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Biodegradation study of enzymatically catalyzed interpenetrating polymer network: Evaluation of agrochemical release and impact on soil fertility

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ABSTRACT

A novel interpenetrating polymer network (IPN) has been synthesized through enzymatic initiation using lipase as initiator, glutaraldehyde as cross-linker, acrylic acid as primary monomer and acrylamide as secondary monomer. Biodegradability of synthesized interpenetrating polymer network was studied through soil burial and composting methods. Synthesized hydrogel was completely degraded within 70 days using composting method, while it was 86.03% degraded within 77 days using soil burial method. This was confirmed by Fourier transform Infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) techniques. Synthesized interpenetrating polymer network hydrogel was used as a device for controlled release of urea and also act as water releasing device. Their impact on soil fertility and plant growth was also studied. The initial diffusion coefficient has a greater value than the later diffusion coefficient indicating a higher fertilizer release rate during the early stage. Fertilizer release kinetic was also studied which showed Non-Fickian diffusion behavior, as the rate of fertilizer release was comparable to the relaxation time of the synthesized matrix. Synthesized IPN enhance the water uptake capacity up to 6.2% and 7.2% in sandy loam and clay soil, respectively.

1. Introduction

Synthetic polymers have been extensively used all over the world due to their excellent physical, chemical and mechanical properties. These properties of the synthetic polymers make them resistant to microorganisms and other natural degradation forces and lead them to remain in the environment after disposal. It causes serious problem worldwide leading to environmental pollution, waste management and land shortage problems for solid waste management. Because of all above problems there is increasing demand of biodegradable polymeric materials as a solution of environment safety, economy and solid waste water management [8,19,26,4,9,10].

Ghosh et al. [7] synthesized novel biodegradable polylmeric flocculant based on polyacrylamide-grafted tamarind kernel polysaccharide and characterized it by NMR spectroscopy, SLS analysis and viscometry. Biodegradation characteristics of starch-polystyrene loose-fill foams in a composting medium were studied by Pushpadass et al. [20]. Biodegradation of lignin through composting method was studied by Tuomela et al. [28]. Sherbiny et al. [5] prepared bioderadable pH-responsive alginate-poly(lactic-*co*-glycolic acid) nano/micro hydrogel matrices for oral delivery of silymarin and characterized synthesized biodegradable hydrogel through SEM and AFM techniques. Novel biodegradable flocculating agents based on cationic amphiphilic polysaccharide was developed by Ghimici and Nichifor [6]. Biodegradable poly(ethylene glycol) hydrogels have self degradation mechanism, which was reported in the literature [29,2,14] Deshmukh et al., 2010).

Many chemical initiators were used in the literature, but using enzyme as a catalyst for the IPN synthesis is a new and greener approach. Enzymatic polymerization is an *in-vitro* polymerization process through a biosynthetic pathway. In many natural polymerization processes, enzyme acted as an environment-friendly natural catalyst. Lipases play an important role in many natural polymerization processes, because of this property it may be possible to exploit lipase for environment-benign industrial polymer processing [15,18,3].

In the present investigation a novel interpenetrating polymer network of *Gum tragacanth*, poly(acrylic acid) and poly(acrylamide) has been synthesized using lipase as an initiator and glutaraldehyde as a crosslinker. The present IPN was synthesized using enzyme as an initiator rather using chemical initiator. The biodegradability of the candidate polymer has been studied

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through soil burial and composting method. The candidate polymer has been evaluated as a device for controlled release of urea and enhancement of moisture content of soils.

2. Experimental

2.1. Materials and methods

Gum tragacanth (Merck) was used as backbone. Lipase (MP Biomedia) was used as an initiator. Glutaraldehyde, acrylic acid, acrylamide and urea (MERCK) were used as crosslinker, monomers and fertilizer, respectively.

FTIR spectra of backbone and hydrogel were recorded on Perkin Elmer Spectrophotometer using KBr pellets. Scanning Electron Micrographs (SEMs) of the backbone and hydrogel were taken on LEO-435VF (LEO Electron Microscopy Ltd.). Weighing was done on electronic balance (LIBROR AEG-220, Shimadzu).

2.2. Synthesis of acrylic acid-*co*-acrylamide based IPN [Gt-cl-poly(AA-ip-AAm)]

Acrylic acid was grafted onto *Gum tragacanth* in an aquous medium using lipase as an initiator and glutaraldehyde as a crosslinker. To get the graft copolymer *Gum tragacanth* (1 g) was taken in a reaction flask containing known amount of water and was stirred thoroughly. A known concentration of lipase was added followed by drop by drop addition of acrylic acid and glutaraldehyde into the reaction mixture. Stirring was continued until the homogenous mixture was obtained. Graft copolymer was extracted using slightly heated distilled water. Finally, hydrogel obtained was dried in hot air oven at 40 °C. The synthesized product was then taken in a flask having known amount of distilled water followed by addition of acrylamide and lipase and kept for 24 h. After 24 h glutaraldehyde was added with constant stirring and kept in oven at 40 °C for 48 h. It was washed with slightly heated distilled water and kept for drying in hot air oven. Percentage grafting (P_g) of synthesized interpenetrating polymer network was calculated using the following equation [22].

$$P_g = \frac{W_f - W_b}{W_b} \times 100 \quad (1)$$

where W_f and W_b are weight of functionalized and backbone, respectively.

The synthesized sample (0.5 g) was immersed in distilled water and after every 2 h interval weight gain of the swollen sample was noted down. After attaining the swelling equilibrium, the swollen sample was separated from the water by filtering using 100- mesh sieve. The percentage swelling (P_s) of the interpenetrating polymer network was calculated from the following equation [23] [25].

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_s and W_d are weight of swollen and dry polymer, respectively.

2.3. Measurement of water uptake by clay and sandy loam soils in presence of swollen interpenetrating polymer network

Clay and sandy loam soil samples were used for laboratory experiment. These samples were collected from the upper layer of respective soil. The soil samples were air dried, mixed and crushed to 2 mm particle size.

Accurately weighed dried interpenetrating network hydrogel samples were taken in tea bags (100 mesh nylon screen) and were immersed in 100 ml of distilled water. The samples were allowed to soak water for 24 h. Tea bags were taken out from the distilled water and were kept in air for two minutes to remove excess water. Tea bags with swollen samples were added to known weight of dry clay and sandy loam soils. After every 4 h time intervals the tea bags with swollen samples were taken-out, wiped with tissue paper and were weighed until equilibrium was attained [24].

2.4. Loading of urea in interpenetrating polymer network

Urea solution was prepared in distilled water. Maximum absorption value of urea was taken using double beam UV–vis spectrophotometer. The standard curve of urea was taken at maximum absorption. Urea solution of 2000 ppm was prepared in distilled water and 2.0 g of candidate polymer was immersed in it and kept overnight. Next day sample was taken out from the urea solution and washed slightly with water to remove any surface adhered urea molecules. The sample was dried in oven and its evaluation of fertilizer release kinetics with respect to time was studied using double beam UV–vis spectrophotometer. Concentration of fertilizer release was carried-out after every 4 h, until the equilibrium was achieved.

2.5. Mathematical analysis of urea release kinetics

Interpenetrating polymer network has properties to absorb and retain a large amount of aqueous liquid in it. These properties make them useful in controlled release of fertilizers. Simple and sophisticated model have been developed to check the release behavior of fertilizer from the interpenetrating polymer device as a function of time. The most applicable mechanism of the solute release behavior from the interpenetrating network is the diffusion mechanism. Urea release behavior was determined through empirical equation. Power law function given by Peppas et al. is used to evaluate the fertilizer release behavior through the interpenetrating polymer network.

$$\frac{M_t}{M_\infty} = Kt^n \quad (3)$$

In diffusion-controlled system, power law equation is valid only for the first 60% release of the urea. Here, n is a release exponent representing the release mechanism, K is a structural constant, M_t is the fractional release of urea at different time intervals and M_∞ is the fractional release of urea at equilibrium. The value of $n = 0.5$ signifies the Fickian diffusion, $n = 1$ reveals the case II diffusion and if the value of n lies between 0.5 and 1.0, it signifies the Non-Fickian or anomalous diffusion.

2.6. Diffusion coefficient of released urea

Analysis of urea release from the interpenetrating polymer network can be performed by calculating diffusion coefficient. Fick's first and second laws were used to describe the diffusion process. Integral diffusion for the cylindrical device can be given as: [12,16,21].

$$\frac{M_t}{M_\infty} = 4 \times \frac{Dt}{\pi l^2} \quad (4)$$

where M_t/M_∞ is the fractional release of urea, M_t is the urea release at time t and M_∞ is the urea release at equilibrium. D is the diffusion coefficient and l is the thickness of the synthesized device.