



# Polyvinyl alcohol based hydrogels for urea release and Fe(III) uptake from soil medium



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## ABSTRACT

Poly(vinyl alcohol) (PVA) based biocompatible, non-toxic and environmentally benign polymeric hydrogels were synthesized by cross-linking with poly(ethylene glycol) (PEG) and sodium sulfate. Further modification was carried out with incorporation of urea into the hydrogel at the time of synthesis. The prepared gels were characterized by scanning electron microscopy (SEM), Fourier Transform Infra Red (FTIR) spectroscopy, nitrogen adsorption desorption isotherms and swelling. Prediction of the possibility of using these hydrogel beads in agriculture fields is the main objective of this work. In this particular article, the release of urea from urea extracted and urea incorporated beads in the soil medium was studied along with inspection of Fe(III) uptake from the same soil sample. The gel matrices were found as potential candidates for slow release of urea and high sorption of Fe(III) from soil sample. Thus the problem of frequent application of urea containing fertilizer to the agricultural field can be overcome and at the same time the trouble for high concentration of Fe(III) in the soil can also be diminished.

## 1. Introduction

Hydrogels are formed of natural or synthetic hydrophilic polymers which form polymeric chain networks and have high degree of flexibility and water absorption capacity [1]. Instead of getting dissolved in water, they swell and retain a significant fraction of water trapped within their structures. Chemical hydrogels are a particular class of macromolecular materials which is obtained by chemical stabilization of hydrophilic polymers in a 3D network through covalent bonds. In physically cross-linked hydrogels the polymeric chains are held together by physical interactions, such as electrostatic interactions, van der Waals forces and H-bonds [2]. The final properties of hydrogels like water uptake capacity, swelling kinetics, mechanical and rheological properties, degradation rate, porosity, toxicity, etc., are related to the method involved in the cross-linking process. These hydrogels are widely used in recent days as drug delivery systems [3–5], biosensing agents [6,7], soft actuators/valves [8], catalysis [9], tissue engineering [10], agriculture [11] and horticulture [12], and every day products [13].

Poly(vinyl alcohol) (PVA) is an interesting material with exceptionally good properties such as biocompatibility, water solubility, biodegradability, non-toxicity, non-carcinogenicity high elasticity and hydrophilic characteristics that possesses the capability to form hydrogels by chemical or physical methods like cross linking,

photopolymerization, freeze-thawing, etc. [14–17]. Various gelling and cross-linking agents, such as aldehydes [18], several inorganic salts like NaCl, KCl, CsCl, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, etc., [19], alginates [20], chitosan [21], starch [22], poly(ethylene glycol) (PEG), [23] etc., are used in recent years to form several hydrogels with PVA. PEG is another polymer that has many kinds of applications in wound healing, tissue engineering scaffolds and drug delivery because of the intrinsic molecular properties of PEG, such as good water solubility, resistance to protein adsorption, low immunogenicity and absence of toxicity which have made it ideal for use in *in vivo* applications [24,25]. These PEG hydrogels are very much versatile materials that can be chemically modified through several methods such as irradiation and chemical cross-linking [26–28] and are very much biocompatible [29,30]. These PVA based hydrogels are extensively used in numerous biomedical applications [31–33]. Apart from medical applications these PVA based polymeric hydrogels have also been widely used in industrial [34] and agriculture fields [35].

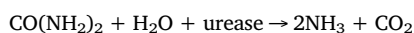
Besides numerous beneficial aspects and being an essential element for life processes and plant growth [36], iron is highly reactive and toxic owing to the Fenton reactions if present in excess amount and may be responsible for a wide range of metabolic disorders in plant tissues [37]. Plants control Fe homeostasis and respond to its deficiency as well as overloaded conditions. It produces toxic hydroxyl radicals like ·OH, and other reactive oxygen species like H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub><sup>·-</sup> [38,39] which

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directly react with polyunsaturated fatty acids, proteins and nucleic acids and destroy numerous endocellular structures [40]. Several articles [41,42] report that the rice roots oxidize Fe(II) to Fe(III), and this results in higher uptake of iron and increases the probability of Fe toxicity in rice. Iron is taken up by the root at the very first step, then transported to the shoot, and finally loaded in the seeds [43,36] and thus enters the food chain. Diseases like leaf bronzing is a common fact due to the iron toxicity and as the disease further progresses, it spreads into the whole body of the crop and then turn brown, dry up and curl inward [44].

On the other hand, urea is a globally used fertilizer for agricultural fields and is directly applied to the soil in blended form with other fertilizers and is superior to most of the other nitrogen sources. But the main problem is, it breaks down via hydrolysis and converts to ammonia and carbon dioxide as soon as it is applied to the soil containing urease and small amount of moisture [45]. The chemical reaction is as follows:



In addition, decomposition becomes faster if the pH of the soil is high. For this reason, farmers are required to apply urea very frequently in the fields. This is definitely a constraint in terms of labour and economy. Research is underway in agricultural sciences [46] for developing a quality matrix to accumulate, store and show sustained release of urea to the soil medium.

Sannino and coworkers developed and patented novel and totally biodegradable and biocompatible class of cellulose-based polyelectrolyte hydrogels loaded with small molecules, such as nutrients, for release in a controlled manner, depending on several conditions including swelling-deswelling transitions and suggested its use for agricultural lands [47–50]. Several other researchers have also reported the sustained release behaviour of several agrochemicals using different matrices during the past few years. Table 1 reflects an idea of the variety of such researches towards agricultural applications [51–66]. Even some interesting reviews are available which clearly indicates the necessity and importance of the work. However, to the best of our knowledge, biocompatible polymers like PVA and PEG have not been reported for such applications before.

In this particular article, we have synthesized two different PVA based hydrogels using PEG and  $\text{Na}_2\text{SO}_4$  as gelling/cross-linking agent. We have characterized them using SEM, FTIR, swelling and porosity measurement using nitrogen adsorption-desorption experiment. Applications of the prepared gels were sought out for the agricultural field by studying the sorption-desorption properties for urea and iron from soil medium.

**Table 1**

Different materials reported in the literature to have sustained release mechanism for different agrochemicals.

Materials	Sustain release of agrochemicals	Ref
Nanocomposites produced from urea or extruded thermoplastic starch/urea blends in a matrix	Urea and P	51
Acrylic polymer	N, P and K containing fertilizer	52
Pectin-based polymer hydrogel	Phosphate, potassium and urea	53
Polyacrylamide and methylcellulose hydrogel	Paraquat pesticide	54
Porous gel of chloroacetic acid and 3-aminopropyl trimethoxysilane	Herbicides	55
Paraffin wax, polyolefin and polyethylene coating, carboxymethyl cellulose, calcium alginate, pectin, hexagonal mesoporous silica, magnesium-aluminium double-layer hydroxide	Pesticides and herbicides	56
Wheat straw cellulose-based semi-IPNs superabsorbent	Fertilizers	57
Corn-cob-based semi interpenetrating polymer network	Fertilizers	58
Waterborne acrylic emulsions modified with organic siloxanes and aziridine crosslinker	Fertilizers	59
Biochar-modified waterborne polyacrylate membrane	Fertilizers	60
polyacrylate/poly(silicone-co-acrylate) emulsions	Fertilizers	61
$\text{Fe}^{\text{III}}$ -tannic acid complexes blended with acrylic latex	Urea	62
Bio-based polymeric hydrogel using gelatin grafted with acrylamide	Fertilizers	63
Ionically crosslinked carboxymethyl cellulose hydrogel	Fertilizers	64
Chitosan nanoparticle based hydrogel	Pesticides, herbicides, plant growth regulators	65
Micro and nanoparticles, beads and hydrogels using polysaccharides such as alginate, cellulose, pectin, cyclodextrin, starch, dextran, chitosan, cyclodextrin, guar gum etc.	Pesticides, chemical fertilizers, manure and other growth agents	66

## 2. Experimental

### 2.1. Reagents

Sodium sulfate, PEG#6000, urea, ferric nitrate, sulfuric acid and hydrochloric acid were procured from Merck, India. PVA (#89,000–98,000, 99 + % hydrolyzed) was obtained from Sigma-Aldrich. Ammonium thiocyanate, para dimethyl amino benzaldehyde (PDAB), ethanol and all other chemicals were of analytical grade and used as received. Soil was obtained from Uttar Banga Krishi Viswavidyalaya (UBKV) NH31, Pundibari, Cooch Behar, West Bengal 736165, India. The collected soil is of alluvial deposit origin and is mildly acidic in nature. Sample collection is done from 0.15 to 1 m deep friable loam to sandy loam.

### 2.2. Apparatus

The absorption spectra were obtained using an Agilent 8453 diode array spectrophotometer. A digital pH/ion meter Mettler Seven Compact (S 220-K) was used to measure and adjust the pH of different solutions. For SEM, Carl Zeiss EVO18 instrument was used. A BOD incubator shaker NOVA Model: SHCI 10(D) was procured from Indian Instruments Manufacturing Co. to maintain the temperature at  $25 \pm 0.5^\circ\text{C}$ . Centrifugation was done using Hermle microprocessor controlled universal refrigerated high speed table top centrifuge (model Z 36 K). IR spectra were recorded in the region  $450\text{--}4000\text{ cm}^{-1}$  with a Perkin Elmer Spectrum Express version 1.03.00. using KBr pellets. The surface area was measured with a Micromeritics Gemini VII surface area analyzer and the nitrogen adsorption/desorption isotherms were recorded 2–3 times to obtain reproducible results and reported by BJH (Barret-Joyner-Halenda) surface/volume analysis.

## 3. Preparation of the hydrogels

- PVA-Sulfate (PS) bead: 5% (w/v) PVA was mixed with 2 M sodium sulfate in equal volume ratio in an eppendorf and was shaken vigorously at room temperature. White round shaped beads were formed.
- PVA-PEG (PP) bead: 5% PVA and 50% (w/v) PEG solution were kept in refrigerator for 2 h to cool and were mixed in equal volume ratios in a test tube with vigorous shaking at room temperature. Cream colored beads were formed.
- Urea incorporated PS bead (U-PS): 5% PVA was prepared in a 100 mM urea solution. This urea incorporated 5% PVA was mixed with 2 M sodium sulfate in equal volumes in an eppendorf and was

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