymer^[17,24]. Therefore the effect of these parameters on water absorbency of ZSAPC was evaluated.

Effect of N,N-Methylene Bisacrylamide (MBA) Content on Water Absorbency

The effect of N,N-methylene bisacrylamide content on water absorbency behavior of prepared composites is shown in Fig. 1. The results indicate that the Q_{H_2O} increased significantly with decrease in cross-linker content in the range 0.015–0.31 wt.%. At cross-linker content lower than 0.015 wt.%, the feed mass remained in sol-gel state and Q_{H_2O} could not be

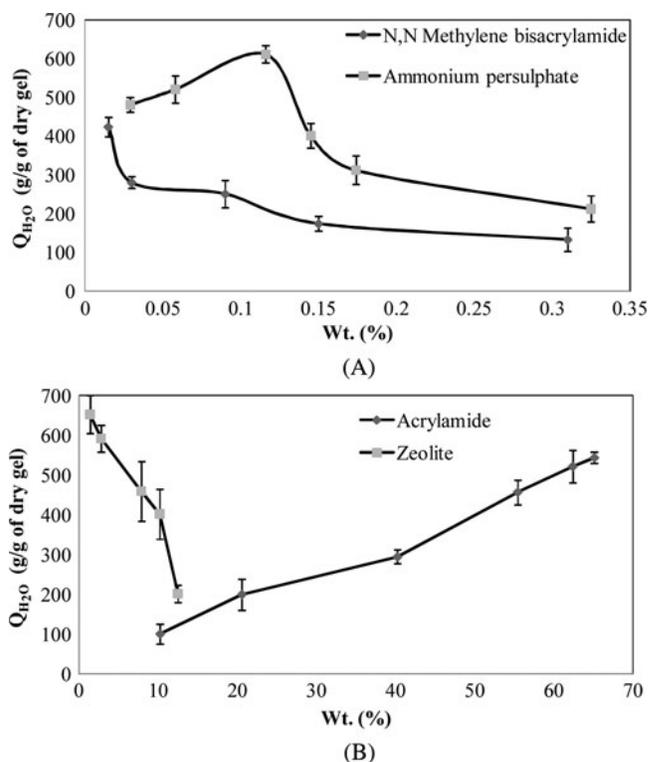


FIG. 1. Effect of monomer content (synthesis parameters: weight ratio of cross-linker, zeolite, and initiator to backbone: 0.0005 : 1, 0.2 : 1, and 0.005 : 1, respectively), cross-linker content (synthesis parameters: weight ratio of monomer, zeolite and initiator to backbone: 2 : 1, 0.2 : 1, and 0.005 : 1, respectively), backbone initiator ratio (synthesis parameters: weight ratio of cross-linker, zeolite, and monomer to backbone: 0.0005 : 1, 0.2 : 1, and 2.5 : 1, respectively), backbone zeolite ratio (synthesis parameters: weight ratio of cross-linker, monomer, and initiator to backbone: 0.0005 : 1, 2.5 : 1, and 0.004 : 1, respectively) on water absorbency (Q_{H_2O} g g⁻¹).

determined. Decrease in water uptake with increase in cross-linker content can easily be explained in terms of generation of extensive cross-link points, resulting in highly cross-linked structures that cannot expand sufficiently to hold large quantities of water^[25].

According to Flory's theory high cross-linker content induces the generation of extensive cross-link points leading to increase in cross-linking density. As a result, the network voids for holding water get minimized and the water absorption is decreased. However, the insufficient cross-linker content lower than the threshold value in the present study causes failure of formation of the three dimensional hydrophilic network, resulting in increase of sol fraction. The relationship between equilibrium water absorption and cross-linker concentration follows the following power law, $Q_{eq} = kC_{MBA}^{(-n)}$ ^[26].

To understand the effect of cross-linker content on water permeation in gel matrix a Voight-based equation ($\frac{M_t}{M_\infty} = 1 - e^{-t/\tau}$)^[27] was used (M_t , swelling at time t (g/g); M_∞ , equilibrium swelling (g/g); t is time (min); τ , "rate parameter" (min)). Because τ is a measure of the resistance to

TABLE 2

Estimated τ , standard error of estimate and R^2 values obtained from fitting swelling data to voight based

$$\text{equation} \left(\frac{M_t}{M_\infty} = 1 - e^{-t/\tau} \right)$$

Zeolite composites	Cross-linker content (wt%)	τ	Std. Error	R^2
ZH1	0.015	0.09	0.0055	0.97
ZH2	0.03	0.15	0.0077	0.98
ZH3	0.15	0.21	0.0186	0.95
ZH4	0.09	0.18	0.0169	0.94

water permeation, the lower the τ value, higher will be the rate of water uptake. Water absorbency values of ZAPC *vis-à-vis* cross-linker content (ZH1, ZH2, ZH3 and ZH4) were fitted in the above Voight-based equation and the predicted rate parameters are shown in Table 2. It was seen that with increase in cross-linker content the predicted rate parameter (τ) increases that may be explained by increase in cross-linker density and simultaneous reduction in water absorbency^[27].

Effect of Acrylamide Content on Water Absorbency

The water absorbency values of ZSPAC prepared by variation of monomer (acrylamide) content are shown in Fig. 1. The highest water absorbency was found at 65.11% acrylamide content. Below 55.44% of acrylamide content, the composite remains in sol-gel state in water, which could be attributed to increase in homopolymer percentages^[28]. At a definite concentration of initiator in reactants, the numbers of free-radicals generated by the initiator decomposition remains constant and the concentration of monomers decides the reaction rate and grafting efficiency. With increase weight ratio of monomer to backbone, the numbers of monomer units that can react at grafting sites also increase, which favors to the enhancement of grafting efficiency and the water absorbency^[29].

Effect of Ammonium Persulphate Concentration on Water Absorbency

The relationship between initiator (ammonium persulphate) and the water absorbency is depicted in Fig. 1. As can be seen, initial increase in ammonium persulphate concentration up to 0.116 wt.% led to increase in water uptake, beyond which further increase led to sharp reduction in swelling ratio. It is well established fact that molecular weight of a polymer in free-radical polymerization will decrease with increasing initiator concentration^[30]. With decrease in molecular weight, the relative amount of polymer chain ends increases, which lead to lower water absorbency^[31]. However, the free radicals on the macromolecular chains of back bone cannot be adequately generated when initiator content is lower than 0.116% in the present study. This restricts the process of chain

transfer reaction and affects the growth of grafting polymer chains. As a result, below the optimal value (0.116%), increase in the initiator enhances the water absorbency of zeolite hydrogel composite.

Effect of Zeolite Content on Water Absorbency in Deionized Water

Water absorbency of ZSAPCs in distilled water, as a function of the zeolite content is shown in Fig. 1. Water absorbency decreased significantly, with increasing weight percentage of zeolite. According to Flory's swelling theory^[32], water absorbency of a gel is directly proportional to the affinity of gel towards water; which in present study was maximum at 1.4 wt.% of zeolite beyond which the swelling ratio decreased with increase in zeolite content. Literature reports that the inorganic clay type mineral provides additional network points in polymerization reaction^[33,34] that results in increase in cross-linking density. Therefore, with increase of zeolite content decreased water absorbency behavior is observed.

Characterization

The XRD patterns of natural zeolite mineral and an optimized ZSAPC (ZH1) are shown in Fig. 2(A). Zeolite show prominent XRD peaks because of its crystalline structure. Appearance of these peaks in X-ray scattering curve of corresponding composites established formation of true composites. The values of average crystallite size of zeolite mineral in pure form and in composite were calculated using Scherer's equation $\left(r = \frac{k\lambda}{\beta \cos \theta} \right)$ (Fig. 2).

FT-IR spectra of zeolite and ZH1 are shown in Fig. 2B. The bands at 1034 cm^{-1} in FT-IR spectrum of zeolite corresponds to the internal Si-O(Si) and Si-O(Al) vibrations in tetrahedra or aluminosilicate and silico-oxygen bridges^[35]. Band observed at 539 cm^{-1} corresponds to Si-O bending in pure zeolite. Modification of aluminosilicate frameworks due to composite formation is visible in the FTIR spectrum of ZH1. Band position of Si-O(Si) and Si-O(Al) vibrations exhibited shift from 1035 cm^{-1} to 1050 cm^{-1} and Si-O bending vibration shifted to 585 cm^{-1} . Additional IR bands observed at 3427 cm^{-1} and 1627 cm^{-1} are characteristic of O-H stretching and C=O stretching vibrations. The characteristic C-H stretching bands at $2925\text{--}2974 \text{ cm}^{-1}$ due to symmetric or asymmetric stretching vibration of the CH_2 groups of polymeric chain are also visible.

Surface morphology of nonzincated and zincated hydrogel composites was examined to investigate the arrangement of filler aggregates in the hydrogel matrix and to see the effect of zinc incorporation on the morphological changes in polymers. Figure 3 compares microscopic surfaces of nonzincated and zincated zeolite composites (A, B), nonzincated and zincated cellulosic noncomposite hydrogels (C, D). Comparison of zeolite-free hydrogel (C) morphology with the corresponding ZSPAC composite (A) showed comparatively smooth surface

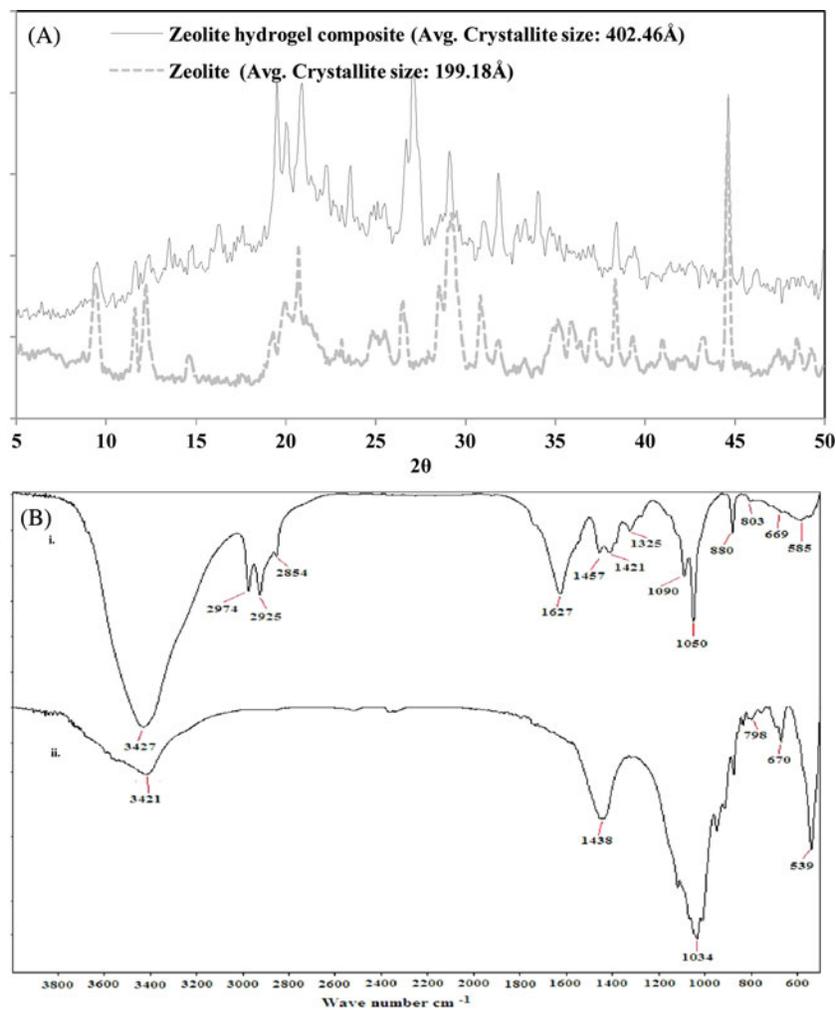


FIG. 2. XRD patterns (A) and FT-IR spectra of poly(CMC-g-cl-PAam/Zeolite) composite (i) and pure natural zeolite (ii).

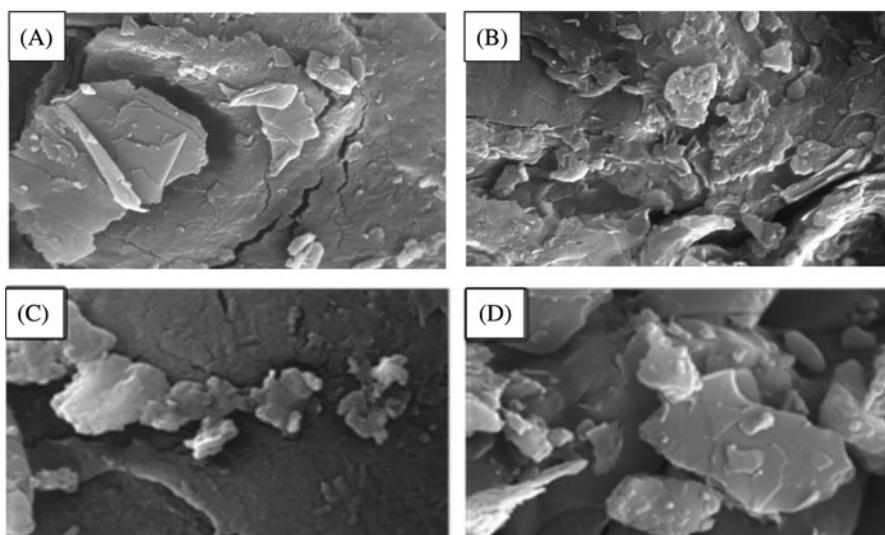


FIG. 3. Scanning electron micrographs (30,000 K) of nonzincated (A) and zincated (B) zeolite hydrogel composites and nonzincated (C) and zincated (D) hydrogels.

TABLE 3
Effect of nature and strength of different swelling media on water absorbency of ZH1 and absorbency rate parameters
(Swelling = k [salt]⁻ⁿ) in salt/alkali solutions

Swelling medium	5 mM	10 mM	20 mM	k	n	R^2
NaCl	135 ± 24	110 ± 13	88.8 ± 19	219.44	0.30	0.9998
NaOH	165 ± 17	141 ± 9	98 ± 35	296.12	0.35	0.9469
NH ₄ (SO ₄) ₂	150 ± 10	122 ± 26	74 ± 14	323.05	0.46	0.9420
Urea	421 ± 45	360 ± 17	320 ± 37	578.49	0.20	0.9937

of filler free gel because of homogenous grafting and cross-linking of monomer onto the backbone, whereas the composites displayed highly fractured and aggregated appearance, this could be because of intercalation of filler particles into the matrix of the hydrogel. Addition of zinc appeared to substantially influence the morphology of all the polymers. Zincated polymers appeared more amorphous as compared to the corresponding nonzincated compositions.

Absorbency Rate Measurements

Evaluation of swelling behavior of superabsorbent composites in ionic solutions, particularly those applied as fertilizers or present in saline and alkaline soils, is very important in view of their agricultural applications. Table 3 depicts the swelling behavior of the optimized ZSAPC (ZH1) in solutions of varying strengths of (NH₄)₂SO₄, NaCl, NaOH and urea. In all test solutions, absorption was less as compared to that in distilled water. In urea solutions of all the test strengths, the reduction in swelling was relatively lesser as compared to other salts. This observation bears significance due to the fact that for most of the crops in agriculture, urea comprises an important fertilizer and test composite (ZH1) can be recommended for simultaneous application with basal dose of urea.

In general, water absorbency decreased with the increase of concentration of salt the salts in solution. This behavior may be attributed to the increased osmotic pressure difference between gel matrix and external environment with increasing ionic strength^[11]. The known relationship between swelling and salt concentration is expressed as, swelling = k [salt]⁻ⁿ, where, k and n are constant^[32]. The k value is the measure of swelling phenomena at increased ionic strength and n value is the measure of salt or ionic sensitivity. As evident from Table 3 the k and n values of ZH1 are different for each swelling medium. The sensitivity of ZH1 is very less to the urea solutions as compared to other test solutions (NaCl, NH₄(SO₄)₂ and NaOH). These salt solutions provide counterion Na⁺/ NH₄⁺, which exerts screening effects on carboxylate anions, preventing expansion and swelling of the network.

Swelling Kinetics

Periodic absorption of water by poly(CMC-g-cl-PAam/Zeolite) superabsorbent composites is depicted in Fig. 4(A). The maximum equilibrium water absorbency (Q_{H_2O}) was

displayed by ZH1. The order of Q_{H_2O} was ZH1 > ZH2 > ZH4 > ZH3. To describe the kinetics of water absorption, the water absorbency data by zeolite hydrogel composites having varied cross-linking densities were fitted to five different models (Table 1) and analyzed. Peppas–Shalin and Ritger–Pappas models were the best models satisfactory describing the experimental data obtained from swelling study of zeolite composites. These models count for the effect of Fickian diffusion and polymer chain relaxation on the overall water absorption mechanism.

The larger SSR (Sum of Square Residual) values obtained from Higuchi and zeroorder models indicate that experimental

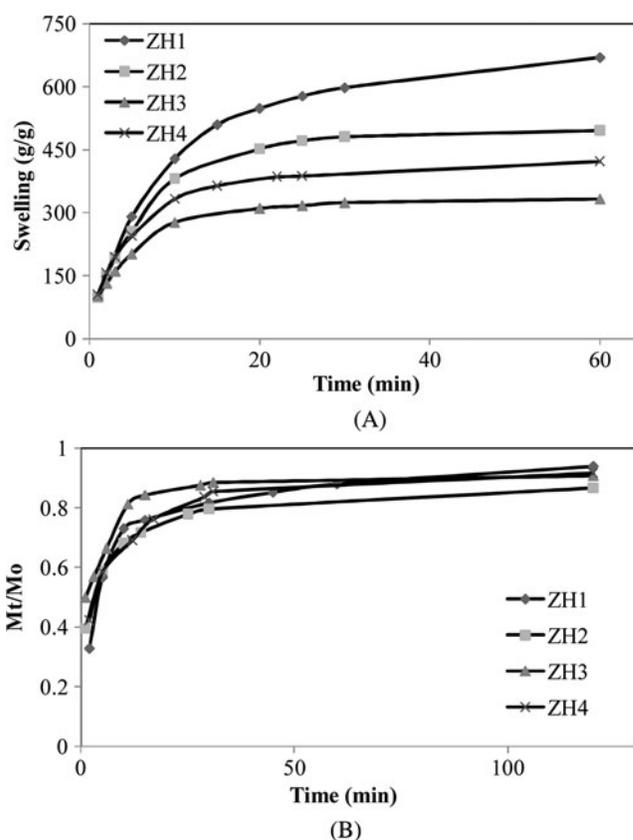


FIG. 4. Absorption (A) and release (B) of water with respect to hydrogel composites having different cross-linker concentrations ZH1, (1: 0.0005); ZH2, (1:0.001); ZH3, (1:0.003); ZH4, (1:0.005).

TABLE 4
Estimated parameters obtained from fitting swelling and deswelling data to Zero order, Higuchi, Ritger-Peppas, Peppas and Shalin model

Composites	Zero-order		Higuchi		Ritger-Peppas				Peppas and Shalin model				
	k_d	R^2	k_H	R^2	k_1	n	Mechanism	R^2	k_1	k_2	m	R^2	
Swelling	ZH1	0.06	0.72	0.19	0.96	0.17	0.56	Anomalous transport	0.98	0.14	-0.006	0.80	0.99
	ZH2	0.09	0.68	0.23	0.98	0.20	0.58	Anomalous transport	0.99	0.20	-0.004	0.61	0.99
	ZH3	0.14	0	0.28	0.97	0.29	0.44	Fickian diffusion	0.99	0.21	0.082	0.32	0.99
	ZH4	0.09	0.26	0.26	0.99	0.26	0.47	Fickian diffusion	0.99	0.27	-0.019	0.60	0.99
Deswelling	ZH1	0.08	0.28	0.24	0.97	0.25	0.47	Fickian diffusion	0.98	0.23	-0.020	0.73	0.99
	ZH2	0.08	0	0.24	0.20	0.40	0.22	Fickian diffusion	0.99	0.42	-0.060	0.40	0.97
	ZH3	0.13	0	0.31	0	0.47	0.21	Fickian diffusion	0.94	0.33	0.140	0.16	0.95
	ZH4	0.06	0	0.23	0.31	0.36	0.25	Fickian diffusion	0.98	0.42	-0.030	0.26	0.96

k_d , rate constant of zero order model; k_H , rate constant for Higuchi model; k_1 and k_2 , rate constant; n , diffusion exponent; m , exponent; R^2 , correlation coefficient.

data did not fit these models properly^[36]. Using the Model 2, (Table 1) the value of exponent n , indicative of the water absorption mechanism, was calculated (Table 4), which ranged from 0.44 to 0.58, indicating significant influence of cross-linking density on water absorption mechanism of zeolite composites. ZH1 and ZH2 having lower cross-linking densities showed n value of 0.56 and 0.58, respectively, indicating that release mechanism was neither solely Fickian diffusion nor polymer chain relaxation but anomalous transport, where as ZH3 and ZH4 having higher cross-linking densities showed an n value of 0.44 and 0.47, respectively, indicating that predominating release mechanism in their case was Fickian diffusion.

Deswelling Kinetics

Swollen gels at equilibrium were transferred to 0.35 M aqueous NaCl solution to study their deswelling kinetics. Release of water from ZSAPC as a function of time is shown in Fig. 4B. When these swollen ZSAPCs were immersed in NaCl solution, the ionic solution pulled out the water from the gel due to the increased osmosis pressure (1.35×10^{-4} KPa). The effect of ionic strength on water absorption can be understood in terms of equation, $Q_{eq}^{5/3} = A + Bi^2/I$ ^[37], where Q_{eq} is the water absorbency at equilibrium, i is the concentration of charges bound to the gel, I is the ionic strength of the external solution and A and B are the empirical parameters. At low ionic strength, the concentration of bound charges within the hydrogel network exceeds the concentration of salt in the external solution and the large ion-swelling pressure causes the hydrogel to expand, thereby lowering the concentration of ions within the hydrogel. As the external ionic concentration rises the difference between the internal and external ion concentration decreases and hydrogel deswells. The deswelling continues with increasing external salt concentration until the mobile ion concentration inside and

outside are almost equal. The deswelling data as function of release of water from swollen zeolite hydrogel composite with time was fitted into different models (Table 1).

As per the values of R^2 shown in Table 5, the Ritger-Peppas and Peppas-Shalin models were the best models that statistically described the deswelling phenomena of swollen composites having different cross-linking densities. The values of diffusion exponent (n) for release of water from fully swollen ZH1, ZH2, ZH3 and ZH4 were 0.47, 0.22, 0.21 and 0.25, respectively, as predicted by Model 2, indicating that release mechanism was purely Fickian diffusion, implying that the deswelling of swollen ZSAPC in the present study was function of ionic strength of outer environment or swelling media irrespective of the structure of gel network.

Release Behavior of ZnSO₄ From Zincated Polymers in Water and Soil

Zinc loading efficiency of prepared compositions is shown in Table 5. The loading capacity varied from 92.5% to 96.88% for all the test formulations. Periodic release of zinc from zincated hydrogel and hydrogel composites in water is shown in Fig. 5A. On first day, maximum release was obtained from zeolite free hydrogel formulations (CHE-1/2/3-Zn) (1.3–1.5%), whereas it was only 0.67 to 0.88% from ZSAPC (ZEO-1/2/3-Zn). On the 30th day 30.92–40.48% of zinc got released from CHE-1/2/3-Zn as compared to 18.64–22.16% from ZEO-1/2/3-Zn. This trend continued and on the 90th day zinc released from CHE-1/2/3-Zn was 46.15–53.76% compared to 29.46–36.89% from ZEO-1/2/3-Zn. This showed that the rate of release of zinc from hydrogel formulation was faster than the hydrogel composites.

Figure 5B depicts the periodic release of zinc from CHE-1/2/3-Zn and ZEO-1/2/3-Zn in soil. In soil, the CHE-1/2/3-Zn exhibited 25.38 to 33.95% zinc release on the 30th day and there after remained almost constant up to 90 days (26.51 to 34.69%). On the other hand, release of zinc from ZEO-1/2/3-Zn was slow

TABLE 5
In-vitro release kinetics parameters of zinc in water and soil from zeolite free gel and zeolite composite

Formulation	Zn Loading (%)	Ritger-Peppas				Higuchi model		First-order model		$t_{0.5}$ (Days)	
		n	Mechanism	k_1	R^2	k_H	R^2	k_f	R^2		
Water	CHE-1-Zn	96.88	0.57	Anomalous transport	0.039	0.95	0.052	0.94	6.62×10^{-5}	0.79	84.71
	CHE-2-Zn	95.95	0.57	Anomalous transport	0.044	0.93	0.057	0.93	7.27×10^{-5}	0.76	71.73
	CHE-3-Zn	92.5	0.57	Anomalous transport	0.047	0.93	0.062	0.92	7.86×10^{-5}	0.76	62.64
	ZEO-1-Zn	96.5	0.60	Anomalous transport	0.024	0.94	0.037	0.92	4.76×10^{-5}	0.81	143.87
	ZEO-2-Zn	96.15	0.60	Anomalous transport	0.025	0.94	0.038	0.93	4.89×10^{-5}	0.82	136.64
	ZEO-3-Zn	95.26	0.61	Anomalous transport	0.026	0.94	0.041	0.92	5.26×10^{-5}	0.83	120.60
Soil	CHE-1-Zn	96.88	0.47	Fickian diffusion	0.037	0.87	0.033	0.87	4.12×10^{-5}	0.55	185.64
	CHE-2-Zn	95.95	0.47	Fickian diffusion	0.043	0.88	0.039	0.87	4.85×10^{-5}	0.55	172.34
	CHE-3-Zn	92.5	0.47	Fickian diffusion	0.048	0.88	0.043	0.88	5.40×10^{-5}	0.56	137.13
	ZEO-1-Zn	96.5	0.65	Anomalous transport	0.016	0.95	0.029	0.92	3.77×10^{-5}	0.86	193.95
	ZEO-2-Zn	96.15	0.65	Anomalous transport	0.016	0.95	0.030	0.92	3.91×10^{-5}	0.87	181.86
	ZEO-3-Zn	95.26	0.64	Anomalous transport	0.018	0.95	0.031	0.92	4.09×10^{-5}	0.86	172.27

k_H , rate constant for Higuchi model; k_1 , rate constant for ritger peppas model; n, diffusion exponent; k_f , rate constant of first order model; R^2 , correlation coefficient; * $t_{0.5}$, -time (days) taken to release 50% of zinc from formulations.

as compared to their release behavior in water. ZEO-1/2/3-Zn showed a gradual increase in release up to the 45th day (22.25

to 25.09%) followed by slowing down of release rate up to the 90th day (25.78 to 29.41%).

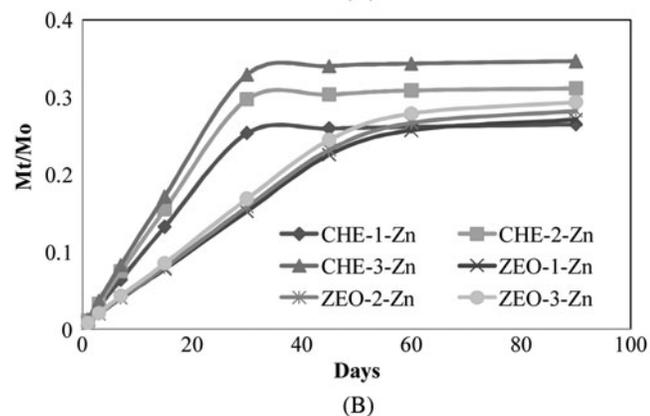
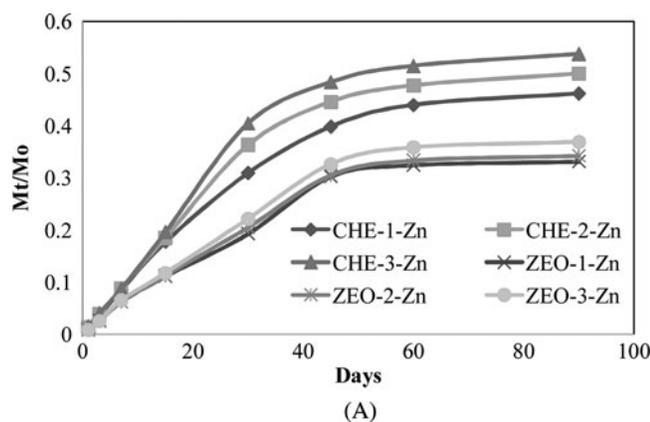


FIG. 5. Cumulative release of zinc in water (A) and soil (B) from CMC-based hydrogels and zeolite-based CMC-graft-PAam composite (ZEO).

To describe the kinetics of zinc release from polymeric matrices, release data was analyzed according to different kinetic equations and coefficient of determination values (R^2) of all batches as shown in Table 3. All the formulations followed the Korsmeyer-Peppas model as its coefficient of determination is nearer to one. The release mechanism of zinc from CHE-1/2/3-Zn and ZEO-1/2/3-Zn were predicted by using the diffusion exponent (n) obtained from the Korsmeyer-Peppas equation. Zinc release in water from CHE-1/2/3-Zn had n values ranging from 0.56 to 0.57 (Table 5), which indicates non-Fickian diffusion or anomalous transport that occurs due to a coupling of Fickian diffusion and polymer relaxation. The same mechanism could also be assigned to zinc release behavior of ZEO-1/2/3-Zn in water as n value equals to 0.6. Interestingly the release of zinc in soil from zincated hydrogels follows a Fickian diffusion mechanism as their n values were very close to 0.43. ZEO-1/2/3-Zn followed non-Fickian or anomalous transport, with n value ranging from 0.64 to 0.65.

The predicted half-life of release ($t_{0.50}$) of zinc from developed CHE-1/2/3-Zn and ZEO-1/2/3-Zn formulations are shown in Table 6. Zinc release in water from the zincated hydrogel formulations had lower $t_{0.50}$ values (62.64 to 84.71 days) than the zincated hydrogel composites (120.60 to 143.87 days). The same trend was observed in the case of release of zinc in soil.

Water Retention Properties of Zeolite Composite Amended Soil

Performance of an optimized ZSAPC (ZH1) for agricultural applications was evaluated in terms of moisture retention characteristics of ZH1 amended sandy loam soil as a function of

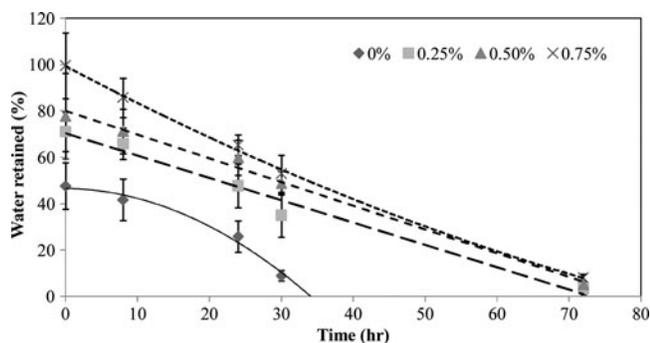


FIG. 6. Effect of zeolite hydrogel composite on water storage of sandy loam soil.

time under laboratory conditions (temp, 40°C and humidity 30%) at three amendment levels (0.25, 0.5 and 0.75% on weight/weight basis). It is clear from Fig. 6 that the soil moisture content decreased with time, but rate of decrease in treated soils was less as compared to control. The control soil lost the absorbed water within 30 h, whereas water retention period of the sandy loam soil amended with various amounts of ZH1 extended to 72 h due to gradual release of water from the composite.

Deswelling experiment exhibited that increased osmotic pressure in the external environment pulled off water from the gel mass due to concentration gradient. Same phenomena happened in soil environment. After addition of water to amended soil, the ionic concentration around the zeolite hydrogel composite particles decreased and at low ionic strength, the concentration of bound charges ($-\text{COO}^-$) within the hydrogel network exceeded the concentration of cations (Na^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Al^{3+} , etc.) in the external solution and a large ion-swelling pressure caused the hydrogel to expand. But with the subsequent evaporation of water from soil, the ionic concentration of external soil solution get increased leading to decrease in difference between the internal and external ion concentration and thus hydrogel released water gradually until the mobile ion concentration inside and outside were approximate equal. The study revealed (Fig. 6) that use of higher level of amendment leads to higher moisture content in soil though there is not much difference between 0.5 and 0.75% level of amendment at later stage of study. Therefore, the zeolite super absorbent composite prepared in the present study can be used as effective water management tool for increasing water use efficiency in agriculture.

CONCLUSIONS

Novel superabsorbent poly(CMC-zeo-g-cl-PAam/Zeolite) superabsorbent composites (ZSAPC) were synthesized by a free radical solution polymerization technique. Effects of synthesis parameters on the swelling characteristics of the composites were studied. The absorbency of the composites was dependent on ionic strength of external swelling media.

Water absorbency and release kinetics study revealed that absorbency of water by ZSAPC was highly dependent on network structure, whereas water release was independent of network structure, and the mechanism was predominately Fickian diffusion. Zeolite hydrogel composite as soil amendment enhanced the water holding capacity of sandy loam soil and the same fortified with zinc sulphate caused controlled delivery of zinc with extended time period.

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