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Psyllium and Acrylic Acid Based Polymeric Networks Synthesized under the Influence of γ-Radiations for Sustained Release of Fungicide

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Abstract: The present study deals with the utilization of psyllium and acrylic acid based hydrogels, synthesized under the influence of γ-radiations, in sustained delivery of copper sulfate, used as a fungicide in agricultural fields. Swelling behavior of the synthesized hydrogel was investigated in distilled water as functions of time, temperature, and pH. It was found that the hydrogel showed maximum of 10,578 % swelling at 25 °C for 24 h. The hydrogel was then checked for its sustained fungicide release behavior. It was observed that the hydrogel has been found to follow Non-Fickian type mechanism for the fungicide release. The 'n' and 'k' have been found to be 0.71 and 7.61×10^{-3}, respectively.

Keywords: Psyllium, Acrylic acid, Fungicide delivery, Water absorption, γ-Radiation

Introduction

Functionalized bio-polymers have successfully taken over the era of synthetic polymers, for being cost-effective, biodegradable, environmentally friendly, and efficient. These bio-polymers have been used in various applications such as waste-water treatment [1], drug-delivery technology [2,3], and membrane technology [4]. Various bio-polymers have been previously modified and used efficiently as flocculants [5,6] and metal ion sorbents [7,8]. These modified bio-polymers have also been used as adsorbents owing to their water absorbing capacity.

Recent years have witnessed tremendous applications of pesticides, herbicides, fungicides, and fertilizers. These chemicals were exploited without considering the disadvantages of the same. After being used for at least two to three decades, the world is witnessing the hazardous effects of these chemicals. The properties of pesticides such as volatility, leaching, and photo-degradation led to increased dosage of pesticides. The presence of excess pesticides in soil can prove harmful in many ways. Also only little amount (5-10 %) of the applied chemicals were effectively used, the rest being washed away by rain and thereby, reaching the human and aquatic life cycle. Pesticides are one of the major components of water pollution which can enter living species through water cycle, thereby disturbing the food chain. These chemicals act on the nervous system, circulatory system, and genetic system, hence, creating disorders which may be carried over to generations together. Controlled release of pesticides can thus be a major remedial factor which can follow the drug release mechanism occurring through diffusion, degradation, or a combination of both. Controlled pesticide delivery by the use of polymeric materials is a field of research which is not much explored by the scientists. Dogan [9] studied the *in vitro* effect of some pesticides such as lambda-cyhalothrin, deltametrin, diozinon, dorzolamide, and brinzolamide on carbonic anhydrase enzyme obtained from the blood of fish *Oncorhynchus mykiss* and *Cyprinus carpio carpio* and compared it with carbonic anhydrase inhibitors. It has been found that the most effective inhibitor of carbonic anhydrase enzyme within pesticides was deltametrin. Fernandez-Perez *et al*. [10] studied the use of polymeric matrix to reduce the leaching of herbicide (diuron) into the soil and hence the ground water contamination. The use of polymeric matrix loaded with pesticides help in attaining sustained activity [11], reducing evaporation, photo-degradation [12], and leaching [13].

Modification of natural polysaccharides for use in sustained fungicide release has not been much explored and hence attracting a lot of attention from scientists.

Experimental

Materials and Method

Psyllium (Sidhpur Sat-Isabgol Factory), acrylic acid (Merck-Schuchardt), hexamethylene tetramine (LOBA Chemie Pvt. Ltd.), and copper sulfate (SD Fine) were used as received.

FTIR spectrum was taken on a Perkin Elmer spectrophotometer and an electronic balance (LIBROR AEG-220, Shimadzu) was used for the weighing purpose. An X-ray diffractometer (BRUKER AXS D8 ADVANCE) was used for X-ray diffraction studies. The X-ray diffraction counts at 2θ angles close to 21.297 and 34.744 ° were used for determining the crystalline index (C.I.), which measures the orientation of the crystals in a polysaccharide to the polysaccharide axis. The counter reading at peak intensity of

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21.297 ° is said to represent the crystalline material and the peak intensities at 34.744 ° corresponds to the amorphous material in psyllium [14]. Percentage crystallinity (%Cr) [15] and the crystalline index [16] were calculated as follows:

$$\%Cr = \frac{I_{21.297}}{I_{21.297} + I_{34.744}} \times 100$$

$$C.I. = \frac{I_{21.297} - I_{34.744}}{I_{21.297}} \times 100$$

where $I_{21.297}$ and $I_{34.744}$ are the crystalline and amorphous intensities at 2θ scale close to 21.297 and 34.744 °, respectively. The drug release studies have been carried out using a UV-VIS spectrophotometer (Systronics 118).

Synthesis

1 g of psyllium is mixed with 7.25×10^{-1} mol·l^{-1} of acrylic acid in a reaction flask containing aqueous medium followed with the addition 7.133×10^{-2} mol·l^{-1} of hexamethylene tetramine to the reaction mixture in the presence of γ-radiations. The reaction was carried out for 600 min. The polymer was separated from the product mixture by stirring it in water for 3-4 h. The hydrogel was then dried in a hot air oven at 40 °C.

Fungicide Loading

Saturated aqueous solution of the fungicide was prepared and its wavelength for maximum absorption was noted down. 750 mg of the polymeric sample was immersed in 100 m*l* of fungicide solution for 24 h. The polymer was then taken out from the solution, wiped off, and was kept for drying. Any fungicide molecule adhering to the polymer surface was removed from the dried fungicide-loaded polymer by washing with distilled water and then was studied for fungicide release kinetics as a function of release time using a UV-VIS spectrophotometer. Release kinetics was studied every 2 hours.

Mathematical Analysis

The empirical equation used to describe the water uptake which is the weight gain (M_s) can be presented as:

$$M_s = kt^n \tag{1}$$

where k and n are constant. $n=0.5$ revealed the normal Fickian diffusion whereas $n=1.0$ signifies Case II diffusion. Non-Fickian or anomalous diffusion is characterized with value of n between 0.5 and 1.0 [17]. Evaluation of drug release from the swellable polymers can be evaluated from the above power law expression [18]. Here, M_s is replaced with M_t/M_∞ and the expression is modified as:

$$\frac{M_s}{M_\infty} = kt^n \tag{2}$$

where M_t/M_∞ is the fractional release of drug in time t. k is the constant which is characteristic of polymer-drug system. n is the diffusion exponent characteristic of the release mechanism. Values of n and k can be evaluated from the slope and intercept of the plot between ln M_s/M_∞ versus ln t, respectively.

Diffusion Coefficients

Diffusion coefficients can be used for the analysis of drug release from various hydrogels. Diffusion process can be adequately described through Fick's first and second laws. Integral diffusion for the cylindrical hydrogel can be given as [19]:

$$\frac{M_t}{M_\infty} = 4 \times \frac{Dt}{\pi l^2} \tag{3}$$

where is the fractional release, M_t is the drug released at time t, M_∞ is the drug release at equilibrium, D is the diffusion coefficient, and l is the thickness of the sample.

The average diffusion coefficient (D_A) for the 50 % release of the drug can be calculated by putting M_t/M_∞=0.5 in Eq. (3), and can be presented as:

$$D_A = \frac{0.049l^2}{t^{1/2}} \tag{4}$$

where $t^{1/2}$ is the time required for the 50 % release of drug.

Equation (5) gives the value of late diffusion coefficient and can be calculated as:

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right)\exp\left(\frac{-\pi^2 Dt}{l^2}\right) \tag{5}$$

The slope of plot between $\ln(1 - M_t/M_\infty)$ and time t can also be used for the evaluation of D_L.

$$D_L = \left(\frac{(slope)l^2}{8}\right) \tag{6}$$

Results and Discussion

Absorption of water from the environment affects the dimensional and physicochemical properties of the hydrogel systems. The diffusion of water or drug in the hydrogels has been classified into three types of mechanisms based on relative rate of diffusion and polymer relaxation: Case-I or Fickian type diffusion, non-Fickian type diffusion, and Case-II diffusion [17].

Hydroxyl groups present in the arabinoxylan, which is composed of xylopyranose straight chain with arabinofuranose branches at 2 or 3 positions and is a mucilage forming fraction of psyllium, are the active sites for the graft copolymerization of monomer onto it [20]. Mechanism for graft copolymerization of the monomer onto psyllium under the influence of γ-radiations can be presented through the following mechanism:

Initiation

$$nM \xrightarrow{\text{Radiatons}} M^*_n \tag{1}$$

$$H_2O \xrightarrow{\text{Radiatons}} H^* + {}^*OH \tag{2}$$

$$\text{Psy-OH} \xrightarrow{\text{Radiatons}} \text{Psy-O}^* + H^* \tag{3}$$

$$\text{Psy-OH} + {}^*OH \longrightarrow \text{Psy-O}^* + H_2O \tag{4}$$

$$M + {}^*OH \longrightarrow {}^*\text{M-OH} \tag{5}$$

Propagation

$$\text{Psy-OH} + {}^*\text{M-OH} \longrightarrow \text{Psy-O-M}^* + H_2O \tag{6}$$

$$\text{Psy-O-M}^* + n\,M \longrightarrow \text{Psy-O-(M)}_n\text{-M}^* \tag{7}$$

$$\text{Psy-O}^* + n\,M \longrightarrow \text{Psy-O-(M)}_{n-1}\text{M}^* \tag{8}$$

$$^*\text{M-OH} + n\,M \longrightarrow \text{HO-(M)}_n\text{-M}^* \tag{9}$$

Termination

$$\text{Psy-O-(M)}_n\text{-M}^* + \text{M}^*\text{-(M)}_n\text{-O-Psy} \longrightarrow \text{Psy-O-(M)}_n\text{-M}_2\text{-(M)}_n\text{-O-Psy Graft co-polymer} \tag{10}$$

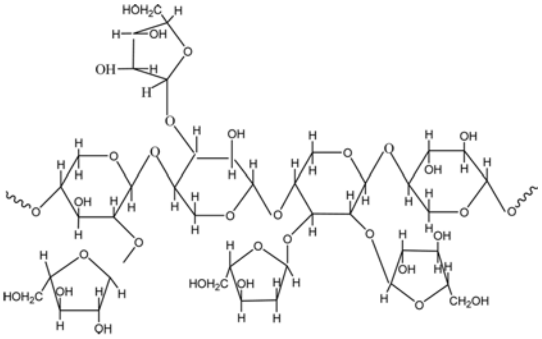
$$\text{Psy-O-(M)}_{n-1}\text{M}^* + \text{M}^*\text{-(M)}_{n-1}\text{-O-Psy} \longrightarrow \text{Psy-O-(M)}_{n-1}\text{-M}_2\text{-(M)}_{n-1}\text{-O-Psy Graft co-polymer} \tag{11}$$

$$\text{Psy-O-(M)}_n\text{-M}^* + {}^*OH \longrightarrow \text{Psy-O-(M)}_{n+1}\text{-OH} \tag{12}$$

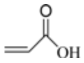
$$\text{HO-(M)}_n\text{-M}^* + {}^*\text{M-(M)}_n\text{-OH} \longrightarrow \text{HO-(M)}_n\text{-M}_2\text{-(M)}_n\text{-OH Homopolymer} \tag{13}$$

where

Psy-OH=



M=



γ-Radiations initiate the monomer moiety and psyllium by creating free radical sites on it. Also, water dissociates to *OH in the presence of radiations. On the other hand, *OH attacks psyllium resulting in the creation of a free radical. Free radicals on monomer moiety are generated through the attacks of OH*. The activated monomer molecules react with the back-bone polymer resulting in the formation of graft copolymers and the reaction propagates further. However, the termination of the reaction takes place either by reaction between *OH and backbone free radical or the reaction between two activated chains.

Table 1. Scheme for optimization of various reaction parameters

Sample No.	Gamma-radiation dose KGy/h	Amount of solvent (m*l*)	Monomer concentration (mol/*l*)	Crosslinker concentration (mol/*l*)	Percent grafting	Percent swelling
1	6.48	20	7.25×10^{-1}	1.783×10^{-2}	98	-
2	12.96	20	7.25×10^{-1}	1.783×10^{-2}	101	-
3	19.44	20	7.25×10^{-1}	1.783×10^{-2}	106	-
4	25.92	20	7.25×10^{-1}	1.783×10^{-2}	124	-
5	32.4	20	7.25×10^{-1}	1.783×10^{-2}	110	-
6	25.92	10	7.25×10^{-1}	1.783×10^{-2}	49	-
7	25.92	15	7.25×10^{-1}	1.783×10^{-2}	65	-
8	25.92	20	7.25×10^{-1}	1.783×10^{-2}	124	-
9	25.92	25	7.25×10^{-1}	1.783×10^{-2}	0	-
10	25.92	30	7.25×10^{-1}	1.783×10^{-2}	0	-
11	25.92	20	3.625×10^{-1}	1.783×10^{-2}	-	2000
12	25.92	20	7.25×10^{-1}	1.783×10^{-2}	-	2175
13	25.92	20	10.87×10^{-1}	1.783×10^{-2}	-	2160
14	25.92	20	14.5×10^{-1}	1.783×10^{-2}	-	1900
15	25.92	20	18.127×10^{-1}	1.783×10^{-2}	-	1990
16	25.92	20	7.25×10^{-1}	1.783×10^{-2}	-	2175
17	25.92	20	7.25×10^{-1}	3.566×10^{-2}	-	8763
18	25.92	20	7.25×10^{-1}	5.349×10^{-2}	-	9422
19	25.92	20	7.25×10^{-1}	7.133×10^{-2}	-	10578
20	25.92	20	7.25×10^{-1}	8.916×10^{-2}	-	8986

Synthesis

The different reaction parameters such as γ-radiation dose, amount of solvent, monomer concentration, and crosslinker concentration were optimized and the scheme for optimization of the reaction parameters is illustrated in Table 1.

Characterization

FTIR Spectroscopy

IR spectrum of psyllium (Figure 1(a)) showed peaks at 3780.9 cm^{-1} and 3427.6 cm^{-1} (O-H stretching absorption of carbohydrates), 2925.8 cm^{-1} (CH_2 asymmetric stretching), 1378.8 cm^{-1} (CH, CH_2, and OH in-plane bending in carbohydrates), 1039.5 cm^{-1} (C-O stretching region as complex bands, resulting from C-O and C-O-C stretching vibrations), 897 cm^{-1}, and 533 cm^{-1} (pyranose rings).

On the other hand, IR spectrum of Psy-cl-poly(AA)-UR (Figure 1(b)) showed peaks at 2856.0 (O-H stretching of carboxylic acid), 1731.3, and 1631.8 cm^{-1} (C=O stretching in carboxylic acid).

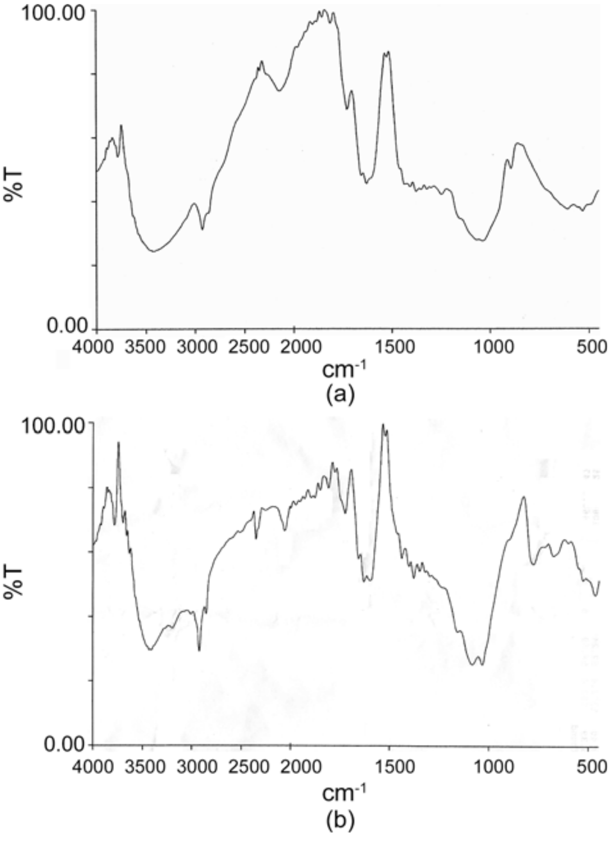


Figure 1. (a) FTIR Spectrum of psyllium and (b) Psy-cl-poly(AA)-UR.

X-ray Diffraction Studies

It has been observed that psyllium exhibited 75.76 % percentage crystallinity and crystalline index was found to be 0.68 and Psy-cl-poly(AA)-UR exhibited 78.12 % *Cr* and 0.72 *C.I.* (Table 2).

It is evident from Figure 2 that Psy-cl-poly(AA)-UR showed higher crystallinity than psyllium. This behavior can be attributed to re-structuring of the crystal lattice during graft copolymerization under the influence of γ-radiations, leading to higher % *Cr*. The 2θ, *I*, and *d*-values of graft copolymer have been found to be quite different than those of psyllium. This behavior is due to the involvement of primary bonding like covalent bonding between psyllium and acrylic acid during graft copolymerization.

Swelling Studies in Distilled Water

Effect of Time on Percent Swelling

It has been observed that P_s increased with an increase in swelling time and a maximum swelling (10,578 %) was found at 24 h time interval at 25 °C. Further increase in time interval resulted in constant P_s (Figure 3). This can be explained on the basis of the fact that after 24 h the porous network of the polymer got saturated with the solvent molecules with no more accommodation for further solvent molecules.

Effect of Temperature on Percent Swelling

As is evident from Figure 3 that P_s increased with an increase in swelling temperature and maximum P_s (10,578 %) was found at 25 °C. Further increase in temperature resulted

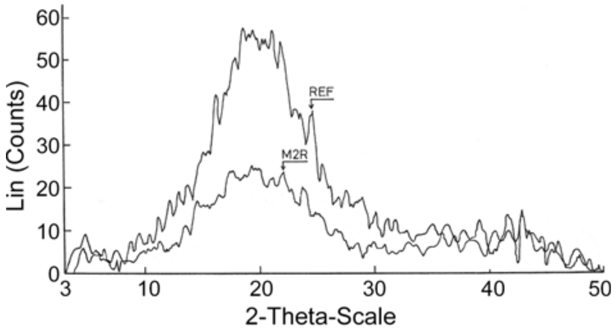


Figure 2. XRD of psyllium (REF) and Psy-cl-poly(AA)-UR (M2R).

Table 2. Percentage crystallinity (%Cr) and Crystalline Index (C.I.) of Psyllium and Psy-cl-poly(AA)-UR

Sr.No.	Sample	P_g	At 2θ-scale		*%Cr*	*C.I.*
			$I_{21.297}$	$I_{34.744}$		
1.	Psyllium	-	100	32	75.76	0.68
2.	Psy-cl-poly(AA)-UR	124.0	100	28	78.12	0.72

where I = relative intensity, UR = under radiations, P_g = percent grafting.

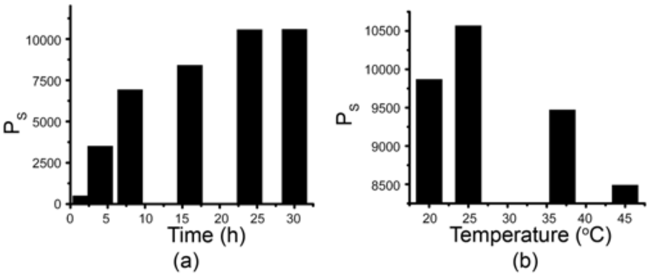


Figure 3. Effect of swelling time and temperature onto P_s of Psy-cl-poly(AA)-UR in distilled water.

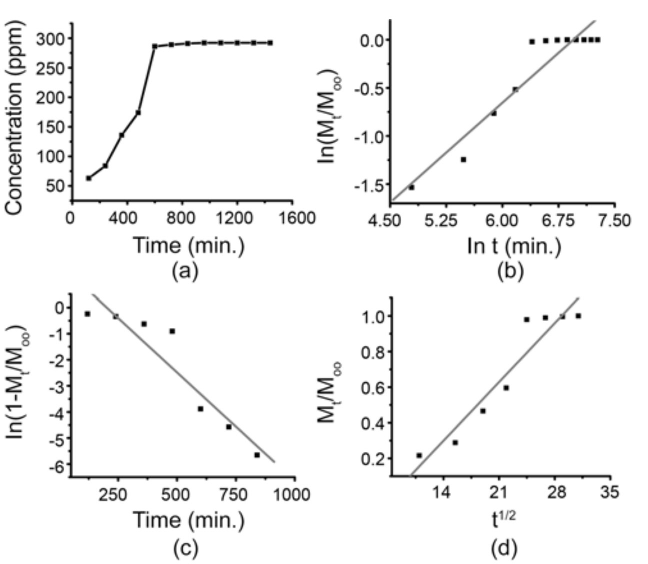


Figure 4. (a) Sustained release of copper sulfate with Psy-cl-poly(AA)-UR as a function of time at pH=6.0, (b) plot of $\ln M_t/M_\infty$ versus $\ln t$ for the copper sulfate release behavior of Psy-cl-poly(AA)-UR at pH=6.0, (c) plot of $\ln(1\text{-}M_t/M_\infty)$ versus time for the copper sulfate release behavior of Psy-cl-poly(AA)-UR at pH=6.0, and (d) plot of M_t/M_∞ versus $t^{1/2}$ for the copper sulfate release behavior of Psy-cl-poly(AA)-UR at pH=6.0.

in decreased P_s. It was due to the fact that beyond optimum temperature, the polymer matrix starts crumbling, thereby, leading to desorption and decreased P_s.

Effect of pH on Percent Swelling

The polymer was found to disintegrate under acidic and alkaline medium, exhibiting maximum P_s in neutral medium. This can be explained on the basis that the backbone polymer was found to be unstable under alkaline and acidic conditions, i.e., it does not form uniform mucilaginous mixture in alkaline and acidic solutions as was formed under neutral medium and hence the polymer got disintegrated under such conditions.

Release Kinetics of Fungicide

Release of copper sulfate by the loaded polymeric gels in the medium (pH-6.0) was carried out at $\lambda_{\max}$=830 nm.

Psy-cl-poly(AA)-UR has been found effective in sustained fungicide delivery. Figure 4(a) shows the fungicide release pattern of Psy-cl-poly(AA)-UR with 63 ppm fungicide release at 2 h interval and 292 ppm release in 16 h, respectively. Psy-cl-poly(AA)-UR showed non-Fickian type mechanism for the fungicide release which is evident from the values of $n=0.71$ and $k=7.61\times10^{-3}$ (Figure 4(b)). The non-Fickian behavior has further been confirmed from Figure 4(d) [21]. Initial diffusion coefficient has been found to be less than late diffusion coefficient indicating lesser fungicide release in the early stages of diffusion that that in the late stages (Table 3 and Figure 4(c)).

Conclusion

The forgone study dealt with the utilization of superabsorbent, based on psyllium and acrylic acid and synthesized under the influence of γ-radiations, in the sustained fungicide delivery system. It was found that the superabsorbent has tremendous water absorbing capacity and is sensitive towards pH as well as temperature. The hydrogel has been found to be quite effective in the sustained release of $CuSO_4$. Hence, the superabsorbent can be efficiently used in the controlled release of fungicide, insecticide, pesticide, and fertilizers.

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Table 3. Diffusion exponent, gel characteristic constant, and diffusion coefficients for the release of copper sulfate through loaded polymeric gels at pH=6.0

Sample code	Diffusion exponent (n)	Gel characteristic constant ($k\times10^{-3}$)	Diffusion coefficients (cm^2/min)		
			$D_i\times10^{-5}$	$D_A\times10^{-5}$	$D_L\times10^{-5}$
Psy-cl-poly(AA)-UR	0.71	7.61	0.304	0.497	0.9287

where D_i = Initial diffusion coefficient, D_L = late diffusion coefficient, D_A = average diffusion coefficient.

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