Release Kinetics and Diffusion Coefficients of Solid and Liquid Pesticides Through Interpenetrating Polymer Network Beads of Polyacrylamide-*g*-Guar Gum with Sodium Alginate

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ABSTRACT: Grafting of acrylamide onto guar gum is achieved by Ce(IV) induced free-radical polymerization to prepare interpenetrating polymer network (IPN) beads of polyacrylamide-*g*-guar gum with sodium alginate by crosslinking with glutaraldehyde. Two widely used pesticides, solid chlorpyrifos and liquid fenvelarate, are loaded up to 60–70% efficiency in the IPN beads. The polymer and beads are characterized by Fourier transform IR spectroscopy to confirm grafting and to understand the possible interactions between the pesticides and the polymer matrix. Scanning electron microscopy is used to study the morphology of the beads. Equilibrium swelling experiments indicate that the swelling of the beads decreases with an increase in crosslinking, as well as an increase in pesticide loading. The *in vitro* release studies are performed under static conditions, and the release data are fitted to an empirical relationship to evaluate the transport parameters. Diffusion coefficients are calculated for the transport of pesticides through the polymeric beads using the initial and later time approximation methods. These values show a decrease with increasing crosslinking and increasing pesticide loading. Long-term diffusion coefficients as computed by Fick's equations are found to be smaller in magnitude when compared to the initial time diffusion coefficients. J Appl Polym Sci 90: 451–457, 2003

Key words: polyacrylamide-*g*-guar gum; sodium alginate; interpenetrating polymer network beads; chlorpyrifos; fenvelarate

INTRODUCTION

Controlled release (CR) formulations containing pesticides have advantages over conventional products to reduce environmental pollution because of direct contact with skin or by inhalation. These formulations are safe to use because of the reduced amount of pesticides, minimum leaching of pesticides, increased persistence of the active ingredient, and the overall ease in handling toxic products.[1,2] In view of this, CR systems have gained widespread usage in agricultural areas because they help to reduce the environmental risk factors. The use of biodegradable polymers is desirable for encapsulation of toxic pesticides, because no polymer residues can remain in the atmosphere after their intended applications.[3]

In continuation of our earlier efforts to develop CR products containing pesticides, we report here the development of CR devices using two naturally occurring polysaccharides: guar gum (GG) and sodium alginate (Na-Alg). These polysaccharides are abundant in nature, cheap, and biodegradable. Hence, they are used as membrane materials in CR applications.[4–8] However, their inherent drawbacks such as poor mechanical strength, uncontrolled degradation, and extensive water uptake properties result in uncontrolled and unpredictable release rates of the active ingredients. In order to overcome some of these difficulties, grafting of acrylamide (AAm) onto GG has been attempted in an effort to develop grafted copolymers that exhibit better CR properties than pure GG.[5] Blending of the copolymer with Na-Alg and its crosslinking will result in the formation of an interpenetrating polymer network (IPN).[7] Therefore, IPNs are better choices to develop CR matrices because their properties can be varied by changing the composition or by crosslinking, thereby regulating the hydrophilic nature of the overall matrix.[9]

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In this study, chlorpyrifos, solid organophosphorus (*o*,*o*′-diethyl *o*-3,5,6-trichloro-2-pyridyl phosphorothioate) pesticide, and fenvalerate [(RS)-α-cyano-3-phenoxybenzyl(RS)-2-(4-chlorophenyl)-3-methylbutyrate], a liquid pesticide, are used as model compounds. Both of the pesticides can be used against pests like flies, nematodes, fungi, white grubs, and larva of chaffer beetles that are considered to be serious soil pests for groundnut and other crops. In order to avoid or minimize their toxic levels, polymeric matrices are used that contain blends of natural polymers with synthetic polymers. Our main objective here is to address the release patterns of the pesticide-loaded formulations with an effort to find a suitable blend to encapsulate solid and liquid pesticides. The effect of physical nature on the release rates and diffusion coefficients is investigated.

EXPERIMENTAL

Materials

A 96.8 mass % pure grade chlorpyrifos and 94.6 mass % fenvelarate were received as gift samples from Rallis India Limited (Bangalore, India). These pesticides were purified by dissolving in AR grade acetone and precipitated in double distilled water to obtain the pure product. Sodium alginate was purchased from Luba Chemicals (Mumbai, India), and GG was purchased from SD Fine Chemicals (Mumbai, India). Polyacrylamide-*g*-GG (PAAm-*g*-GG) was prepared as described earlier.[10] Ceric ammonium nitrate (CAN), hydrochloric acid, glutaraldehyde (GA, 25% w/v) solution, and methanol were AR grade samples (SD Fine Chemicals) and were used as received. Double distilled water was used throughout the research.

Synthesis of PAAm-*g*-GG

PAAm-*g*-GG was synthesized by free-radical polymerization of AAm with GG at 60°C using CAN as an initiator.[10] Briefly, a 2% aqueous GG solution was prepared and stirred well for 1 h with 0.105 mol of AAm at 60°C. The initiator solution containing 5.47×10^{-4} mol of CAN was added to the mixture and stirred well for an additional 5 h. The product was precipitated in acetone and washed with a water/methanol (7:3) mixture to remove any homopolymer that was formed. This solid mass was dried in an electrically controlled oven at 40°C until attainment of constant mass.

The percentage of grafting was estimated from the mass of the polymer before and after grafting using the following relationship:

$$\% \text{ grafting} = \left(\frac{W_g - W_o}{W_o}\right) \times 100 \qquad (1)$$

where W_g and W_o are the masses of the grafted copolymer and GG. The percentage of grafting of AAm onto GG and the grafting efficiency were calculated as follows:

$$\text{AAm \% grafting} = \left(\frac{\text{mass of pAAm}-g-\text{GG} - \text{mass of GG}}{\text{mass of GG}}\right) \times 100 \qquad (2)$$

$$\text{grafting efficiency} = \left(\frac{\text{mass of PAAm}-g-\text{GG} - \text{mass of GG}}{\text{mass of PAAm}-g-\text{GG} + \text{mass of PAAm homopolymer}}\right) \times 100 \qquad (3)$$

Preparation of pesticide encapsulated IPN beads

The PAAm-*g*-GG (2.5 g) and Na-Alg (2.5 g) were dispersed in hot water and stirred to form a homogenous mixture. Different amounts (10, 20, and 30 mass % of dry mass of the polymer) of chlorpyrifos or fenvelarate were added to this solution, mixed thoroughly using a magnetic stirrer, and sonicated to ensure complete mixing. Using a 25-mL hypodermic syringe (1-mm i.d. needle) under constant stirring, the polymer solution containing the pesticide was added dropwise into 30% methanol in water containing 5, 10, and 15 vol % GA and 3 vol % 1.0*N* HCl. The resulting beads were removed from the antisolvent after 30 min and repeatedly washed with water to remove the adhered GA and the acid; the beads were then dried completely. The formulations were given the codes Chlor-1 to Chlor-9 and Fen-1 to Fen-9 to indicate the increasing crosslinking and increasing amounts of pesticide loading for chlorpyrifos and fenvelarate, respectively.

To estimate the size of the beads, five samples of the completely dried beads from different formulations were selected and their sizes were measured using a micrometer screw gauge (Sargent) with an accuracy of ±0.01 mm.

Equilibrium swelling of beads

Equilibrium swelling of the beads was done at 35°C in water and the percentage of water uptake was measured gravimetrically. Three different beads were selected that had been exposed to different amounts of GA at three different loadings of chlorpyrifos or fenvelarate at different times, and they were incubated by placing them in distilled water on a watch glass. The mass measurements were taken until attainment of equilibrium and the average value was considered for all calculations. During this process, handling of the swollen beads should be smooth in order to avoid any

mass loss due to breaking or erosion of solvent from the beads. All the mass measurements were done on a Mettler single pan balance (model AE 240). The percentage of water uptake (Q) was calculated as

$$Q=\left[\frac{\text{mass of swollen beads} - \text{mass of dry beads}}{\text{mass of dry beads}}\right] \times 100 \quad (4)$$

Content uniformity

The beads were evaluated for pesticide content by refluxing a known mass of the beads with 100 mL of methanol at 30–40°C for 4 h to ensure complete extraction of chlorpyrifos or fenvelarate. The absorbance of methanol containing the extracted amount of chlorpyrifos or fenvelarate was measured at λ_{max} values of 230 and 277 nm, respectively, using a UV spectrophotometer (Secomam, Anthelie, France). Methanol was used as the blank.

Fourier transform IR (FTIR) measurements

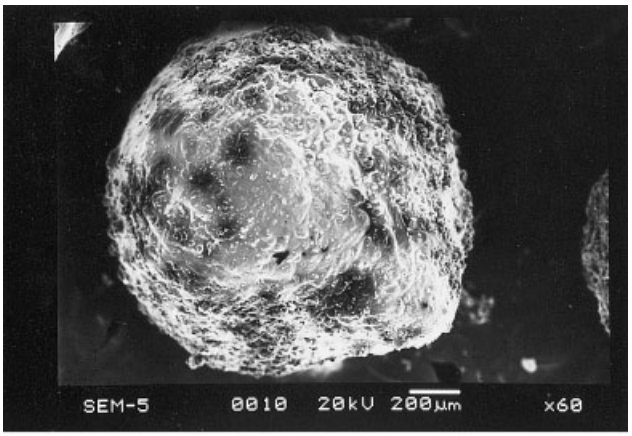
FTIR measurements (using a Nicolet Impact 410) were taken to confirm the grafting of AAm onto GG and to understand the interactions between pesticides and the polymer matrix. Individual spectra were taken for the neat GG, PAAm-*g*-GG, IPN beads without pesticide, IPN beads with pesticide, and neat two pesticide samples. The FTIR samples were prepared in KBr pellets under a hydraulic pressure of 400 kg. The FTIR spectrum of fenvelarate was obtained by taking a thin film of the pesticide in between two KBr windows.

Dissolution studies

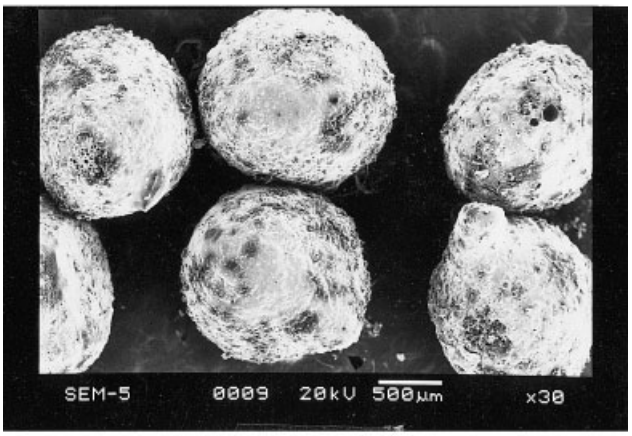
Static dissolution experiments were carried out in 250-mL conical flasks containing a 40% (w/v) solution of methanol in distilled water as the dissolution media with closer caps; an incubator (WTB Binder) was used that was maintained at 35°C. Beads weighing about 150 mg were taken in 100 mL of the dissolution media, and the flasks were shaken well. We removed 10-mL aliquot samples at regular time intervals and analyzed them for chlorpyrifos or fenvelarate using UV spectrophotometer at the λ_{max} values of 230 and 277 nm, respectively. Dissolution experiments were performed in triplicate and the average values were considered for data treatment and graphical display.

Scanning electron microscopy (SEM)

SEM photographs to study the surface topology of the beads were taken using a JSM 6400 scanning microscope. The photographs of the samples were taken by depositing the samples on a brass holder and sputtering them with gold at the required magnification. The working distance of 39 mm was maintained using an acceleration voltage of 5 kV with a secondary electron image as a detector.



(a)



(b)

Figure 1 Scanning electron micrographs of (a) a single bead and (b) a group of beads.

RESULTS AND DISCUSSION

Grafting of AAm onto GG was achieved successfully by Ce(IV) ion induced free-radical polymerization. We achieved 100% grafting efficiency of AAm at the optimized temperature and initiator concentration.[10] Further, 94% grafting of AAm onto GG and 94% conversion of AAm to PAAm were observed. Both chlorpyrifos and fenvelarate were successfully encapsulated in the IPN beads. The SEM photographs [see Fig. 1(A,B)] revealed the absence of pores on the surface and the beads were almost spherical in shape with smooth surfaces.

The FTIR spectra of PAAm-*g*-GG discussed in an earlier study[11] showed a strong and broad band at ~3357 cm^{-1}, which corresponds to O—H stretching vibrations due to GG, indicating that all the O—H

TABLE I
Formulation Data of Pesticide Entrapped Beads

Amount of GA Used (%)	Sample Code	Loading of Pesticide (%)	Bead Diameter (mm)	Encapsulation Efficiency (%)	Equilibrium Water Uptake (%)
			Chlorpyrifos		
5	Chlor-1	10	1.25 ± 0.18	61.31 ± 1.26	60.51 ± 3.25
10	Chlor-2	10	1.23 ± 0.31	65.51 ± 1.07	48.38 ± 1.89
15	Chlor-3	10	1.20 ± 0.21	76.29 ± 2.38	32.58 ± 2.58
5	Chlor-4	20	1.35 ± 0.23	64.35 ± 2.18	51.48 ± 1.41
10	Chlor-5	20	1.33 ± 0.15	70.59 ± 2.68	41.37 ± 2.64
15	Chlor-6	20	1.31 ± 0.16	78.39 ± 3.54	37.57 ± 3.48
5	Chlor-7	30	1.41 ± 0.46	67.37 ± 1.21	43.74 ± 4.58
10	Chlor-8	30	1.39 ± 0.42	72.58 ± 2.48	30.63 ± 3.94
15	Chlor-9	30	1.38 ± 0.41	79.57 ± 3.61	27.61 ± 5.68
			Fenvelarate		
5	Fen-1	10	1.24 ± 0.21	58.36 ± 2.38	64.23 ± 2.54
10	Fen-2	10	1.20 ± 0.27	60.21 ± 1.97	53.29 ± 2.11
15	Fen-3	10	1.18 ± 0.18	61.29 ± 2.13	42.36 ± 3.11
5	Fen-4	20	1.32 ± 0.23	62.45 ± 3.12	55.87 ± 1.78
10	Fen-5	20	1.30 ± 0.17	64.32 ± 1.87	48.36 ± 3.11
15	Fen-6	20	1.28 ± 0.14	65.98 ± 2.68	42.36 ± 2.88
5	Fen-7	30	1.38 ± 0.37	67.38 ± 3.12	52.64 ± 2.56
10	Fen-8	30	1.36 ± 0.34	69.29 ± 3.12	43.18 ± 1.98
15	Fen-9	30	1.34 ± 0.28	71.89 ± 3.58	35.23 ± 3.19

groups are not involved in grafting. The characteristic band at 1665 cm^{-1} corresponding to the amide group confirms grafting of AAm onto the GG backbone. The presence of a shoulder band at 3191 cm^{-1} corresponding to the primary amide N—H stretching further supports the grafting of AAm onto GG.

The FTIR of blank IPN beads and pesticide-loaded beads did not show any alteration in the positions of the bands corresponding to characteristic functional groups of the neat pesticides and the polymer as discussed in our earlier communication.[12] It thus appears that there were no chemical interactions between the

TABLE II
Transport Data of Pesticide Entrapped Beads

Sample Code	$k \times 10^2$ (h^{-n})	n	Corr. Coeff.	Initial Time $D \times 10^6$ (cm^2/h)	Later Time $D \times 10^8$ (cm^2/h)
			Chlorpyrifos		
Chlor-1	3.91	0.564	0.988	2.18	15.88
Chlor-2	3.25	0.541	0.948	1.74	7.82
Chlor-3	2.03	0.568	0.990	1.08	4.45
Chlor-4	2.37	0.566	0.995	1.58	12.51
Chlor-5	1.96	0.577	0.998	1.44	12.13
Chlor-6	1.34	0.611	0.981	1.05	4.21
Chlor-7	1.95	0.551	0.982	1.58	10.46
Chlor-8	0.98	0.678	0.992	1.54	3.11
Chlor-9	1.05	0.636	0.975	1.13	2.66
			Fenvelarate		
Fen-1	2.01	0.236	0.999	1.98	8.42
Fen-2	1.07	0.294	0.959	1.22	4.64
Fen-3	0.47	0.410	0.948	1.41	8.49
Fen-4	1.42	0.306	0.957	1.71	8.64
Fen-5	1.58	0.219	0.967	1.19	7.94
Fen-6	0.64	0.364	0.956	1.58	3.07
Fen-7	1.82	0.235	0.998	1.50	9.50
Fen-8	1.42	0.270	0.997	1.62	7.25
Fen-9	1.03	0.311	0.983	1.69	5.93

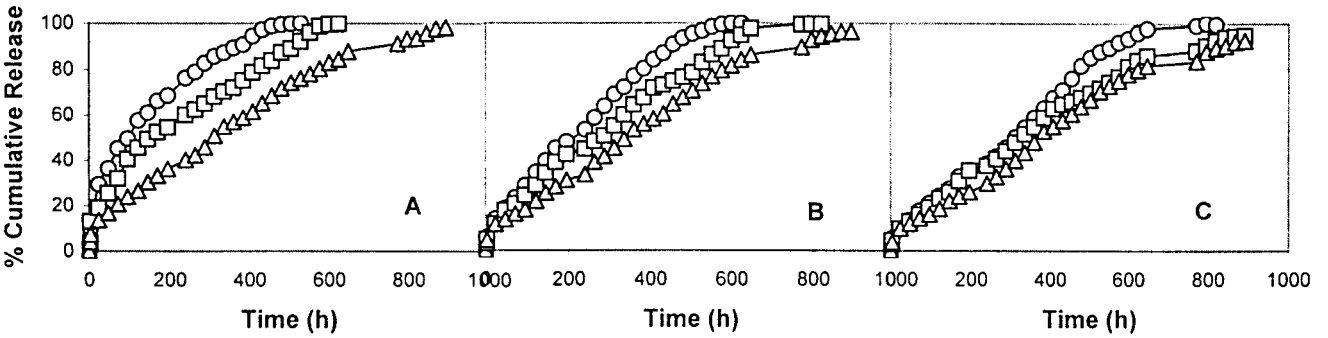


Figure 2 The cumulative (%) release of chlorpyrifos from (A) (○) Chlor-1, (□) Chlor-2, and (△) Chlor-3; (B) (○) Chlor-4, (□) Chlor-5, and (△) Chlor-6; and (C) (○) Chlor-7, (□) Chlor-8, and (△) Chlor-9 formulations.

membrane matrix and the pesticide. This indicates that the pesticides are physically encapsulated within the beads.

Table I gives details of the bead size, the percentage of entrapment efficiency, and the percentage of equilibrium water uptake as a function of the amount of GA used and percentage of loading. The SEM photographs (Fig. 1) indicate that the beads are spherical with diameters ranging from 1.25 to 1.41 mm for chlorpyrifos and 1.24–1.38 mm for fenvelarate. Even though the particle size did not change much, it showed a systematic trend with crosslinking, the percentage of loading, and the physical nature of the pesticide. With an increase in crosslinking, the particle size decreases then increases with increasing loading of the pesticide. This may be attributable to the formation of a more rigid network by increased crosslinking. The chlorpyrifos-loaded particles have a higher particle size than fenvelarate. This may be due to the formation of larger crystal domains by the solid chlorpyrifos particles.

The encapsulation efficiency varied between 61 and 79% for chlorpyrifos and 58 and 71% for fenvelarate, and it also varies systematically. It increases with increasing crosslinking and an increasing percentage of loading of the pesticide (see Tables I, II). A slightly higher encapsulation efficiency is observed for chlorpyrifos than fenvelarate because of their solubility[13] in the antisolvent used while preparing the beads. Fenvelarate is more soluble than chlorpyrifos at a particular solvent composition (30% methanol).

The percentages of equilibrium water uptake for the IPN beads varied widely between 60 and 27% for chlorpyrifos and 64 and 35% for fenvelarate-loaded formulations. A systematic trend is observed for the uptake capacity in all the formulations. Chlor-1 showed an equilibrium water uptake of 60%, whereas 27% uptake is observed for Chlor-9. This is due to the lesser availability of free volume space because of the formation of a more rigid network at higher crosslinking and higher pesticide loading. A similar situation exists for the fenvelarate-loaded formulations.

In vitro release kinetics

The *in vitro* release studies were performed in 40% methanol in water. Figures 2 and 3 represent the plots of the percentage of cumulative release versus the time for 10, 20, and 30% chlorpyrifos- or fenvelarate-loaded beads with 5, 10, and 15% GA crosslinking. The release of chlorpyrifos shows a systematic trend: it decreases with increasing crosslinking and an increasing amount of pesticide loading. For instance, Chlor-1 releases 50% in 96 h, whereas Chlor-2 and Chlor-3

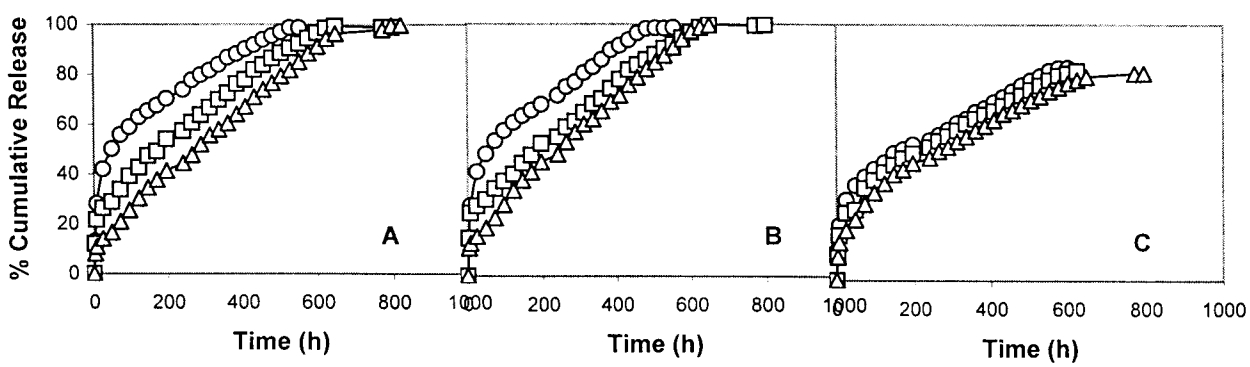


Figure 3 The cumulative (%) release of (A) (○) Fen-1, (□) Fen-2, and (△) Fen-3; (B) (○) Fen-4, (□) Fen-5, and (△) Fen-6 (△); and (C) (○) Fen-7, (□) Fen-8, and (△) Fen-9 fenvelarate from formulations.

release the same amount in 146 and 312 h, respectively [see Fig. 2(A)]. This is because of the increasing amount (5–15 % GA) of crosslinking of the matrix, resulting in the formation of a more rigid network. This is also supported by the percentage of equilibrium water uptake data presented in Table I. The hydrophilicity of the polymer also influences the release of pesticides. With an increasing amount of pesticide loading, the release decreases. The Chlor-4 and Chlor-7 formulations' release is 50% in 240 and 312 h, respectively. This may be due to the formation of increased crystal domains inside the polymer matrix as discussed earlier.[6] However, the release continues for more than 820 h in all the formulations.

The release data of fenvelarate are presented in Figure 3. The release of fenvelarate is somewhat quicker than chlorpyrifos-loaded formulations. Formulation Fen-1 releases 50% in 48 h, whereas Chlor-1 releases the same amount in 96 h. This may be due to the crystalline nature of chlorpyrifos inside the polymer matrix. Fenvelarate is a liquid that diffuses fast, but the release of fenvelarate from Fen-2 is slower than Fen-1. Fen-3 is the slowest for 10% loading, which is attributable to an increased amount of crosslinking, thereby resulting in a more rigid matrix. The Fen-7, Fen-8, and Fen-9 formulations release 50% of the pesticides quicker than formulations Fen-4, Fen-5, and Fen-6 [see Fig. 2(B)], which is somewhat unexpected. Such a release at higher loading may be due to an increased concentration gradient inside the polymer matrix, making it diffuse more quickly. In all the formulations studied here, the release of fenvelarate is faster in comparison to chlorpyrifos. Fenvelarate release continued up to 700 h, whereas chlorpyrifos release continued for up to 820 h.

The *in vitro* release data were fitted to an empirical equation.[14,15]

$$\frac{M_t}{M_\infty} = kt^n \tag{5}$$

Here, the values of n suggest the nature of transport and k is a parameter indicating the interaction between the pesticide and the polymer. Fractional release data up to 60% of release [i.e., $\log(M_t/M)$ vs. $\log t$] were plotted. The initial linear portions of these plots were fitted by the least squares method to estimate k and n at a 95% confidence limit. If $n = 0.5$, the transport becomes Fickian; if $n = 1$, case II transport occurs. The intermediary values of n are suggestive of the non-Fickian (anomalous) transport.[14,15] Ritger and Peppas[15] obtained values of n as low as 0.3 and 0.45 for Fickian and case II transport, respectively.

The results for n and k value are presented in Table II. For chlorpyrifos, n varies between 0.54 and 0.67, indicating that the release follows anomalous transport, which slightly deviates from the Fickian transport. In the case of fenvelarate, the n values vary between 0.22 and 0.41, indicating a Fickian trend. The values of k range between (0.98 and 3.91) $\times 10^{-2}$ for chlorpyrifos whereas for fenvelerate these values range between (0.47 and 2.01) $\times 10^{-2}$, indicating negligible interactions of the pesticides with the polymeric matrices.

Release data were used to calculate the apparent diffusion coefficients from the IPN beads. To do this, the initial ($0 < M_t/M_\infty < 0.4$) and long-term ($0.6 < M_t/M_\infty < 1.0$) release profiles were analyzed using Fick's theory[16] in the most simplified form to calculate the diffusion coefficients from the initial and long-term approximations.[17]

$$\frac{M_t}{M_\infty} = \left(\frac{36Dt}{\pi r^2}\right)^{1/2} - \left(\frac{3Dt}{r^2}\right) \tag{6}$$

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\exp - \left(\frac{\pi^2 Dt}{r^2}\right) \tag{7}$$

where r is the average radius of the bead in eq. (6) in the dry state whereas it is the average diffusional distance corresponding to the radius of the fully swollen bead in eq. (7). The data presented in Table II show a relationship between the extent of crosslinking and pesticide loading.

The diffusion coefficients estimated by the initial (D_1) and long-term (D_2) approximations decrease with an increase in the amount of crosslinking and an increase in the amount of pesticide loading. For the Chlor-1, Chlor-2, and Chlor-3 formulations, the D_1 values decrease from (2.182 to 1.076) $\times 10^{-6}$ cm^2/h whereas the D_2 values decrease from (15.878 to 4.445) $\times 10^{-8}$ cm^2/h. Release of the active ingredients from hydrogels is controlled by polymer chain relaxation, which is followed by rapid water uptake. Therefore, the initial release of the active ingredients from the hydrogels is fast and hence the values of D_1 are higher. The later part of the release from a completely swollen hydrogel might be completely governed by a diffusion mechanism and thus the values of D_2 might be smaller. The diffusion coefficient data presented in Table II have the same order of magnitude for both pesticides.

CONCLUSIONS

In the present study, grafting of AAm onto GG was done by Ce(IV) induced free-radical polymerization to prepare the IPN beads of PAAm-*g*-GG with sodium alginate after crosslinking with GA. Both chlorpyrifos and fenvelarate containing beads were encapsulated successfully with higher percentages of efficiency. Pesticide release from the beads continued up to 1 month.

Fenvelarate release was faster than chlorpyrifos in all the beads. The present article is a continuation of our ongoing research on the development of ecofriendly polymeric matrices for the release of toxic pesticides. However, the fieldwork studies on these matrices will be the goal of our future research activity.

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