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Designing Swellable Beads of Alginate and Gelatin for Controlled Release of Pesticide (Cypermethrin)

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In the present study biopolymeric beads of sodium alginate and gelatin were prepared by employing $CaCl_2$ as a crosslinking agent. A series of such microspheres of different compositions were prepared by varying the amounts of sodium alginate, gelatin and $CaCl_2$ in the feed mixture. The beads were loaded with an insecticide like cypermethrin. The prepared loaded and unloaded beads were characterized by FTIR spectral and Environmental scanning electron microscopy (ESEM) techniques, to gain insight into the molecular structure and morphology of beads, respectively. The swelling experiments were performed for different composition of beads and at varying pH and temperature of the swelling media. The swelling controlled release of insecticide was also investigated for 8 days in bi-distilled water as a release medium. The release experiments were performed under the static and varying experimental conditions and the data obtained were fitted to Fick's equation to evaluate diffusion coefficients of insecticide. The results were further analyzed by Fick's power law equation, and the possible mechanisms of the insecticide release were explored at different experimental conditions. Soil–pot experiments were also performed to demonstrate the applicability of the present controlled release technique to agricultural fields.

Keywords: Biopolymer, hydrogel, swelling, insecticide, controlled release

1 Introduction

Hydrogels also coined as 'hungry networks' are hydrophilic architecture of macromolecular chains held up with each other by physical or chemical crosslinks possessing unusual property of water uptake without undergoing dissolution (1). The water reservoir in these polymeric networks develop certain critical biophysical properties such as soft and rubbery texture, living tissue like resemblance, physiological stability towards biofluids, permeability to biomolecules, blood compatibility, etc. These typical properties of hydrogels result in their massive applications in biomedical fields (2), agriculture (3), controlled release of agrochemicals (4), environment engineering (5), etc.

In recent years, the use of ionic hydrogels in soil applications has become increasingly popular because these hydrogels exhibit response to soil conditions. Additionally, in agricultural areas, it is advantageous to employ hydrogels that can encapsulate toxic pesticides or micronutrients so as to regulate their release to keep the environment safe (6,7). The hydrogels carrying protonable groups show sensitive response to external stimuli such as pH (8), temperature (9) and presence of ions (10). Controlled release (CR) formulations containing insecticides have advantages over conventional products to reduce environmental pollution because of their direct contact with skin or by inhalation (11). Recently, hydrogel based pesticide devices have become very popular. They consist of a pesticide loaded into a polymer network in the form of a microcapsule or granule. Such systems exhibit many advantages including controlled or slow release of the core active ingredient (AI) leading to longer application intervals, reduction in dosage, stabilization of the core AI against environmental degradation (light, air, humidity, micro organisms), reduction in mammalian toxicity and human mucous membrane irritation, reduction in phytotoxicity and ease of handling of the toxic materials (12). Insecticides are beneficial to the agriculture sector and in water borne diseases control. They may cause both illness and other physiological disorders in humans. These problems arise from various circumstances through either direct or indirect contact with insecticides. The direct contact of insecticide comes from the ingestion of insecticide residue in food, which leads to its increased level.

Cypermethrin is a well known synthetic pyrethroid insecticide used to kill insects on cotton and lettuce, and to kill cockroaches, fleas and termites in houses and

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*Address correspondence to: A. K. Bajpai, Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur (M.P.) - 482001, India. E-mail: akbmrl@yahoo.co.in or akbajpailab@yahoo.co.in other buildings (13). On soils, cypermethrin photodegrades rapidly with a half life of 8–16 days. Its major photodegradation products are DCVA [3-(2,2-dichloro vinyl-2,2-dimethylcyclopropanecarboxylic acid)], 3–phenoxy benzaldehyde and 3–phenoxy benzoic acid. Cypermethrin is also subject to microbial degradation under aerobic conditions (14).

Recently, there has been growing considerable interest in natural polymers like sodium alginate (15), carboxymethyl cellulose (16), starch (17), chitosan (18), pectin(19), etc. due to their non-toxic and biodegradable nature. These natural polymers have been extensively investigated as controlled release carrier for drugs (20), bioactive agents (21) and agrochemicals (22). The present study aims at developing binary polymeric beads of sodium alginate and gelatin with $CaCl_2$, as a crosslinker, and evaluating their potential as a controlled release device of cypermethrin.

It is important to mention here that due to controlled delivery of cypermethrin, a much smaller amount will go into soil and consequently, its photodegradation and microbial degradation will be significantly suppressed. Alginate is a linear polyuronate obtained from marine algae and contains variable amounts of D–mannuronic acid and L–guluronic acid, which can be crosslinked by Ca^{++} ion. Biopolymers are very useful in pharmaceuticals (23,24). Several properties of alginate such as biodegradability, non-toxicity, biocompatibility (25), immunogenecity (26), and ability to form gel with a variety of crosslinking agents in mild and aqueous conditions, make it a useful carrier for controlled delivery of biologically active agents.

Gelatin is a natural macromolecular protein containing a wide variety of amino acids in its polymer structure. Moreover, it is a potential source of N and P, therefore it may be added to soil as organic waste for enhancement of microbial biomass that results in a change in enzymatic activity (27). This has motivated authors to undertake the present study as done by other workers also (28).

2 Experimental

2.1 Materials

Sodium alginate and gelatin were obtained from Research Lab, Pune, India and used without pretreatment. Calcium chloride (dihydrate) (Loba Chemie, Mumbai, India) was used as a crosslinker. Cypermethrin (Unikil Pesticide Pvt. Ltd., Mumbai, India) was purchased from a local agrochemical supplier. All other chemicals used in this study were of analytical quality, and triple distilled water was used throughout the experiment.

2.2 Preparation of Loaded Beads

In order to prepare cypermethrin loaded polymeric beads of sodium alginate and gelatin, a viscous solution was prepared by dissolving precalculated amounts of sodium alginate and gelatin into a definite volume of distilled water with constant stirring. The prepared viscous solution was added dropwise into a crosslinking bath containing 92.0% (w/w) $CaCl_2$ solution, by syringe and with gentle stirring. The beads so prepared were cured in the same solution for 48 h. The prepared hard beads of nearly identical spherical shapes and sizes were purified by equilibrating them in water for a week. The beads so purified were further dried at 30°C for 1 week and stored in airtight polyethylene bags. A similar procedure was repeated for preparing unloaded beads, but without the addition of cypermethrin.

2.3 Characterization of Beads

The prepared biopolymer beads were characterized by various techniques as discussed below.

2.4 FTIR Spectral Analysis

Unloaded and cypermethrin loaded beads were characterized by Fourier Transform Infrared Spectrophotometer (Perkin-Elmer 1000 Paragon).

2.5 Environmental Scanning Electron Microscopy

ESEM analysis of unloaded and loaded (cypermethrin) beads were performed for the morophological characterization of their surfaces on a ESEM apparatus (STEREO SCAN, 430, Leica SEM, USA).

2.6 Swelling Kinetics

A conventional gravimetric procedure (29) was adopted for monitoring the progress of the water sorption process. In a typical experiment, a preweighed quantity of beads were immersed in a definite volume of water at definite pH and temperature and taken out at predetermined time intervals. The removed swollen beads were gently pressed in between two filter papers to remove excess water and finally weighed on a digital balance (APX–203 Denver, Germany). The swelling ratio (SR) was calculated by the following equation:

$$\text{Swelling ratio} = \frac{\text{Wt. of swollen beads } (W_s)}{\text{Wt. of dry beads } (W_d)} \tag{1}$$

2.7 Release of Cypermethrin

To study the release of cypermethrin from loaded beads, its known weights were placed in a measured volume (25 mL) of distilled water (release medium) without stirring. The released amount of cypermethrin at different time intervals (W_t) was determined by recording the absorbance of the release medium by UV–Vis spectrophotometer (Systronics 2201, Ahamdabad India) at 272 nm. This was related to the

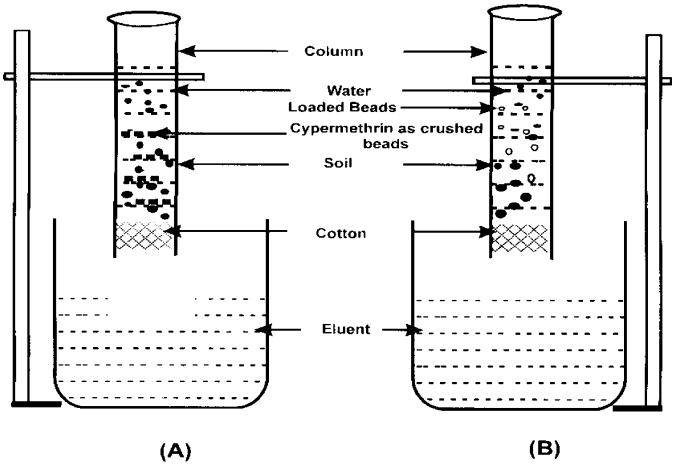

Fig. 1. A schematic presentation of soil–pot experiment.

amount of cypermethrin using a calibration plot. Similarly, the equilibrium release (W_∞) of cypermethrin was determined by recording the absorbance of the release medium after 8 days. In order to gain insight into the operative release mechanisms, the following equations based on Fick's law, but applicable to a spherical device were used (30–31).

$$\frac{W_t}{W_\infty} = k\,t^n \qquad (2)$$

$$\frac{W_t}{W_\infty} = 4\left[\frac{D\,t}{\pi\,r^2}\right]^{0.5} \qquad (3)$$

Where W_t and W_∞ represent the amounts of cypermethrin released at time t and equilibrium, respectively, k is the swelling front factor, n is the release exponent, and r is the radius of the dry spherical bead. The value of 'n' determines the nature of the involved release mechanism, i.e., when $n = 0.43$, the release is Fickian and when 'n' lies between 0.43 and 0.85, the release mechanism is non-Fickian in nature. Moreover, for n being equal to 0.85, the mechanism is coined as Case II, the most desirable condition in controlled release technology.

2.8 Soil–Pot Experiment

In order to mimic the release experiment in agricultural fields, the release studies were also performed in a well defined soil–pot system under nearly similar conditions as are prevalent in a common agriculture field. The whole experiment may be described as below.

2.9 Preparation of Column

First of all, the specific samples of soil were collected from a 2 feet deep pit and it was made certain that the collected sample materials were of identical type.

Two different columns were prepared by initially putting a definite amount of cotton at the end of the columns to protect the loss of soil and insecticide. Each column was filled with 50 g of soil. It was confirmed again that the soil filling process is slow enough to produce uniform porosity and texture of the sample inside the columns, which results in the almost constant rate of insecticide flow. The whole experimental setup is schematically depicted in Figure 1.The column is filled up to its 1/3rd of length by soil, and now

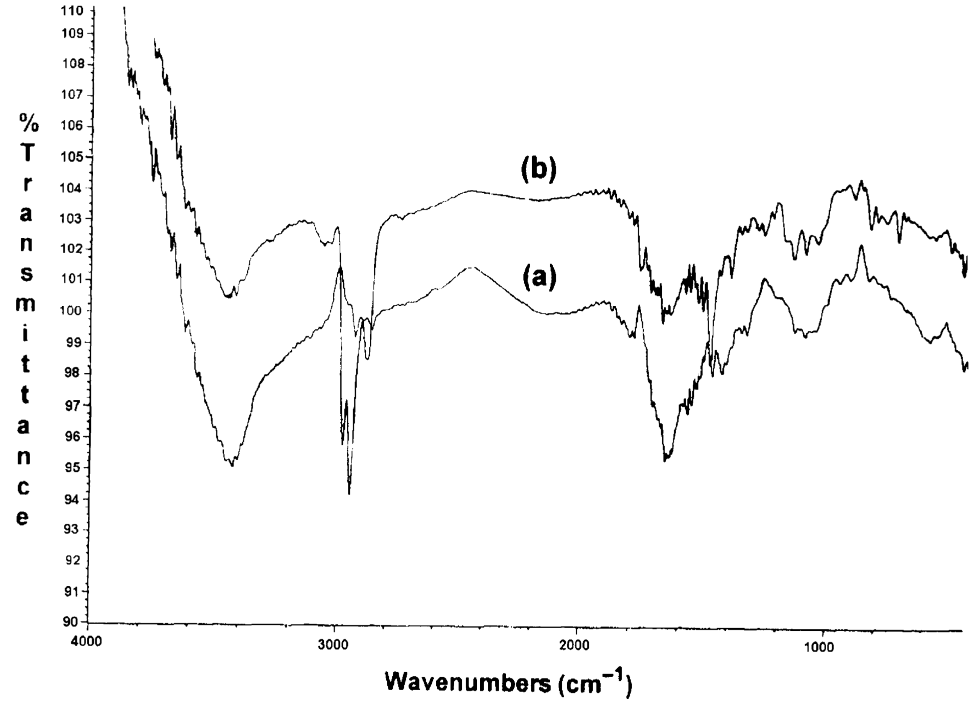

Fig. 2. FTIR spectra of (a) unloaded, and (b) cypermethrin–loaded beads.

the release of insecticide was studied in two different conditions:

(i) When insecticide is released from loaded beads due to their swelling, and
(ii) When insecticide is released directly from crushed beads.

The amount of released insecticide was monitored up to 14 days.

In order to fill up the first column, 50 gm of soil and a definite amount of beads were initially mixed thoroughly and then carefully packed in the columns to produce uniform porosity. Similarly, to prepare the several columns, 50 gm of soil was mixed thoroughly with the same amount of well crushed beads and then filled into the column up to the same height as that of the previous one. In each case, the column were filled up to $1/3^{rd}$ of length by the soil beads mixture and release was facilitated by running down definite volumes of water along the two columns with slow flow rates. The filterate collected in the beaker was periodically analyzed for the release amount of cypermethrin.

3 Results and Discussion

3.1 FTIR Spectra

The FTIR spectra of unloaded and cypermethrin–loaded beads are shown in Figure 2(a) and (b), respectively which confirm the presence of alginate, gelatin and cypermethrin in the loaded beads.

The evidence for the presence of alginate comes from the O–H stretching of hydroxyl at 3434 cm^{-1} and C(=O)$_2$ stretching of carboxylate ion at 1428 cm^{-1}, respectively. The FTIR spectra shows N–H stretching at 3419 cm^{-1} and 1667 cm^{-1} (C=O) stretching, respectively, which are characteristics of proteins and peptides and, thus confirm the presence of gelatin. The spectra (b) also confirm the presence of cypermethrin as evident from the sharp band at 2930 cm^{-1} (C–H stretching of methyl) and C$\equiv$N stretching at 1128 cm^{-1}, C=O stretching at 1662.8 cm^{-1}, respectively.

3.2 ESEM

Environmentally Scanning Electron Micrographs of the unloaded and cypermethrin loaded beads are shown in Figure 3(A) and (B), respectively. A close examination of the photographs indicates that the image (A) of the unloaded bead presents a smooth and homogeneous surface, which suggests a fair level of compatibility between the components of the bead, i.e., gelatin and alginate. On the other hand, the image of the cypermethrin loaded beads, as shown in Figure 3(B), clearly indicates the heterogeneous nature of the surface which could be due to the interaction between the insecticide molecules and polymer components of the bead. The heterogeneity developed on the loaded bead surface could also be due to a lack of compatibility between the polymer components and cypermethrin.

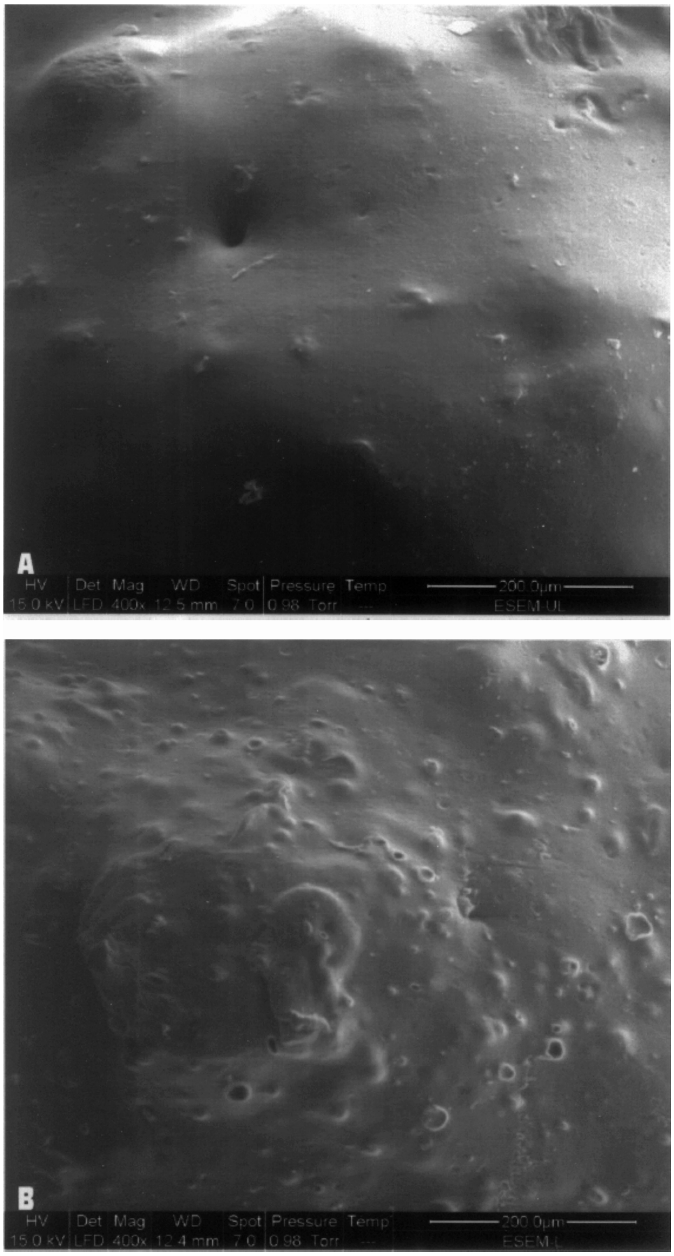

Fig. 3. ESEM images of (A) native beads and (B) cypermethrin–loaded beads.

3.3 Modeling of Release Mechanism

In the present study, the cypermethrin loaded beads of polymeric blend of crosslinked alginate and gelatin could be visualized as a network of macromolecular chains of gelatin and alginate, and the release mechanism may be understood as below.

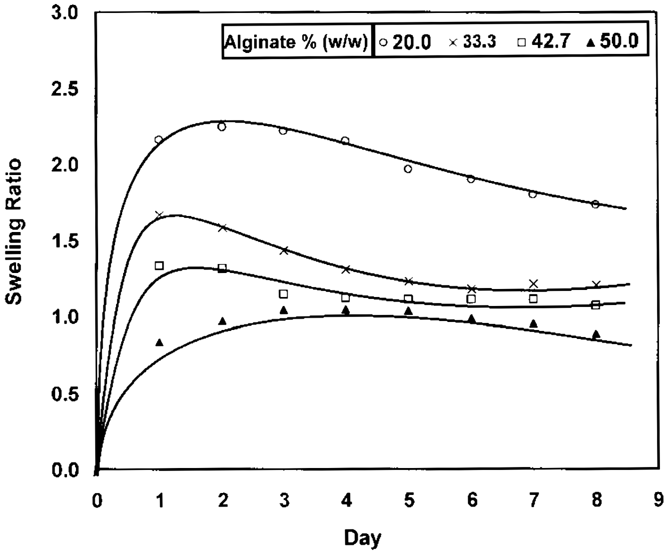

Fig. 4. Influence of varying concentration of alginate on the swelling ratio of the beads at fixed composition of [gelatin] =50%, [$CaCl_2$] = 92.0% (w/w), Temp. = 25 ± 0.2°C.

Case I : Fickian diffusion occurs when the diffusion of insecticide is significantly slower than the rate of relaxation of polymer chains.

Case II : Non–Fickian diffusion occurs when the rate of penetrant diffusion is greater than the rate of relaxation.

Case III : Diffusion is anomalous when the rate of penetrant diffusion is comparable to that of the relaxation of polymer chains.

3.4 Effect of Bead Composition on Swelling

A common architecture of a hydrogel consists of hydrophilic polymer chains crosslinked with a suitable crosslinking agent. The degree of water sorption is not determined by chemical composition only, but it is also regulated by the physical forces and subsequent elastic responses of the constituent macromolecular chains of the matrix. According to Flory's swelling theory (32), the following equation can be given for the swelling ratio (Q).

$$Q^{5/3} = \frac{\{(i/2V_N \cdot S^{3/2}) + (1/2 - X_i)/V_i\}}{V_e/V_o} \tag{4}$$

Where i/V_N is the concentration of the fixed charges referred to unswollen network, S is the ionic concentration in the external solution, $(\frac{1}{2} - X_i)/V_i$ is the affinity of matrix for water, and V_e/V_o is the crosslink density of the network. The above equation reveals that the swelling ratio has a direct relation to ionic osmotic pressure, crosslinked density and the affinity of the hydrogel for water. Therefore, the swelling of a hydrophilic macromolecular matrix can be effectively controlled by varying its chemical composition.

3.5 Effect of Alginate

Alginate is a biopolymer that contains different types of hydrophilic functional groups. When the amounts of alginate is increased in the feed mixture in the range 20 to 50% (w/w), a significant decrease occurs in the swelling ratio as is evident from Figure 4. The results can be explained as below. It is well known that alginate is anionic in nature and its increasing concentration in the bead produces a greater number of carboxylate ions along the chains. This should result in an enhanced repulsion between COO^- ions and cause network chains to undergo a larger relaxation. This allows a greater number of water molecules to enter the bead and should result in increased swelling. However, the results obtained are just the opposite, i.e., the swelling ratio decreases with increasing concentration of alginate in the feed mixture. The observed fall in the swelling ratio could be attributed to the fact that because of crosslinking of alginate by Ca^{2+} ions, the negative charges of the COO^- groups are reduced and as a result, the network undergoes shrinkage due to electrostatic attraction. The shrinkage produced in the network decreases the mesh sizes of the network, which ultimately lowers the swelling ratio.

Another typical feature revealed by Figure 4 is that with an increasing amount of alginate, the rate of decrease of swelling also decreases. This is due to the fact that with the increasing number of alginate molecules, the number of uncrosslinked COO^- groups increases which tend to enhance the swelling ratio due to electrostatic repulsion. However, due to predominance of charge neutralization of COO^- groups due to crosslinking by Ca^{2+} ions and reduced mesh size, the swelling ratio eventually decreases (33).

If the swelling ratio–time curves are examined on a time scale, it is noticed that during the initial time period, the swelling ratio increases while after a definite period (2 to 3 days) a decrease in swelling ratio is noticed. The observed decrease in swelling ratio could be assigned to the partial erosion of surface layers of loaded polymeric beads.

3.6 Effect of Gelatin

Gelatin is a known biopolymer that contains in its molecule variety of hydrophilic functional groups. When the concentration of gelatin is increased in the feed mixture of the hydrogels in the range 33.3 to 50% (w/w), with 50% (w/w) of alginate, the swelling ratio is found to increase as shown in Figure 5. The observed increase in water content may be attributed to the reason that gelatin is a hydrophilic polymer and increasing its amount in the hydrogel, the gel gains more hydrophilicity, which eventually results in a greater swelling ratio (34).

3.7 Effect of $CaCl_2$

Calcium chloride is a well-known crosslinking agent of alginate and assumed to act by the complexation of the

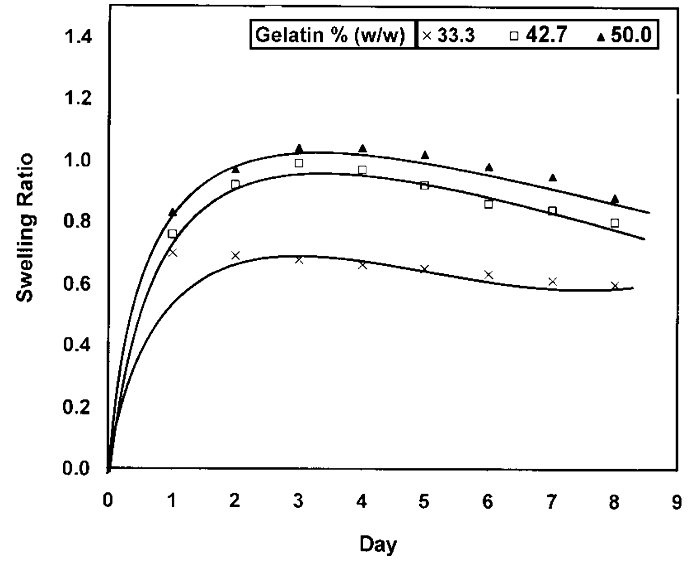

Fig. 5. Effect of varying concentration of gelatin on the swelling ratio of the beads at fixed composition of [alginate] =50%, [$CaCl_2$] = 92.0% (w/w), Temp. = 25 ± 0.2°C.

carboxylate anions of alginate by its bivalent calcium ions, thus, forming a cavity type of network (35). In the present investigation, the effect of $CaCl_2$ on the swelling ratio of the beads has been investigated by crosslinking concentration in the range 36.7% (w/w) to183.5 % (w/w). The results are shown in Figure 6, which indicate that the degree of water sorption constantly decreases with increasing concentration of crosslinker. The observed decrease in swelling ratio may be attributed to the fact that enhanced number of crosslinks results in a reduction in mesh sizes of the polymeric bead, which inhibits penetration of water molecules into the bead network. This brings about a fall in the swelling ratio. Similar type of results have also been reported elsewhere (36).

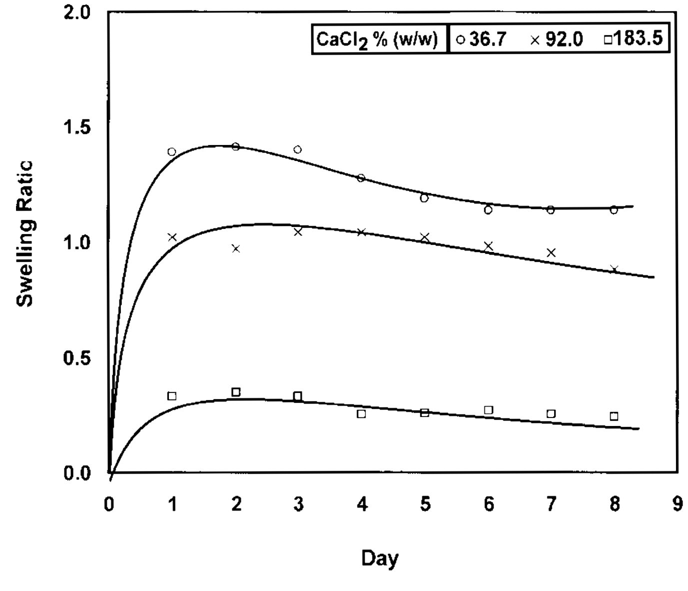

Fig. 6. Effect of varying concentration of crosslinker ($CaCl_2$) on the swelling ratio of the beads at fixed composition of [alginate] =50%, [gelatin] =50%, Temp. = 25 ± 0.2°C.

3.8 Effect of Salts

The presence of an electrolyte in a swelling medium is of importance in agriculture and biomedical fields, namely for water reservoirs in agriculture and hydrogels as implants for drug release application. The effect of electrolytes on the extent of swelling is normally determined by the balance between the π ion and the elastic response of the network chains. π ion is given by the following equation:

$$\pi_{\mathrm{ion}} = \mathrm{R\,T} \sum_{\mathrm{i}} (\mathrm{Ci}^{g} - \mathrm{Ci}^{s}) \qquad (5)$$

Where Ci is the mobile ion concentration of species i, the superscripts g and s represent the gel and solution phases, respectively, R is the gas constant, T is the absolute temperature of swelling medium. Equation 5 clearly implies that the greater the difference between the concentration of mobile ions inside and outside the gel, the larger the ion and, therefore, the greater the swelling of the gel.

In the present investigation, the influence of salts on the swelling of the beads was studied by the addition of various salts of sodium (0.5 M) and chlorides of cations (0.5 M) to the swelling bath, respectively. The results are shown in Figure 7, which indicate that in both cases the swelling ratio decreases. These results also reveal that although various anions exerted an almost identical impact on the swelling ratio in the case of cations, the degree of suppression of the swelling ratio increases in the following sequence.

$$K^{+} > Ba^{2+} > Al^{3+}$$

The obtained results may be explained as follows: Once the hydrogel swells to an optimum value, the gel pores widen, which allow cation from the swelling bath to diffuse into the bulk of the swollen gel. These cations bind to the negatively charged $-COO^{-}$ ions present along the network chains and obviously result in a shrinking of the network chains, bringing about a fall in the swelling ratio (37).

The observed order of the relative effectiveness of added cations may be explained by the fact that the cations, due to their smaller sizes, diffuse into the network and bind electrostatically to the anionic centers of the biopolymeric molecules. This results in a decrease in electrostatic repulsion between the chain and thus, which causes reduction in the swelling of the bead. The binding of the cations to the anionic ends inside the beads is greatest in the case of Al^{3+} ions, while it is smallest with K^{+} ions. This explains the least effectiveness of K^{+} ions in lowering the swelling ratio of beads. In the case of anions, the added ions diffuse into the swollen network through the pores and bind to the positively charged centers of gelatin molecules such as $-NH-.-NH_{3m}$, etc. This consequently results in a shrinkage

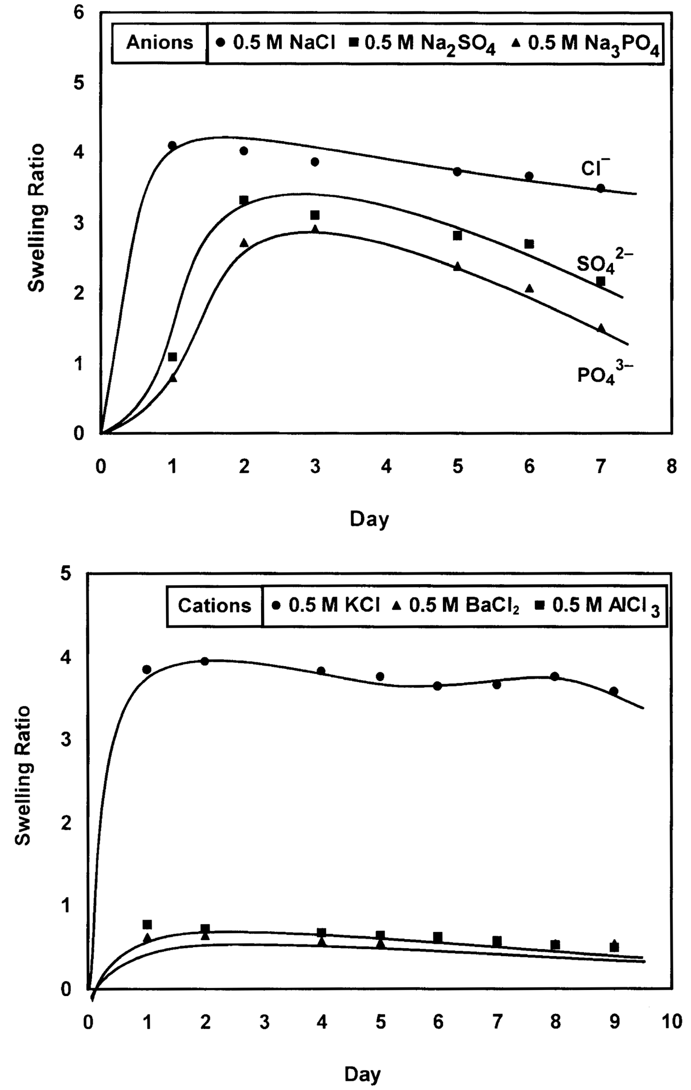

Fig. 7. Effect of salts on the swelling ratio of beads of definite composition. [gelatin] =50%, [alginate] =50%, [$CaCl_2$] =92.0(w/w), Temp.= 25 ± 0.2°C.

of the network pores which brings about a fall in the water sorption, since the greater reduction in charge is about by PO_4^{3-} ions, obviously the relative order of effectiveness of added anions is also justified. The binding of salts to protein molecules (gelatin) is well documented in the literature (38).

It is worth mentioning here that the studied salt ions were also added to the $CaCI_2$ solution to see if there is any effect of those ions on the degree of crosslinker. The results showed that the added ions did not influence the degree of crosslinker.

3.9 Effect of Temperature

The effect of temperature on the swelling ratio of the beads was investigated by the variation of the temperature of the swelling medium in the range 12°C–35°C.

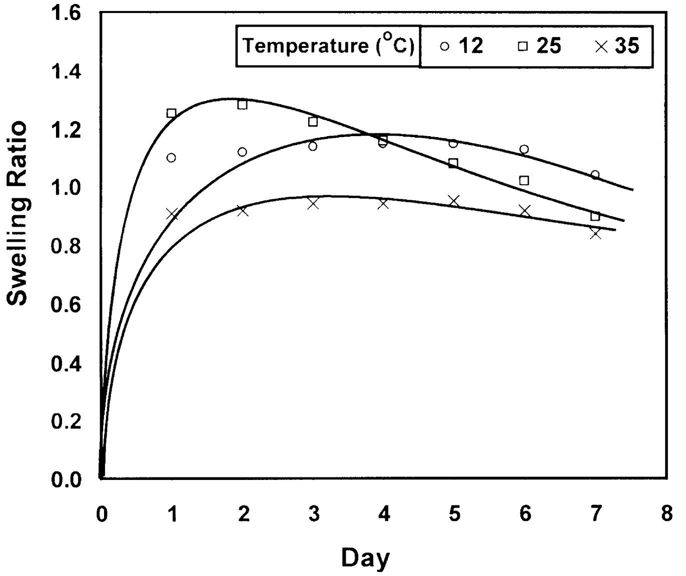

Fig. 8. Effect of temperature on the swelling ratio of beads of definite composition [gelatin] = 50%, [alginate] = 50%, [$CaCl_2$] = 92.0(w/w).

The results depicted in Figure 8 clearly reveal that in the temperature range 12°C to 25°C, the swelling ratio initially increases with increasing temperature, while after a definite time period (7 days for 12°C and 3 days for 25°C) the swelling ratio constantly decreases. However, beyond 25°C, i.e., at 35°C, the swelling ratio is significantly suppressed. The results may be explained as below.

At this higher temperature, the swelling initially increases with a swelling period up to 2.5 days and thereafter decreases constantly with increasing swelling time. The obtained results may be explained as below.

When the temperature increases from 12°C to 25°C, the segmental mobility of biopolymeric chains also increases which in turn, causes more relaxation of chains, thus, allowing greater number of water molecules to enter the bead. This results in a greater swelling ratio of the gel. However the observed decrease in swelling ratio with increasing time could again be attributed to continuous erosion of surface layers of swelling beads which lowers the swelling ratio.

The observed decrease in swelling ratio could again be attributed to continuous erosion of surface layers of the swelling bead which lowers the swelling ratio. It is worth mentioning here that the erosion of bead becomes faster with increasing temperature and, therefore, erosion starts earlier at higher temperature.

However, at the highest temperature (35°C) of the studied range, the swelling ratio is appreciably lower than 25°C, which may be due to the fact that at a higher temperature, the hydrogen bonds hold water molecules to the polymer chains get broken and therefore, the swelling ratio decreases (39).

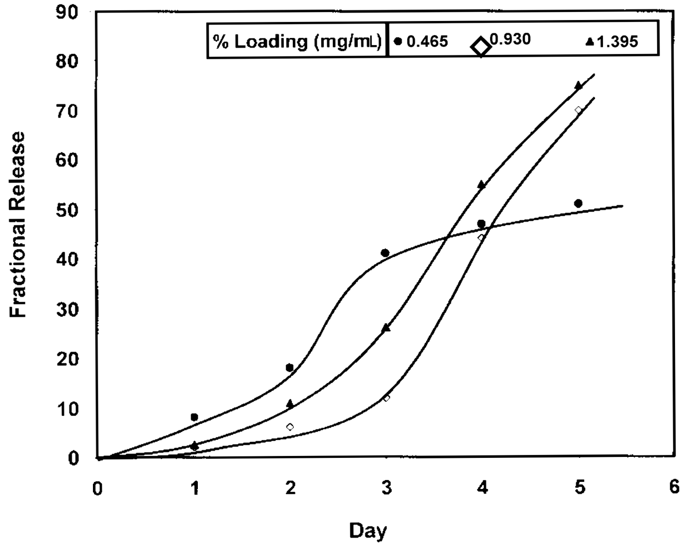

Fig. 9. Effect of percent loading on the fractional release of cypermethrin from the beads of definite composition [gelatin] =50%, [alginate] = 50%, [$CaCl_2$] = 92.0(w/w), Temp. = 25 ± 0.2°C.

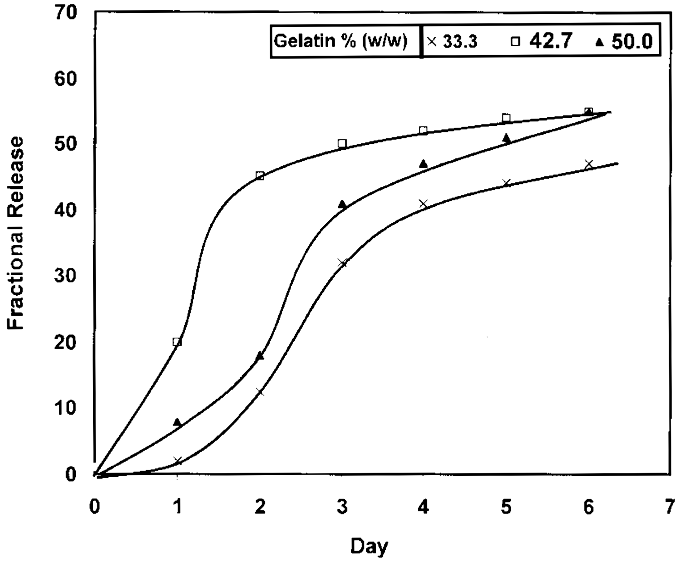

Fig. 10. Effect of gelatin on the fractional release of cypermethrin from the beads of definite composition [alginate] = 50%, [$CaCl_2$] = 92.0(w/w), Temp. = 25 ± 0.2°C.

3.10 Release Study

Since the present study basically aims at designing a swelling controlled slow release system, the release dynamics of cypermethrin is expected to show a close dependence on the chemical composition of the carrier beads and on the external experimental conditions such as temperature and presence of electrolyte in the release medium. The forthcoming part of the paper describes the kinetic results of the fractional release of cypermethrin from loaded alginate–gelatin beads.

3.11 Effect of Percent Loading

The influence of percent loading of the insecticide on its release profiles has been studied by equilibrating the known amount of beads into a cypermethrin solution of varying concentration in the range 0.465 mg/mL to 1.39 mg/mL. The dry beads loaded to various extents were investigated for release dynamics of the cypermethrin and the results obtained are shown in Figure 9. The results that indicate when the percent loading, increases from 0.465 to 1.39 mg/mL, the fractional release decreases up to 3 days, while after it, the release of cypermethrin steeply increases. It is also revealed that at highest loading (1.39 mg/mL) the fractional release again starts increasing which further accelerates after the second day. The results are quite unusual and may be explained as below.

At the lowest percent loading (0.465 mg/mL), the cypermethrin is uniformly loaded into the biopolymer matrix and when immers into the release media the encapsulated insecticides releases smoothly showing no abnormal trend (40). However, at higher (or moderate) loading (1.39 mg/mL) the pores of the matrix get blocked due to accumulation of the cypermethrin which results in a shrinkage of the matrix pores. This leads to a fall in the released cypermethrin. However, an enhanced release pulse is seen beyond the third day which may be attributed to the fact that after the initial swelling of the loaded beads, the pore size of the polymer matrix increases which results in an enhanced rate of fractional release.

A similar type of fall in the released amount has also been reported by other workers (41). Some authors (42) however, reported an increase in the released amount due to a higher percent loading. In the present study, therefore, both types of results have been obtained.

3.12 Variation of Gelatin

Gelatin, being a hydrophilic functional biopolymer, is expected to affect the release profile of cypermethrin to a significant extent. Thus, the influence of gelatin content in the beads has been investigated on the fractional release of cypermethrin by varying its amount in the range 33.3 to 50% (w/w) of alginate in the feed composition. The results are presented in Figure 10 which clearly indicates that the fractional release of cypermethrin increases from 33.3 to 42.7% (w/w) of gelatin content while beyond 42.7% (w/w) of gelatin, a decrease in fractional release is noticed.

The obtained results may be explained on the basis of the fact that with an increase in concentration of gelatin, the hydrophilicity of the network also increases which in turn, absorbs water from the release medium and thus causes expulsion of the insecticide molecules from the loaded beads. This obviously results in an increase in fractional release of cypermethrin. However, a fall in fractional release is noticed when the gelatin content in the polymeric beads

Table 1. Kinetic data of the release process of Cypermethrin from the swelling biopolymeric beads

S. No.	*Gelatin (%)*	*Sodium alginate (%)*	*$CaCl_2$ (w/w)*	*$t_{1/2}$ (days)*	*n*	*$D \times 10^{-10}$ (cm^2/s)*	*Mechanism*
1	33.3	50.0	92.0	6.0	0.50	2.35	Non-Fickian
2	42.7	50.0	92.0	5.0	0.60	2.35	Non-Fickian
3	50.0	50.0	92.0	5.0	0.30	3.68	Non-Fickian
4	50.0	20.0	92.0	3.0	0.30	3.68	Nearly Fickian
5	50.0	33.3	92.0	3.0	0.60	3.68	Non-Fickian
6	50.0	42.7	92.0	$2^{1/2}$	0.60	1.8	Non-Fickian
7	50.0	50.0	36.7	4.0	1.0	3.68	Super Case II
8	50.0	50.0	183.5	5.0	0.69	2.35	Non-Fickian

exceeds. The observed fall in the fractional release of cypermethrin may be attributed to the fact that at much higher content of gelatin, the polymer matrix acquires a compact configuration that not only restrains the mobility of polymeric chains, but also brings about shrinkage in the matrix pores which lowers the insecticide release (43).

3.13 Variation of Alginate

Alginate being a anionic biopolymer is present as crosslinked calcium alginate in the biopolymeric beads and is expected to affect the fractional release profiles of cypermethrin. To study its impact on the release dynamics of the insecticide, its concentration has been varied in the feed mixture in the range 20 to 50% (w/w) of gelatin, and the results are depicted in Figure 11. The Figure reveals that the fractional release increases with increasing concentration of alginate in the range 20 to 42.7% (w/w) of alginate while a decrease is seen beyond 42.7% (w/w). The reason for the observed initial increase in fractional release may be attributed to the fact that an increased content of alginate in the bead results in greater electrostatic repulsion among macromolecular chains, which facilitates the inclusion of water molecules into the bead networks. This consequently results in a greater release of the loaded insecticide. The enhanced release of cypermethrin may further be quantified in terms of half life period ($t_{1/2}$) which are summarized in Table 1. The results reveal that with increasing alginate content in the bead, the half-life period gradually decreases which is to a certain extent expected as an alginate rich bead will have a faster release rate and, consequently, half life period will be lowered.

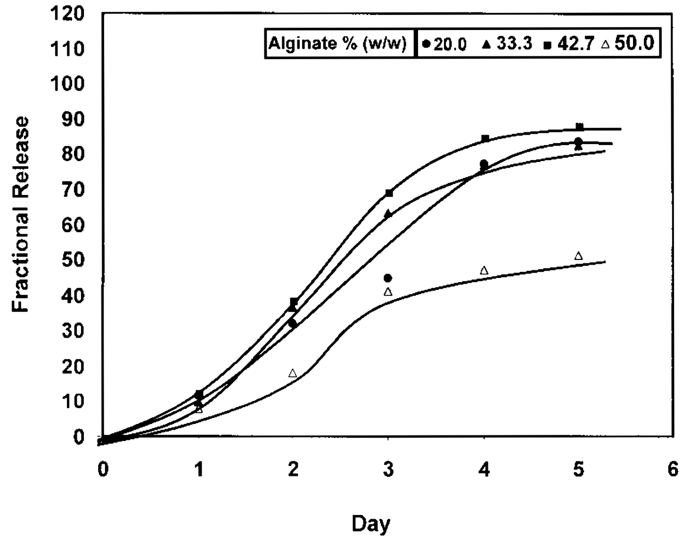

Fig. 11. Effect of alginate on the fractional release of cypermethrin from the beads of definite composition [gelatin] = 50%, [$CaCl_2$] = 92.0(w/w), Temp. = 25 ± 0.2°C.

The results shown in Figure 11 also indicate that beyond 42.7% (w/w) of alginate, the fractional release decreases which could be attributed to the reason that at greater alginate content, the polymeric matrix becomes quite compact and, therefore, reduced mesh sizes of the pores causes a fall in the released cypermethrin. Alternatively, at higher alginate content, the volume fraction of polymer increases in the polymeric bead due to which the entering water molecules have to travel a longer path to swell the polymer network. This lowers the degree of swelling of the bead which consequently results in a fall in the insecticide release.

3.14 Effect of Crosslinker

The extent to which a polymer matrix is crosslinked, either physically or chemically exerts a pronounced effect on the physicochemical properties of the polymer matrix and determines its end application. In the present study, alginate has been crosslinked with $CaCl_2$ to a different extent by varying the concentration of the crosslinker solution in the range 36.7 to 183.5% (w/w) of alginate. The results are depicted in Figure 12, which clearly indicate that the fractional release of cypermethrin decreases as the degree of crosslinking increases in the biopolymeric bead. The observed results are quite obvious and may be explained by the fact that with increasing crosslink density of the polymer network, the mesh sizes of the free volumes available between the polymer network chains decreases which restrains the mobility of macromolecular chains. Thus, the transport of water molecules into the bead network and subsequent release of insecticide is suppressed resulting a fall in the released amount of cypermethrin.

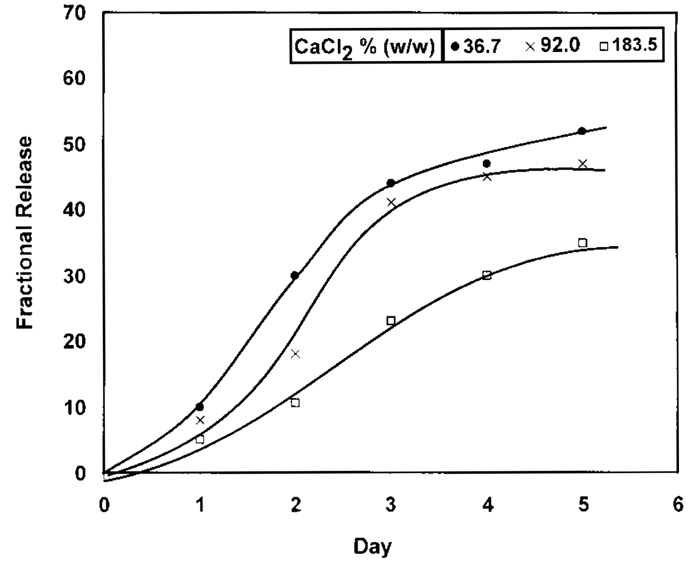

Fig. 12. Effect of crosslinker on the fractional release of cypermethrin from the beads of definite composition [gelatin] =50%, [alginate] = 50%, Temp. = 25 ± 0.2°C.

The influence of enhanced crosslinker on the release of cypermethrin has also been quantified in terms of the half-life period ($t_{1/2}$), which are summarized in Table 1. The half life period data indicate that with increasing degree of crosslinking, $t_{1/2}$ also increases as due to suppressed release rate at higher crosslinker content, greater time will be required for the release of half of the loaded insecticide.

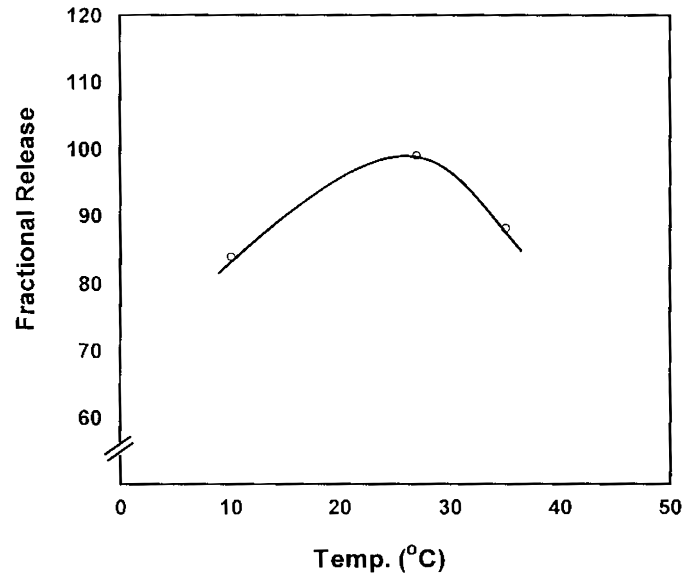

Fig. 13. Effect of temperature on the fractional release of cypermethrin from the beads of definite composition [gelatin] = 50%, [alginate] = 50%, [$CaCl_2$] = 92.0(w/w).

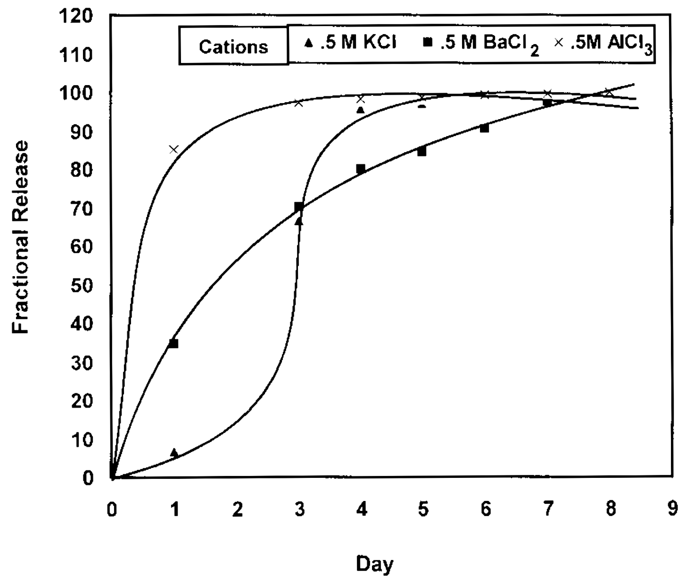

Fig. 14. Effect of cations on the fractional release of cypermethrin from the beads of definite composition [gelatin] = 50%, [alginate] = 50%, [$CaCl_2$] = 92.0(w/w), Temp. = 25 ± 0.2°C.

3.15 Effect of Temperature

The influence of temperature on the fractional release of cypermethrin has been investigated by performing the release experiments in the temperature range of 12°C to 35°C. The results are depicted in Figure 13, which show that whereas in the temperature range 12°C to 27°C, a fractional release increases with increasing temperature, while beyond 27°C, just the opposite order of release is obtained, that is, the fractional release decreases with increasing temperature. The observed increase in fractional release of cypermethrin may be explained by the fact that in the temperature range 12°C to 27°C, both the mobility of polymeric chains and diffusion of water and cypermethrin molecules increases which brings about an overall increase in the fractional release. However, beyond 27°C, the observed decrease in fractional release could be attributed to the fact that at higher temperature, the binding forces between the water molecules and polymeric chains decreases which results in a lower absorption of water molecules by the loaded polymeric beads. This consequently decreases the released amount of cypermethrin (44).

3.16 Salt Effect

The presence of electrolytes in the release medium exert a significant influence on the fractional release profile of the cypermethrin. The effect of salts has been studied in two parts, viz. cationic and anionic effect as discussed below.

3.16.1. *Effect of cations*

When equimolar cations (0.5 M) such as K^+, Ba^{2+}, Al^{3+} of increasing charge are added to the release medium, the

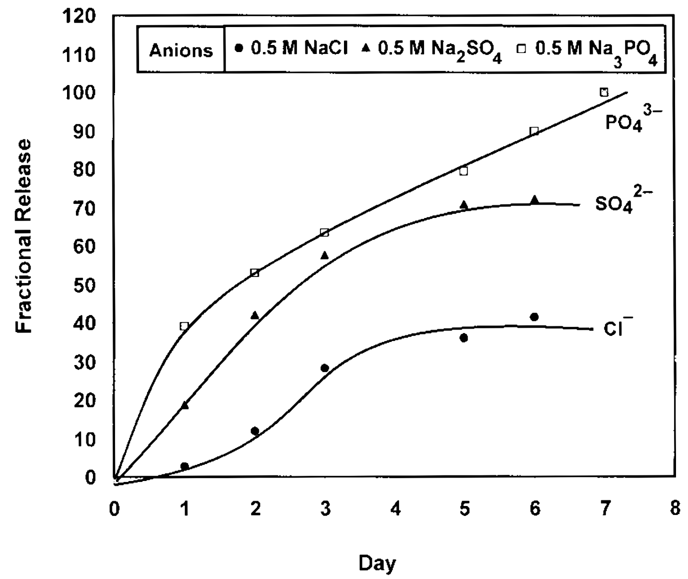

Fig. 15. Effect of anions on the fractional release of cypermethrin from the beads of definite composition [gelatin] = 50%, [alginate] = 50%, [CaCI$_2$] = 92.0(w/w), Temp. = 25 ± 0.2°C.

fractional release is found to increase as shown in Figure 14 with increasing change of the added cation. Thus, the fractional release increases in the following order,

$$K^+ < Ba^{2+} < Al^{3+}$$

The observed order of effectiveness and increased fractional release is quite unexpected and opposite to the previously obtained swelling results. The enhanced fractional release with increasing charge may be explained by the fact that the added cations interact with the carboxylic groups of alginate on the bead surface and causes dissolution of the bead. This obviously results in a rapid release of cypermethrin as is evident from the steep portion of the release profile curves.

The relative order of effectiveness is also justified as greater the charge over the added cation, more strongly it interacts with the bead surface and consequently greater would be the dissolution of the bead. In this way, K^+ ion produces minimum interaction while Al^{3+} ions a greater interaction with alginate component of the bead. The half-life period ($t^{1/2}$) also decreases with an increasing charge over the ion as summarized in Table 1.

3.16.2. *Effect of anions*

The effect of anions on to the release of cypermethrin has been investigated by adding Cl^-, SO_4^{2-}, PO_4^{3-} ions into the release medium in the form of sodium salts (0.5 M). The results are depicted in Figure 15, which show an increase in fractional release with increase in charge over the added ions. The order of effectiveness of added anions obey the following sequences:

$$Cl^- < SO_4^{2-} < PO_4^{3-}$$

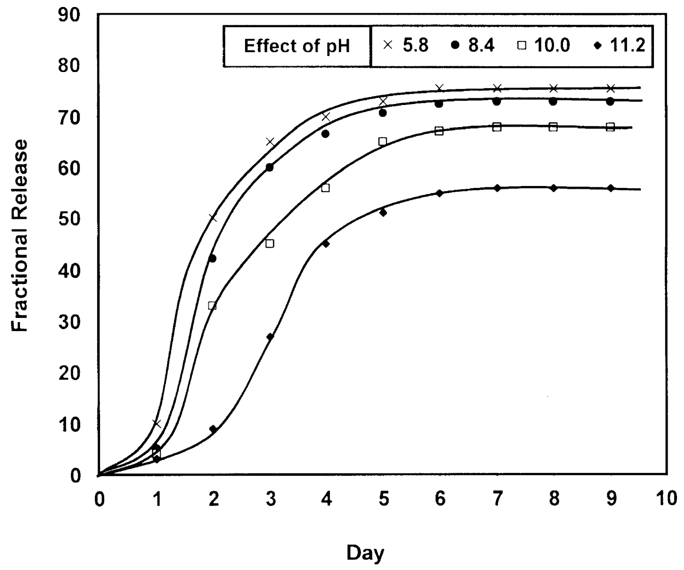

Fig. 16. Effect of pH on the fractional release of cypermethrin from the beads of definite composition composition [gelatin] = 50%, [alginate] = 50%, [CaCI$_2$] = 92.0 (w/w), Temp. 25± 0.2°C.

The results may be explained by the fact that the added anions may interact with the protonated amine groups of gelatin and may facilitate bead dissolution, which subsequently results in a faster release.

3.17 Effect of pH

The release of a bioactive agent is influenced by varying pH of the release media. In agricultural studies also, the pH has to be considered as a prime factor to affect the release process. Thus, in the present study, the effect of pH on the release of cypermethrin has been investigated by varying pH of the release medium in the range 5.8 to 11.2.The results are depicted in Figure 16, which clearly reveals that the amounts as well as rate of released cypermethrins constantly decreases with increasing pH of the release medium. The observed results may be explained as below.

The beads taken in this study are made up of gelatin (alkali processed, isoelectric point 4.8) and alginate which at pH bear a net negative charge and almost no charge, respectively. Thus, due to a negatively charged gelatin chains, the repulsive forces operate causing relaxation of blend chains. This in turn, results in expulsion of entrapped of (loaded) cypermethrin molecules into the release medium giving rise to an optimum release at pH 5.8.

However, when the pH increases and enters the alkaline range and the gelatin molecules acquire a net negative charge, the alginate molecules may undergo dissociation of their carboxylic groups leading to formation of COO^- ions which may further produce a greater repulsion. But, surprisingly, the released amount decreases with increasing pH. The possible reason for this unexpected result may be that due to a large number of carboxylate ions, the

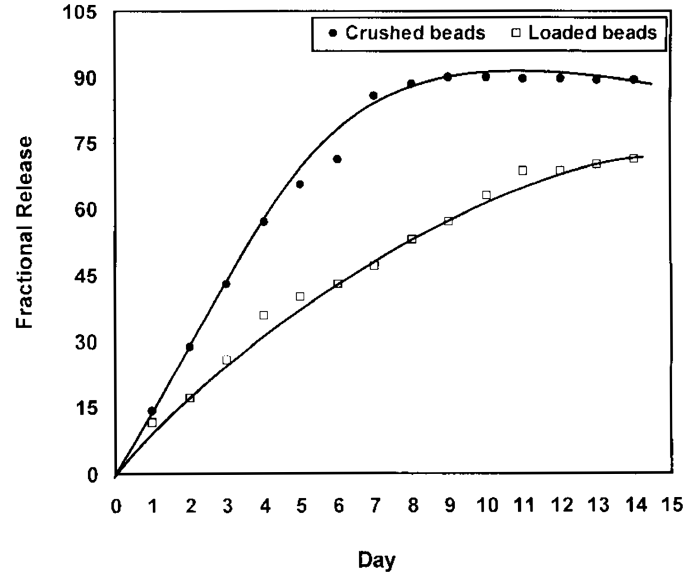

Fig. 17. Release of Cypermethrin when applied (a) as crushed beads, and (b) through swelling polymeric beads.

cypermethrin molecules may more firmly bind to alginate chains, which brings about a fall in the amount of cypermethrin.

3.18 Soil–Pot Experiments

In order to demonstrate the utility of swelling controlled release of cypermethrin in agricultural fields, soil–pot experiments were done, the details of which have already been given in the Experimental section. The cumulative release results are shown in Figure 17, which clearly indicate that the release rate of insecticide is significantly higher when the cypermethrin is applied directly (in crushed bead form) than that when applied and released through swelling biopolymeric beads. It is clear from the release profile that in the case of direct application, the released amount of cypermethrin acquires a limiting value only after 10 days, whereas in the case of release through biopolymeric beads, the release rate is quite slow and the release process is continuous even after 14 days. Moreover, the released amount of insecticide is 75 percent after 14 days, in comparison to what has been released through direct application after 6 days only. Thus, the controlled release formulations of cypermethrin appear to serve the purpose well.

3.19 Analysis of Kinetic Data

The kinetics of cypermethrin release is mainly determined by the contributions of relative rates of diffusion (R_{diff} cypermethrin) and relaxation (R_{relax}). The values of 'n' are summarized in Table 1, which indicate that in all of the cases of bead compositions, the values of n vary from Fickian to Super case II transport mechanism.

4 Conclusions

Crosslinking of alginate by calcium ions in the presence of gelatin results in ionotropic hydrophilic beads, which offers a great potential to serve as a biopolymeric carrier for swelling controlled release of cypermethrin, a well known and widely applied insecticide.

Whereas the FTIR confirms the presence of alginate, gelatin and cypermethin in the bead, the ESEM analysis reveals that whereas the native beads have homogeneous and smooth morphology, the cypermethrin loaded beads develop unevenness on the surface which may be attributed to the insecticide–polymer interaction, which reduces the mutual compatibility of the two components.

The water sorption capacity of beads depends greatly on their chemical composition. It is found that in the case of alginate, an initial increase in swelling ratio is noticed with increasing alginate concentration, while with a further rise in concentration, the water sorption capacity decreases. However, in the case of gelatin and calcium chloride (crosslinker) increases in concentrations results in an increase and a decrease in the swelling ratio, respectively.

The swelling ratio of the hydrogel is significantly reduced when inorganic salts are added to the swelling bath. The influence of temperature on the swelling ratio shows that whereas an initial rise in temperature leads to a rise in swelling ratio, a further increase in temperature tends to lower water sorption capacity of the beads.

The fractional release of the cypermethrin is found to increase with greater percent loading of the pesticide. The extent of release is found to be dependent on the chemical architecture of the bead. When the amount of gelatin is varied, in the feed composition, the fraction release initially increases and then decreases. The release also increases with increasing gelatin but decreases with a crosslinking agent.

The temperature and ionic strength of the release medium also affect fractional release. An increase in temperature brings about an increase in the fractional release initially, but further rise results in a fall in the released amount. The presence of salts, on the other hand causes a constant increase in fractional release.

The utility of the present study has also been judged by performing soil–pot experiments which clearly suggests that the release rate is significantly lower with polymeric carrier in comparison to that when the cypermethrin is applied directly (in crushed beads form). The release process is controlled by swelling of the polymer matrix and follow non–Fickian transport mechanism.

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