

Controlled Release of Insecticide Carbaryl from Sodium Alginate, Sodium Alginate/Gelatin, and Sodium Alginate/Sodium Carboxymethyl Cellulose Blend Beads Crosslinked with Glutaraldehyde

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ABSTRACT: Interpenetrating network polymeric beads of sodium alginate (NaAlg) and its blend with gelatin (gels) or sodium carboxymethyl cellulose (NaCMC) have been prepared by crosslinking with a common crosslinking agent, glutaraldehyde (GA), for the release of insecticide carbaryl (Carb). The prepared beads were characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. Scanning electron microscopy confirmed the spherical nature and surface morphology of the particles. Bead characteristics, such as carbaryl entrapment efficiency, particle size, equilibrium swelling degree, and carbaryl release kinetics, were determined. The effects of the preparation conditions, such as Carb/NaAlg ratio, time of exposure to GA, blend ratio, and temperature of release medium on the carbaryl release, were investigated for 25 days at 25°C. It was observed that the carbaryl release decreased with in-

crease in crosslinking of network, while it increased with increase in Carb/NaAlg ratio and temperature. The release of carbaryl also increased with increase in Gel or NaCMC content in the blend beads. The highest carbaryl release was found to be 100%, for the beads that were prepared with 1 : 1 NaAlg/Gel at 16 days. The diffusion coefficients have been calculated for the transport of insecticide through the polymeric beads, using initial time approximation method. These values were also consistent with the carbaryl release data. The carbaryl release from most of the bead formulations followed the Fickian trend. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1310–1319, 2006

Key words: crosslinking; water soluble polymers; beads; blends; carbaryl

INTRODUCTION

Controlled release (CR) technology is a recent technology, which has considerable potential in the fields of medicine, pharmacy, and agriculture.^{1–4} The aims of CR formulations are to protect the supply of the agent, to allow the automatic release of the agent to the target at a controlled rate, and to maintain its concentration in the system within the optimum limits, over a specified period of time, thereby providing great specificity and persistence.⁵

The parameters that affect the properties of such CR formulations depend upon the nature and type of the polymer used. Several research work have contributed to the development of formulations for the CR of chemicals in agriculture.^{6–12} Despite of several polymers used in these work, natural polymers are often preferred to synthetic polymers because of their non-toxic, low cost, free availability, and biodegradability

characteristics.^{13,14} However, several natural biopolymers, especially the class of polysaccharides, have some inherent disadvantages, such as poor mechanical strength, uncontrolled water uptake, and microbial contamination.¹⁴ To overcome these problems, efforts have been made to develop chemically modified matrices by grafting^{15–18} or blending^{19–22} with other polymers. The polymer blending technique can be considered a useful tool for the new properties of polymer.

Among such natural polymers, alginate is a linear chain structure of (1→4)- β -D-mannuronic acid (M) and α -L-guluronic acid (G) residues, arranged in a blockwise fashion.¹² Sodium alginate (NaAlg) is a bioerodible natural polymer that has been widely used in CR applications of drugs^{23–25} and pesticides,^{10,20,26,27} because it forms strong gels in aqueous media and is bioerodible. The development of interpenetrating polymer networks (IPNs) of NaAlg is attractive because, by definition, IPNs contain two polymers, each in a network form, which can be crosslinked in the presence of each other to give a three-dimensional network structure, producing free volume for easy encapsulation of drugs or pesticides.

In the present study, preparation of IPNs of NaAlg and its blending with two other biodegradable natural

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polymers, Gel or sodium carboxymethyl cellulose (NaCMC), were investigated. These matrices were used to study CR of carbaryl, which is a wide spectrum insecticide, used in controlling 100 species of insects.²⁸ In an earlier study, crosslinked carboxymethyl cellulose beads have been prepared to deliver carbaryl for agricultural applications.²⁹ Carbaryl has very low chemical stability because of its rapid hydrolysis to 1-naphthol in alkaline media.³⁰ It is formulated as a wettable powder, which makes its handling very difficult, mainly because of the fast absorption by nasal, oral, and transdermal routes. CR formulations of carbaryl would potentially extend its effective lifetime, reduce risks, leach or runoff on application, and safer to the user and nontarget organisms. For these reasons, pesticide carbaryl (as a model active substance) was encapsulated with NaAlg matrices, using glutaraldehyde (GA) as a crosslinking agent, and to improve release properties and entrapment efficiency of NaAlg, the polymer was blended with Gel or NaCMC polymers. The release characteristics, in terms of entrapment efficiency, bead diameter, equilibrium swelling degree (ESD), and carbaryl diffusion coefficient, have been investigated. The effects of exposure time to GA, Carb/NaAlg ratio, blend ratio, and release temperature on the carbaryl release from the polymeric beads were studied.

EXPERIMENTAL

Materials

Sodium alginate, with a viscosity of 3500 cps (2% solution at 25°C), was purchased from Sigma (Louis, USA). Hexavin 85 (containing 85% w/w carbaryl) was chosen as an active substance, supplied from Hektaş T.A.Ş. in Turkey, and used after purification by recrystallization with ethyl alcohol. Gel and NaCMC were obtained by Fluka Chemie AG (Buchs, Switzerland). GA (25% w/w) solution and ethanol were supplied by Merck AG (Darmstadt, Germany).

Preparation of the NaAlg beads

NaAlg (1.5%, w/v) solution in distilled water was prepared by heating it gently. After complete cooling, different amounts of carbaryl were added and mixed thoroughly using a magnetic stirrer (Corning, USA). The polymer solution containing carbaryl was added dropwise into 4% GA and 1% 10N HNO₃ solution, using a 25-mL hypodermic syringe (1 mm diameter), with constant stirring. Experimental conditions, such as the distance between the syringe and crosslinking solution level, number of drops/min and temperature, were maintained constant. The beads formed were removed from the crosslinking solution, at selected time intervals of 5, 10, and 15 min. The beads were

filtered, and washed with water repeatedly to remove the adhered GA and acid, and then allowed to dry in an oven at 40°C.

NaAlg/Gel and NaAlg/NaCMC blend beads were prepared in a similar way. Aqueous Gel and NaCMC solutions were prepared. Then, the mixture of NaAlg with Gel or NaCMC solutions at the specified blend ratios of 1 : 1, 2 : 1, 4 : 1 (w/w) were stirred at room temperature for 1 day to form homogeneous solutions. To this solution, carbaryl was added and mixed thoroughly using a magnetic stirrer to ensure complete mixing. The polymer solution containing carbaryl was added dropwise into 4% GA and 1% 10N HNO₃ solution. The beads thus formed were removed from the crosslinking solution after 5 min and were washed with water. The beads were then dried completely.

To estimate the bead diameters, 10 samples of the completely dried beads from the different formulations were selected, and their diameters were measured by using electronic digital caliper (Cole-Parmer, USA).

Swelling of the beads

Swelling property of the beads was studied by measurement of ESD. ESD values for individual formulation of the beads were determined by measuring the extent of swelling of the beads in water at 25°C. To ensure complete equilibration, the bead samples were allowed to swell for 48 h. The excess surface-adhered liquid drops were removed by blotting, and the swollen beads were weighed using electronic balance (Shimadzu, Japan). The beads were then dried in an oven (Nuve, Turkey) at 40°C, until there was no change in the dried mass of samples. The ESD percent was calculated as follows:

Equilibrium swelling degree (%)

$$= \frac{(M_s - M_d)}{M_d} \times 100 \quad (1)$$

where M_s and M_d are the mass of the swollen beads and dry beads, respectively.

Carbaryl content

The known mass of beads was crushed in an agate mortar with a pestle, and then, the polymeric powder was taken in a flask. Ethanol (50 mL) was added and refluxed at 25°C for 2 h, to ensure the complete extraction of carbaryl from the beads. At the end of 2 h, precipitated NaAlg was filtered, and carbaryl was analyzed by using a UV-visible spectrophotometer (Ultrospec 2000, Cambridge, England) at a wavelength of 280 nm, using pure ethanol as a blank. The percentage

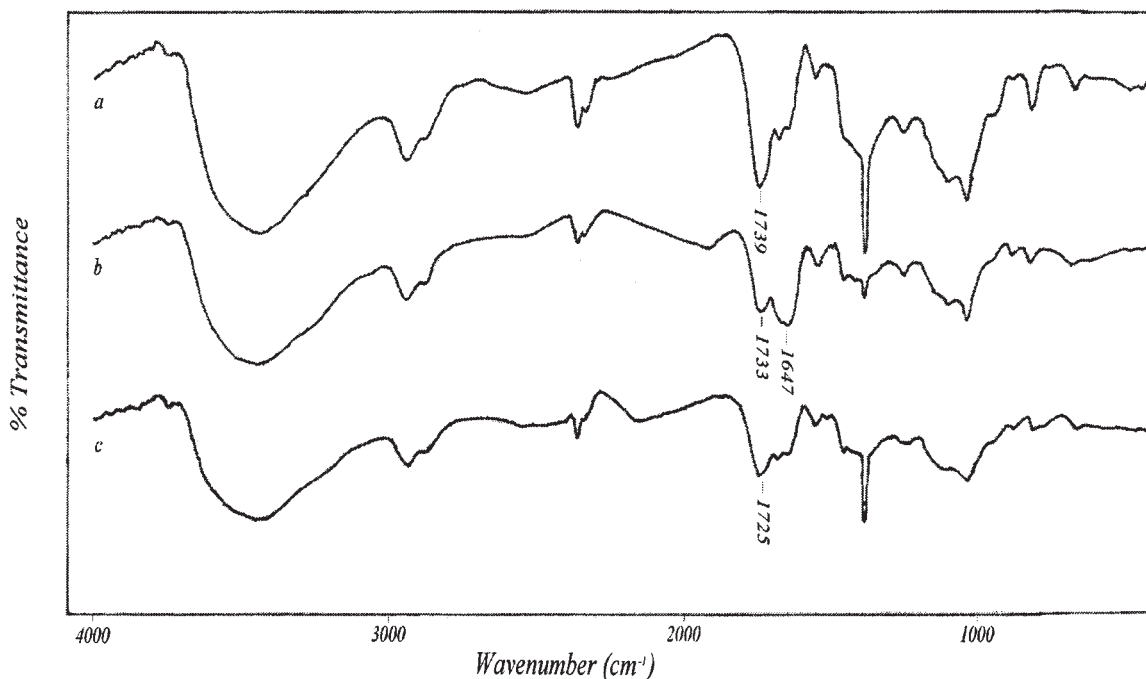


Figure 1 FTIR spectra of (a) NaAlg, (b) NaAlg/Gel, and (c) NaAlg/NaCMC (c) beads.

of entrapment efficiency was then calculated as follows:

Entrapment efficiency (%)

$$= \frac{\text{Practical carbaryl loading}}{\text{Theoretical carbaryl loading}} \times 100 \quad (2)$$

Fourier transform infrared measurements

Polymer samples or beads were crushed to make KBr pellets under a pressure of 600 kg/cm². Fourier transform infrared (FTIR) spectra were taken in the wavelength region between 400 and 4000 cm⁻¹ at ambient temperature, using Mattson 1000 FTIR spectrometer (with a resolution of 4 cm⁻¹).

Scanning electron microscope

Scanning electron microscope (SEM) photographs were taken with JSM 5600 SEM (Japan), to examine the morphology and surface structure of the beads at the required magnification at room temperature. The beads were deposited on brass hold and sputtered with a thin coat of gold under vacuum. Acceleration voltage used was 20 kV, with the secondary electron image as a detector.

Carbaryl release studies

Crosslinked beads (50 mg) were placed in a conical flask, containing 500 mL dissolution media (distilled

water), and incubated in a shaking water bath (Nüve ST 402, Turkey) at 25 or 35°C, with a speed of 50 rpm. At specific time intervals, 4 mL solution was withdrawn and carbaryl content was determined by UV-visible spectrometer at 280 nm. Analyzed solution was added back to the dissolution media to maintain a constant volume. From the absorbance values, the cumulative percent released was determined. All experiments were performed in triplicate to minimize the variational error. The average values were used for further data treatment and plotting.

RESULTS AND DISCUSSION

Properties of NaAlg based IPN beads

Carbaryl containing NaAlg, NaAlg/Gel, and NaAlg/NaCMC blend beads were successfully prepared using GA. In the present research, Gel and NaCMC were found to be compatible for forming blends with NaAlg.

The FTIR spectra of NaAlg, NaAlg/Gel, and NaAlg/NaCMC blend beads, with the exposure time to GA of 5 min, are shown in Figure 1. All the bead formulations showed a broad band between the 3100 and 3700 cm⁻¹, which was attributed to O—H stretching vibrations. Compared with the spectrum of NaAlg bead, the bond of NaAlg/Gel at 1647 cm⁻¹ was characteristic of the imine stretching vibrations, which is due to the reaction between —NH₂ groups of Gel and —CHO groups of GA.^{14,31}

The strong band of NaAlg beads at 1739 cm^{-1} was assigned to the carboxyl group. Interestingly, the carboxyl group band for NaAlg/Gel and NaAlg/NaCMC beads shifted from 1739 to 1733 cm^{-1} and 1725 cm^{-1} , respectively, indicating the specified intermolecular hydrogen bonds between the carboxyl group of NaAlg and the amine group of Gel or hydroxyl group of NaCMC forms. Similar results were found in literature.^{21,32}

SEM micrographs and typical surface morphology of dried NaAlg, NaAlg/Gel, and NaAlg/NaCMC beads, loaded in 1 : 2 Carb/NaAlg ratio, are shown in Figure 2. As it is reflected from the figure, all the beads almost maintain a spherical form at various conditions. Beads produced using Gel and NaCMC have more pore structure on the surface than does NaAlg bead [See in Fig. 2(b,d,f)]. It is also clearly seen that particle size of blend beads are greater than that of NaAlg bead.

The spherical shape of beads in the wet state was usually changed to collapse shape after drying, especially in blend beads and in low carbaryl content beads. Compared with NaAlg beads, the collapse shape of blend beads after drying was possibly attributed to their more heterogeneous structure. It was reported by Shu and Zhu²⁵ that chitosan coated calcium-alginate gel beads usually had a heterogeneous structure with dense surface layer and loose core, because of heterogeneous gelation mechanism, which resulted in the collapse of beads during the drying process.

The results of percentage entrapment efficiency and particle size are presented in Table I. As can be seen, the diameter of the beads depends on the preparation conditions of beads, such as Carb/NaAlg ratio, NaAlg/Gel, and NaAlg/NaCMC blend ratio. The bead diameter increased from $1.93 \pm 0.17\text{ mm}$ to $2.71 \pm 0.16\text{ mm}$ when Carb/NaAlg ratio was decreased from 1 : 1 to 1 : 8, respectively. As the Carb/NaAlg ratio decreases, the carbaryl content in the bead decreases. Hence, decrease in the carbaryl content causes the bead shape to change from spherical to collapse form. Therefore, the diameter of the beads increased with decreasing Carb/NaAlg ratio. Similar observation was found in literature.³³ Also, the diameters of the blend beads, with different blend ratio, are larger than that of NaAlg beads, which may be due to the heterogeneous structure of the beads. When NaAlg/Gel ratio of the beads increased from 1 : 1 to 4 : 1, the diameter of the beads decreases from $3.77 \pm 0.15\text{ mm}$ to $2.99 \pm 0.16\text{ mm}$, respectively. On the other hand, the diameter of NaAlg/NaCMC beads at the same blend ratio decreases from $4.68 \pm 0.15\text{ mm}$ to $3.16 \pm 0.16\text{ mm}$, respectively.

The percentage entrapment efficiency depends upon the type of matrix material, the extent of the crosslinking agent, and preparation conditions of the

beads. The results of entrapment efficiency (%) are also included in Table I. These data show an increase with decreasing carbaryl loading. In the NaAlg beads, Carb/NaAlg ratio decreases from 1 : 1 to 1 : 8, and the entrapment efficiency increases from 51.5 to 68.7%. This phenomenon is explained as follows: when the Carb/NaAlg ratio decreases, NaAlg is bound to trap more carbaryl, and thus, increase the entrapment efficiency. With increasing time of exposure to the crosslinking agent, the percentage entrapment efficiency decreased, and this might be attributed to the release of carbaryl to the external water. In the case of NaAlg beads, formed at 5 min of exposure to GA, the entrapment efficiency was 55.7%, whereas for the beads formed with a 15-min exposure time to GA it was 52.5%. Similar results were found in literature.^{27,34,35} On the other hand, it was observed that the entrapment efficiency of the blend beads are higher than that of NaAlg bead for the 1 : 2 Carb/NaAlg ratio. Increase in the amount of Gel or NaCMC in the bead causes increasing of the entrapment efficiency.

Effect of Carb/NaAlg ratio on the carbaryl release

The effect of Carb/NaAlg ratio on the release kinetics for the NaAlg beads exposed to the crosslinking agent for 5 min is presented in Figure 3. The release profiles indicate that the amount of carbaryl released increases with increasing Carb/NaAlg ratio of NaAlg beads. The cumulative release (%) of 1 : 1 Carb/NaAlg ratio beads have shown 67% release, whereas that of 1 : 8 Carb/NaAlg ratio beads have shown 35% at 25 days. The results are as expected because of larger initial load and faster movement of the water front penetrating the surface of the loaded bead. Larger loading of the bead may also facilitate the relaxation of polymer chains. Similar finding was reported for the liquid pesticide, neem seed oil, loaded formulations by Kulkarni et al.²⁷

Bajpai and Giri³⁶ studied swelling dynamics of a ternary interpenetrating polymer and CR of potassium nitrate, as a model agrochemical. They observed that the amount of the released KNO_3 increases with increasing percent loading of the IPN.

Carbaryl release data are also in agreement with the ESD values presented in Table II. As the Carb/NaAlg ratio increases from 1 : 8 to 1 : 1, ESD increases from 31 to 70%. A greater swelling with larger carbaryl loading may be attributable to the polar carbaryl molecules, thus producing a larger chain relaxation within the polymer bead.

Effect of exposure time to GA on carbaryl release

Carbaryl release from beads were subjected to a number of physical and chemical parameters, including those related directly to the release medium (water),

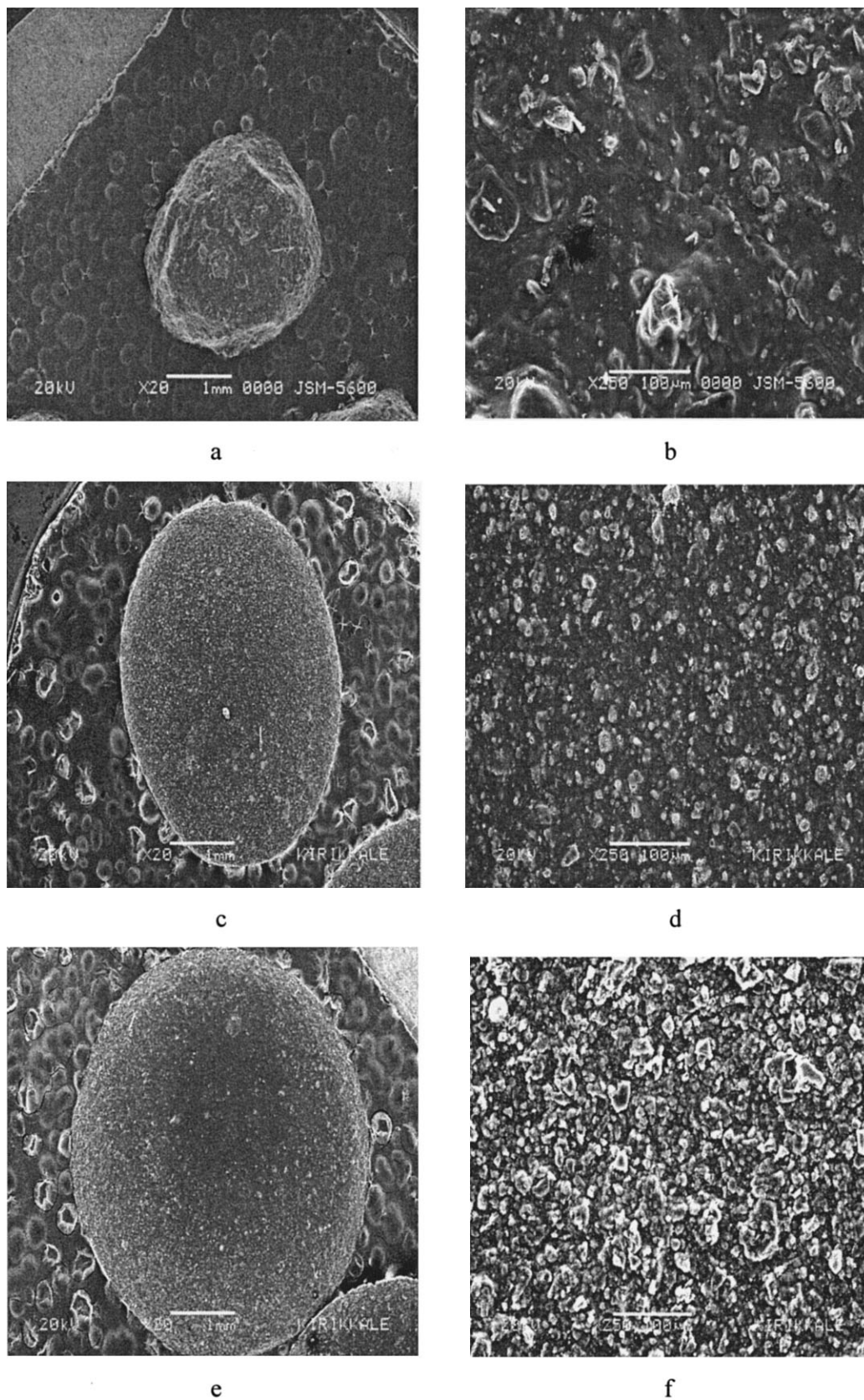


Figure 2 SEM photographs of NaAlg bead (a), magnification $\times 250$ (b), NaAlg/Gel bead (c), magnification $\times 250$ and (d), NaAlg/NaCMC bead (e), magnification $\times 250$ (f).

TABLE I
Results of Bead Diameter and Percentage of Entrapment Efficiency for Carbaryl Loaded Beads Prepared at Different Conditions

Formulation code	Polymer	Time of exposure to GA (min)	Carb/NaAlg ratio (w/w)	Bead diameter (mm)	Entrapment efficiency (%)
SA1	NaAlg	5	1 : 1	1.93 ± 0.17	51.5
SA2	NaAlg	5	1 : 2	2.04 ± 0.13	55.7
SA3	NaAlg	5	1 : 4	2.10 ± 0.12	61.5
SA4	NaAlg	5	1 : 8	2.71 ± 0.16	68.7
SA5	NaAlg	10	1 : 2	2.49 ± 0.14	53.7
SA6	NaAlg	15	1 : 2	2.46 ± 0.20	52.5
SG1	NaAlg/Gel (1 : 1)	5	1 : 2	3.77 ± 0.15	71.6
SG2	NaAlg/Gel (2 : 1)	5	1 : 2	3.63 ± 0.17	60.4
SG3	NaAlg/Gel (4 : 1)	5	1 : 2	2.99 ± 0.16	56.7
SC1	NaAlg/NaCMC (1 : 1)	5	1 : 2	4.68 ± 0.17	65.8
SC2	NaAlg/NaCMC (2 : 1)	5	1 : 2	4.31 ± 0.12	57.2
SC3	NaAlg/NaCMC (4 : 1)	5	1 : 2	3.16 ± 0.29	51.5

the release conditions (temperature, pH), preparation conditions, and those resulting from change in the characteristics of beads. One of the most effective ways to change the release rate of beads is to change the crosslink density of the matrix, by employing varying time of exposure to crosslinking agent or concentrations of the crosslinking agent. The effect of exposure time to GA on the release rate of carbaryl has been investigated by varying the time of exposure to GA at 5, 10, and 15 min, respectively. The results are shown in Figure 4, which clearly indicate that with increasing exposure time to GA (5–15 min), the release rate constantly decreases. The observed decrease in the cumulative release is because increasing exposure time to GA results in an increase in the crosslink density of the bead, which gives rise to a compact network of macromolecular chains. Consequently, the free volume reduces, and penetration of water molecules and the diffusion of the carbaryl molecules become difficult. Release results are also supported with swelling measurement results. As it is seen from the

Table II, as the exposure time to GA increases from 5 to 15 min, a significant decrease in ESD occurs from 59 to 47%, respectively, because of increase in crosslinking degree. SEM photographs also show a dense surface structure of the bead (at the exposure time to GA, 15 min) in Figure 5. Similar results were reported by many workers.^{5,13,20,27,34,37,38}

Kulkarni et al.²⁷ prepared GA-crosslinked sodium alginate beads, containing liquid pesticide in methanol medium, and studied the effects of extent of crosslinking and amount of loading on pesticide release. They reported that swelling of the polymeric beads and pesticide release decreases with increasing exposure time to the crosslinking agent.

Effect of NaAlg/Gel and NaAlg/NaCMC blend ratio on carbaryl release

The polymer blending technique can be considered a useful tool for the preparation of new alginate beads. Figures 6 and 7 display the cumulative percent release

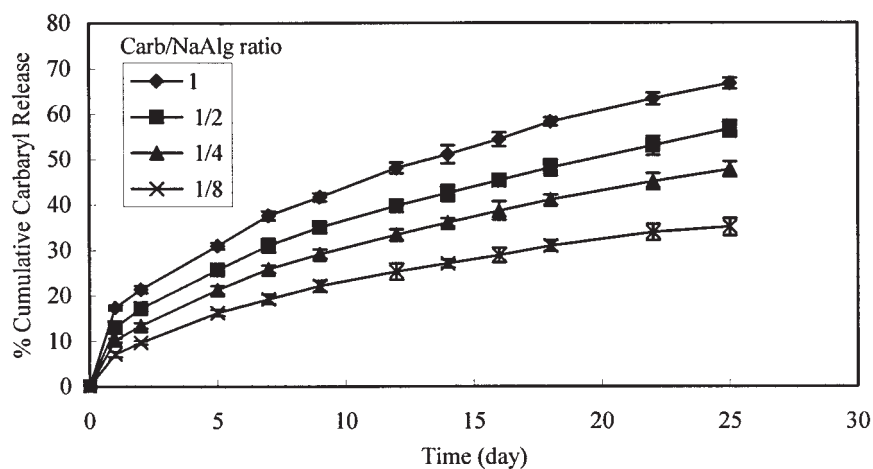


Figure 3 Effect of Carb/NaAlg ratio on carbaryl release from GA-crosslinked alginate beads. Exposure time to GA, 5 min.

TABLE II
Equilibrium Swelling Degrees for Beads at 25°C

Formulation code	Equilibrium swelling degree (%)
SA1	70
SA2	59
SA3	33
SA4	31
SA5	48
SA6	47
SG1	118
SG2	87
SG3	63
SC1	96
SC2	68
SC3	58

data of NaAlg beads, blended with different ratios of Gel or NaCMC in 1 : 2 Carb/NaAlg ratio and at 5 min of exposure time to GA. From the figures, it is observed that the release rate of carbaryl is much slower for the NaAlg beads than that of NaAlg/Gel and NaAlg/NaCMC blend beads. The maximum carbaryl release is obtained with 1 : 1 NaAlg/Gel bead as 100% in 16 days, whereas that of NaAlg/NaCMC bead is obtained as 82% in 25 days. Also, increase in blend ratio from 1 : 1 to 4 : 1 decreases the carbaryl release in both the blend beads. These results are attributed to the hydrophilic nature of Gel or NaCMC polymers. With increasing amounts of Gel and NaCMC, cumulative release from the blend beads increases. The results are quite expected, and as these polymers are hydrophilic in nature their increasing amounts will result in a greater swelling (see in Table II) and a faster carbaryl release. Similar observations were found in literature.^{35,36,38,39} The results also indicate that the NaAlg/Gel beads exhibit a greater swelling and drug release than that of NaAlg/NaCMC beads.

Kurkuri and Aminabhavi³⁵ prepared poly(vinyl alcohol) and poly(acrylic acid) interpenetrating network

microspheres for the delivery of diclofenac sodium, and they observed that equilibrium swelling and cumulative release increase with increase in the content of poly(acrylic acid).

Parasad and Kalyanasundaram³⁹ studied swelling behavior, ionotropically crosslinked carboxymethyl cellulose, and carboxymethyl cellulose–Gel matrices. Matrices were crosslinked with cupric or ferric ions, and they reported that swelling ratio of matrices increases with increasing hydrophilic Gel content.

Effect of release medium temperature

The effect of temperature of the release medium on carbaryl release for the various bead formulations was investigated at two different temperatures (25 and 35°C), and the obtained results were given in Figure 8. As can be seen from the figure, the carbaryl release from the beads increases with increase in the temperature. In Figure 8, the highest carbaryl release was observed to be 100%, at 35°C in 18 days, for the beads prepared with the exposure time of 5 min to GA, while the lowest carbaryl release was observed to be 50%, at 25°C in 25 days, for the beads prepared with an exposure time of 10 min to GA.

According to the free volume theory,⁴⁰ thermal motion of polymer chains in the amorphous regions randomly produces free volume. As the temperature increases, the frequency and amplitude of the chain jumping increase and the resulting free volumes become larger. Penetration of water molecules through these free volume and diffusion of carbaryl molecules become easier at higher temperatures. Hence, release rate of carbaryl from NaAlg beads are high when the temperature is high. Similar results concerning the effect of temperature on release were reported in literature.^{5,36,38}

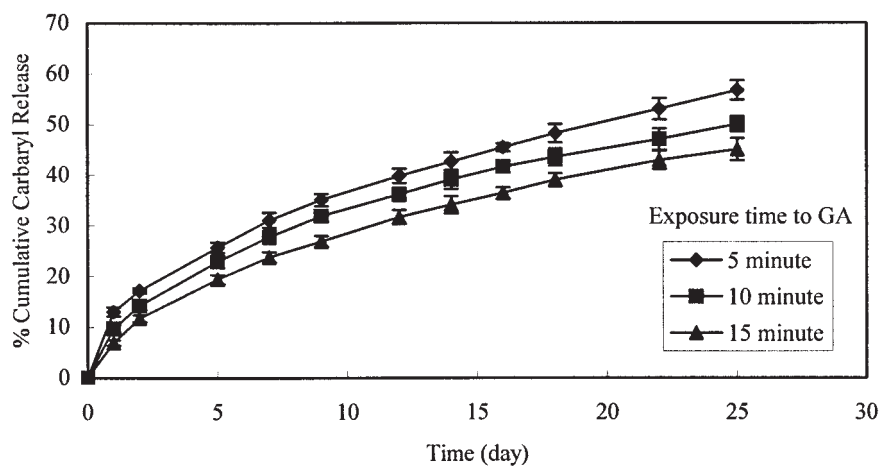


Figure 4 Effect of exposure time on carbaryl release. Carb/NaAlg ratio, 1 : 2.

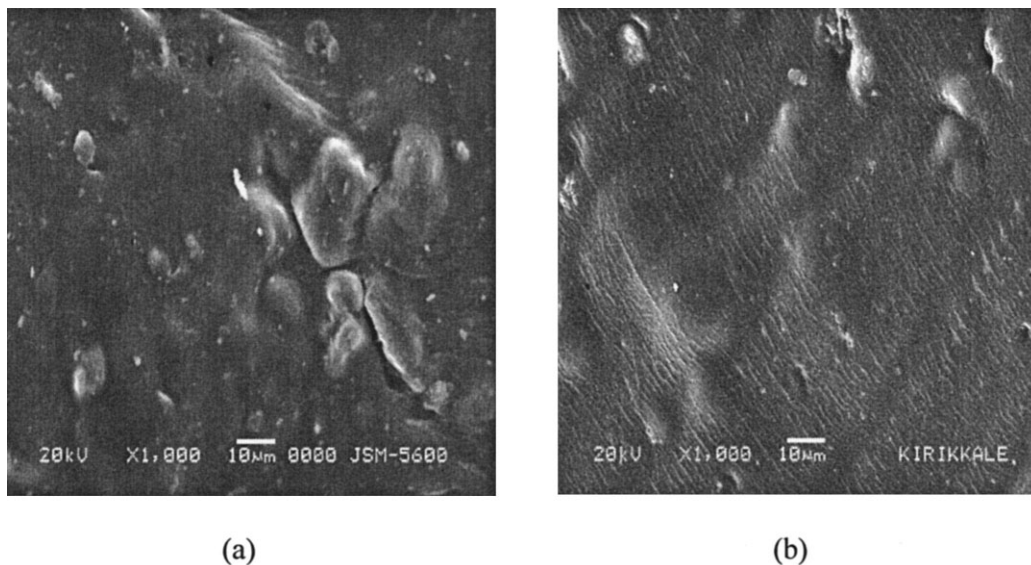


Figure 5 SEM photographs of NaAlg bead with (a) exposure time to GA, 5 min and (b) exposure time to GA, 15 min (magnification $\times 1000$).

Analysis of kinetic results

The phenomenon of solvent sorption by a polymeric bead depends mechanistically on the diffusion of water molecules into the gel matrix and subsequent relaxation of macromolecular chains of the bead.⁵ The release data of all the systems have been further substantiated by fitting the fraction release data M_t/M_∞ to an empirical equation proposed by Peppas:⁴¹

$$\frac{M_t}{M_\infty} = kt^n \tag{3}$$

where M_t is the amount of carbaryl released at time t ; M_∞ , the drug released at equilibrium time; k , a constant characteristic of the pesticide-polymer system;

and n is the diffusional exponent, which suggests the nature of the release mechanism. A value of $n = 0.5$ indicates the Fickian transport (mechanism), while $n = 1$ is of Case II transport. The intermediary values, ranging between 0.5 and 1.0, are indicative of the anomalous transport.^{13,14,20} The least-squares estimations of the fractional release data, along with the estimated correlation coefficient values, r , are presented in Table III. From these data, the n value ranged between 0.35 and 0.57, with correlation coefficient values of 0.99, indicating that the carbaryl release from most of beads have Fickian transport, but some of them deviate slightly from the Fickian transport.

The k values increase with increase in percentage loading of carbaryl, and in amount of Gel or NaCMC,

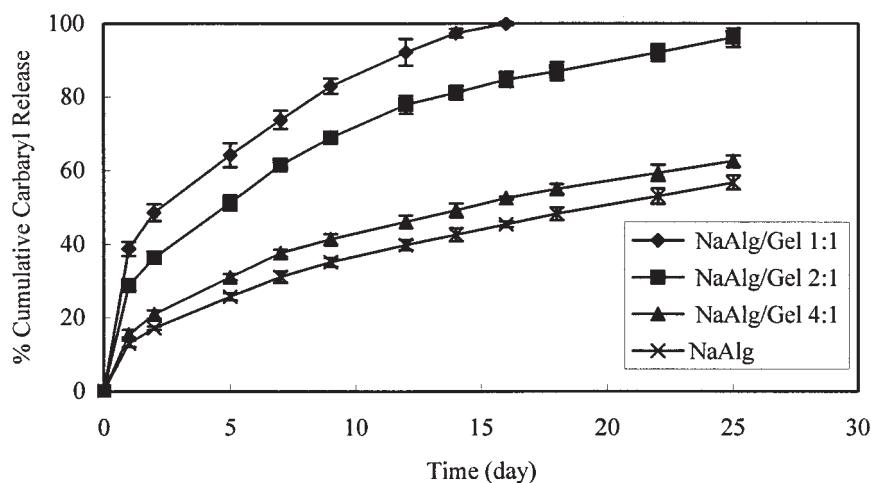


Figure 6 Effect of NaAlg/Gel ratio on carbaryl release from the blend beads. Exposure time to GA, 5 min; Carb/NaAlg ratio, 1 : 2.

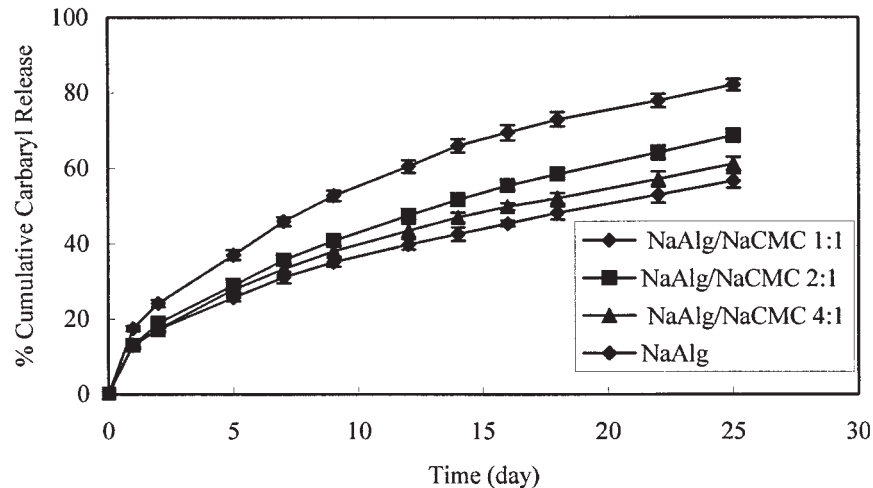


Figure 7 Effect of NaAlg/NaCMC ratio on carbaryl release from the blend beads. Exposure time to GA, 5 min; Carb/NaAlg ratio, 1:2.

but decrease with increase in crosslinking exposure time to GA. Similar observation was found in the literature.²⁷ Kulkarni et al.²⁷ found the same trend analysis of kinetic results. Also, in previous study,²⁹ the same observation was found.

To calculate the values of the apparent diffusion coefficients, the D of carbaryl from the beads, the initial portions of the release profiles (i.e.) $0 < M_t/M_\infty < 0.4$ as shown in Figures 3, 4, 6, and 7, were analyzed by the Fickian theory.⁴² This equation, given in the most simplified form, calculates the diffusion coefficients from the initial time approximation as follows⁴³:

$$\frac{M_t}{M_\infty} = \left(\frac{36Dt}{\pi r^2} \right)^{1/2} - \left(\frac{3Dt}{r^2} \right) \quad (4)$$

where r is the average radius of the beads. The data reported in Table III show a relationship involving the exposure time of GA, Carb/NaAlg ratio and NaAlg/Gel or NaAlg/NaCMC ratio. The D value decreases from $0.66 \times 10^{-7} \text{ cm}^2/\text{s}$ to $0.27 \times 10^{-7} \text{ cm}^2/\text{s}$, with decrease in Carb/NaAlg ratio from 1 : 1 to 1 : 8, respectively. As the Gel or NaCMC content in the blend beads diffusion coefficient increases a good agreement with release results. The highest diffusion constant was determined to be $4.11 \times 10^{-7} \text{ cm}^2/\text{s}$ for the 1 : 1 NaAlg/Gel beads.

CONCLUSIONS

NaAlg, NaAlg/Gel, and NaAlg/NaCMC blend beads were prepared by crosslinking with GA and used for

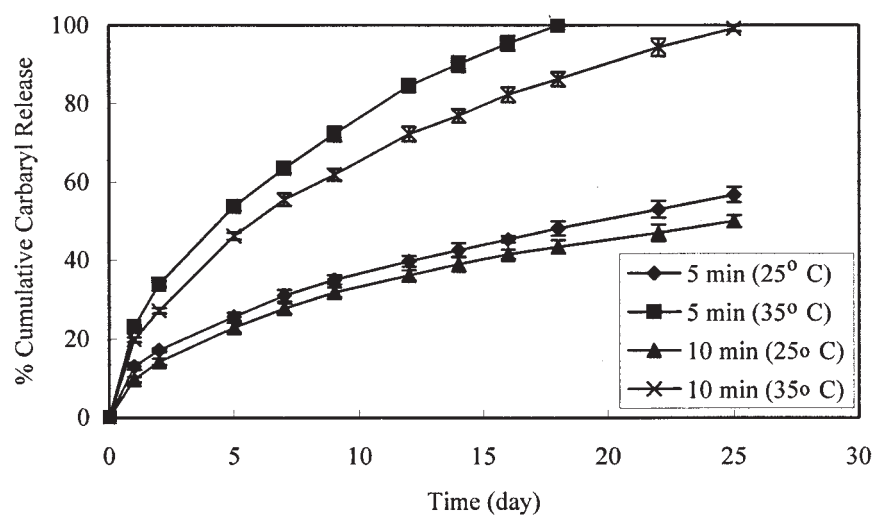


Figure 8 Effect of release medium temperature on carbaryl release. Carb/NaAlg ratio, 1 : 2.

TABLE III
Analysis of Release Kinetics from Eqs. (3)
and (4) of the Carbaryl Loaded Beads

Formulation code	D (10^{-7} cm ² /s)	k (10^{-1} day ⁻ⁿ)	n	r
SA1	0.66	1.64	0.43	0.998
SA2	0.47	1.27	0.46	0.999
SA3	0.40	0.99	0.49	0.998
SA4	0.27	0.71	0.51	0.999
SA5	0.63	1.00	0.51	0.999
SA6	0.51	0.75	0.57	0.998
SG1	4.11	3.81	0.35	0.998
SG2	3.01	2.85	0.39	0.998
SG3	1.51	1.56	0.44	0.999
SC1	4.03	1.74	0.49	0.999
SC2	2.84	1.33	0.51	0.999
SC3	1.29	1.29	0.49	0.999

the delivery of carbaryl. Formed beads were characterized with SEM and FTIR. SEM results indicate that the occurred beads have almost spherical shape, with rough surface. Also, it is observed from FTIR analysis that hydrogen bonding interaction were found between the NaAlg and Gel or NaCMC. Bead particle size, entrapment efficiency, and ESD of the beads were determined, and it is observed that these parameters effected beads preparation conditions, such as exposure time to GA, Carb/NaAlg ratio, and blend ratio with Gel or NaCMC. It is found that addition of Gel or NaCMC to NaAlg polymer increases the entrapment efficiency of beads. Preparation conditions also affect the results of carbaryl release. Carbaryl release studies indicate that carbaryl release from the beads increases with the increase in Carb/NaAlg ratio, temperature, and increase in content of Gel or NaCMC, whereas decreases with the increase of exposure time to GA. ESD of all the formulations are consistent with the release results. From the release data, bead formulations almost display transport for Fickian mechanism, but some of them deviate slightly from Fickian to anomalous mechanism. It is also observed that the diffusion coefficient decreases with increasing exposure time to GA and with decreasing carbaryl amount of the beads, whereas it increases with increasing Gel or NaCMC content. Finally, carbaryl release from the beads is changed to depend on the polymer and crosslinking agent used and preparation conditions. The effective CR formulations can be obtained by varying them. From these results, crosslinked alginate and blend beads appear to be very interesting as a CR system for agrochemical applications.

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