

Evaluation of the Water Sorption and Controlled-Release Potential of Binary Polymeric Beads of Starch and Alginate Loaded with Potassium Nitrate as an Agrochemical

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ABSTRACT: Binary polymeric beads of sodium alginate and starch were prepared and characterized by IR spectral and scanning electron microscopy (SEM) techniques. The beads were examined for water uptake potential, and the influence of various factors, including chemical composition of the macromolecular matrix, pH, ionic strength, and temperature of the swelling medium, were investigated on the degree of water sorption. The prepared beads were loaded

with KNO_3 , as a model agrochemical, and the release kinetics of KNO_3 were studied under varying experimental conditions, as mentioned previously. The release data were analyzed by Fick's equation, and the mechanism of KNO_3 release was worked out at different experimental conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1815–1826, 2004

Key words: hydrogels; swelling FTIR; morphology

INTRODUCTION

Hydrogels are three-dimensional physically and/or chemically bonded polymeric matrices that absorb and swell with a significant proportion of water without undergoing dissolution.¹ Their ease of preparation and the control over physicochemical properties by the simple manipulation of chemical architecture make them a material of choice for many significant applications in diversified areas, including biomedicine,² bioengineering,³ pharmaceuticals,^{4,5} the food industry,⁶ and agriculture.⁷ A major property of hydrogels is the encapsulation of bioactive agents into their internal structure and the delivery of these at a desirable rate and at the targeted site. This obviously forms the very foundation of controlled drug delivery technology and has been exhaustively used in pharmaceutical science⁸ and agriculture.⁹ Controlled-release polymer matrix systems offer a number of potential advantages over conventional applications.¹⁰ A potential advantage is that these systems allow much less active agent to be used.

The recent past has witnessed growing interest in the chemical combination of agrochemicals with polymeric materials, and this has emerged as one of the approaches designed for the enhanced production of crops.¹¹ The conventional application of agrochemicals can result in ground water contamination,¹²

which has become an issue of great concern as this normally leads to the unnecessary spreading of toxic substances in the environment. This obviously results in potential hazards to nontarget organisms by direct action or by residues in food. Thus, there is a need for the more controlled application of agrochemicals to reduce the amount of active ingredient without the diminution of efficiency. The replacement of conventional agrochemical formulations by controlled-release systems not only helps to avoid treatment with excess amounts of active substances, but it also offers the most suitable technical solution in special fields of application, such as aquatic weed control and pest management in paddy fields. The most common controlled-release formulations are hydrophilic polymers that not only maintain the local concentration of active ingredients in the soil but also show the ability to alter soil characteristics by influencing infiltration rates, density soil structure, compaction, soil texture, and water-holding capacity.¹³ Changes to soil properties can be permanent or temporary, depending on the situations in which they are used.

An alarming problem that three-fourths of the world is facing is nitrate leaching and the subsequent pollution of ground water.¹⁴ The seriousness of the problem can be assessed by the fact that nitrates and nitrites are implicated in many fatal physiological disorders, including methemoglobinemia in babies,¹⁵ oral cancer,¹⁶ cancer of the colon and rectum, and other gastrointestinal cancers.¹⁷ A number of approaches to remedy ground water contamination by nitrates have been undertaken, including physical methods such as

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reverse osmosis and nanofiltration,¹⁸ chemical methods such as the catalytic removal of nitrates from water,¹⁹ abiotic degradation of nitrates with zero-valent iron, and electrokinetic processes.²⁰ However, these methods are considered costly even in advanced and developed countries.²¹ Thus, the application of nitrate-loaded carriers with a technology based on the controlled release of nitrates by the swelling of the polymeric carrier could prove a suitable measure against ground water pollution.

Recently, various polymer-supported or microencapsulated biocides have been introduced in agriculture to limit the undesirable side effects associated with conventional formulations of agrochemicals and related biocides.²² Biodegradable matrices are especially preferred to prevent further environmental pollution by nondegradable carriers.

Thus, as we realized the contribution of polymers in the controlled release of agrochemicals, in this study aims, we aimed to develop a hydrophilic matrix of a binary polymeric blend of sodium alginate (SA) and starch (ST) and to evaluate its potential as a controlled-release device with KNO₃ as a model agrochemical. SA and ST were chosen as components of the KNO₃ carrier because they are naturally occurring hydrophilic, biodegradable, and nontoxic biopolymers and possess great potential as carriers for the controlled release of bioactive compounds.²³

EXPERIMENTAL

Materials

Water-soluble corn ST and SA were obtained from Thomas Baker Chemicals, Ltd. (Mumbai, India) and Research Lab (Pune, India) and were used without any pretreatment. Epichlorohydrine and calcium chloride (dihydrate), used as crosslinkers for ST and SA, respectively, were obtained from Thomas Baker Chemicals and were used as received. All other chemicals used in this study were of analytical quality, and triple-distilled water was used throughout the experiment.

Preparation of beads

To prepare polymeric beads of ST and SA, a series of blends were prepared by the dissolution of precalculated amounts of ST (33.33–66.67% w/w) and SA (109.5–219.0% w/w alginate) into 25 mL of distilled water with constant stirring. The blends so prepared were added dropwise into CaCl₂ solutions (109.5–219.0% w/w alginate) with gentle stirring with the help of a syringe, and the beads so prepared were placed in the same solution for 48 h. The cured beads were further hardened by placement in epichlorohydrine solutions (12.6–31.7% w/w ST) for 72 h. The

hard beads of nearly identical spherical shapes and sizes were purified by equilibration in distilled water for a week. The beads so prepared were further dried at 30°C for 1 week and were stored in airtight polyethylene bags.

Characterization of beads

IR spectral analysis

The beads prepared as described previously were characterized with IR spectra of unloaded and KNO₃-loaded beads on a Fourier transform infrared (FTIR) spectrophotometer (PerkinElmer, 1000 Paragon).

Scanning electron microscopy (SEM)

SEM analysis of unloaded and KNO₃-loaded beads were performed for the morphological characterization of their surfaces on a SEM apparatus (STEREO SCAN, 430, Leica SEM).

Swelling kinetics

A conventional gravimetric procedure²⁴ was adopted to monitor the progress of the water sorption process. In a typical experiment, a preweighed quantity of beads was immersed in a definite volume of water at a definite pH and temperature and taken out at predetermined time intervals. The swollen beads so taken out were gently pressed between two filter papers to remove excess water and finally weighed on a digital balance (APX-203 Denver, Germany). The swelling ratio was calculated with the following equation:

$$\text{Swelling ratio} = \frac{W_d}{W_s} \quad (1)$$

where W_d is the weight of the swollen beads and W_s is the weight of the dry beads.

Loading of potassium nitrate

In this study, we performed the loading by equilibrating preweight dry beads in an aqueous solution of KNO₃ of known concentration (1% w/v) and thereafter drying and weighing again. The percentage loading was calculated by the following equation:

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

where m_1 and m_0 are the weights of KNO₃ in the loaded and dry beads, respectively.

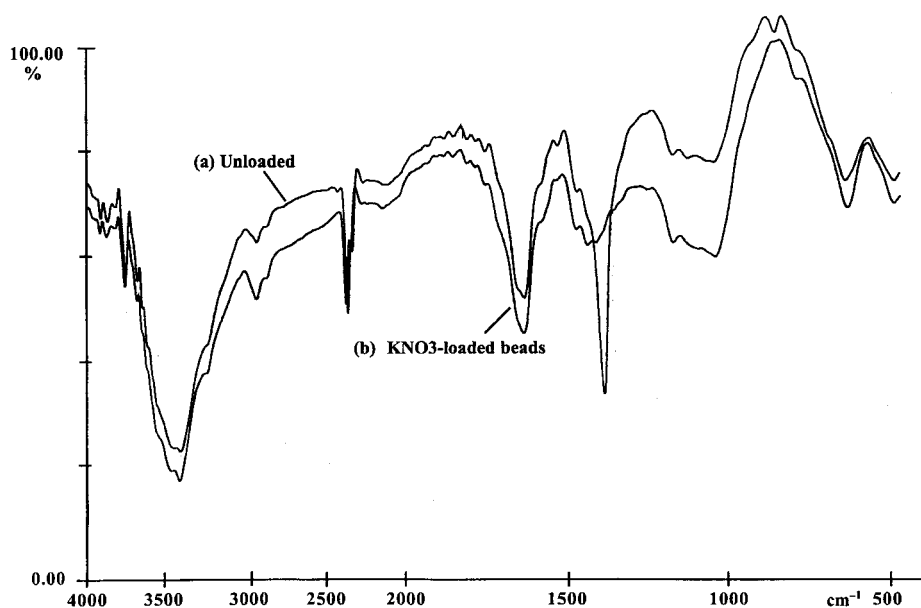


Figure 1 FTIR spectra of (a) unloaded and (b) KNO₃-loaded beads.

Release of potassium nitrate

To study the release of KNO₃, loaded gels of known weights were placed in a measured volume (25 mL) of distilled water (release medium) with no stirring. The released amount of KNO₃ at different time intervals (M_t) was determined by the measurement of the conductivity of the release medium with a conductivity meter (model no. 303, Systronics, India). This was related to the amount of KNO₃ with a calibration plot. Similarly, the equilibrium release (M_∞) of KNO₃ was determined by the conductivity of the release medium after 5 days. To gain insights into the operative release mechanisms, the following equation based on Fick's law but applicable to a spherical device was applied:^{25,26}

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

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

where M_t and M_∞ represent the amounts of KNO₃ released at time t and at equilibrium, respectively; k is the swelling front factor, n is the release exponent, and r is the radius of the spherical bead. The value of n determines the nature of release mechanism. That is, when $n = 0.5$, the release is Fickian, when n lies between 0.5 and 1.0, the release is anomalous, and when $n = 1$, the release mechanism is case II.

RESULTS AND DISCUSSION

Characterization of beads

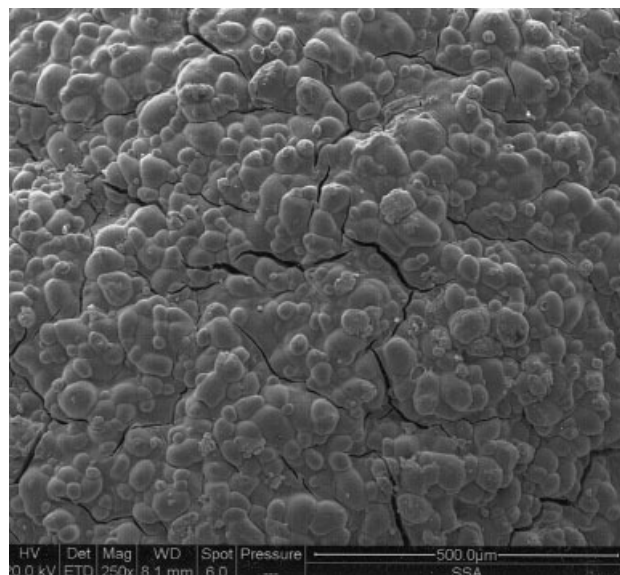
FTIR spectra

The FTIR spectra of unloaded and KNO₃-loaded beads are shown in Figure 1(a,b), which clearly confirms the presence of ST, alginate, and KNO₃ in the loaded beads as discussed later.

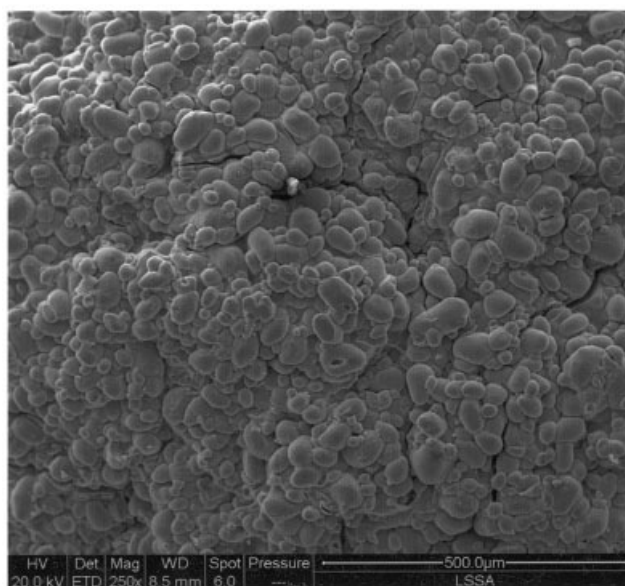
The evidence of ST came from peaks observed at 3683, 3755, and 3864 cm⁻¹ (all because of O—H stretching²⁷); 2933 cm⁻¹ due to C—H stretching, 1629 cm⁻¹ [δ (O—H), bending of absorbed water], and 1032 cm⁻¹ (C—O stretching). The spectra clearly marked the presence of alginate, as confirmed by the O—H stretching of hydroxyls at 3419 cm⁻¹ and C(O)2 stretching of the carboxylate ion. Figure 1(b) also confirms the presence of KNO₃ within the bead, as evident from the vibrational frequency of the nitrate ion at 1384 cm⁻¹.²⁸ The previously mentioned bands were observed at wave numbers that were shifted a little bit, which confirmed the blend nature of the material as reported elsewhere.²⁹

SEM

Scanning electron micrographs of the unloaded and KNO₃-loaded beads are shown in Figure 2(a,b). A close examination of the photographs clearly indicates that the beads had a multilayered morphology containing an accumulation of irregularly shaped bead particles ranging in size between 6 and 90 μ m. The unloaded beads had prominent cracks on their surfaces, which had a maximum width of 1 μ m. The fractured surface clearly implied a phase separation between the crosslinked ST



(a)



(b)

Figure 2 Scanning electron micrographs of (a) unloaded and (b) KNO_3 -loaded beads.

and the crosslinked alginate. Also noticeable was the fact that on the surface of the unloaded beads, the particle density was lower than that on the loaded beads, which may have been due to the loading of KNO_3 on the beads, which resulted in a deposition of the latter on the bead surfaces.

Modeling of the release mechanism

In this study, the KNO_3 -loaded beads of the polymeric blend of crosslinked ST and SA could be visualized as

a network of macromolecular chains of ST and SA bonded to one another via physical forces and the formation of pockets of molecular dimensions between them. These pockets (or voids) of varying mesh sizes were further occupied by the active ingredient KNO_3 . When the loaded bead came in contact with the still aqueous release medium, the penetrant water molecules invaded the bead surface, and a moving solvent front was observed that clearly separated the unsolvated glassy polymer region ahead of the front from the swollen and rubbery gel phase behind it (Fig. 3).³⁰ Just ahead of the front, the presence of solvent plasticized the polymer and caused it to undergo a glass-to-rubber transition.³¹ Then, the following possibilities arose:

1. If the glass-transition temperature (T_g) of the polymer was well below the experimental temperature, the polymer would be in the rubbery state, and the polymer chains would have had a higher mobility that allowed an easier penetration of water molecules into the bead and, as a consequence, the expulsion of KNO_3 into the outer release medium. If the rate of diffusion of KNO_3 into the outer medium [$R_{\text{diff}(\text{KNO}_3)}$] was slower than that of chain relaxation (R_{relax}), the release mechanism would be diffusion-controlled or Fickian and n would be equal to 0.5
2. However, if the experimental temperature was below T_g , the polymer chains were not sufficiently mobile to permit immediate penetration of the solvent into the polymer core (or the release of KNO_3 into the outer medium). Thus, $R_{\text{diff}(\text{KNO}_3)}$ may have been greater than R_{relax} , and this gave rise to a relaxation-controlled (or non-Fickian) release mechanism, which would be quantified by a unity value of n . This is also known as *case II transport*.
3. In an intermediate situation, the two rates, that is, $R_{\text{diff}(\text{KNO}_3)}$ and R_{relax} may have been nearly equal, and this is called an *anomalous diffusion* or, simply, *non-Fickian diffusion*.

These three situations are modeled in Figure 3(a–c).

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 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):

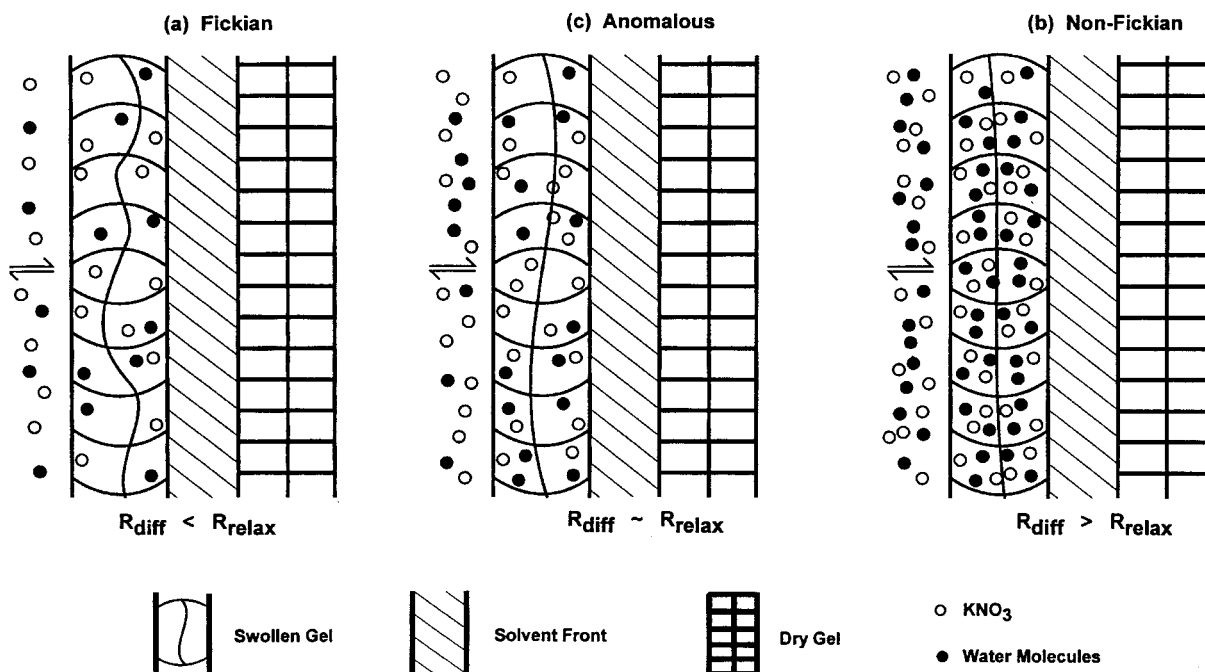


Figure 3 Hypothetical model depicting the (a) Fickian, (b) anomalous, and (c) non-Fickian release of KNO₃.

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

where i/V_N is the concentration of the fixed charges of the unswollen network, S is the ionic concentration in the external solution, $(1/2 - X_i)/V_i$ is the affinity of the matrix for water, and v_e/V_o is the crosslink density of the network. Equation (5) reveals that the swelling ratio has a direct relation to ionic osmotic pressure (π_{ion}), crosslink density, and affinity of the hydrogel for water. Therefore, the swelling of a hydrophilic macromolecular matrix can be controlled by the variation of its chemical composition.

Effect of ST

The influence of ST on the swelling ratio of the beads was investigated by the variation of its concentration in the feed mixture in the range 33.33–66.67% (w/w). The results are shown in Table I, which clearly indicates that the swelling ratio constantly increased up to 50% ST in the feed mixture of the bead, whereas beyond 50%, a fall in the degree of water sorption was noticed. The initial increase observed in the swelling ratio may be explained on the basis of the fact that ST is a mixture of one linear and one branched hydrophilic macromolecule and its increasing amount in the bead resulted in the enhanced hydrophilicity of the network, which obviously resulted in larger swelling. However, the decrease observed beyond 50% ST may have been due to the fact that a much higher ST

content in the matrix gave rise to a compact network of biopolymeric chains, which caused greater interaction between the ST molecules, resulting in restrained mobility of the network chains. Moreover, a compact structure resulted in small pore sizes in the network, which also slowed down the diffusion of water molecules into the bead, which also brought about a decrease in the swelling ratio.

Effect of SA

The effect of SA, an anionic biopolymer, on the swelling ratio of the beads was studied by the variation of

TABLE I
Effect of the Composition of the Blends on Their Equilibrium Swelling Ratios

ST (%)	SA (%)	CaCl ₂ (%)	Epichlorohydrine (%)	Equilibrium swelling ratio
33.33	66.67	182.5	31.7	4.0
42.86	57.14	182.5	31.7	4.5
45.00	55.00	182.5	31.7	7.0
50.00	50.00	182.5	31.7	13.0
55.56	44.44	182.5	31.7	9.0
57.14	42.86	182.5	31.7	6.2
66.67	33.33	182.5	31.7	5.2
50.00	50.00	109.5	31.7	3.2
50.00	50.00	146.0	31.7	3.5
50.00	50.00	182.5	31.7	13.0
50.00	50.00	219.0	31.7	3.0
50.00	50.00	182.5	12.6	6.5
50.00	50.00	182.5	19.0	8.0
50.00	50.00	182.5	25.3	10.0
50.00	50.00	182.5	31.7	13.0

the concentration of SA in the range 33.33–66.67% (w/w). The results are presented in Table I, which clearly indicates that although the swelling ratio initially increased up to 50% SA, a decrease was observed beyond 50%. The observed findings may have been due to the fact that alginate is an anionic polymer and its increasing concentration in the bead produced a greater number of carboxylate ions along its molecules, which because of enhanced repulsions between COO^- ions, caused the network chains to undergo a larger relaxation. This obviously allowed a greater number of water molecules to enter the bead and resulted in increased swelling. However, beyond 50% SA, when the concentration of alginate became high, the increased number of alginate chains produced a dense network, which permitted a lower number of water molecules into the beads and, thus, resulted in decreased swelling.

Effect of CaCl_2

Calcium chloride, a known crosslinking agent of alginate, was assumed to act by the complexation of the carboxylate anions of alginate by its bivalent calcium ion, thus forming a cavity-type network. In this investigation, the effect of CaCl_2 on the swelling ratio of the beads was investigated by the variation of the concentration of CaCl_2 in the range 109.5–219.0% w/w alginate. The results are summarized in Table I, which clearly indicates that the degree of water sorption constantly increased up to 182.5%, whereas beyond this concentration, a constant decrease in the swelling ratio was noticed.

The observed initial rise in the swelling ratio may have been due to the fact that with increasing number of calcium ions in the crosslinking bath, alginate beads containing larger cavities were produced, which could have accommodated a greater amount of water. This obviously resulted in greater swelling in the polymeric beads. We also observed that beyond 182.5% CaCl_2 solution, the swelling ratio decreased, which was because if number of calcium ions became much greater, they screened the electrostatic repulsion operative between the carboxylate ions inside the cavity, thus, causing shrinking of the bead. This clearly resulted in a decrease in the swelling ratio.

Effect of epichlorohydrine

The addition of varying concentrations of crosslinker to a hydrogel is an effective route for the modification of the water sorption properties as it also influences the physical properties of the polymer, such as the T_g . In this study, the effect of the crosslinker epichlorohydrine on the swelling ratio of the bead was studied by the variation of its concentration in the range 12.6–31.7% w/w ST. The results are displayed in Table I,

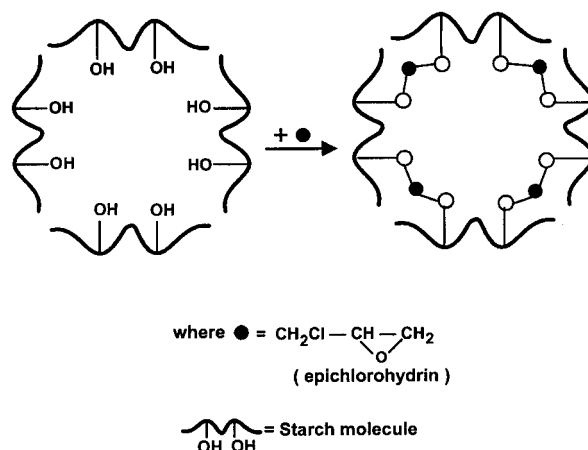


Figure 4 Hypothetical reaction model showing the crosslinking of ST molecules with epichlorohydrine.

which clearly reveals that the swelling ratio constantly increased with increasing epichlorohydrine. The results were quite surprising, as in majority of investigations a decrease in the degree of swelling has normally been observed with an increasing concentration of crosslinking agent.³³ The results obtained in this case, however, may be explained as follows.

Epichlorohydrine is a low-molecular-weight crosslinking agent of ST, which at its two terminals reacts with the hydroxyls of ST and crosslinks them. Thus, a crosslinked ST network could be imagined as a ultra-high-molecular-weight ST molecule that generates wide pore sizes in the whole network and, therefore, possesses an abnormal capacity for accommodating water into its network (Fig. 4). This obviously resulted in a greater water sorption by the polymeric bead.

Effect of pH

pH plays an important role in influencing the swelling of hydrogels where the hydrogel components are of a polyelectrolyte nature. In this study, where SA was of an anionic nature, the effect of pH was investigated on the swelling ratio of the beads in the pH range 3.0–10.0. The results are shown in Figure 5, which indicates that the swelling ratio increased up to 8.0, although beyond this, a decrease was observed. The results may be explained by the fact that with increasing pH of the swelling medium, the extent of ionization of the carboxylic groups of alginate also increased, which produced a greater number of carboxylate ions along the alginate molecule. These anionic charged centers repelled each other and produced a rapid relaxation in the network chains, which facilitated the inclusion of water molecules into the bead network. This clearly resulted in a rise in the degree of water uptake.

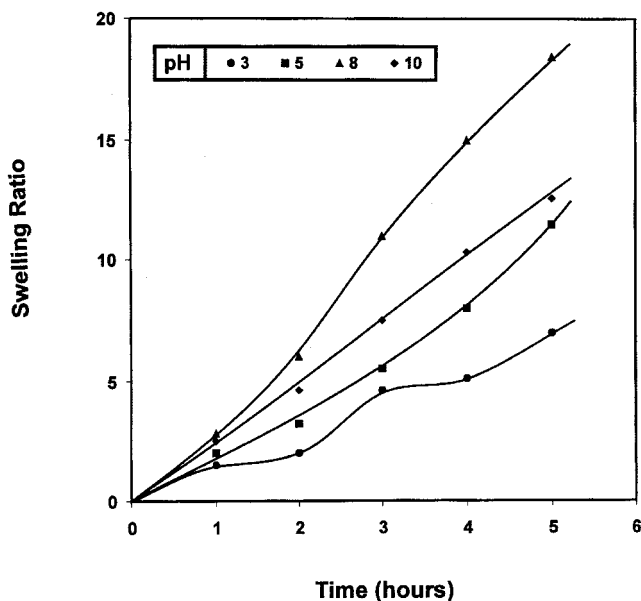


Figure 5 Effect of the pH of the swelling medium on the swelling ratio of the beads of fixed composition: [ST] = 50% (w/w) [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), and temperature = 30 ± 0.2°C.

However, beyond pH 8.0, a decrease in the swelling ratio was noticed, which may have been due to the fact that at a higher alkaline range (pH > 8.0), the network chains acquired a greater charge density, which restricted the entrance of polar penetrant water molecules into the bead, and thus, the swelling ratio decreased.

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 applications.³⁴ The effect of electrolytes on the extent of swelling is normally determined by the balance between π_{ion} and the elastic response of the network chains. π_{ion} is given by the following equation:³⁵

$$\pi_{ion} = RT \sum_i (C_i^g - C_i^s) \quad (6)$$

where C_i 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; and T is the absolute temperature of swelling medium. Equation (6) clearly implies that the greater the difference between the concentration of mobile ions inside and outside the gel is, the larger π_{ion} and, therefore, the swelling of the gel will be.

In this investigation, the influence of salts on the swelling of the beads was studied by the addition of

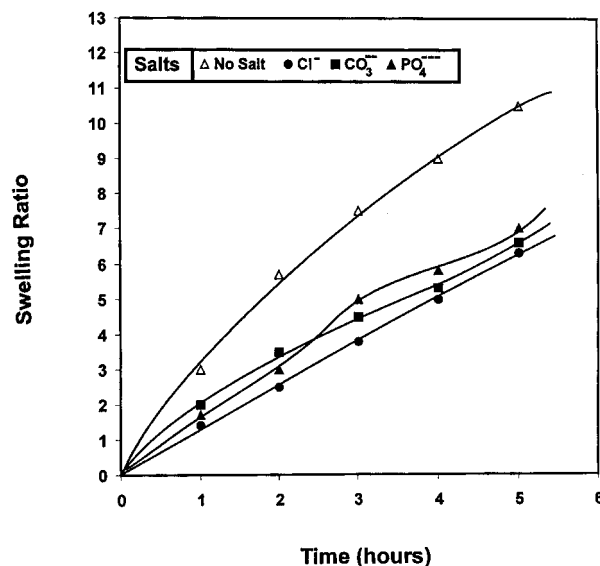


Figure 6 Effect of the addition of anions to the swelling medium on the swelling ratio of the beads of fixed composition: [ST] = 50% (w/w), [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), pH = 7.2, and temperature = 30 ± 0.2°C.

various salts of sodium (0.5M) and chlorides of cations (0.5M) to the swelling bath, respectively. The results are shown in Figures 6 and 7, which indicate that in both cases, the swelling ratio decreased. These figures also reveal that although various anions exerted an almost identical impact on the swelling ratio, in the

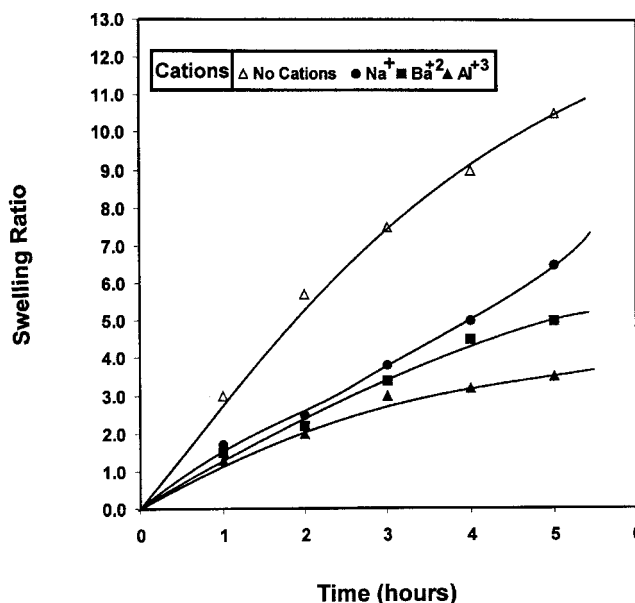
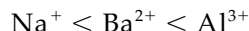


Figure 7 Effect of the addition of cations to the swelling medium on the swelling ratio of the beads of fixed composition: [ST] = 50% (w/w), [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), pH = 7.2, and temperature = 30 ± 0.2°C.

case of cations, the degree of suppression of the swelling ratio increased in the following sequence:



The observed results can be explained as follows: The addition of salts into the swelling medium increased the term C_i^s in eq. (6), which in turn decreased π_{ion} and, thus, caused a fall in the swelling ratio. In the case of anion addition, the added anions, because of their negative charges, may not have diffused into the bead network, as the network chains also had the same charge. Thus, the added ions, namely, Cl^- , CO_3^{2-} , and PO_4^{3-} , produced a similar decrease in the swelling.

However, the added cations may have diffused into the bead, and their concentrations inside the bead may have determined their relative effectiveness. Because Na^+ ion was the largest and Al^{3+} was the smallest ion, a greater diffusivity was expected with Al^{3+} ions, which inside the bead network deshielded the coulombic repulsive forces and caused the shrinking of the gel. This obviously produced the largest swelling with Al^{3+} ions. The larger Na^+ ions may have diffused into the bead in lower numbers and caused a lower degree of shrinking effect.

Effect of temperature

The effect of temperature on the swelling ratio of the blends was investigated by the variation of the temperature of the swelling medium in the range 5–40°C. The results are displayed in Figure 8, which implies that the swelling ratio constantly increased with increasing temperature. The results may have been due to the fact that a higher temperature resulted in both a greater diffusion of water molecules and a larger relaxation of network chains, which as a consequence, enhanced the swelling ratio of the beads.

More quantitative information could be obtained by application of the Clausius–Claxpron equation, according to which³⁶

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

where ΔH_m is the enthalpy of mixing between the dry polymer and an infinite amount of water. When W_∞ was plotted against the reciprocal of temperature ($1/T$), a straight line with a negative slope was obtained, which implied an endothermic process. The value of ΔH_m was calculated to be 17.5 kcal/mol.

Release study

The release kinetics of a loaded hydrogel is intimately related to its water sorption kinetics³⁷ because a highly

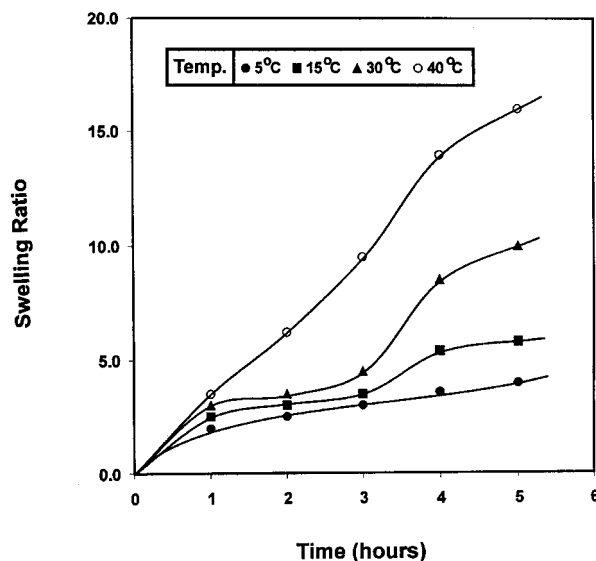


Figure 8 Influence of temperature on the swelling ratio of the beads of fixed composition: [ST] = 50% (w/w), [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), and pH = 7.2.

swelling loaded gel is expected to release a greater amount of bioactive agent entrapped within the network. The forthcoming section discusses the results of KNO_3 release from the loaded beads, and as discussed later, the release results were very consistent with the swelling results.

Effect of percentage loading

The effect of percentage loading of KNO_3 on its release by the polymeric beads was studied by the variation of the amount of percentage loading in the range 0.6–1.0%. The results are shown in Figure 9, which clearly indicates that the amount of released KNO_3 decreased with increasing percentage loading. The observed decrease in the release rate may have been due to the fact that a larger loading of the bead resulted in an accumulation of KNO_3 in the pores of the blend network, which caused a reduction in the mesh size of the pores. This consequently restricted both the entrance of water molecules into the network and the subsequent release of KNO_3 from within the blend network into the outer release medium, thus resulting in a decrease in the released KNO_3 .

Effect of ST

The influence of ST content in the bead on the release profile of KNO_3 was investigated by the variation of the amount of ST in the range 33.3–55.5% (w/w). The release results are shown in Figure 10, which clearly reveals that the amount of released KNO_3 increased up to 50% ST, whereas beyond this, a decrease was

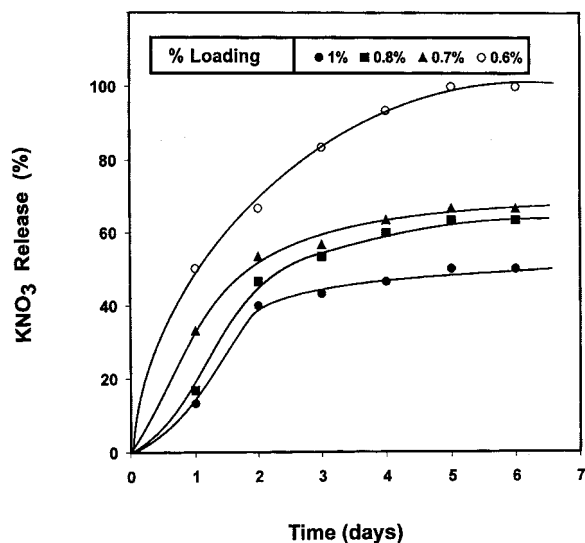


Figure 9 Effect of the percentage loading of beads on released amount of KNO₃ for beads of fixed composition: [ST] = 50% (w/w), [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), pH = 7.2, and temperature = 30 ± 0.2°C.

noticed. The observed results can be explained on the basis of the swelling results, which clearly indicate that the swelling ratio increased up to 50% ST, beyond which the swelling decreased. Obviously, a higher swelling of beads implied a greater expulsion of entrapped KNO₃ into the release medium.

Effect of SA

When the SA was varied in the range 33.3–55.5% (w/w) in the feed mixture of the loaded beads, the

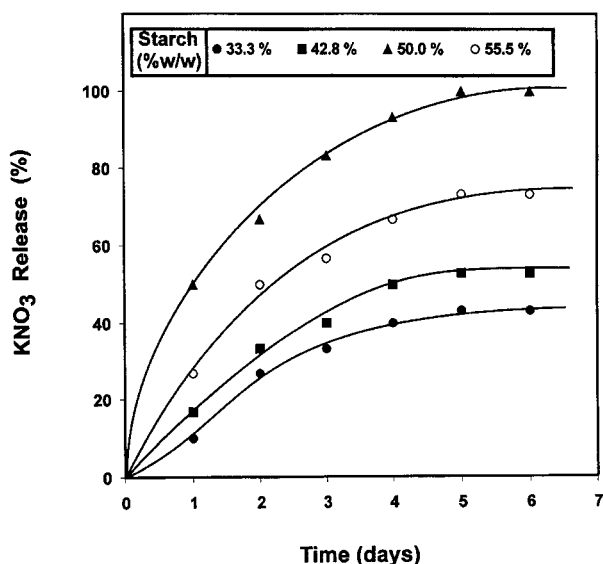


Figure 10 Effect of ST content in the beads on the released amount of KNO₃ for beads of fixed composition: [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), pH = 7.2, temperature = 30 ± 0.2°C, and percentage loading = 30%.

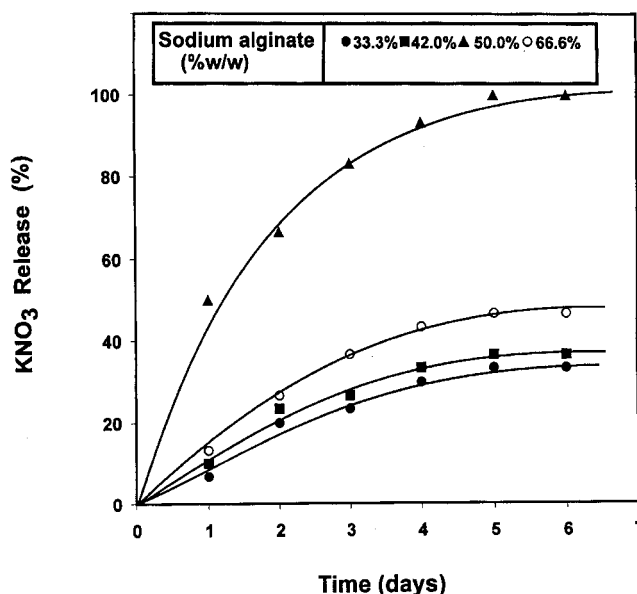


Figure 11 Effect of SA content in the bead on the released amount of KNO₃ for beads of fixed composition: [ST] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), pH = 7.2, temperature = 30 ± 0.2°C, and percentage loading = 30%.

amount of released KNO₃ increased initially up to 50% SA, whereas beyond this, a significant decrease was noticed (Fig. 11). The results may be explained on the basis of the swelling behavior of the beads as discussed previously.

The observed results may also be attributed on the basis of KNO₃ polymer interaction. With increasing alginate content in the bead, the NO₃⁻ ions and carboxylate ions of alginate produced electrostatic repulsion within the bead network and, therefore, caused a larger relaxation of the network chains. This obviously allowed a greater number of water molecules into the bead, and as a consequence, a higher amount of nitrate was delivered into the release medium. However, at a much greater concentration of alginate, the charge density within the network increased so much that the entrance of water molecules became unlikely, and as a result of suppressed swelling, the amount of released KNO₃ decreased.

Effect of CaCl₂

The effect of CaCl₂, which is a crosslinker of SA, was investigated on the release profile of KNO₃ by the variation of the concentration of CaCl₂ solution in the range 109.5–219.0% (w/w alginate). The results are depicted in Figure 12, which clearly indicates that the amount of released KNO₃ constantly increased up to 182.5% CaCl₂ solution, whereas a decrease was observed beyond 182.5%. The results can be well explained on the basis of

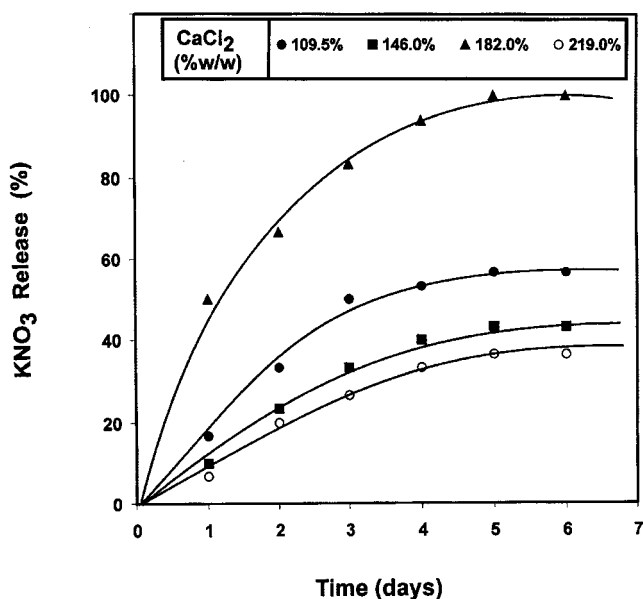


Figure 12 Effect of CaCl_2 content in the bead on the released amount of KNO_3 for beads of fixed composition: $[\text{ST}] = 50\%$ (w/w), $[\text{SA}] = 50\%$ (w/w), $[\text{epichlorohydrine}] = 31.7\%$ (w/w), $\text{pH} = 7.2$, temperature = $30 \pm 0.2^\circ\text{C}$, and percentage loading = 30%.

the swelling response of the beads to the variation in concentration of CaCl_2 solution.

Another important consideration is 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 interacted with the Ca^{2+} ions and were entrapped within the bead. On the entrance of water molecules into the loaded beads, the electrostatic attractive forms between the Ca^{2+} and nitrate ions were broken, and nitrate was released into the outer medium. When the concentration of Ca^{2+} ions exceeded 182.5%, the nitrate ions were so firmly held with the large number of Ca^{2+} ions that they did not move apart on dissolution when water molecules entered the bead. This obviously decreased the release of KNO_3 .

Effect of epichlorohydrine

A variation in epichlorohydrine concentration largely influenced the release rate of KNO_3 , as shown in Figure 13. It is clearly revealed by this figure that when the concentration of epichlorohydrine solution was varied from 12.6 to 31.7% (w/w ST), the released amount of KNO_3 constantly increased. The observed increase may again be attributed to similar type of swelling results obtained with the beads prepared with epichlorohydrine in the same concentration range.

Effect of pH

The effect of pH on the release of KNO_3 was investigated by the variation of the pH of the release medium

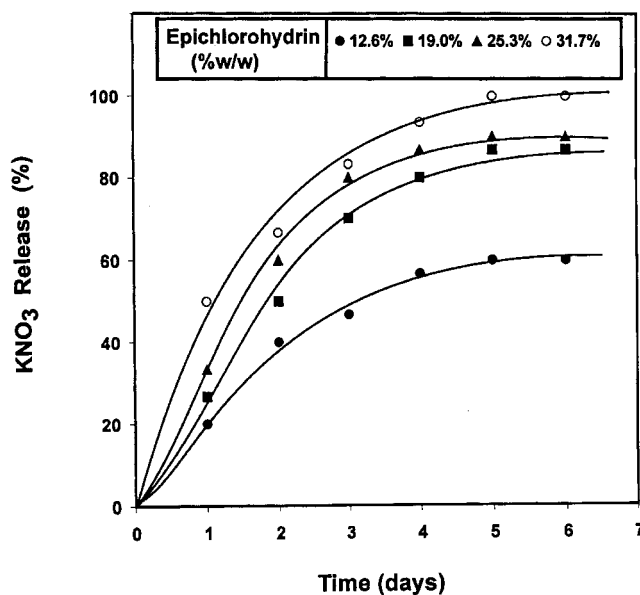


Figure 13 Effect of epichlorohydrine content in the bead on the released amount of KNO_3 for beads of fixed composition: $[\text{ST}] = 50\%$ (w/w), $[\text{SA}] = 50\%$ (w/w), $[\text{CaCl}_2] = 182.5\%$ (w/w), $\text{pH} = 7.2$, temperature = $30 \pm 0.2^\circ\text{C}$, and percentage loading = 30%.

in the range 3–10; the results are displayed in Figure 14. It is clear from this figure that the amount of released KNO_3 constantly increased up to 8.0, whereas a decrease was observed beyond pH 8.0, that is, in the higher alkaline range. One of the possible explana-

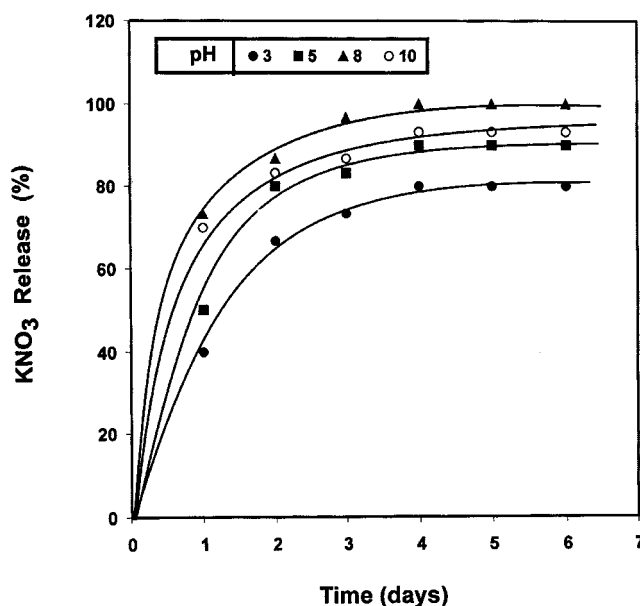


Figure 14 Effect of the pH of the release medium on the released amount of KNO_3 for beads of fixed composition: $[\text{ST}] = 50\%$ (w/w), $[\text{SA}] = 50\%$ (w/w), $[\text{CaCl}_2] = 182.5\%$ (w/w), $[\text{epichlorohydrine}] = 31.7\%$ (w/w), temperature = $30 \pm 0.2^\circ\text{C}$, and percentage loading = 30%.

tions for the observed findings is a similar type of swelling behavior of the beads as explained in a previous section of this article.

Another cause for the observed results may have been the screening effect of added H⁺ ions. At low pH (say, 3.0), the H⁺ ions entered the bead network and deshielded the electrostatic repulsion operative between the NO₃⁻ ions and carboxylate ions of the alginate molecule. Thus, a decreased repulsion produced a lower relaxation of bead chains and resulted in a lower release of KNO₃. When the pH of the solution increased, the lower concentration of H⁺ ions produced a relatively larger relaxation of the alignate chains and resulted in the enhanced release of KNO₃. However, at much higher pH, that is, beyond 8.0, a greater number of hydroxyl ions in the release medium may have restricted the expulsion of the NO₃⁻ ions from within the bead because of repulsion between the two ions and, thus, may have resulted in a smaller release of KNO₃.

Effect of temperature

When temperature of the release medium was varied in the range 15–40°C, a constant increase in KNO₃ release was obtained, as shown in Figure 15. The observed increase may be explained on the basis of a faster relaxation of network chains and a greater diffusion of NO₃⁻ ions into the release medium. Both of these factors brought about an enhanced release of KNO₃.

When the Clausius–Clayperon equation is applied to the release process, the following equation may be written:

$$\frac{d \ln(M_{\infty})}{d(1/T)} = - \Delta H_{rel}/R$$

where M_{∞} is the amount of KNO₃ released at the equilibrium time and ΔH_{rel} is the enthalpy of the KNO₃ release process. With the help of a linear plot drawn between $\ln M_{\infty}$ and $1/T$, the value of ΔH_{rel} was calculated and was found to be 8.2 kcal/mol. This clearly indicated that the release process was endothermic in nature.

Analysis of kinetic data

The kinetics of KNO₃ release were mainly determined by the contribution of relative $R_{diff(KNO_3)}$ and R_{relax} . The values of n are summarized in Table II, which clearly indicates that in all of the cases of bead compositions, the values of n were almost 0.50, which indicated a Fickian diffusion, that is, a diffusion-controlled release mechanism. D is defined as diffusion constant.

The results reveal that variation in the chemical composition of the blend did not influence the nature of the release mechanism. In other words with variation in ST, alginate, CaCl₂, and epichlorohydrine concentrations, the rate of relaxation of the macromolecular chains was not affected to that extent, which could have made it a rate-determining step. Thus, under all variations of chemical composition, $R_{diff(KNO_3)}$ was always smaller than R_{relax} , and this, of course, resulted in a Fickian release mechanism.

CONCLUSIONS

The sequential crosslinking of a polymeric blend of SA and ST by calcium chloride and epichlorohydrine, respectively, produced a hydrophilic matrix in the form of beads. The resulting beads possessed a multilayered morphology with 1 μm wide cracks on their surfaces.

The binary polymeric beads displayed a fair affinity for water sorption that greatly depended on the chemical architecture of the beads. When the concentration of ST was varied in the range 33.33–66.67% (w/w), the swelling ratio increased up to 50% ST, and thereafter, a decrease was observed. A similar type of swelling behavior was shown by the bead when the other component, SA, was varied between 33.33 and 66.67% (w/w) in the feed mixture of the beads. The two crosslinkers showed different results. When CaCl₂ was varied between 109.5 and 219.0% (w/w alginate), the degree of water sorption increased up to 182.5% (w/w ST), whereas a decrease was observed thereafter. However, with an increase in the concentration of epichlorohydrine, an optimum swelling was achieved with 31.7% (w/w) pure epichlorohydrine.

The swelling ratio of the beads increased with an increase in the pH of the swelling bath in the range

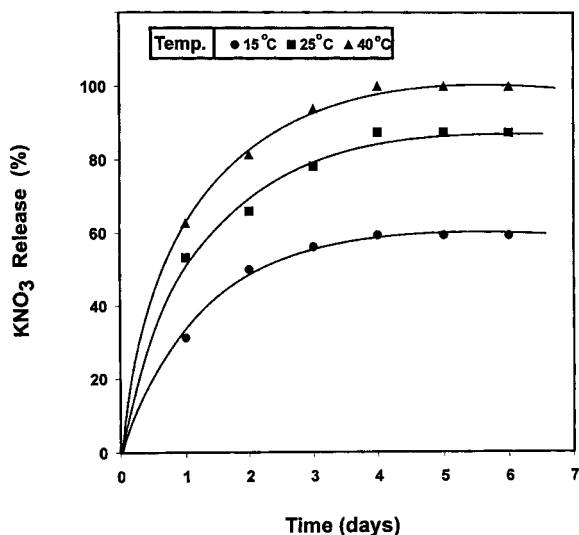


Figure 15 Effect of the temperature of the release medium on the released amount of KNO₃ for beads of fixed composition: [ST] = 50% (w/w), [SA] = 50% (w/w), [CaCl₂] = 182.5% (w/w), [epichlorohydrine] = 31.7% (w/w), pH = 7.2, and percentage loading = 30%.

TABLE II
Influence of the Composition of the Blends on the Release Mechanism of KNO₃

ST (%)	SA (%)	CaCl ₂ (%)	Epichlorohydrine (%)	<i>n</i>	<i>D</i> × 10 ⁸ (cm ² /S)	Mechanism
33.33	66.67	182.5	31.7	0.42	0.96	Fickian
42.86	57.14	182.5	31.7	0.46	0.81	Fickian
45.00	55.00	182.5	31.7	0.45	1.67	Fickian
50.00	50.00	182.5	31.7	0.45	0.60	Fickian
55.56	44.44	182.5	31.7	0.45	1.06	Fickian
58.00	42.00	182.5	31.7	0.44	0.96	Fickian
66.67	33.33	182.5	31.7	0.45	1.06	Fickian
50.00	50.00	109.5	31.7	0.45	0.96	Fickian
50.00	50.00	146.0	31.7	0.45	1.67	Fickian
50.00	50.00	182.5	31.7	0.45	1.67	Fickian
50.00	50.00	219.0	31.7	0.45	1.67	Fickian
50.00	50.00	182.5	12.6	0.45	0.35	Fickian
50.00	50.00	182.5	19.0	0.42	0.45	Fickian
50.00	50.00	182.5	25.3	0.45	0.96	Fickian
50.00	50.00	182.5	31.7	0.45	1.11	Fickian

3.0–8.0 whereas beyond pH 8.0, a decrease in the swelling ratio was obtained. In the case of the addition of electrolytes into the swelling medium, a depression in the swelling ratio was obtained. The anions Cl⁻, CO₃²⁻, and PO₄³⁻ ions exerted an almost equal influence on the swelling, whereas the cations showed an increasing order of depression in the sequence Na⁺ < Ca²⁺ < Al³⁺. A constant increase in the swelling ratio was also observed.

The polymeric beads showed a great potential for the release of KNO₃ as a model agrochemical. The release results clearly indicate that the release process was directly controlled by the swelling properties of the beads and displayed a similar type of variation in the released amount of KNO₃, as shown in their swelling ratio by the beads. Apart from the swelling qualities of the beads, the release was also influenced by the KNO₃-polymer interaction. A variation in the chemical composition of the bead resulted in a Fickian or diffusion-controlled release mechanism of KNO₃.

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