Dynamics of Controlled Release of Potassium Nitrate from a Highly Swelling Binary Polymeric Blend of Alginate and Carboxymethyl Cellulose

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ABSTRACT: Highly water absorbing and homogeneous binary biopolymeric blends in bead form were prepared of calcium alginate and carboxymethyl cellulose by solution cast method. The prepared blends were evaluated for controlled delivery of KNO_3 taking it as a model agrochemical. The beads characterized by Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) were used to investigate the molecular structure and morphology of beads. The swelling experiments were performed for different compositions of beads and at varying pH and temperature of the aqueous media. The release experiments were performed under static and varying experimental conditions and the release data obtained were conductometrically fitted to Ficks equation to evaluate diffusion coefficients of released KNO_3. The release results were further analyzed by Ficks power law equation, and the possible mechanisms of KNO_3 release were explored at different experimental conditions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 961–972, 2007

Key words: calcium alginate; CMC; swelling; potassium nitrate; release

INTRODUCTION

Macromolecular formulations like the graft, random and blocks copolymers,[1] interpenetrating polymeric networks,[2] and hydrogels[3] are currently the focus of considerable scientific research due to their potential for application in a large variety of areas such as biomedicine,[4] food industry,[5] pharmaceuticals,[6–8] bioengineering,[9] and agriculture.[10] The reason for this vast potential is not only because of their ability to respond reversibly to external stimuli such as pH,[11,12] temperature,[13] ionic strength,[14] electric fields,[15,16] etc, but also to their capacity to act as a carrier of a variety of bioactive compounds like proteins,[17,18] vitamins,[19] drugs,[20] etc. Such loaded polymeric carriers swell and subsequently deliver the entrapped compound into the aqueous reservoir when allowed to contact a still release medium. Such controlled release polymer matrix systems offer a number of potential advantages over the conventional means of applications.[21]

Although various polymeric carriers have been used for controlled release of pesticides,[22] agrochemicals,[23] and pharmaceuticals,[24] however, biodegradable matrices are especially preferred as carriers to prevent different kind of pollution created by residues of depleted, non-degradable carriers.

Agriculture represents one of the important areas of international requirement for health, nutrition, and economic development. Agrochemicals are bioactive agents concerned with the utilization of chemicals to control either plant or animal life that is disadvantageous to humans and animals, and to improve production of crops both in quality and quantity. Hence, a great increase in the quantities of these chemicals are necessary for enhancing any substantial increase in farm production of food-stuff.[25] Depending on the method of application and climatic conditions, as much as 90% of applied agrochemicals never reach their target, to produce the desirable biological response.

A very serious problem that the three-fourth of the world is facing is nitrate leaching and subsequent pollution of ground water. The seriousness of the problem can be assessed by the fact that nitrates and nitrites are implicated in many fatal physiological disorder such as methmoglobinemia in babies,[26] oral cancer, cancer of colon, rectum or other gastrointestinal cancers,[27] etc. Thus, the application of nitrate loaded carriers with a technology based on the controlled release of nitrates by the swelling of polymeric carriers could prove to be a suitable means against pollution of ground water. These systems are currently the focus of considerable scientific research due to their potential technological applica-

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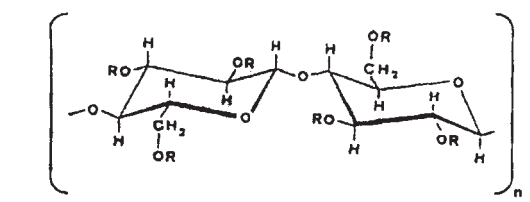
tion in large number of areas such as medicine, agriculture, biology, and environmental remediation. Craig et al.[28] have shown that nitrate consumption leads to a decrease in the ascorbate/nitrate ratio in gastric juice, which regulates the synthesis of potentially carcinogenic *N*-nitroso compound and decrease in the ratio leads to increased risk of gastric cancer.

Recently various polymer-supported or microencapsulated biocides have been introduced in agriculture to limit the undesirable side effects associated with conventional formulation of agrochemicals and related biocides.[29] The present study aims at developing a hydrophilic matrix of binary polymeric blend of calcium alginate and carboxymethyl cellulose (CMC) and evaluating their potential as controlled release device using KNO_3 as a model agrochemical.

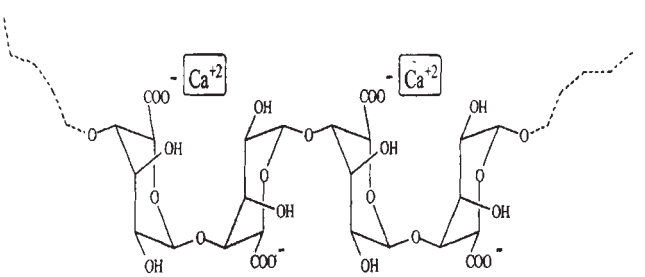
CMC, a major commercial derivatives of cellulose[30] is a highly water soluble anionic polysaccharides [Fig. 1(a)] which is widely used in pharmaceutical,[31] cosmetic, and food[32] applications. In biomedical field, it is used to prevent the postoperative adherences[33] and epidural scarring.[34] It also possesses the advantages of being biodegradable and economic.

Alginate is an unbranched binary copolymer constituted of (1,4) linked α-L-guluronic acid and β-D-mannuronic acid. It is a high-molecular mass polysaccharide and very useful for application in pharmaceuticals,[35,36] biomedicals,[37] and bioengineering.[38] Several properties of alginate, like its biodegradability, nontoxicity, biocompatibility,[39] immunogenicity,[40] 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.



Structure of carboxymethyl cellulose (CMC).

(a)



Structure of Calcium Alginate

(b)

Figure 1 Structures of (a) CMC, and (b) calcium alginate.

EXPERIMENTAL

Materials

Water soluble carboxymethyl cellulose (CMC-Mol. Wt-90,000) and sodium alginate (SA Mol. Wt-45,000) were obtained from Loba Chemie, Mumbai, India and Research Lab, Pune, India, respectively, and used without any pretreatment. Calcium chloride (dihydrates) (Loba Chemie, Mumbai, India) was used as a crosslinker for both carboxymethyl cellulose (CMC) and sodium alginate. All other chemicals used in the study were of analytical quality and triple distilled water was used throughout experiments.

Preparation of beads

To prepare polymeric beads of CMC and SA, a viscous solution was prepared by dissolving precalculated amounts of CMC and SA into a definite volume of distilled water with constant stirring. The viscous solution so prepared was added dropwise into 0.1*M* $CaCl_2$ solutions with gentle stirring with the help of a syringe, and the beads so prepared were cured in the same solution for 48 h. The hard beads of nearly identical spherical shapes and sizes were purified by equilibrating them in distilled water for a week. The beads so prepared were further dried at 30°C for 1 week and stored in air tight polyethylene bags.

Characterization of beads

IR spectral analysis

The beads prepared as described above were characterized by recording infrared spectra of unloaded and KNO_3-loaded beads on a FTIR spectrophotometer (Perkin–Elmer, 1000 Paragon, Ontario, Canada).

SEM analysis

Scanning electron micrographs analyses of unloaded and KNO_3-loaded beads were performed for morphological characterization of their surfaces on a SEM apparatus (STEREO SCAN, 430, Leica SEM Zeis-Leica, Heidelberg GmbH, Germany).

Swelling kinetics

Conventional gravimetric procedure[41] was adopted for monitoring the progress of water sorption process. In a typical experiment, 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 swollen beads so taken out were gently pressed in between the 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.

$$\text{Swelling Ratio} = \frac{\text{Weight of Swollen beads } (W_s)}{\text{Weight of the dry beads } (W_d)} \quad (1)$$

Loading of potassium nitrate

In the present work, the loading was performed by equilibrating preweighed dry beads in the aqueous solution of KNO_3 of known concentration (1% w/v) and thereafter drying and weighing again. The percent loading was calculated by the following formula.

$$\%\text{Loading} = \frac{m_1 - m_0}{m_0} \times 100 \quad (2)$$

where m_1 and m_0 are the weights of KNO_3 loaded and unloaded dry beads, respectively.

Release of potassium nitrate

To study the release of KNO_3, the loaded beads of known weights were placed in a measured volume (25 mL) of distilled water (release medium) under unstirred condition. The released amount of KNO_3 at different time intervals (M_t) was determined by measuring the conductivity of the release medium using a conductivity meter (Model No. 303, Systronics, Ahamdabad, India). This was related to the amount of KNO_3 using a calibration plot. Similarly, the equilibrium release (M_∞) of KNO_3 was determined by measuring the conductivity of the release medium after 5 days. To gain insights into the operative release mechanisms, the following equations based on Ficks law but applicable to a spherical device may to applied[42,43]

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

and,

$$\frac{M_t}{M_\infty} = 6\left(\frac{Dt}{\pi r^2}\right)^{0.5} \quad (4)$$

where M_t and M_∞ represent the amounts of KNO_3 released at time t, and equilibrium time, respectively, D is diffusion coefficient, k is the swelling front factor, n is release exponent and r being the radius of the dry spherical bead. The value of n determines the nature of release mechanism, i.e., when $n = 0.5$, release is Fickian; when n lies between 0.5 and 1.0, the release is said to be anomalous and when $n = 1$, the release mechanism is said to be (Case II).

RESULTS AND DISCUSSION

Characterization of beads

FTIR spectra

The FTIR spectra of unloaded binary polymeric beads are shown in Figure 2, which clearly confirms the presence of CMC, alginate beads as discussed below:

The IR spectra clearly marks the presence of CMC unit bearing carboxylate ion at 1632 cm^{-1} (strong asymmetrical stretching band), 1387 cm^{-1} (OH bending of carboxylate ion) and 2933 cm^{-1} due to C—H stretching. The presence of alginate is confirmed by O—H stretching of hydroxyls at 3424 cm^{-1} and C=O stretching of carboxylate ion.

SEM analysis

The morphological features of the unloaded and KNO_3 loaded blends have been investigated by recording their SEM images as shown in Figure 3(a) and (b), respectively. A close examination of the photograph of unloaded beads clearly reveal that the blends surface is quite heterogeneous and possesses a multilayer morphology containing agglomerated clusters of CMC and SA of varying sizes in the range of 25–150 μm. The surface of the blend also shows significant fractures having width in the range of 25–50 μm.

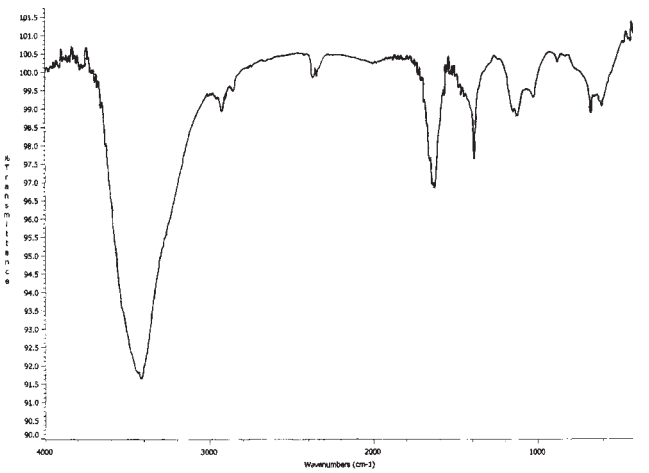


Figure 2 FTIR spectra of unloaded binary polymeric beads.

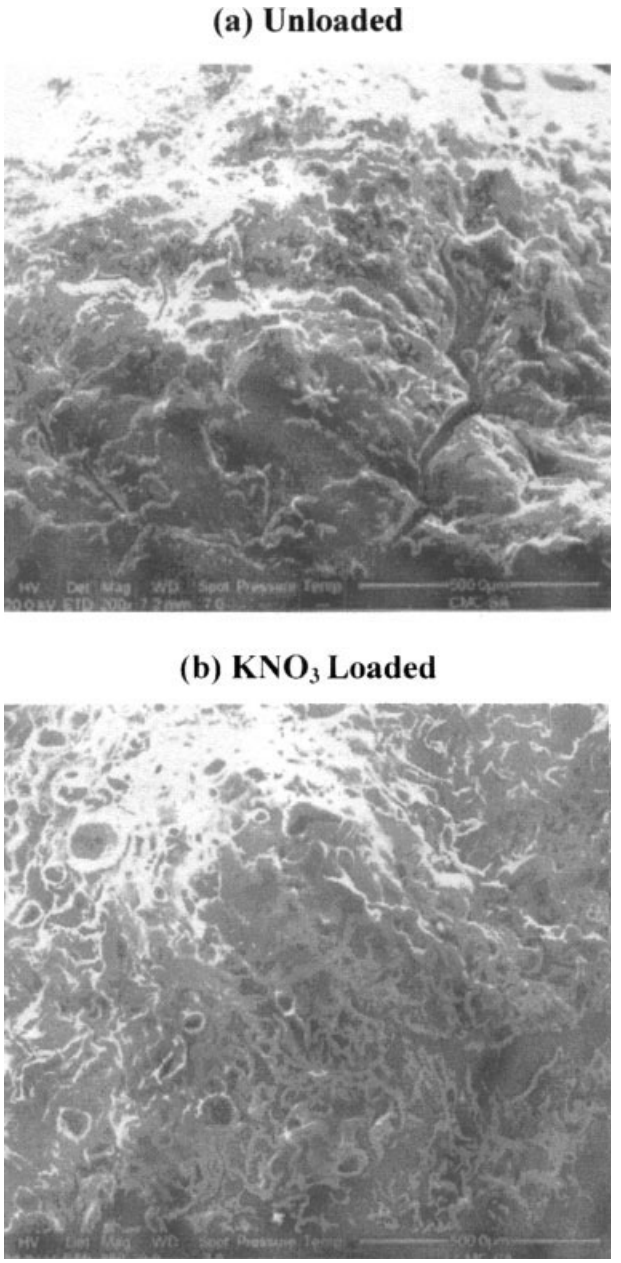


Figure 3 Scanning electron micrographs (SEMs) of (a) unloaded, and (b) KNO_3-loaded beads.

On the other hand, the loaded beads depict a distinct morphology with shell type structures having pore sizes in the range 15–80 μm. This entirely different morphology of KNO_3 loaded beads may be attributed to the fact that during the loading of KNO_3 onto the beads the diffusion of water and KNO_3 molecules into the polymer blend generates pores on the surface, which become more prominent upon drying the loaded beads during the device preparation.

Modeling of release mechanism

In the present study, the KNO_3 loaded beads of polymeric blend of crosslinked CMC and calcium alginate (CA) could be visualized as a network of macromolecular chains of CMC and CA bonded to one another via physical forces and forming pockets of molecular dimension in between them. These pockets (or voids) of varying mesh sizes are further occupied by the active ingredient like KNO_3. When the loaded beads come in contact with a still aqueous release medium, the penetrated water molecules invade the bead surface and a moving solvent front is observed that clearly separates the unsolvated glassy polymer region ahead of the front from the swollen and rubbery gel phase behind it[44] (Fig. 4). Just ahead of the front, the presence of solvent plasticizes the polymer and causes it to undergo a glass to rubber transition.[45] Now, the following possibilities arise:

i. If the glass transition temperature (T_g) of the polymer is well below the experimental temperature, the polymer will be in the rubbery state and polymer chains will have a higher mobility that allows an easier penetration of water molecules into the bead and as a consequence expulsion of KNO_3 into the outer release medium. Now, if the rate of diffusion of KNO_3 into the outer medium ($R_{\text{diff}([KNO_3])}$) is slower then that of chain relaxation (R_{relax}) then the release mechanism is said to be diffusion controlled or Fickian and the release exponent n becomes equal to 0.5.
ii. However, if the experimental temperature is below T_g, the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent into the polymer core (or release of KNO_3 into the outer medium). Thus, $R_{\text{diff}([KNO_3])}$ may be greater than R_{relax} and this gives rise to a relaxation controlled (or non-Fickian) release mechanism which is quantified by a unity value of n. This is also known as Case II transport.
iii. In an intermediate situation, the two rates, i.e., $R_{\text{diff}([KNO_3])}$ and R_{relax} may be nearly equal and

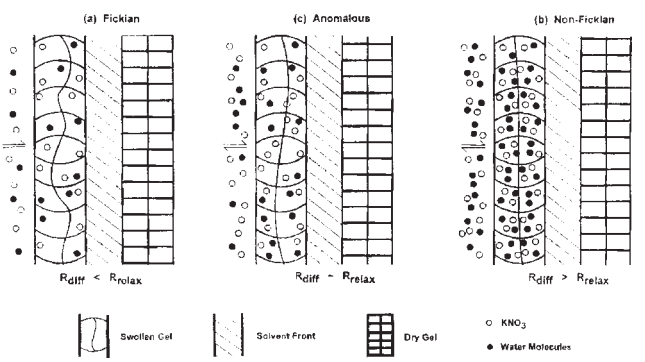


Figure 4 A hypothetical model depicting (a) Fickian, (b) anomalous, and (c) non-Fickian release of KNO_3.

this is called an ''anomalous diffusion'' or simply non-Fickian diffusion.

The above three situations are modeled in Figure 4(a–c), respectively.

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 also regulated by the physical forces and subsequent elastic responses of the constituent macromolecular chains of the matrix. According to Flory's swelling theory,[46] the following equation can be given for the swelling ratio (Q),

$$Q^{5/3} = \left[\frac{\{(i/2V_N.S^{1/2}) + (1/2 - X_1)/V_i\}}{V_e/V_o}\right] \quad (5)$$

where i/V_N is the concentration of the fixed charges referred to unswollen network, S is the ionic concentration in the external solution, $(1/2-X_i)/V_i$ 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 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 controlled by varying its chemical composition.

Effect of CMC

The observed large swelling ratio can be explained by the fact that increased CMC content in the hydrogel renders the network more hydrophilic such that when the polymer matrix contacts the dissolution medium, the molecules of water penetrate the gel and swells the macromolecular chains. Influence of CMC on the swelling ratio of the beads has been investigated by varying its concentration in the feed mixture in the range of 66.6–77.7%. The results shown in Table I that clearly indicate that the swelling ratio constantly increases up to 75.0% of carboxy methyl cellulose concentration in the feed mixture of the bead while beyond 75.0% a fall in degree of water sorption is noticed. The initial increase observed in the swelling ratio may be explained on the basis of the fact that CMC is a linear hydrophilic polymer and its increasing amount in the bead results in an enhanced hydrophilicity of the network that obviously results in a larger swelling. However, the decrease observed beyond 75.0% g of CMC may be attributed to the fact that much higher CMC content in the matrix gives rise to a compact network of biopolymeric chains, which became of greater interaction between the CMC molecules results in a restrained mobility of the network chains. Moreover, a compact structure results in small pore sizes of the network that also slows down diffusion of water molecules into the bead which also brings about a fall in the swelling ratio.

TABLE I
Data Showing the Effect of Composition of the Blend on its Equilibrium Swelling Ratio

CMC (%)	Sodium alginate (%)	$CaCl_2$ (M)	Equilibrium swelling ratio
66.67	33.33	0.1	22.0
71.42	28.58	0.1	25.0
75.00	25.00	0.1	34.0
77.78	22.22	0.1	28.0
75.00	25.00	0.1	34.0
66.67	30.33	0.1	18.0
60.00	40.00	0.1	13.0
54.54	45.46	0.1	11.0
75.00	25.00	0.05	11.0
75.00	25.00	0.08	10.0
75.00	25.00	0.10	34.0
75.00	25.00	0.15	9.5

Effect of sodium alginate

The effect of sodium alginate, an anionic biopolymer, on the swelling ratio of the beads has been studied by varying the concentration of sodium alginate in the range 25.0–45.4%. The results are presented in Table I that clearly indicate that whereas the swelling ratio initially increases up to 45.4% of sodium alginate while it decreases with further increase in concentration. The observed finding may be attributed to the fact that alginate is an anionic polymer and its increasing concentration in the bead produce greater number of carboxylate ions along its molecules which because of enhanced repulsion between $-COO^-$ ion cause the network chains to undergo a larger relaxation. This obviously allows greater number of water molecules to enter the bead and results in an increased swelling. However, beyond 45.4% of sodium alginate, when the concentration of alginate becomes high, the increased number of alginate chains produces a dense network that permits less number of water molecules into the beads and thus results in a decreased swelling.

Effect of $CaCl_2$

Calcium chloride, a known crosslinking agent of alginate, is assumed to act by complexing carboxylate anions of alginate by its bivalent calcium ion,

thus forming a type of network. In the present work, the effect of crosslinkers on water sorption capacity of blend has been studied by varying the concentration of $CaCl_2$ in the range 0.05–0.15*M*. The results are summarized in Table I that clearly indicate that the degree of water sorption constantly increases up to 0.1*M*, while beyond this concentration a fall in the swelling ratio is noticed.

The observed initial rise in the swelling ratio may be attributed to the fact that with increasing number of calcium ions in the crosslinking bath, the alginate beads containing larger cavity are produced which could accommodate greater amount of water. This obviously results in a greater swelling of the polymeric beads. It is also observed that beyond 0.1*M* of $CaCl_2$ solution the swelling ratio decreases which is because of the reason that if number of calcium ions becomes much greater, they screen the electrostatic repulsion operative between the carboxylate ions inside the cavity, thus causing shrinking of the bead. This clearly results in a decrease in the swelling ratio.

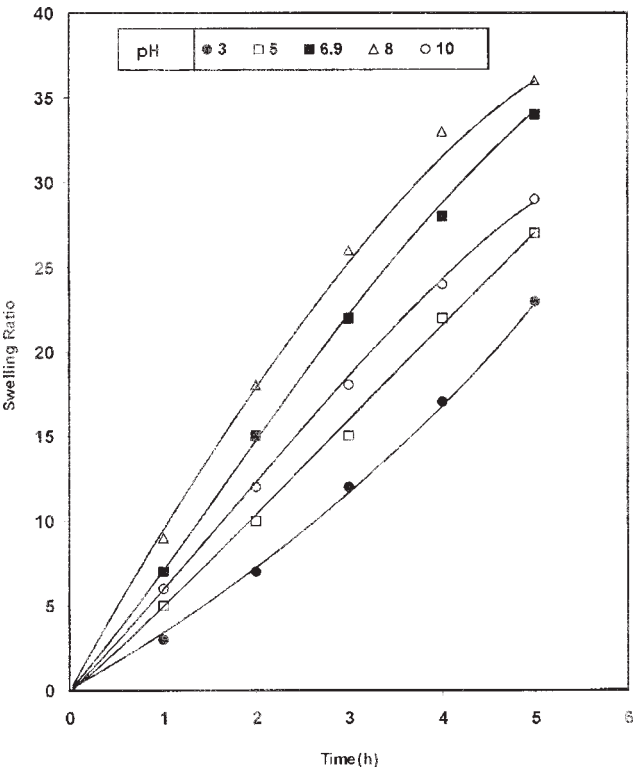


Figure 5 Effect of pH of the swelling medium on the swelling ratio of the beads of fixed composition, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, Temp. = (30 ± 0.2)°C.

Effect of pH

Macromolecules matrices containing either carboxyl groups or carboxylate ions as pendent functional of network chains have been found to respond greatly to the external stimuli such as pH of the swelling medium. In the present study, since the polymer used was the sodium salt of CMC, the network contained both $—COO^-$ and COOH groups along the CMC chains. In the present study, where sodium alginate is of anionic nature, the effect of pH has been investigated on the swelling ratio of the beads in the pH range 3.0–10.0. The results are indicate an increase in the swelling ratio that can be explained by the fact that with rising pH of the swelling medium, the ratio COO^-/COOH on CMC also increases because of increasing ionization of carboxylic groups and this results in a greater repulsion among the $—COO^-$ bearing CMC chains. In Figure 5, which indicate that the swelling ratio increases up to 8.0 while beyond it a decrease is observed, the results may also be explained by the fact that with increasing pH of the swelling medium the extent of ionization of carboxylic groups of alginate also increases which produce greater number of carboxylate ions along the alginate molecule. These anionic charged centers repel each other and produce a rapid relaxation in the network. This clearly results in a rise in the degree of water uptake.

However, beyond pH 8.0, a fall in the swelling ratio is noticed that may be attributed to the fact that at higher alkaline range (pH > 8.0) the network chains acquire greater charge density which restricts the entrance of polar penetrant water molecules into the bead and thus the swelling ratio decreases.

Effect of salt

The presence of an electrolyte in a swelling medium is of importance in agriculture and biomedical fields, viz., water reservoirs in agriculture and hydrogels as implants for drug release applications.[47] The effect of electrolytes on the extent of swelling is normally determined by the balance between the osmotic pressure and elastic response of the network chains. The osmotic pressure (π_{ion}) is given by the following equation,[48]

$$\pi_{ion} = RT \, \Sigma_i \, (C_i^g - C_i^s) \tag{6}$$

where C_i is the mobile ion concentration of species i and superscripts g and s represent gel and solution phases, respectively. The above equation clearly implies that greater the difference between the concentration of mobile ions inside and outside the gel, larger would be the osmotic pressure and, therefore, the swelling of the gel.

In the present investigation, the influence of salts on the swelling of the beads has been studied by adding various salts of sodium (0.1*M*) and chlorides of cations

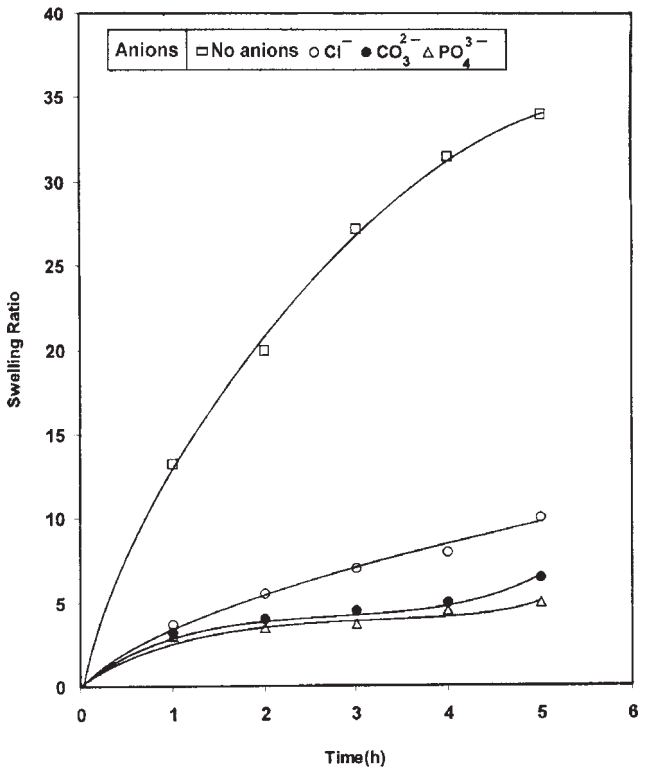


Figure 6 Effect of addition of anions to the swelling medium on the swelling ratio of the beads of fixed composition, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.9, Temp. = (30 ± 0.2)°C.

(0.1*M*) to the swelling bath respectively. The results are shown in Figures 6 and 7 which indicates that in both the cases the swelling ratio constantly decreases. It is also revealed by the Figure 6 that whereas various anions exert almost identical impact on the swelling ratio, the effectiveness of cations increases in the following sequence

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

The observed results may be explained as below:

The addition of salts into the swelling medium increases the term C_i^s in Eq. (6) which in turn decreases the osmotic pressure (π_{ion}) and thus cause a fall in the swelling ratio. In case of anion addition, the added anions because of their negative charges may not diffuse into the bead network as the network chains also have the same charge. Thus, the added ions, viz. Cl^-, CO_3^{2-}, and PO_4^{3-} produce a nearly similar degree of fall in the swelling.

On the other hand, the added cations may diffuse into the bead and their concentrations inside the bead may determine their relative effectiveness. Since Na^+ ion is the larger and Al^{3+} is the smaller ion, a greater diffusivity is expected with Al^{3+} ions which inside the bead network deshield the coulombic repulsive forces and cause shrinking of the gel. Thus, the Al^{+3} ion obviously produce a largest shrinking of the gel. The larger Na^+ ions may diffuse into the bead in less number and cause lower degree of shrinking effect.

Effect of temperature

The effect of temperature on the swelling ratio of the blends has been investigated by varying temperature of the swelling medium in the range 15–40°C. The results are shown in Figure 8 which clearly indicates that the swelling ratio increases with increasing temperature of the swelling bath. The observed increase may be attributed to the fact that on increasing the temperature both the segmental mobility and diffusion of water molecules increase, which leads to an enhanced swelling.

A more quantitative information may be obtained by applying Clausius-Clayperon equation, according to which,[49]

$$\frac{d\ln(W_\infty)}{d(1/t)} = -\Delta H_m/R \qquad (7)$$

where R is a gas constant, and ΔH_m is the enthalpy of mixing between the dry polymer and infinite amount of water. When W_∞ is plotted against reciprocal of temperature ($1/T$), a straight line with

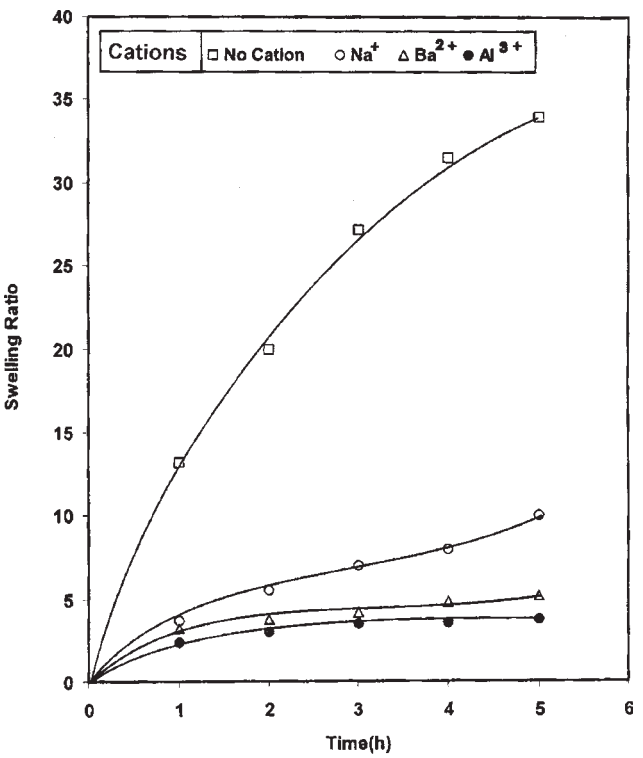


Figure 7 Effect of addition of cations to the swelling medium on the swelling ratio of the beads of fixed composition, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.9, Temp. = (30 ± 0.2)°C.

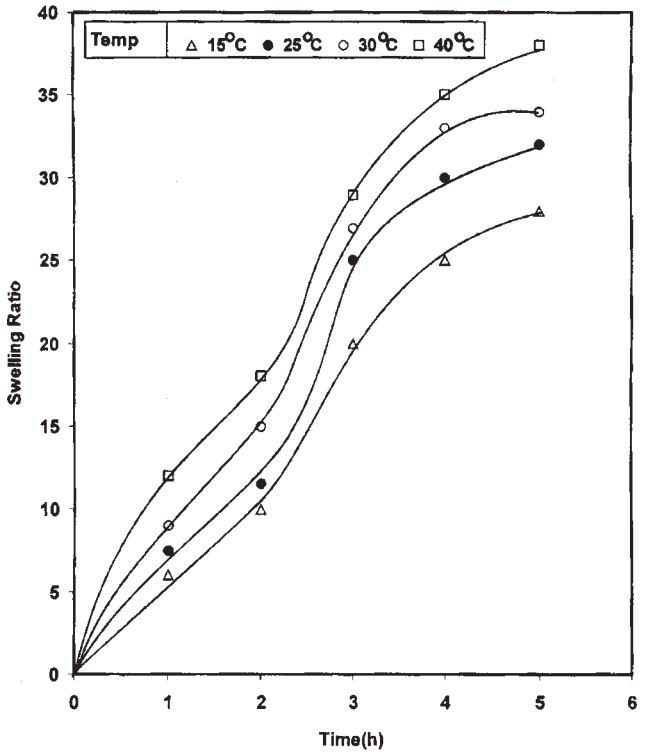


Figure 8 Influence of temperature on the swelling ratio of the beads of fixed composition, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.9.

negative slope is obtained that implies for an endothermic process. The value of ΔH_m was calculated to be 11.9 kcal/mol.

Release study

Effect of percent loading

The release kinetics of a loaded carrier is intimately related to its water sorption kinetics,[50] since a highly swelling loaded gel is expected to release a greater amount of bioactive agent entrapped within the network. The forthcoming section discusses the results on KNO_3 release from the loaded beads and, as may be seen later on, the release results are very consistent to the swelling results.

The effect of percent loading of KNO_3 on its release by the polymeric beads has been studied by varying the amount of percent loading in the range 0.6–1.0%. The results are shown in Figure 9 which clearly indicate that the amount of released KNO_3 decreases with increasing percent loading. The observed decrease in release rate may be attributed to the fact that a larger loading of the bead results in an accumulation of KNO_3 in the pores of the blend network, which brings about a reduction in mesh size of the pores. This consequently restricts both the entrance of water molecules into the network and subsequent release of KNO_3 from within the blend network into the outer release medium, thus resulting in a fall in the released KNO_3.

Effect of CMC

The effect of CMC content in the loaded hydrogel and its release behavior is shown in Figure 10 which reveal that the release amount of KNO_3 (in mg) increases when the CMC content increases in the feed mixture in the range 66.6–77.7%. The release results are shown in Figure 10 which clearly reveals that the amount of released KNO_3 increases up to 75.0% of CMC while beyond it a decrease is noticed. The observed results can be explained on the basis of the swelling results which clearly indicate an increased swelling up to 75.0% of CMC and a fall thereafter.

Effect of sodium alginate

When the sodium alginate is varied in the range 25.0–45.4% in the feed mixture of the loaded beads the amount of released KNO_3 decreases with increases of SA. The results shown in Figure 11 can be attributed to the fact that a large crosslinked produces a matrix with small mesh sizes of the free vol-

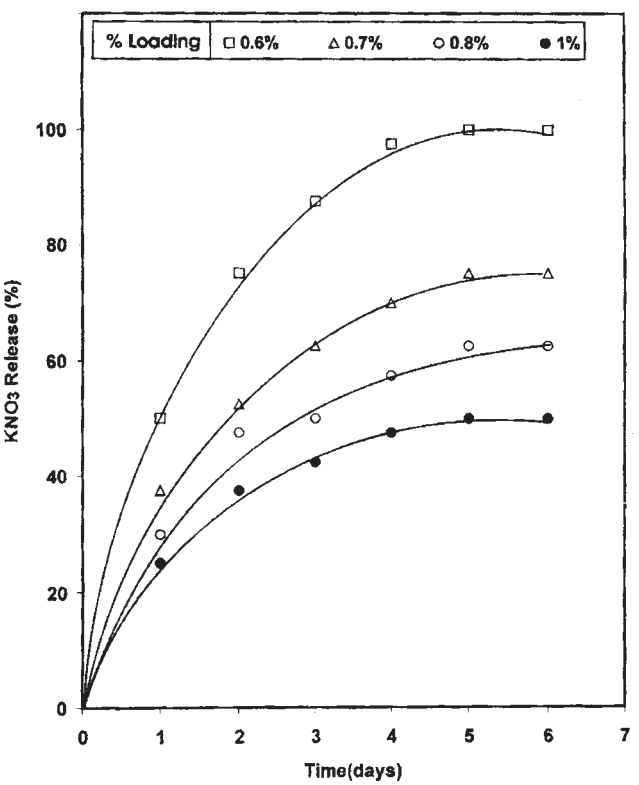


Figure 9 Effect of % loading of beads on released amount of KNO_3 for fixed composition of the [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.9, Temp. = (30 ± 0.2)°C.

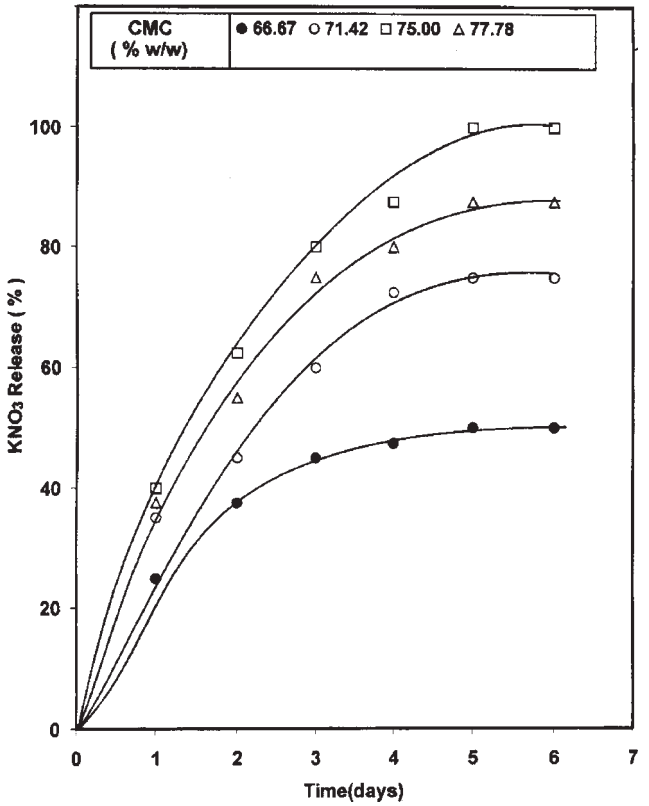


Figure 10 Effect of CMC content in the bead on the released amount of KNO_3 for fixed composition of beads, [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH 6.9 Temp. = (30 ± 0.2)°C, % loading = 50%.

umes and therefore, accommodate less amounts of KNO_3. This clearly explains the lower release rate and the lower released amount of KNO_3. Another cause may be that because of small mesh size of the free volumes, the diffusion of water molecules into the gel matrix and that of KNO_3 from within the matrix become relatively slower and this as a consequence, results in a lower release rate of KNO_3. A fall in the release rate and released amounts of KNO_3 may also be due to a poor relaxation rate of macromolecular chains of the loaded beads of SA which will obviously result in slow release kinetics.

Effect of $CaCl_2$

The effect of $CaCl_2$, which is a crosslinker of sodium alginate, has been investigated on the release profile of KNO_3 by varying the concentration of $CaCl_2$ solution in the range 0.05–0.15*M*. The results are depicted in Figure 12 which clearly indicates that the amount of released KNO_3 constantly increases up to 0.1*M* concentration of $CaCl_2$ solution while a decrease is observed beyond 0.1*M*. The results can be well explained on the basis of the swelling response of the beads to the variation in concentration of $CaCl_2$ solution.

Another important consideration could be the possible interaction between the KNO_3 and calcium ions within the bead network. With increasing concentration of Ca^{2+} ions in the crosslinked beads the nitrate ions favorably interact with the Ca^{2+} ions and entrapped within the bead. Upon entrance of water molecules within the loaded beads, the electrostatic attractive forces between the Ca^{2+} and nitrate ions get broken and nitrate is released into the outer medium. When the concentration of Ca^{2+} ions exceeds 0.1*M*, the nitrate ions get so firmly held with the large number of Ca^{2+} ions that they do not move apart on dissolution when water molecules enter the bead. This obviously lowers the release of KNO_3.

Effect of pH

The effect of pH on the release of KNO_3 has been investigated by varying pH of the release medium in the range 3–10 and the results are displayed in Figure 13. It is clear from the figure that the amount of released KNO_3 constantly increases up to 8.0 while a fall is observed beyond pH 8.0, i.e., in the higher alkaline range. One of the possible explanations of

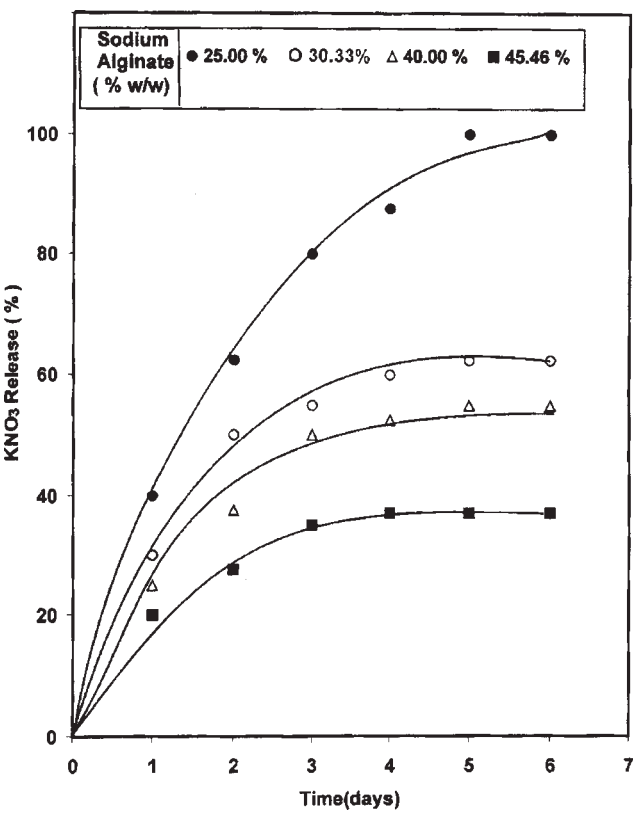


Figure 11 Effect of sodium alginate content in the bead on the released amount of KNO_3 for fixed composition of beads [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.9, Temp. = (30 ± 0.2)°C, % loading = 50%.

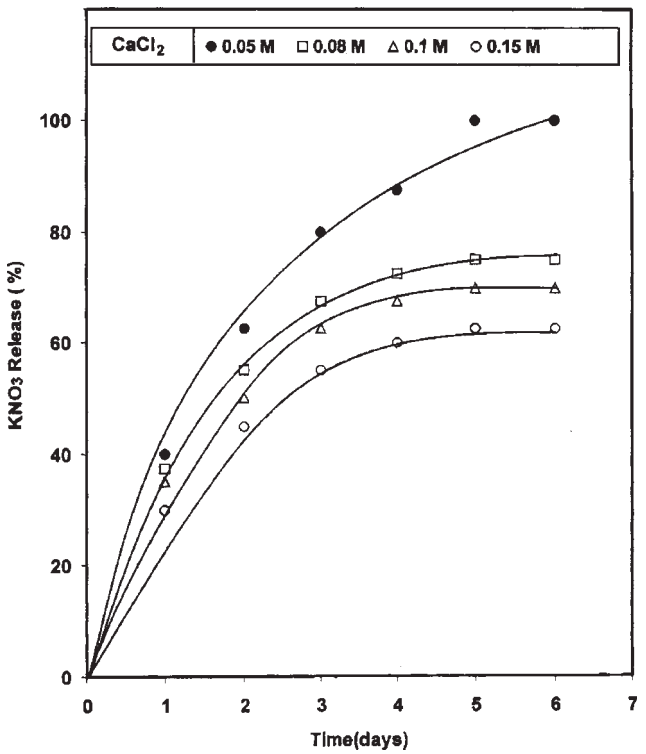


Figure 12 Effect of $CaCl_2$ content in the bead on the released amount of KNO_3 for fixed composition of bead, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.8, Temp. = (30 ± 0.2)°C, % loading = 50%.

the observed findings is due to the similar type of swelling behavior of the beads as explained in the previous section of the article.

Another cause for the observed results may be due to the screening effect of added H^+ ions. At low pH (say, 3.0) the H^+ ions enter the bead network and deshield the electrostatic repulsion operative between the NO_3^- ions and carboxylate ions of the alginate molecule. Thus, a decreased repulsion produces a less relaxation of bead chains and results in a lower release of KNO_3. When pH of the solution increases, the lower concentration of H^+ ions produces relatively more relaxation of alignate chains and result in an enhanced release of KNO_3. However, at much higher pH, i.e., beyond 8.0, greater number of hydroxyl ions in the release medium may restrict the expulsion of the NO_3^- ions and thus, results in a lower release of KNO_3.

Effect of temperature

When the temperature of the release medium is varied in the range 15–40°C, a constant increase in KNO_3 release is obtained as shown in Figure 14. The observed increase may be explained on the basis of a faster relaxation of network chains as well as greater diffusion of NO_3^- ions into the release medium. Both of these factors bring about an enhanced release of KNO_3.

On applying the Clausius – Clayperon Eq. (7) to the release process, the value of ΔH_{rel} may be calculated with the help of the linear plot drawn between ln M_∞ and $1/T$ (where M_∞ being the amount of KNO_3 released at equilibrium time). The value of ΔH_{rel} was calculated and found to be 15.1 kcal/mol. This clearly indicates that the release process is endothermic in nature.

Analysis of kinetic data

The kinetics of KNO_3 release is mainly determined by the contribution of relative rates of diffusion of KNO_3 into the release medium and relaxation of polymeric chains of the bead network. The values of n are summarized in Table II which clearly indicate that in all the cases of bead compositions, the value of n is almost near to 0.50 which indicate a Fickian diffusion, i.e., diffusion controlled release mechanism.

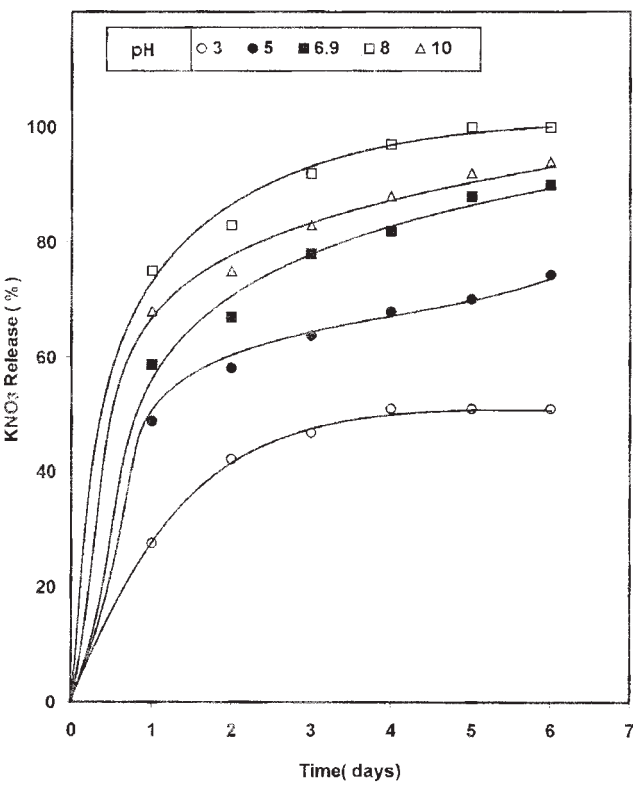


Figure 13 Effect of pH of the release medium on the released amount of KNO_3 for fixed composition of bead, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, Temp. = (30 ± 0.2)°C, % loading = 50%.

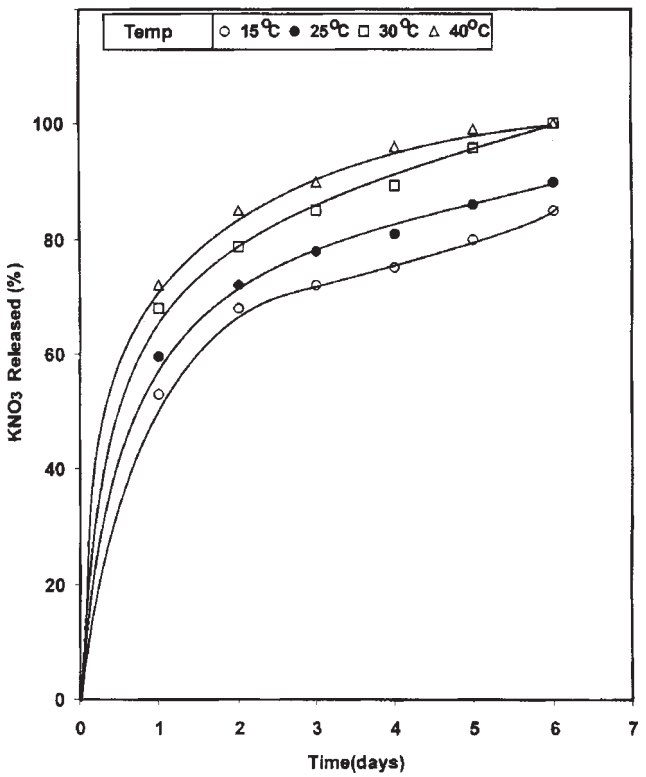


Figure 14 Effect of temperature of the release medium on the released amount of KNO_3 for fixed composition of bead, [CMC] = 75% (w/w) [sod. alginate] = 25% (w/w), [$CaCl_2$] = 0.1*M*, pH = 6.9, % loading = 50%.

The results also reveal that the variation in chemical composition of the blend does not influence the nature of the release mechanism. In other words, with variation in CMC, alginate, and $CaCl_2$ concentrations, the rate of relaxation of macromolecular chains is not affected to that extent which can make it a rate determining step. Thus, under all variations of chemical compositions, the rate of KNO_3 diffusion (R_{diff}) is always smaller than that of chain relaxation (R_{relax}) and this, of course, results in a Fickian release mechanism.

CONCLUSIONS

A sequential crosslinking of a polymeric blend of sodium alginate and CMC by calcium chloride produces a hydrophilic matrix in the form of beads. The resulting beads possess a multilayered morphology with 25–50 μm wide cracks on their surfaces.

The binary polymeric beads display a fair affinity for water sorption that greatly depends on the chemical architecture of the beads. When the concentration of CMC varies in the range 66.6–77.7%, the swelling ratio increases up to 75.0% of CMC and thereafter a fall is observed. A similar type of swelling behavior is shown by the bead when the other component, sodium alginate, varies between 25.0% and 77.7%, in the feed mixture of the beads. The crosslinkers show different results. When $CaCl_2$ varies between 0.05*M* and 0.15*M*, the degree of water sorption increases up to 0.1*M*, while a decrease is observed thereafter.

The swelling ratio of the bead increases with increase in the pH of the swelling bath in the range 3.0–8.0 while beyond pH 8.0, a decrease in swelling ratio is obtained. In the case of addition of electrolytes into the swelling medium, a depression in the swelling ratio is obtained. It is found that the added anions Cl^-, CO_3^{2-}, and PO_4^{3-} ions exert almost equal influence on the swelling while the cations show an increasing order of depression in the sequence $Na^+ < Ca^{2+} < Al^{3+}$. A constant increase in swelling ratio is also observed.

The polymeric beads show a great potential for release of KNO_3 taken as a model agrochemical. The release results clearly indicate that the release process is directly controlled by the swelling property of the beads and display a similar type of variation in released amount of KNO_3 as shown in their swelling ratio. Apart from the swelling quality of the beads, the release is also influenced by the KNO_3-polymer interaction. A variation in the chemical composition of the bead results in a Fickian or diffusion controlled release mechanism of KNO_3.

TABLE II
Data Showing the Influence of Composition of the Blend on the Release Mechanism of KNO_3

CMC (%)	Sodium alginate (%)	$CaCl_2$ (*M*)	*n*	$D \times 10^8$ (cm^2S^{-1})	Mechanism
66.67	33.33	0.1	0.40	0.78	Nearly Fickian
71.42	28.58	0.1	0.40	0.78	Nearly Fickian
75.00	25.00	0.1	0.45	1.23	Fickian
77.78	22.22	0.1	0.42	1.07	Nearly Fickian
75.00	25.00	0.1	0.45	1.23	Fickian
66.67	30.33	0.1	0.50	1.52	Fickian
60.00	40.00	0.1	0.43	1.12	Nearly Fickian
54.54	45.46	0.1	0.43	1.12	Nearly Fickian
75.00	25.00	0.05	0.50	1.52	Fickian
75.00	25.00	0.08	0.44	1.18	Nearly Fickian
75.00	25.00	0.10	0.50	1.52	Fickian
75.00	25.00	0.15	0.50	1.52	Fickian

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