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Slow-release NPK fertilizer encapsulated by carboxymethyl cellulose-based nanocomposite with the function of water retention in soil

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ABSTRACT

In this study, new slow release fertilizer encapsulated by superabsorbent nanocomposite was prepared by in-situ graft polymerization of sulfonated-carboxymethyl cellulose (SCMC) with acrylic acid (AA) in the presence of polyvinylpyrrolidone (PVP), silica nanoparticles and nitrogen (N), phosphorous (P), and potassium (K) (NPK) fertilizer compound. The prepared materials were characterized by FT-IR, XRD and scanning electron microscopy (SEM) techniques. The incorporation of NPK fertilizer into hydrogel nanocomposite network was verified by results of these analyses. Also, the swelling behavior in various pH and saline solutions as well as water retention capability of the prepared hydrogel nanocomposite was evaluated. The fertilizer release behavior of the NPK loaded hydrogel nanocomposite was in good agreement with the standard of Committee of European Normalization (CEN), indicating its excellent slow release property. These good characteristics revealed that the hydrogel nanocomposite fertilizer formulation can be practically used in agricultural and horticultural applications.

1. Introduction

Water and fertilizer are two main operative factors which put limitations on agricultural production [1,2]. Excessive application of agrochemicals to increase food production not only causes large economic and resource losses, but also causes serious environmental pollution [3]. Nowadays, water deficiency is one of the global problems. Considering these issues, effort to find controlled release fertilizer formulations (CRFs) or slow–release fertilizer formulations (SRFs) with high selectivity and effectiveness is one of the scientist's serious challenges [4–7]. Compared with conventional fertilizers, these formulations (CRFs or SRFs) prevent the loss of chemicals during irrigation and mitigate their degradation by microbial decomposition, photolysis and hydrolysis. At the same time, considering the water deficiency problem, development of efficient water reservoir systems such as superabsorbent hydrogels is necessary [8,9].

Superabsorbent hydrogels (SHs) are cross-linked polymers that can absorb large amount of water and saline solutions due to the presence of hydrophilic functional groups in their unique three-dimensional network structure [10]. SHs due to their good water retention and thereafter slow release of water from swollen SH have found extensive applications in various industries such as agriculture and horticulture [11–15]. In these industries, especially in desert regions, utilization of SHs can be advantageous in the reduction of irrigation of water consumption and improving the fertility of the soil [16,17]. Therefore, the soluble NPK fertilizer encapsulated by hydrogel would be an ideal slow release SH formulation. Carboxymethyl cellulose (CMC) based SH hydrogels synthesized by graft polymerization with acrylic acid (AA) monomers has been widely used in agriculture [18–22]. However, the high production cost and low mechanical strength of SH hydrogels (especially in natural-based hydrogels) limited their use in agriculture. Recently, to overcome these limitations, addition of low cost inorganic compounds such as clays and silicates has attracted great attention [23–26]. Silica (SiO_2) particles have been widely used in ceramic technology, electronic devices, and polymer material industries including thixotropic agent, thermal insulators, and composite fillers. Some studies have been shown that the usage of silica nanoparticles in hydrogel composition significantly influences its physical, mechanical, and also swelling characteristics. Addition of silica nanoparticles will increase the swelling capacity of the hydrogel nanocomposite due to their hydrophilic hydroxyl groups. Moreover, hydroxyl groups of the silica can interact with the functional groups of hydrogel components which results in the formation of additional physical cross-linking points within the hydrogel network. These additional cross-linking points will improve the mechanical strength of the nanocomposite [27–29]. Also, using water soluble linear nonionic polymers (such as

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polyvinylpyrrolidone (PVP)) being compatible with CMC, creates a highly porous hydrogels and increases their water absorption capacity [30].

On the basis of described background and to obtain such controlled release formulation, we attempted to prepare a novel SRF formulation based on SCMC-g-poly(AA)/PVP/Silica (Hyd/PVP/Silica) in this work. Also, the effect of silica nanoparticles on the water retention and slow release property of the prepared SH nanocomposite formulation was studied. Furthermore, repeatable swelling of prepared SH nanocomposite at various pH values and salt solutions were investigated.

2. Experimental

2.1. Materials

Acrylic acid (AA), *N*,*N*′-methylene bisacrylamide (MBA), ammonium persulfate (APS), sodium hydroxide, chlorosulfonic acid, urea, potassium dihydrogen phosphate, ammonium dihydrogen phosphate, polyvinylpyrrolidone (PVP, M_w 25,000 − 30,000), and dimethylformamide (DMF) were purchased from Merck company. Carboxymethyl cellulose sodium salt (NaCMC) (> 99.5%) (viscosity of 1000–1500 mPas for a 4% aqueous solution at 25°) was purchased from Fluka BioChemika. Ethanol (96%) was purchased from Mojallali reagent chemicals Co. (Iran, Tabriz). Rice husk (RH) was provided from a supplier in Rasht, Iran. All other reactants were of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of silica nanoparticles

Silica nanoparticles were prepared according to our reported procedure [31]. Briefly, rice husk was washed with distilled water to remove its soil and dust. Then, it was acid-washed two times. In the first step, rice husk was acid-leached by reflux boiling in HCl aqueous solution (3% V/V) with the ratio of 50 g/L under stirring in a round-bottomed flask at 100° for 2 h. The obtained mixture was filtered and then rice husk was washed with distilled water for several times. Thereafter, the filtered rice husk was dried in an oven at 100° for 24 h. In the second step, the rice husk was acid-leached by reflux boiling in H_2SO_4 aqueous solution (10% V/V). In continue filtration and drying processes were performed similar to the previous step. Finally, the dried rice husk sample was calcined in a furnace at 900° for 5 h, yielding white-colored ash which contained 90–97% silica.

2.3. Preparation of Hyd/PVP/silica nanocomposite

Sulfonation of CMC was performed according to the method of Gamzazade et al. [32]. One gram of SCMC was mixed adequately with 30 mL distilled water in a three necked glass round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a nitrogen purge line. The prepared mixture was stirred continuously at 40° for 10 min to obtain a homogeneous solution. Then, 1 g PVP and 0.05 g silica nanoparticles were added to the prepared solution while stirring. A few minutes later, 7.2mL of 65% neutralized AA and 0.018 g cross-linker agent (MBA) were added to the mixture. After purging with nitrogen to remove the dissolved oxygen, 0.05 g APS was added to the mixture as initiator agent. Thereafter, temperature of the reaction mixture was raised up to 60° and kept at this condition for 4 h to complete the polymerization process. The gel like product was cut into small pieces, and then it was immersed in ethanol for 24 h to remove unreacted species. Afterwards, the dehydrated hydrogel sample was dried in an oven at 70° for 24 h. For comparison, a neat hydrogel sample without addition of PVP and silica nanoparticles was also synthesized similar to the above described method.

2.4. Preparation of Hyd/PVP/silica/NPK formulation

To prepare SRF formulation based on Hyd/PVP/Silica/NPK by in-situ polymerization method, a pre-determined amount of urea (10 g), ammonium dihydrogen phosphate (5 g), and potassium dihydrogen phosphate (5 g) was dissolved in a solution of SCMC under constant stirring. Next steps for the synthesis of SRF formulation were performed in compliance with the described procedure in Section 2.3.

2.5. Characterization methods

The FTIR spectra of Hyd/PVP/Silica, NPK and Hyd/PVP/Silica/NPK were recorded by a Bruker Tensor 27 FTIR at the wavenumber range of 400–4000 cm^{-1} using samples prepare as KBr pellets. Wide angle X-ray diffraction patterns of Hyd/PVP/Silica, NPK and Hyd/PVP/Silica/NPK were also measured using a Siemens D500 X-ray diffractometer (Siemens AG, Karlsruhe, Germany) with Cu Kα radiation in 2Θ range of 2° to 70°. The surface morphologies of Hyd/PVP/Silica and Hyd/PVP/Silica/NPK formulation were studied using MIRA3 FEG-SEM (Tescan, Czech) scanning electron microscope.

2.6. pH-sensitivity and pulsatile behavior

To investigate on-off switching behavior as well as reversible swelling (pH = 8) and deswelling (pH = 2) property of the prepared hydrogels, diluted 0.1 M aqueous solutions of NaOH and HCl were used. First, 0.05 g dried hydrogel sample was transferred into a tea bag and then, it was immersed in distilled water at room temperature. The swollen hydrogel samples were removed from the distilled at certain time intervals and were weighted after removing the surface water by a filter paper. Each experiment was performed in 4 times. The equilibrium swelling ratio (S_{eq} (g/g)) was calculated using the following equation:

$$S_{eq}(g/g) = \frac{W_s - W_d}{W_d} \quad (1)$$

where S_{eq} (g/g) is equilibrium swelling ratio, W_s (g) is the weight of the swollen hydrogel sample, and W_d (g) is the weight of the dry hydrogel sample.

2.7. Saline sensitivity and pulsatile behavior

To investigate on-off switching behavior of prepared samples, 1 g of dried hydrogel sample was immersed in distilled water and 0.1 M aqueous solution of NaCl, periodically. The equilibrium swelling capacity was calculated similar to the previously mentioned method.

2.8. Water retention behavior of soil with and without SRF formulation

To investigate water retention of soil containing synthesized SRF formulation, a plastic cup containing well-mixed dry sample of SRF formulation and 100 g of dry loamy sand soil (below 20 mesh) was prepared. Thereafter, 50 mL distilled water was poured into the plastic cup and weighed (W_0). As comparison, another 100 g of dry loamy sand soil without SRF formulation was placed in an identical plastic cup and after addition of 50 mL distilled water weighed (W). The plastic cups were kept at room temperature and weighed every day (W_t) over a period of 30 days. Finally, the water retention percent (WR%) of soil was determined by following equation:

$$WR\% = \frac{W_t - W}{W_0 - W} \times 100 \quad (2)$$

2.9. Slow release behavior of synthesized SRF formulation

To study release of NPK fertilizer from synthesized SRF formulation,