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Dynamics of Controlled Release of Potassium Nitrate from a Highly Swelling Binary Biopolymeric Blend of Alginate and Pectin

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Novel polymeric sodium alginate (Na-Alg) beads have been prepared by crosslinking Na-Alginate–pectin blend using CaCl_2 as a crosslinking agent to form biopolymeric beads. A series of beads of varying composition were prepared by varying the amounts of sodium alginate, pectin and CaCl_2 in the feed mixture. These beads were loaded with KNO_3 taking as a model agrochemical and used for release of KNO_3 . The prepared unloaded and loaded sodium alginate and pectin beads were characterized by FTIR spectral and Scanning Electron Microscopy (SEM) techniques to investigate the molecular structure and morphology of beads, respectively. The swelling experiments were performed for different compositions of beads and at varying pH and temperature of the aqueous media. The release of KNO_3 was investigated for 8 days in 25 ml of distilled water as a release medium. The release experiments were performed under static and varying experimental conditions and the release data obtained conductometrically were fitted to Ficks equation to evaluate diffusion coefficients of released potassium nitrate. 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.

Keywords calcium alginate, pectin, swelling, potassium nitrate, release

Introduction

Hydrogels are a unique class of crosslinked polymeric materials, which imbibe enormous amounts of water without dissolution when left in a water reservoir for long periods of time (1). The water sorption property of hydrogels accounts for a great number of biomedical and technological applications such as artificial implants (2), enzyme immobilization (3), contact lenses (4), tissue engineering (5), etc. Applications of hydrogels also cover the area of controlled release technology, which is being intensively used in pharmaceuticals (6) and agriculture (7). Controlled release polymer matrix systems offer a number of potential advantages over the conventional means of applications (8). The principle advantage is that these systems allow a much less active agent to be used for the desired of activity (9).

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Agrochemicals are bioactive agents used to improve the production of crops (10). The conventional application of agrochemicals can result in ground water contamination (11), which is further intensified by over application and point source contamination.

Thus, there is a need for more controlled application of agrochemicals to reduce the amounts of active ingredients without diminishing efficiency. The replacement of conventional agrochemical formulations by controlled release system 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 aim of controlled release formulations are to protect the agent supply to allow 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. Agriculture represents one of the important areas of international requirements for health, nutrition, and economic development.

One of the most alarming problems which 3/4 of the world is facing is nitrate leaching and subsequent pollution of ground water (12). The seriousness of the problem can be assessed by the fact that nitrates and nitrites are implicated in many fatal physiological disorders such as methemoglobinemia in babies (13), oral cancer (14), cancer of the colon, rectum or other gastrointestinal cancers (15), etc. Craig et al. (16) 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 compounds and a decrease in the ratio leads to an increased risk of gastric cancer. A number of approaches to remedy ground water contamination by nitrate have been taken, which include physical methods, such as reverse osmosis and nano filtration (17), chemical methods, such as catalytic removal of nitrate from water (18), abiotic degradation of nitrate using zero valent iron, and electrokinetic process(19). However, these methods are considered costly in advanced and developed countries (20). Thus, the application of nitrate-loaded carriers based on the controlled release of nitrates by swelling of the polymeric carrier could prove to be suitable technology against pollution of ground water. Recently, there has been growing considerable interest in natural polymers like sodium alginate (21), carboxymethyl cellulose (22), starch (23), chitosan (24), pectin (25), etc. due to their non-toxic and biodegradable nature. The present study is aimed at developing binary polymeric blends of calcium alginate and pectin and evaluating their potential as a controlled release device of KNO_3 selected as a model agrochemical.

Pectins are polysaccharides that act as a cellular binder in the peel of many different fruits and vegetables. Basically, they are polymers of α -D-(1-4)-linked galacturonic acid, but they also contain neutral sugars such as L-rhamnose, D-galactose, L-arabinose, D-xylose, etc. Pectins gel by calcium dication bridging between adjacent two-fold helical chains forming 'egg-box' junction zone structure in which minimum 14-20 residues can cooperate. Pectins are mainly used as gelling agents (26), but also act as a thickener, water binder, and stabilizer in many food products (27) and also find medical (28) and pharmaceutical applications (29).

Alginate is a linear polyuronate obtained from marine algae and contains variable amounts of D-manuronic acid and L-guluronic acid, which can be crosslinked by using Ca^{++} ion. Polysaccharides are very useful for application in pharmaceuticals (30, 31), biomedical (32), bioengineering (33), etc. Several properties of alginate, such as its biodegradability, nontoxicity, biocompatibility (34), immunogenicity (35), 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.

Experimental

Materials

Water soluble pectin and sodium alginate were obtained from Research Lab, Pune, India and used without pretreatment. Calcium chloride (dihydrate) (Loba Chem., Mumbai, India) was used as a crosslinker for both pectin and sodium alginate. All other chemicals used in the study were of analytical quality and triple distilled water was used throughout the experiments.

Preparation of Beads

In order to prepare polymeric beads of pectin and sodium alginate, a viscous solution was prepared by dissolving precalculated amounts of pectin and sodium alginate (SA) into a definite volume of distilled water with constant stirring. The prepared viscous solution was added dropwise into a 0.05 M CaCl₂ solution with the help of a syringe and gentle stirring, 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 prepared bio-polymeric beads were further dried at 30°C for one week and stored in airtight polyethylene bags.

Characterization of Beads

FTIR Spectral Analysis. The beads prepared as described above were characterized by recording infra red spectra of unloaded and KNO₃-loaded beads on a FTIR spectrophotometer (Perkin Elmer, 1000 Paragon).

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

Swelling Kinetics

A conventional gravimetric procedure (36) was adopted for monitoring the progress of the water sorption process. In a typical experiment, a pre-weighed quantity of beads were immersed in a definite volume of water at definite pH and temperature and taken out at predetermined time intervals. The removed swollen beads were gently pressed in between two filter papers to remove excess water and finally weighed on a digital balance (APX-203 Denver, Germany). The swelling ratio (SR) was calculated by the following Equation (1):

$$\text{Swelling ratio} = \frac{\text{Weight of swollen beads (Ws)}}{\text{Weight of the dry beads (Wd)}} \quad (1)$$

Loading of Potassium Nitrate

In the present work, the loading was performed by equilibrating pre-weight dry beads in the aqueous solution, KNO₃, in a known concentration (1% w/v) and, thereafter, dried and

weighed 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 gels of known weights were placed in a measured volume (25 ml) of distilled water (release medium) under unstirred conditions. 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, India). This was related to the amount of KNO_3 using a calibration plot. It is worth mentioning here, that in 25 ml of release medium, the values of specific conductivity were found significant, while in a lower volume of release medium, no appreciated change in conductivity was noticed. This made us select 25 ml of distilled water as a release medium. Similarly, the equilibrium release (M_∞) of KNO_3 was determined by measuring the conductivity of the release medium after 5 days. In order to gain an insight into the operative release mechanisms, the following equation based on Ficks law, applicable to a spherical device, may be used (37, 38).

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

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, k is the swelling front factor, n is the release exponent, and r being the radius of the dry spherical bead. The value of n determines the nature of the release mechanism, i.e., $n = 0.43$ is Fickian diffusion. 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 $n = 0.85$, the release mechanism is said to be Case II.

Statistical Analysis

All release experiments were performed at least three times, and the plots were drawn, taking average values of the released amounts. The standard deviation (S.D.) values have also been included in the respective curves as error bars.

Results and Discussion

Characterization of Beads

FTIR Spectra. The FTIR spectra of unloaded and KNO_3 -loaded beads are shown in Figure 1(a) and (b), respectively, which clearly confirm the presence of pectin, alginate, and KNO_3 in the loaded beads as discussed below.

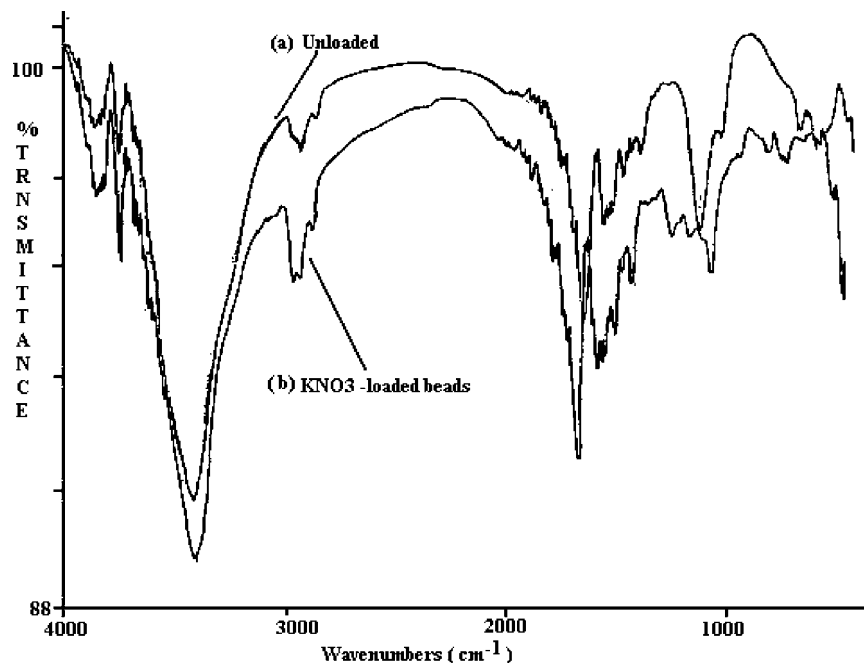


Figure 1. FTIR spectra of (a) unloaded and (b) KNO_3 loaded binary polymeric beads.

The evidence of pectin comes from the peaks observed at 3750 cm^{-1} and 3870 cm^{-1} (due to O–H stretching (39), 2956 cm^{-1} due to C–H stretching, 1642 cm^{-1} ($\delta(\text{O–H})$ bending of absorbed water), and 1031 cm^{-1} (C–O stretching). The spectra clearly marks the presence of alginate as confirmed by O–H stretching of hydroxyls at 3424 cm^{-1} and $\text{C}(=\text{O})_2$ stretching of carboxylate ion. The spectra (b) also confirms the presence of KNO_3 within the bead as is evident from vibrational frequency of nitrate ion at 1380 cm^{-1} . It is worth mentioning here that the above bands have been observed at slightly shifted wave numbers, which confirm the blend nature of the material as reported elsewhere.

SEM Analysis. Morphology of the surfaces of the unloaded and loaded blends has been investigated by recording their SEM images as shown in Figure 2(a) and (b), respectively. It is clear from micrograph (a), that the mixing of sodium alginate and pectin does not produce a homogeneous blend as is evident from the uneven surface and aggregated domains of the constituent bio-polymers. A possible reaction for the observed heterogeneous morphology could be the anionic nature of both biopolymers, which due to electrostatic repulsion, may not permit perfect mixing. Loading potassium nitrate onto the blends results in the formation of cracks on the blend surfaces as depicted in micrograph (b). The developed cracks may be attributed to the enhanced repulsive forces within the blend, due to the loading of KNO_3 .

Modeling of Release Mechanism

In the present study, the KNO_3 loaded beads of a polymeric blend of crosslinked pectin (P) and sodium alginate (SA) could be visualized as a network of macromolecular chains of

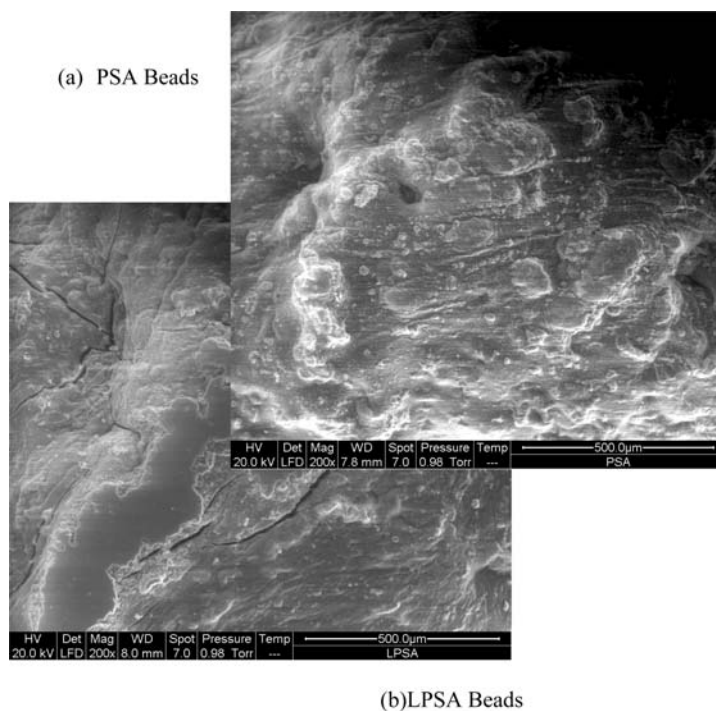


Figure 2. Scanning electron micrographs (SEM) of (a) unloaded, and (b) KNO_3 loaded beads.

pectin and SA 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 bead comes in contact with a still aqueous release medium, the penetrant 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 (40) (Figure 3). Just ahead of the front, the presence of the solvent plasticizes the polymer and causes it to undergo a glass to rubber transition (41). 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 ($R_{\text{diff}(\text{KNO}_3)}$) is slower than 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 (and subsequent release of KNO_3 into the outer medium). Thus, $R_{\text{diff}(\text{KNO}_3)}$ 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.

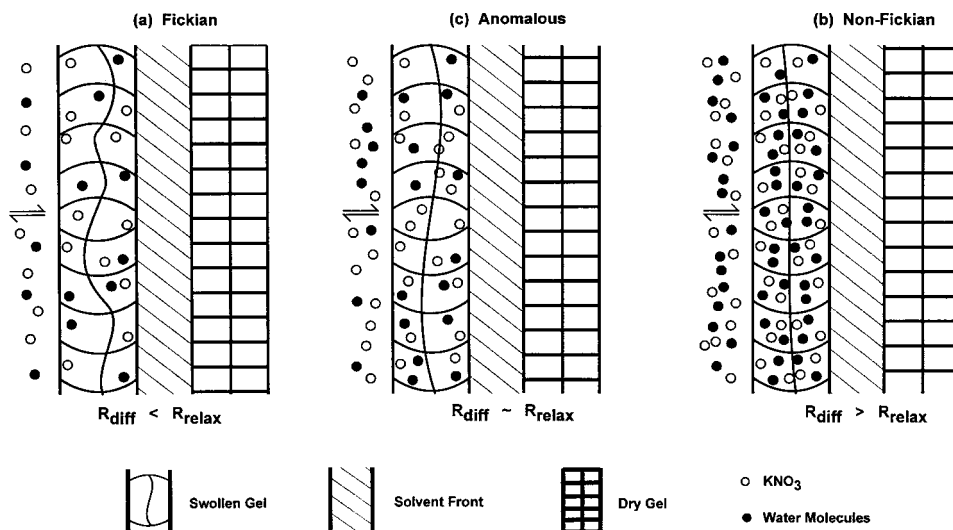


Figure 3. A hypothetical model depicting (a) Fickian, (b) anomalous, and (c) non-Fickian release of KNO_3 .

- iii. In an intermediate situation, the two rates, i.e. $R_{\text{diff}(\text{KNO}_3)}$ and R_{relax} may be nearly equal, and this is called an ‘anomalous diffusion’ or simply non-Fickian diffusion.

The above three situations are modeled in Figures 3(a), (b) and (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 it is also regulated by the physical forces and subsequent elastic responses of the constituent macromolecular chains of the matrix. According to Flory’s swelling theory (42), the following equation can be given for the swelling ratio (Q),

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

where i/V_N is the concentration of the fixed charges 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 a direct relation to ionic osmotic pressure, crosslinked density and the affinity of the hydrogel for water. Therefore, the swelling of a hydrophilic macromolecular matrix can be controlled by varying its chemical composition.

Effect of Pectin

Pectin (Figure 4(a)) is a polysaccharide that contains a different type of hydrophilic functional groups. When the concentration of pectin is increased in the reaction mixture of the hydrogels in the range of 37.50–71.00% (w/w), the swelling ratio is found to increase

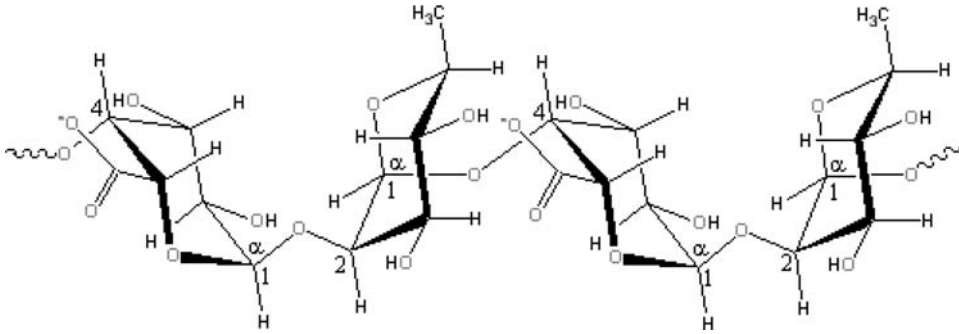


Figure 4a. Structure of pectin.

substantially as shown in Table 1. The observed increase in swelling ratio can be explained by the fact that increased pectin contained in the hydrogel renders the network more hydrophilic so that when the polymer matrix contacts the dissolution medium, the molecules of water penetrate the gel and swells the macromolecular chains. Molecularly, individual chains, originally found in their unperturbed state, absorbed water so that their end-to-end distance and radius of gyration expand to a new solvated state.

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 28.58% to 62.50%. The results are presented in Table 1, which clearly indicate that whereas the swelling ratio initially increases up to 60.0% of sodium alginate, it decreases with a further increase in concentration. The observed findings may be attributed to the fact that alginate is an anionic polymer, and its increasing concentration in the bead produces a greater number of carboxylate ions along its molecules since enhanced

Table 1
Data showing the effect of composition of the blend on its equilibrium swelling ratio

Pectin (%)	Sodium alginate (%)	CaCl ₂ (M)	Equilibrium swelling ratio
37.50	62.50	0.05	4.2
42.86	57.14	0.05	11.6
50.00	50.00	0.05	12.6
60.00	40.00	0.05	13.0
66.00	33.34	0.05	13.8
71.00	28.58	0.05	14.0
60.00	40.00	0.02	20.0
60.00	40.00	0.05	13.0
60.00	40.00	0.08	8.0
60.00	40.00	0.10	6.0

repulsions between $-\text{COO}^-$ ions cause the network chains to undergo a larger relaxation. This obviously allows a greater number of water molecules to enter the bead and results in an increased swelling. However, beyond 60.0% of sodium alginate, when the concentration of alginate becomes high, the increased number of alginate chains produces a dense network, which permits less number of water molecules into the beads, and thus results in a decreased swelling.

Effect of CaCl_2

Calcium chloride is a well-known crosslinking agent of alginate, as well as pectin. The acid group in pectin can react with calcium ion, which have two positive charges, and can link two acid anion groups with negative charges. The crosslinking of pectinate molecules occurs according to a egg box model (43). A calcium pectinate gel network incorporates two solubilizing features-rhamnosyl "Kinks" and estrification. (Figure 4(b) egg box model).

In the present work, the effect of a crosslinker on water sorption capacity of blend has been studied by varying the concentration of calcium chloride in the range 0.02 to 0.10 M. The results are summarized in Table 1, which clearly indicate that the degree of water sorption constantly increases to 0.10 M. The observed initial rise in the swelling ratio may be attributed to the fact that with an increasing number of calcium ions in the crosslinking bath, the alginate beads containing a larger cavity are produced, which could accommodate a greater amount of water. This obviously results in a greater swelling of bio-polymeric beads.

Effect of pH

Macromolecular matrix containing either carboxyl groups or carboxylate ions as pendent functionals of network chains have been found to respond greatly to the external stimuli such as the pH of the swelling medium. In the present study, since the polymer used was the sodium salt of pectin, the network contains both $-\text{COO}^-$ and $-\text{COOH}$ groups along the pectin chains. In the present study, where sodium alginate is of an anionic nature, the pH effect has been investigated on the swelling ratio of the beads in the pH range 3.0 to 10.0. The results are shown in Table 2, which indicate an increase in the swelling ratio that can be explained by the fact that with a rising pH of the swelling medium, the ratio of $-\text{COO}^-/-\text{COOH}$ on pectin also increases because of increasing ionization of carboxylic groups. This results in a greater repulsion among the $-\text{COO}^-$ bearing pectin

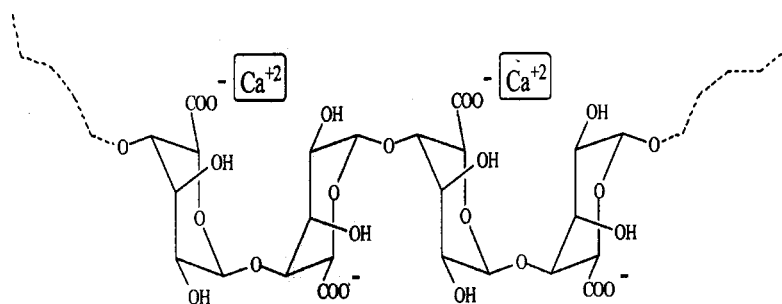


Figure 4b. Structure of calcium alginate (egg-box model).

Table 2
Data showing the influence of composition of the blend on the release mechanism of KNO_3

Pectin (%)	Sodium alginate (%)	CaCl_2 (M)	n	$D \times 10^8$ ($\text{cm}^2 \text{S}^{-1}$)	Mechanism
37.50	62.50	0.05	0.40	1.42	Nearly Fickian
42.86	57.14	0.05	0.45	1.71	Fickian
50.00	50.00	0.05	0.35	0.15	Nearly Fickian
60.00	40.00	0.05	0.42	1.52	Nearly Fickian
66.00	33.34	0.05	0.38	1.28	Nearly Fickian
71.00	28.58	0.05	0.45	1.71	Fickian
60.00	40.00	0.02	0.45	1.71	Fickian
60.00	40.00	0.05	0.42	1.52	Nearly Fickian
60.00	40.00	0.08	0.45	1.71	Fickian
60.00	40.00	0.10	0.45	1.71	Fickian

chains. It is clear from Figure 5 that the swelling ratio increases up to pH 8.0, while beyond it, a decrease is observed. The results may also be explained by the fact that with an increasing pH of the swelling medium, the extent of ionization of the carboxylic groups of alginate also increases, which produce a greater number of carboxylate ions along the alginate molecules. These anionic charged centers repel each other and produce a larger relaxation in network chains, which facilitate inclusion of water molecules into the bead 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 which may be attributed to the fact that at a higher alkaline range ($\text{pH} > 8.0$), the network chains acquire a greater charge density, which restrict the entrance of polar penetrant water molecules into the bead and, thus the swelling ratio decreases.

Effect of Salts

The presence of an electrolyte in a swelling medium is of importance in the agriculture and biomedical fields, viz., water reservoirs in agriculture. 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 (42):

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

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 the greater the difference between the concentration of mobile ions inside and outside the gel, the larger osmotic pressure would be 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 (0.05 M) and chlorides of cations (0.1 M) to the swelling bath, respectively. The results are shown in Figures 6 and 7, which indicate that in both cases the swelling ratio constantly decreases. The figures also reveal that various

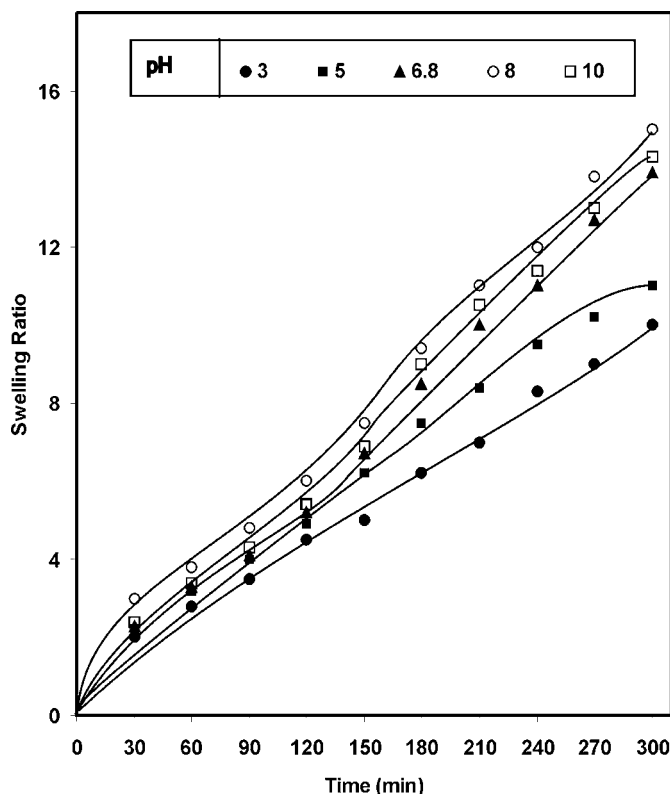
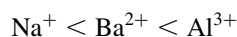


Figure 5. Effect of pH of the swelling medium on the swelling ratio of the beads of fixed composition, [Pectin] = 60% (w/w), [sod. alginate] = 40% (w/w), [CaCl₂] = 0.05 M, Temp. = 30 ± 0.2°C.

anions exert an almost identical impact on the swelling ratio and the effectiveness of cations increases in the following sequence:



The observed results may be explained as below.

The addition of salts into the swelling medium increases the term C_i^s in Equation (6), which in turn decreases the osmotic pressure (π_{ion}) and thus, causes a fall in the swelling ratio. In the case of anion addition, because of their negative charges, the added anions 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 largest and Al^{3+} is the smallest ion, a greater diffusivity is expected with Al^{3+} ions, which deshield the coulombic repulsive forces inside the bead network and cause shrinking of the gel. This obviously produces the largest swelling with Al^{3+} ions. The larger Na^+ ions may diffuse into the bead in a smaller number and cause a lower degree of shrinking effect.

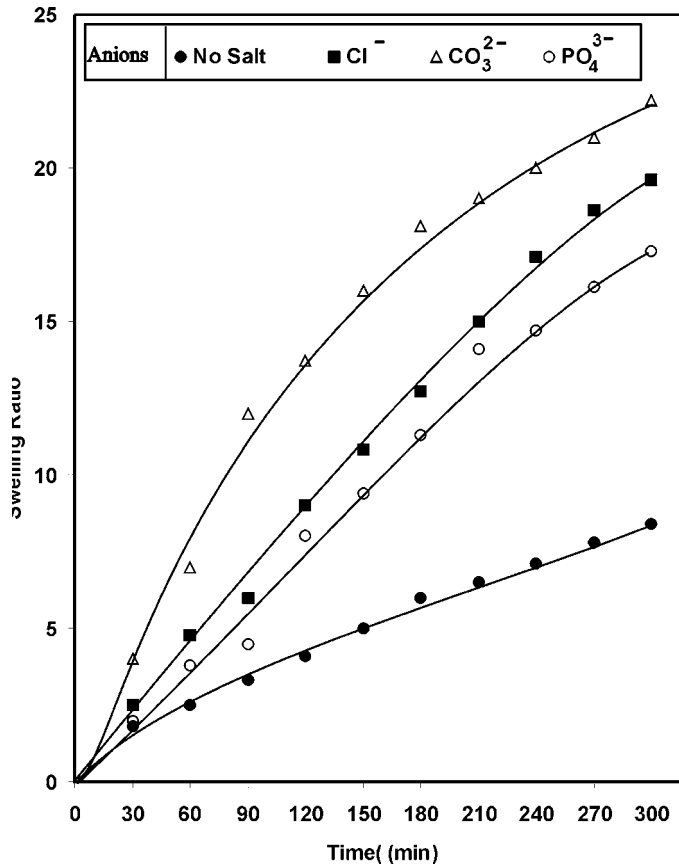


Figure 6. Effect of addition of anions to the swelling medium on the swelling ratio of the beads of fixed composition, [Pectin] = 60% (w/w), [sod. alginate] = 40% (w/w), [CaCl₂] = 0.05 M, pH = 6.8, Temp. = 30 ± 0.2°C.

Effect of Temperature

The effect of temperature on the swelling ratio of the beads has been investigated by varying temperature of the swelling medium in the range 15 to 40°C. The results are displayed in Figure 8, which imply that the swelling ratio constantly increases with increasing temperature. The results may be attributed to the fact that a higher temperature results in both greater diffusion of water molecules and larger relaxation of network chains, which as a consequence enhance the swelling ratio of the beads.

A more quantitative information may be obtained by applying Clausius-Clayperon equation, according to which (44):

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

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 negative slope is obtained which implies for an endothermic process. The value of ΔH_m was calculated to be 1.37 Kcal/mole.

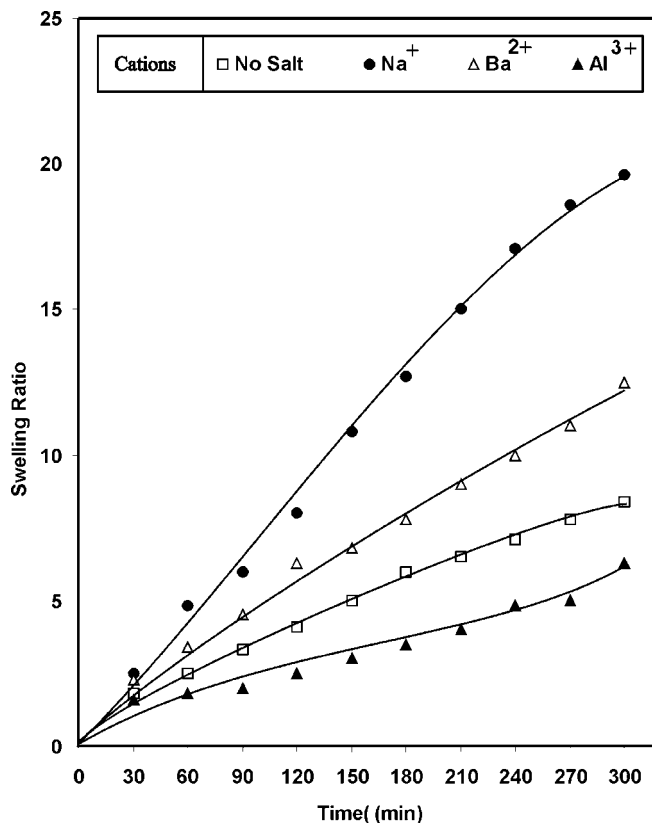


Figure 7. Effect of addition of cations to the swelling medium on the swelling ratio of the beads of fixed composition, [pectin] = 60% (w/w), [sod. alginate] = 40% (w/w), [CaCl₂] = 0.05 M, pH = 6.8, Temp. = 30 ± 0.2°C.

Release Study of KNO₃

An important object of the prepared biopolymeric beads is to study the release of an active agent from swellable polymeric matrix, which is based on the glassy–rubbery transition of the polymer occurring as a result of imbibing water into the matrix (45). Whereas, the interaction between water, polymer, and active agent are the primary factors in the controlled release. The release process is also affected by various other factors, such as the dissolution of the surface area, molecular size and permeability of the diffusate molecules.

The release kinetics of a loaded hydrogel is clearly related to its water sorption kinetics. It has been already established that a highly swelling hydrogel should release a greater amount of solute entrapped within the biopolymeric bead. The release of solute from a loaded bead (initially dried at 30°C for 3 days) involves the absorption of water into the matrix and simultaneous release of solute via diffusion, as governed by Ficks law. The process can be modeled using a free volume approach or a swelling controlled release mechanism.

Effect of Percent Loading

One of the primary factors in the use of a hydrogel as the carrier of an active compound is the effect of percent loading on the rate of solute release. For this purpose, the beads were

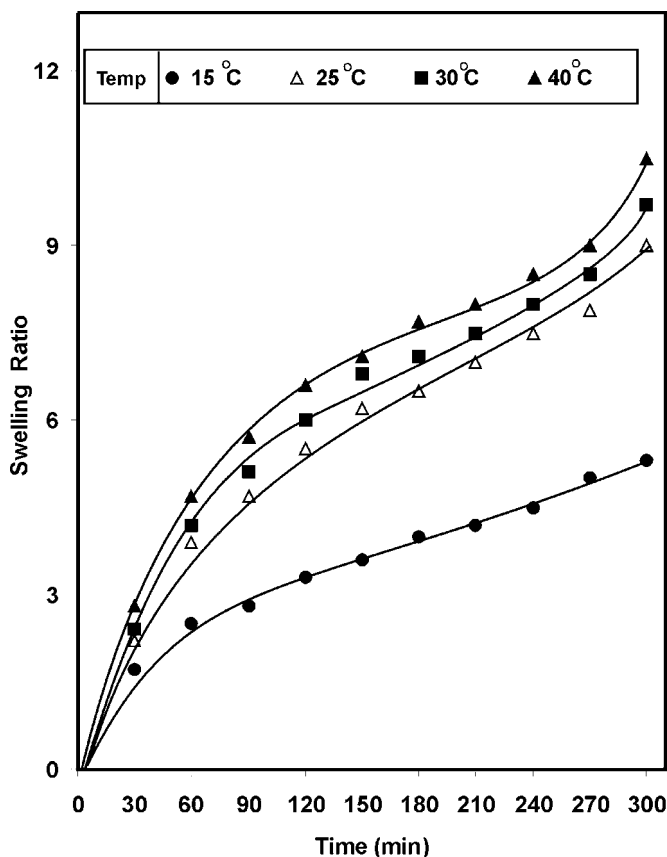


Figure 8. Influence of temperature on the swelling ratio of the beads of fixed composition, [pectin] = 60% (w/w), [sod. alginate] = 40% (w/w), [CaCl₂] = 0.05 M, pH = 6.9.

equilibrated with a KNO₃ solution of varying concentrations (0.6 to 1.0% w/v) for 1 day. The loaded beads of definite composition (pectin 60.0%, SA 40.0%, and CaCl₂ 0.05 M) were mildly agitated in a release medium and the progress of the release process was monitored conductometrically. The release profiles (Figure 9) indicated that the amounts of KNO₃ released increases with increasing percent loading of the hydrogels. The results are as expected, because the larger the initial load, the faster the movement of the solvent front penetrating the surface of the loaded bead (46). A larger loading of the hydrogel may also facilitate the relaxation of macromolecular chains because of enhanced repulsion between the ionic species within the network.

Effect of Pectin

The effect of the pectin content in the loaded hydrogel and its release behavior is shown in Figure 10, which reveals that the amount of released KNO₃ increases when the pectin content increases in the feed mixture in the 50.0–71.4% range. The progress of the release process was monitored conductometrically. The results are shown in Figure 10, which indicate that the release rate, as well as the amounts of released KNO₃, increase with increasing pectin. The increase observed in the released rate with increasing pectin

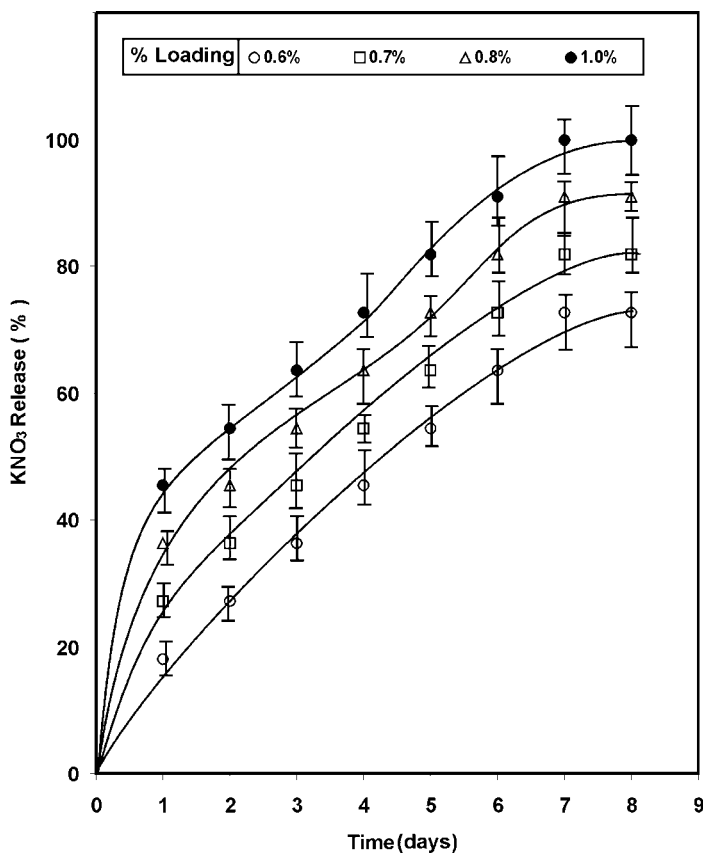


Figure 9. Effect of % loading of beads on released amount of KNO_3 for fixed composition of the [pectin] = 60% (w/w), [sod. alginate] = 40% (w/w), $[\text{CaCl}_2]$ = 0.05 M, pH = 6.8, Temp. = $30 \pm 0.2^\circ\text{C}$.

content in the bead may be explained by the reason that pectin is a hydrophilic biopolymer and therefore, its increasing concentration in the bead results in a greater hydrophilicity of the polymer network, which consequently absorbs a large amount of water. Thus, the greater amount of absorbed water results in large relaxation of network chains, which finally results in increasing the release of KNO_3 . Another reason may be that since pectin is also an anionic biopolymer like alginate. Therefore, their presence together in the beads produces electrostatic repulsions among the network chains which facilitates expulsion of KNO_3 into the release medium.

Another notable observation from the release profiles is that a 'burst-effect' is obtained after the first day, which could be due to the reason that during the device preparation KNO_3 migrates to the surface and when the dried and loaded bead is put in the release medium there occurs an instantaneous release of KNO_3 thus producing a 'burst-effect'.

Effect of Sodium Alginate

When the sodium alginate is varied in the 37.5%–60.0% (w/w) range in the feed mixture of the loaded beads the amount of released KNO_3 decreases with increase of sodium

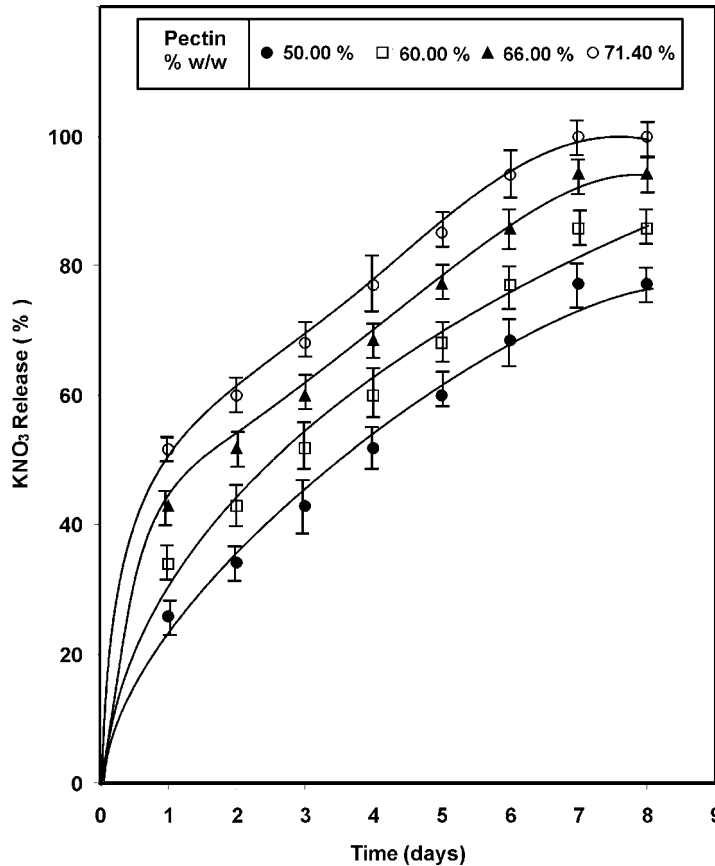


Figure 10. Effect of pectin content in the bead on the released amount of KNO_3 for fixed composition of beads, [sod. alginate] = 40% (w/w), $[\text{CaCl}_2]$ = 0.05 M, pH = 6.8, Temp. = $30 \pm 0.2^\circ\text{C}$, % loading = 30%.

alginate. The results shown in Figure 11 can be attributed to the fact that a largely cross-linked bead produces a matrix with small mesh sizes of the free volumes 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 the 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 becomes relatively slower and 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 slow relaxation rate of macromolecular chains of the loaded beads of SA which will obviously result in a suppressed release kinetics.

Effect of Calcium Chloride

The effect of CaCl_2 , which is a crosslinker of both sodium alginate and pectin, has been investigated on the release profile of KNO_3 by varying the concentration of CaCl_2 solution in the range 0.02 M to 0.10 M. The results are depicted in Figure 12, which clearly indicate that with an increasing crosslinking concentration (0.02 M to 0.10 M)

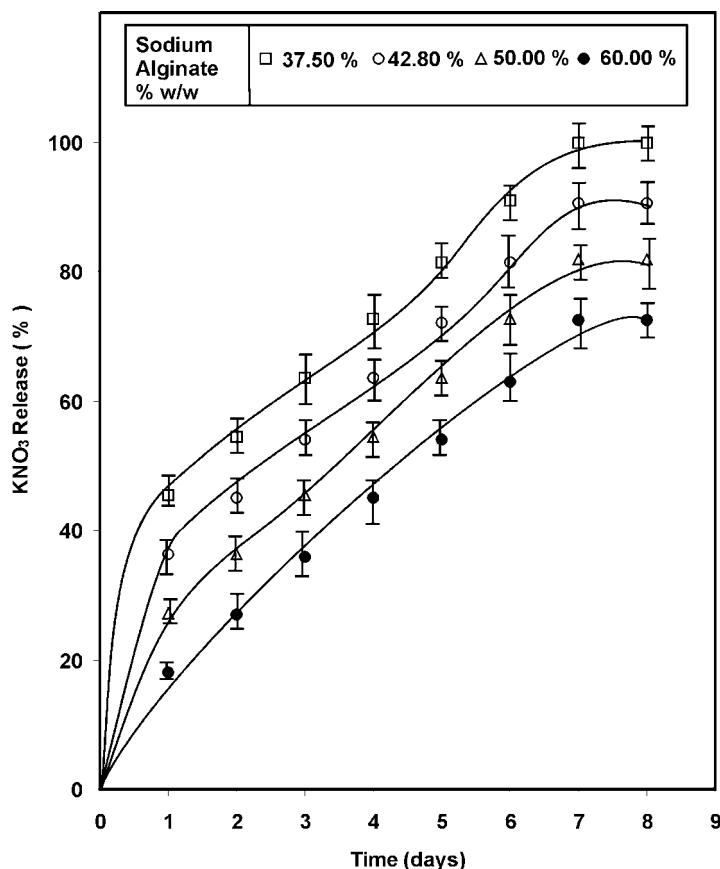


Figure 11. Effect of sodium alginate content in the bead on the released amount of KNO_3 for fixed composition of beads [pectin] = 60% (w/w), $[\text{CaCl}_2]$ = 0.05 M, pH = 6.8, Temp. = $30 \pm 0.2^\circ\text{C}$, % loading = 30%.

the release rate of KNO_3 constantly decreases. The reason for the observed decrease is consistent with swelling results. Some workers (47) reported an increase in the glass transition temperature (T_g) of the polymer with increasing crosslink density and thus, a glassy nature of the matrix does not permit loosening of the macromolecular chains, which results in lower water sorption with concomitant slow release kinetics.

Another important consideration could be the possible interaction between the KNO_3 and calcium ions within the bead network. With an increasing concentration of Ca^{2+} ions in the crosslinked beads the nitrate ions interact favorably 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.

Effect of pH

The effect of pH on the release of KNO_3 has been investigated by varying the pH of the release medium in the range 3 to 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

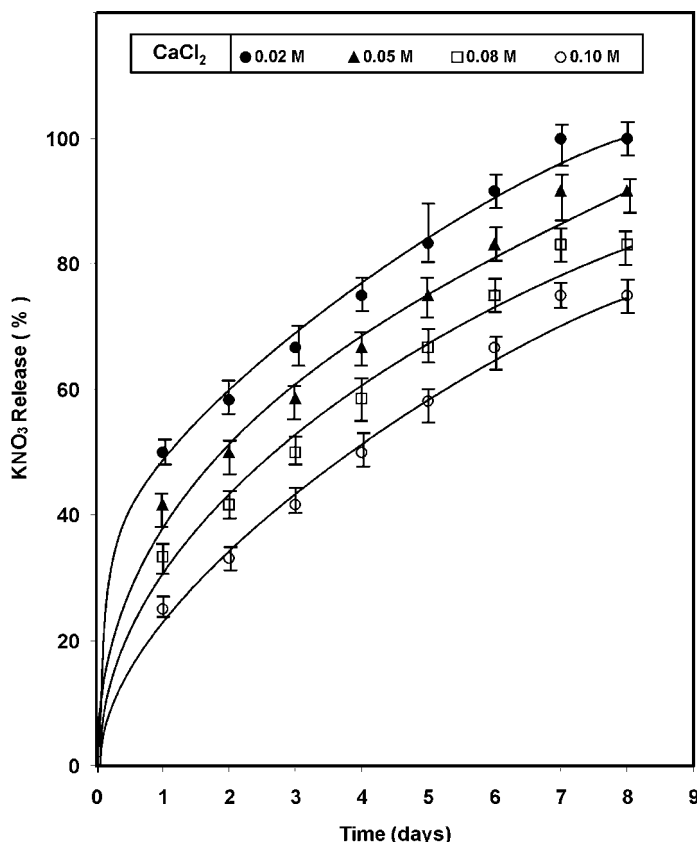


Figure 12. Effect of CaCl_2 content in the bead on the released amount of KNO_3 for fixed composition of bead, [Pectin] = 60% (w/w) [sod. alginate] = 40% (w/w), pH = 6.8, Temp. = $30 \pm 0.2^\circ\text{C}$, % loading = 30%.

fall is observed beyond pH 8.0, i.e., in the higher alkaline range. One of the possible explanations of the observed findings is due to the similar type of swelling behavior of the beads as discussed previously.

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 less relaxation of bead chains and results in a lower release of KNO_3 . When the pH of the solution increases, the lower concentration of H^+ ions produces relatively more relaxation of alginate chains and results in an enhanced release of KNO_3 . However, at a much higher pH, i.e., beyond 8.0, a 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 15 to 40°C range, 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

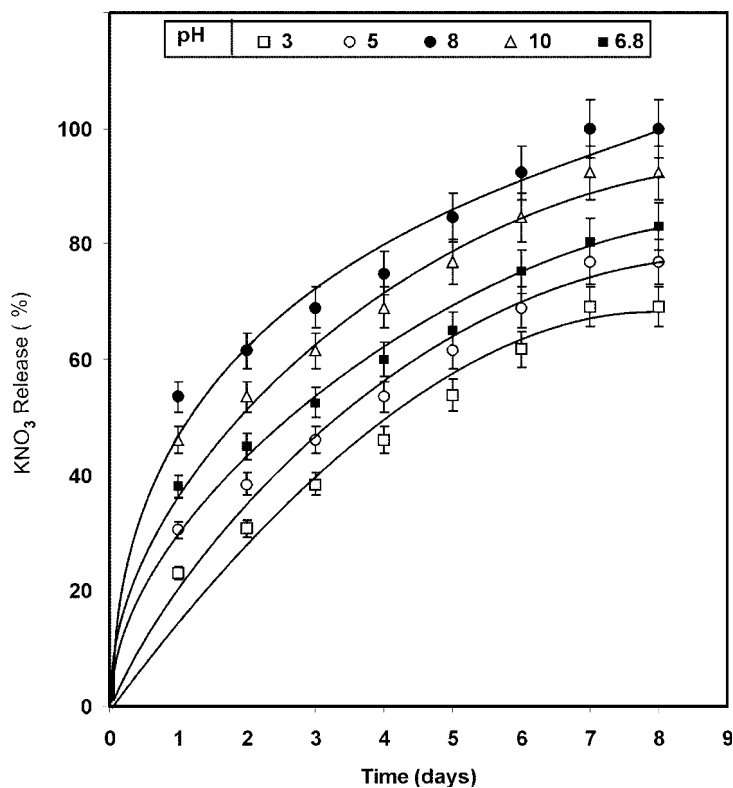


Figure 13. Effect of pH of the release medium on the released amount of KNO_3 for fixed composition of bead, [pectin] = 60% (w/w) [sod. alginate] = 40% (w/w), $[\text{CaCl}_2] = 0.05 \text{ M}$, Temp. = $30 \pm 0.2^\circ\text{C}$, % loading = 30%.

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 Equation (7) to the release process, the value of ΔH_{rel} may be calculated with the help of the linear plot drawn between $\ln M_\infty$ 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 0.93 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 2, which clearly indicate that in all the cases of bead compositions, the value of n is almost 0.50, which indicates a Fickian diffusion, i.e., diffusion controlled release mechanism.

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 pectin, alginate and CaCl_2 concentration, the rate of relaxation of macromolecular chains is not affected to that extent which can make it a rate determining step. Thus,

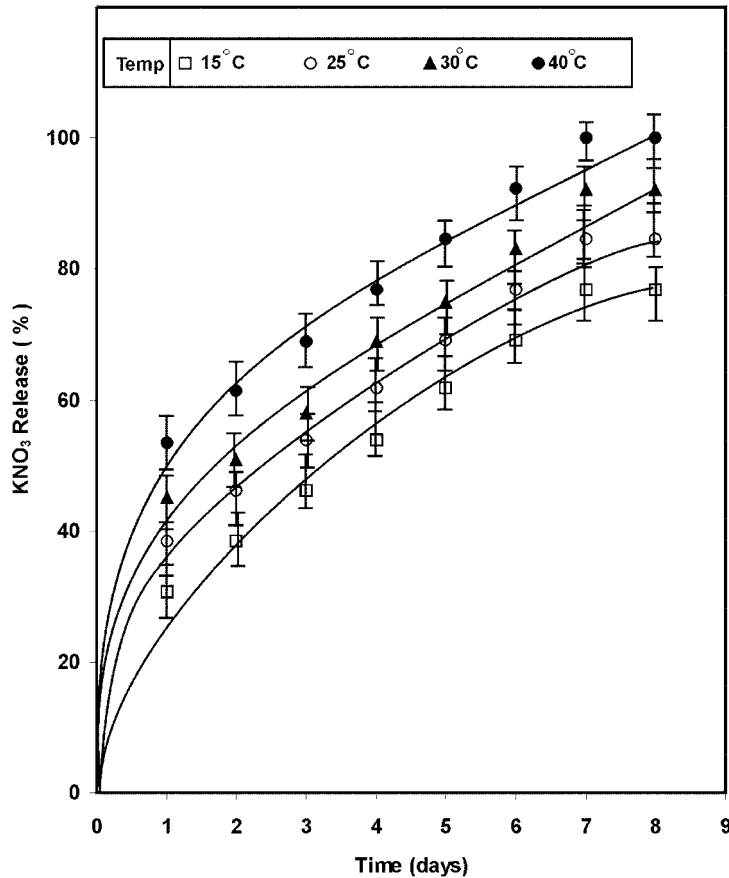


Figure 14. Effect of temperature of the release medium on the released amount of KNO_3 for fixed composition of bead, [pectin] = 60% (w/w) [sod. alginate] = 40% (w/w), $[\text{CaCl}_2] = 0.05 \text{ M}$, $\text{pH} = 6.8$, %loading = 30

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 bio-polymeric bead of sodium alginate and pectin by calcium chloride produces a hydrophilic matrix in the form of a bead. The resulting beads possess a multi-layered morphology with cracks on their surfaces.

The binary bio-polymeric beads display a fair affinity for water sorption, which greatly depends on the chemical architecture of the beads. When the pectin concentration varies in the 50.0% to 71.4% range, the swelling ratio simultaneously increases up to 71.4% of pectin. A similar type of swelling behavior is shown by the bead when the other component, sodium alginate varies between 37.5% to 60.0%, in the feed mixture of the beads. The crosslinkers show different results. When CaCl_2 varies between 0.02 M to 0.10 M, the degree of water sorption increases up to 0.10 M.

The swelling ratio of the bead increases with an increase in the pH of the swelling bath in the 3.0 to 8.0 range, while beyond pH 8.0, a decrease in 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 $\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}$. A constant increase in swelling ratio is also observed.

The bio-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 displays a similar type of variation in the released amount of KNO_3 with varying experimental conditions 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 .

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