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Facile preparation of iron loaded calcium alginate nanocarriers and study of controlled release of iron

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ABSTRACT

The deficiency of micronutrient such as iron in the soil has become a problem of major and global concern in agriculture sector. The direct application of micronutrient to soil does not serve the purpose well as most of the added active ingredient is leached out due to watering. Thus, a constant and sustained supply of micronutrient deserves attention. In the present study iron loaded calcium alginate nanocarriers were prepared via microemulsion technique. The prepared iron nano-reservoirs were characterized by analytical techniques like Fourier transform infra-red (FTIR) and X-ray diffraction (XRD) spectroscopy, transmission electron microscopy (TEM), electron diffraction (ED), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy(SEM), and particle size and zeta potential measurements. The iron loaded calcium alginate nanocarriers were studied for their water holding capacity and the effect of alginate, crosslinker, pH and temperature was examined on their water sorption capacity. The release of iron from calcium alginate nanocarriers was investigated and the influence of various factors such as composition of nanocarriers, pH and temperature of the release medium was studied. The suitability of developed formulation to agricultural fields was examined by performing soil − pot experiments which demonstrated that the iron loaded nanocarriers caused better growth of plants in comparison to that when iron was directly applied to soil.

1. Introduction

In the past decades the green revolution has steeply enhanced the agricultural production thus to meet the increasing demand of food. At the same time, however, it has also adversely affected the nutritional value of the soil and developed severe deficiency of micronutrients. Furthermore, it has also brought about undesirable changes in the soil characteristics like higher porosity, poor micronutrients retention, enhanced porosity, loss in water holding capacity and poor fertility. Thus, maintaining a healthy level of micronutrients in the agricultural lands is a challenging task. All these consequences can only be overcome by the frequent and rational application of nanoscience and nanotechnology in each and every steps of agricultural production. The new and newer strategies in chemical synthesis of nanomaterials have resulted in production of large variety of nanomaterials such as nano-pesticides, nanofertilizers, controlled delivery of agricultural active agents etc which not only increase the crop production but also meticulously maintain the soil quality and environmental protection [1].

Nanotechnology has been quite successful in designing controlled release formulations which desirably regulate the delivery of agrochemicals such as micronutrients, pesticides, fertilizers, herbicides etc [2]. The advantages of controlled release technology include longer persistence of active agents in the soil − water system and less requirement of active agents that make the agricultural practices more economical. Furthermore, this also protects ground water from the applied toxic pesticides, insecticides etc. It is well known that besides fertilizers, the micronutrients like Cu, Zn, Mn, Fe etc are also essential for the growth of plants and eventual production of agricultural crops [3]. Unfortunately, less attention has been paid to address the problems of micronutrients deficiency in the soil and its proper and effective remediation [4]. One of the possible strategies to tackle the deficiency of micronutrients is the use of nanocarriers which act as vehicles of the essential micronutrients and deliver them with desired quantity and duration of time [5]. Among various materials employed for fabrication of micronutrients loaded nanocarriers, the use of natural occurring polymers has greatly increased in the recent years [6]. The fundamental reason behind the selection of biopolymers is due to their abundance in nature, low cost [7], easy availability [8], biodegradability [9], eco-friendly nature [10], non toxicity and ease of functionalization. These biopolymers are versatile materials because of certain unusual characteristics like the presence of multifunctional groups such as amino groups in chitosan [11], carboxylic groups in polysaccharides [12] etc.

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which may be easily crosslinked either with low molecular weight organic compounds like aldehyde or multivalent cations such as Ca^{2+}, Ba^{2+} etc, respectively, to produce micro or nanogels [13]. The literature is richly documented with investigations reporting the use of biopolymers such as chitosan, sodium alginate, starch, polysaccharide [14] etc. in biomedical [15], domestic and agricultural [16] fields.

Thus, being motivated by the interesting properties of crosslinked alginate, the authors have adopted a novel strategy to design agricultural formulations [17] that include iron loaded calcium alginate nanocarriers. Due to the hydrophilic nature of alginate the iron loaded calcium alginate nanocarriers swell in aquatic environments and release iron into the soil which are iron deficient. The extent to which the alginate has been crosslinked with Ca^{2+} ions regulates the swelling behavior of nanocarriers which, in turn, controls the amount of iron releasing into the soil [18]. The suitability of the prepared formulation in agricultural field will also be evaluated by performing soil pot experiments.

2. Experimental

2.1. Materials and methods

Sodium alginate was purchased from Merck, India and used as such. Iron chloride and calcium chloride (di hydrate) were used as micronutrient and crosslinking agent of alginate, respectively (Loba Chemie, Mumbai, India). Paraffin oil (Merck, India) was used to prepare microemulsion and double distilled water was used throughout the experiments. For conducting soil-pot experiments the sandy soil was collected from the Leh-Laddakh region of India which is known to be highly deficient in iron. The moisture content in the soil was determined by a Digital Moisture-meter (Universal Traders, New Delhi, India).

2.2. Preparation of native and micronutrient (Fe) loaded nanocarriers

In order to prepare iron loaded calcium alginate nanocarriers, an emulsion crosslinking method was adopted. In a typical experiment, 1 g of sodium alginate was dissolved in 30 mL distilled water at 60 °C, and to this solution of sodium alginate 10 mL paraffin oil was added with vigorous stirring (Capacity 5 MLH 300 rpm, Remi India) for 40 min to produce a stable emulsion. Now, for crosslinking of sodium alginate emulsions and subsequent loading of iron, 10 mL solution of calcium chloride (0.5 M) and an equal volume of 0.5 M ferric chloride solution were added to sodium alginate emulsion under constant stirring to allow crosslinking reaction to take place. The reaction mixture was continuously stirred for 3 h at room temperature so that alginate was completely crosslinked by Ca^{2+} ions to form iron loaded calcium alginate nanocarriers which were precipitated on the bottom of the reaction vassal. The iron loaded calcium alginate nanocarriers were left in solution for 24 h at room temperature and thereafter filtered and intensively washed with water and acetone, respectively to remove unreacted chemicals and paraffin oil. Following the same procedure, unloaded calcium alginate nanocarriers were also prepared [19]. The preparation of calcium alginate nanocarriers and iron loaded alginate nanocarriers are shown in Fig. 1.

2.3. Characterization

FTIR spectrophotometer (8400S, Shimadzu) was used to seek structural information about the calcium alginate nanocarriers in the range 4000–400 cm^{-1}. The shape and size of the nanocarriers were determined using a transmission electron microscope (Morgagni-268-D) at an acceleration voltage of 80.0 kv. The XRD studies were conducted to determine the crystalline nature of the native alginate and iron loaded alginate nanocarriers using a rotating X-ray diffractometer scanned at 0.005°, (2θ)/s in the 2θ range 10–60°. The size and zeta potential of nanocarriers were measured using a Zetasizer ZS 90(Malvern Instruments, Malvern, UK). All experiments were done in triplicate. A scanning electron microscope with an electron dispersive X-ray spectrometer (SEM/EDX, Jeol, JSM-5800LV) was used to study the surface morphologies and elemental composition of the native and iron loaded nanocarriers. Electron diffraction study was performed to determine the crystalline nature of the native calcium alginate and iron loaded sodium alginate nanocarriers, respectively on Morgagni 268-D transmission electron microscope.

2.4. Swelling experiments

The water sorption capacity of the nanocarriers was quantified gravimetrically [20]. In a typical experiment, a pre-weighed quantity of nanocarriers was placed in water and allowed to swell till equilibrium. The swollen weight was recorded by a digital balance (APX-203 Denver, Germany) and the following equation was used to calculate the swelling ratio,

$$\text{Swelling Ratio} = \text{Wt. of swollen nanocarriers } (W_s)/\text{Wt. of dry nanocarriers } (W_d) \quad (1)$$

2.5. Micronutrient (iron) release study

For performing iron release experiments under static conditions, accurately weighed iron loaded calcium alginate nanocarriers were placed in 25 mL of distilled water taken as release medium. The amount of released iron at different time intervals (Wt) was assayed spectrophotometrically at 328 nm [21]. The following equations derived from Fick's law and applicable to a spherical release device were applied to the release data to gain information about the mechanisms of iron release,

$$W_t/W_\infty = Kt^n \quad (2)$$

$$W_t/W_\infty = 4[Dt/\pi L^2]^{0.5} \quad (3)$$

In the above Eq. W_t and W_∞ represent the amount of iron released at time t and equilibrium, respectively, k is the swelling front factor, n is the release exponent, D is the diffusion constant and L is the radius of the dry nanocarriers.

The type and nature of the release mechanism is reflected by the value of 'n' For instance, when $n = 0.43$, the release process is said to be Fickian whereas the value of 'n' lying between 0.43 and 0.85 suggests for a non-Fickian release mechanism. When n is equal to 1, the release process is said to follow Case II transport which is the most desired mechanistic route in controlled release processes.

2.6. Soil-pot experiments

In these experiments, the columns were prepared by using standard burettes (Borosil) of 50 mL capacity. The soils samples were collected from the depth of 2 feet and 50 g of soil was used to prepare the columns. The soil was filled in the column to the one third of the length of the columns and their lower ends were blocked by cotton so that the soil could be retained in the columns. Thereafter, a definite volume of micronutrient solution (iron) of known concentration was filled in the columns and the release of iron was monitored under the following conditions:

i) When iron is released from loaded nanocarriers, and
ii) When iron is released directly from the soil without nanocarriers.

The experimental setup for soil pot experiment is shown in Fig. 2.