Carrageenan-based semi-IPN nanocomposite hydrogels: Swelling kinetic and slow release of sequestrene Fe 138 fertilizer
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ABSTRACT
Nanocomposite hydrogels based on kappa-carrageenan were synthesized by incorporating natural sodium montmorillonite (Cloisite) nanoclay. Acrylamide (AAm) and methylenebisacrylamide (MBA) were used as a monomer and a crosslinker, respectively. Effects of reaction variables on the swelling kinetics were studied. The results revealed that the rate of swelling for nanocomposites with high content of MBA was higher than those of nanocomposites consisting of low content of MBA. Similar to the effect of MBA, the rate of swelling enhanced as the carrageenan content was decreased. The influence of clay content on swelling rate was not remarkable. The experimental swelling data were evaluated by pseudo-first-order and pseudo-second-order kinetic models. The swelling data described well by pseudo-second-order kinetic model. Sequestrene Fe 138 (Sq) as an agrochemical was loaded into nanocomposites and releasing of this active agent from nanocomposites was studied. The clay-free hydrogel released the whole loaded Sq; whereas the presence of clay restricted the release of Sq.

INTRODUCTION
Hydrogels as a crosslinked or partially crosslinked polymeric matrix, exhibit extensive hydrogen bonding between polymeric chains and water to stabilize a three-dimensional network (Chen et al. 2004). The water sorption of hydrogels as well as their unique behaviors opens a lot of applications in different fields e.g., medicine, pharmaceutical, agriculture, biotechnology, waste water treatment, etc. (Chen et al. 2004; Kaplan and Kasgoz 2011).

Many industrial sources lead to pollute of groundwater. But, evidence reveals that agriculture is a major contributor of groundwater contamination. For instance, highly water soluble potassium/ammonium nitrate are mostly consumed as nitrogen fertilizers. During irrigation of agricultural land, the water dissolves the nitrate fertilizer. Because of negatively charge on the both nitrate and soil solid, nitrate is not attracted onto soil solid. So, solution containing nitrate moves freely through soil strata and subsequently, it will be caused to contaminate the groundwater (SE-IK 1992).

Because of their water retention property and subsequently, the slow release of water from swollen hydrogels, hydrogels with high swelling capacity are of special interest as potential water retainer systems for agriculture fields. Also, the slow release of water from the polymeric matrix opens another potential area of application that is related to load of agrochemicals into hydrogels. In the swollen hydrogels containing agrochemicals, not only the water releasing takes place, but also the agrochemical will be released together with water. Therefore, by loading of agrochemical into hydrogels, the utilization efficiency of water and agrochemical is improved (Zhang et al. 2006). Recently, hydrogels as agrochemical carriers have been used to slow or controlled release of fertilizers (Abd El-Mohdy 2007; Mahdavinia et al. 2009), herbicides (Li et al. 2008; Li et al. 2009), and pesticides (Darvari and Hasirci 1996; Rudzinski et al. 2003).

The higher production cost and low gel strength of these hydrogels, however, restrict their application widely. To improve these limitations, inorganic compounds with low cost can be used.
The introduction of inorganic fillers to a polymer matrix increases its strength and stiffness properties. Among inorganic compounds, special attention has been paid to clay minerals in the field of nanocomposites because of their small particle size and intercalation properties. Nanocomposite hydrogels based on synthetic or natural polymers have been widely investigated (Okay and Oppermann 2007; Deng et al. 2008).

In the previous work (Mahdavinia et al. 2009), we reported synthesis of carrageenan-based Semi-IPN nanocomposite hydrogel. The effect of reaction variables and salt solution on the swelling, as well as water retention capacity of nanocomposites under heating has been investigated. In this part of our work, we attempt to study swelling kinetics of carrageenan-based Semi-IPN nanocomposite hydrogels and their application for releasing of sequestrene Fe 138 (Sq) (Scheme 1) as agrochemical. Sq is a chelated iron product that is used for iron deficient plants in alkaline and calcareous soils (Davenport 1983). The chelating agent in Sq is ethylenediamine di-O-hydroxyphenyl acetic acid. The effect of reaction variables and salt solution on the release kinetics of Sq was studied.

**Scheme 1. Structure of Sequestrene Fe 138.**

**MATERIALS AND METHODS**

**Materials**

kappa-Carrageenan (Carra) was obtained from Condinson Co., Denmark. N,N-methylenebisacrylamide (MBA) and ammonium persulfate (APS) from Fluka, and acrylamide (AAm) from Rotterdam, the Netherlands, were of analytical grade and were used as received. Sq was supplied from Fronboon International Company (China). Natural sodium-montmorillonite (sodium Cloisite, Na-MMt) as a clay with cation exchange capacity of 92 meq/100 g of clay was provided by Southern Clay Products. All other ingredients were analytical grades and were used as received.

**Synthesis of Nanocomposite Hydrogels**

Table 1 shows the reaction variables contents used to synthesize of the nanocomposite hydrogels. The suffix m, n, and z in Clay, Carra, and MBAz are wt% of Clay and Carra, and mmol of MBA, respectively. In general, clay was dispersed in 30 mL of distilled water and sired under magnetic stirrer for 24 h. Dispersed clay solution was transferred in a one-liter reactor equipped with mechanical stirrer. To control the reaction temperature, the reactor was placed in a water bath preset at 60 °C. Then, 0.5 g of Carra was added to the solution containing clay and stirred for 2 h until completion of dissolution. AAm and MBA (MBA dissolved in 3 mL of water) were simultaneously added into solution and allowed to stir for 1 h. It may be noted that the synthesis of nanocomposite hydrogels was carried out under air condition (Mahdavinia et al. 2009). Finally, APS (0.05 g in 2 mL of water) as initiator was added into solution and stirred for 3 min. After this time, the solution was transferred into a test tube (interior size: 12 mm in diameter and 160 mm long) and was kept in an oven at 60 °C for 4 h. The nanocomposite hydrogels were cooled to ambient temperature and cut into discs with 0.5 cm long. For removing the un-reacted substrates, the hydrogels were immersed in excess amount of de-ionized water for 6 days with daily refreshment of water. After this time, the purified hydrogels discs were dried at ambient temperature for 1 week.

**Swelling Study**

Dried nanocomposite discs were used to determine the degree of swelling. The equilibrium swelling (ES) was determined by immersing the
nanocomposite hydrogels (~0.2 g, two discs of dried nanocomposites) in distilled water (100 mL) or saline solutions (0.15 M of CaCl₂ or NaCl) and was allowed to swell for 72 h at room temperature. The swelling data are illustrated in Table 1 and the results have been discussed in our previous work (Mahdavinia et al. 2009). After this time, they were removed from the water, blotted with filter paper to remove surface water, weighed and the ES was calculated using Eq (1):

\[
ES = \frac{(W_s - W_d)}{W_d}
\]

where \(W_s\) and \(W_d\) are the weights of the samples swollen in water and in dry state, respectively. For studying the swelling kinetics of the nanocomposites, a certain amount of samples (~0.2 g, two discs of dried hydrogels) was poured into weighed tea bags and was immersed into 200 ml distilled water. At consecutive time intervals, the water absorbency of the nanocomposites was measured according to the above mentioned method.

To evaluate the reaction yields, a part of samples were not purified. The un-purified samples were dried and the gel content of samples was examined. For this purpose, a known amount of dried sample was weighed \((W_{dp}, \text{g})\) and immersed into excess water for 6 days with daily refreshment of water. After this time, the purified hydrogel discs were dried in an oven at 60 °C for 1 week \((W_{dp}, \text{g})\). The gel content was calculated according to Eq 2:

\[
\text{Gel Content} (\%) = \frac{(W_d - W_{dp})}{W_d}
\]

Where \(W_d\) and \(W_{dp}\) are the weights of un-purified and purified samples (g).

**Loading and Release of Sequestrene**

Loading of Sq as active agent into nanocomposites was carried out by immersing dried nanocomposite discs into 15 mL of 4% wt of Sq solution and allowed to swell for 4 days. Then, loaded nanocomposites were withdrawn and dried at ambient temperature for 10 days. To sure drying of loaded nanocomposites, they were kept in an oven at 50 °C for 3 days. For estimation of the percentage of loaded Sq, after withdrawing loaded hydrogel, the volume of remained solution was reached up to 15 mL by adding distilled water and loading content was estimated using UV spectrophotometer method. Distilled water and solutions of 0.15 M of calcium and sodium chloride salt were chosen as a release medium to study the percentage release of Sq. In general, dried Sq loaded nanocomposites were immersed in 200 mL deionized water or salt solutions under unstirred condition. At intervals, the amount of released Sq was evaluated using UV spectrophotometer at 480 nm. The percentage of released Sq was determined from the calibration curve.

**Instrumental Analysis**

For SEM studies, purified hydrogel nanocomposites were coated with a thin layer of gold and imaged in a SEM instrument (Philips, XL30). One-dimensional, wide angle X-ray diffraction patterns were obtained by using a Siemens D-500 X-ray diffractometer with wavelength, \( \lambda = 1.54 \AA \) (Cu-Kα), at a tube voltage of 35 KV, and tube current of 30 mA. A thermal analyzer (TA60, Shimadzu) was used for differential scanning calorimetry (DSC) under nitrogen. The heating rate was 10°C/min. An UV-Visible (UNICO, 2102 Series) was used to study release of Sq. The FTIR spectra were performed using UNICUM 4600 spectrophotometer (KBr pellets).

**RESULTS AND DISCUSSION**

**Synthesis and Characterization**

Nanocomposite hydrogels based on kappa-carrageenan were synthesized using solution polymerization. Na-MMt was used as nanoclay. The XRD patterns of pristine clay and nanocomposites are shown in Fig. 1a. As shown in this figure, the XRD profile of pristine Na-MMt shows a diffractive peak at 2θ=7.6 corresponding to the distance of clay sheets with d spacing 11.61 Å. Stirring of clay for 24 h and subsequently in situ polymerization of AAm in the presence of MBA...
crosslinker leads to a nanocomposite hydrogel that the XRD profile of this hydrogel shown in Fig. 1a. No diffraction peak was observed in nanocomposite and it can be concluded that the clay layers are completely or partially exfoliated. To study the structure of Na-MMt structure in nanocomposite with details, we investigated the TEM image of Clay5 nanocomposite and the result was shown in Fig. 1b. The dark and thin lines corresponded to Na-MMt layers. It can be seen that Na-MMt layers were obtained and indicates that the clay layers exists in exfoliated type.

Fig. 2 shows the FTIR spectra of pristine clay, carrageenan biopolymer, and Clay5 nanocomposite hydrogel. In the Fig. 2a, the characteristic vibration bands of the clay (-OH stretch from lattice hydroxyl, -OH stretch from free H₂O, -OH bending and Si-O stretch) are shown at 3633, 3447, 1641 and 1043 cm⁻¹, respectively. In the Fig. 2(b), the sulfate stretching of carrageenan, respectively. The broad band at 3200–3400 cm⁻¹ is due to stretching of -OH groups of carrageenan. The nanocomposite hydrogel comprises carrageenan backbone, PAAm, and clay. According to Fig. 2(c), PAAm chains carry carboxamide functional groups that are evidenced by peaks at 1659 cm⁻¹ due to the primary amides and 3200 cm⁻¹ corresponds to amide –NH stretching vibrations and asymmetric –N-H bending. The presence of clay and carrageenan in nanocomposite is confirmed by appearing band at 1038 and 926 cm⁻¹.

Differential scanning calorimetry (DSC) was used to study the effect of clay on glass transition temperature (Tg). Fig. 3 depicts the DSC thermograms for nanocomposites with various content of clay. According to data, inclusion of clay into hydrogel composition causes an increase in Tg. While the Tg of hydrogel containing no-clay is 156.6 °C, the Tg of all nanocomposites is higher than 162.7 °C. In fact, because of insertion of polymeric chains into clay layers, the mobility of these chains will decrease and subsequently the glass transition temperature will increase (Pourjavadi et al. 2010).

One of the most important properties of nanocomposites which can be considered is hydrogel microstructure morphology. Fig. 4 depicts surface morphology of clay-free hydrogel (Fig. 4a) and nanocomposite hydrogels containing 3, 5, 12, and 17 wt% of clay (Fig. 4b, c, d, e). While the clay-free hydrogel shows a relatively smooth surface, the nanocomposites contain coarse and undulant surface. This observation can be attributed to insertion of nanoclay into hydrogel.

The reaction condition can affect the yield of reaction. So, we tried to evaluate the gel content of selected samples. The results were shown in Table 1. In the Carra series, the gel contents were
obtained 90, 91, and 81 %, respectively. As it is clear from data, at high content of carrageenan, the gel content is decreased. This observation can be attributed to the increase in viscosity of medium in the presence of high content of carrageenan that restricts the movement of monomers (Hosseizadeh 2010). In the case of Clay series, similar to Carra series, at high content of clay, the gel content was decreased that the reason can be explained as Carra series.

**Swelling Kinetics**

The rate of swelling is an important factor in using of hydrogel for different applications. Fig. 5 shows the effect of reaction variables on the dynamic swelling of nanocomposites. In the MBA series (Fig. 5a), it seems that the rate of water uptake is higher for MBA4. But, according to the data, after 25 h while the nanocomposite MBA4 with low content of crosslinker reaches to 80 % of its swelling capacity, the MBA16 uptakes 95 % of its swelling capacity at the same time. In fact, increase in crosslinker concentration causes an increase in micropores in the hydrogels that causes ease of water diffusion into hydrogels (Omidian et al. 1998). A similar behavior was observed for the Carra series (Fig. 5b). In this series, carrageenan content was varied from 0 to 24 wt%. While the slope of water uptake for Carra24 is higher, but it reached to 79% of its swelling capacity after 25 h. Carra4 reached to 84% of its water uptake capacity during this time. The effect of nanoclay content on the dynamic swelling of nanocomposite is shown in Fig. 5c. As can be seen from this figure, the difference in initial water uptake rates is not significant as MBA and Carra series. For example, Clay12 and Clay5 reach to 69 and 67 % of their swelling capacity after 25 h, respectively. But, for Clay17, it reaches 75 % of its swelling capacity. In this sample, the clay content is high and may results in high micropores in nanocomposite and subsequent the water diffusion will be higher.

We analyzed the swelling kinetics to see whether the swelling follows the first order or second order kinetics. We adopted the procedure proposed by Quintana et al. (Quintana et al. 1999), (Martinez-Ruvalcaba et al. 2009). For the first order kinetics, the rate of swelling at any time \( t \) is directly proportional to the water content that the hydrogel has to obtain before the equilibrium water content \( W_\infty \) reaches. The swelling is then expressed as:

\[
\frac{dW}{dt} = K(W_\infty - W)
\]

where \( W \) is the water content of the hydrogel at time \( t \) and \( K \) is the proportionality constant between the swelling rate and the unrealized swelling capacity \( (W_\infty - W) \).

Upon integration of Equation 3 between the limits \( t=0 \) to \( t \) and \( W=0 \) to \( W \), the following expression can be obtained.

\[
\ln \left( \frac{W}{W_\infty - W} \right) = Kt
\]

(4)

If the swelling process of the hydrogel followed the first order kinetics, the plot of the \( \ln (W/W_\infty-W) \)
versus $t$ gives a straight line. But none of the swelling followed Equation 3.

Considering the second order kinetics, the swelling rate at any time may be expressed as:

$$\frac{dW}{dt} = K(W_\infty - W)^2$$

(5)

Integration Equation 5 with the limits $t=0$ to $t$ and $W=0$ to $W$ and after rearrangement, the following equation 6 is obtained.

$$\frac{t}{W} = \frac{1}{KW_\infty^2} + \frac{1}{W_\infty}t$$

(6)

According to this equation, the swelling data must fit a straight line with a slope of $1/W_\infty$ and an ordinate intercept of $1/KW_\infty^2$. The variation of $t/W$ against $t$ is plotted in Fig. 6-a, -b, and -c for nanocomposite series. It was found that the swelling data for all nanocomposites gives a straight line. So, the swelling behaviors of nanocomposites samples obey the second order kinetics.

**Release Behavior of Sq from Nanocomposites**

The release of an active agent from hydrogel matrix can be affected by hydrogel composition and release media nature. So, in this study we attempt to investigate the effect of MBA and carrageenan concentrations as well as the clay amount on the release kinetic of Sq from nanocomposite matrix. Also, the effect of salt solution on the release kinetic was studied.

![Figure 5. Swelling kinetic of nanocomposites as a function of MBA concentration (a), amount of carrageenan (b), and various content of clay (c).](image1)

![Figure 6. Plotting of $t/W$ versus $t$ for nanocomposites with various content of crosslinker (a), various content of carrageenan (b), and various content of clay (c).](image2)
Release of Sq as a function of MBA concentration was shown in Fig. 7-a. While the water uptake content was higher for nanocomposite with high concentration of MBA, the percentage of Sq release was higher for nanocomposite with low content of crosslinker. It may be attributed to decrease in pore size between nanocomposite chains that limit ease of diffusion of large Sq molecules into releasing media. When the effect of Carra content was studied on the release of Sq (Fig. 7-b), it was observed that the cumulative release for Carra0, Carra7, Carra14, and Carra20 is 88, 88, 92, and 85, respectively. But for Carra24 this content was 75. This observation can be attributed to high swelling capacity of the Carra24 nanocomposite that causes an increase in diameter of hydrogel and subsequent the release of Sq from interior of hydrogel into outside will be difficult.

In the case of clay series (Fig. 7-c), Clay0, Clay1.5, Clay5, Clay12, and Clay17 were chosen to study Sq releasing from nanocomposites matrix with various clay content. It was expected that clay content affect the releasing percentage by varying clay content. But, no significant difference in the releasing of Sq content was observed.

An interest point was observed for all nanocomposite samples after releasing. The results showed that while all the loaded Sq was released for hydrogel with no clay, the fractional release of the Sq from nanocomposites samples does not reach 100%. Maximum Sq releasing was 97 wt% for nanocomposites. These samples were kept for 3 months in 500 mL of distilled water and no difference in releasing was observed. This observation was shown in Fig. 8. We attempted to study this observation using XRD patterns. The XRD patterns of pristine clay and pure Sq were shown in Fig. 9. A peak at 2θ=7.6 and 4.4 can be seen for pristine clay and pure Sq, respectively. Sq was dissolved in the clay dispersion and allowed to stir for 5 h. The water was evaporated and clay-Sq mixture was dried. The XRD pattern of clay-Sq
was shown in Fig. 9. The peaks at 2θ=4.8 and 7.25 are attributed to the Sq and clay, respectively. Also, a new peak at 2θ=9.5 is appeared. This observation may be attributed to non-perfect releasing of Sq from nanocomposite samples. In fact, the results may be confirmed interaction between Sq and clay. Also, Sq may be entrapped in the clay layers and releasing will be difficult.

As mentioned above, the composition of releasing media can be a variable for releasing of active agent from hydrogel matrix. Chloride solutions of sodium and calcium with same concentration were chosen to release study of Sq from Carra14. As it clear from Fig. 10, the nature of releasing media can affect the percentage of release. After 6 h, the amount of released Sq from Carra14 is 84, 71, and 60 in the distilled water, NaCl solution, and CaCl$_2$ solution, respectively. Slow release in salt solution can be attributed to low swelling capacity of nanocomposite (Table 1). Also, in the case of CaCl$_2$ solution, calcium cation can act as crosslinker [25] and then the diffusion of active agent will be difficult.

The release curves of nanocomposites in distilled water and saline solutions were used to study diffusion kinetic of Sq from nanocomposites into release media. The following equation (Fick's equation) was used to determine the nature of diffusion of Sq into release media:

\[
\frac{M_t}{M_\infty} = K t^n
\]

(7)

Where, $M_t/M_\infty$ is the fractional Sq release, $M_t$ is the amount of diffusant released at time $t$, $M_\infty$ is the maximum amount released, $k$ is a constant incorporating characteristic of polymer network system and the diffusant, $n$ is the diffusional exponent, which is indicative of transport mechanism (Line and Metters 2006). The mechanism of release will be Fickian diffusion, Case II, and non-Fickian when $n$ is around 0.5, $n=1$, and $n$ between 0.5-1, respectively (Piai et al. 2010). To study the diffusion mechanism of Sq into releasing media, the initial releasing data were fitted to the exponential heuristic equation for

| Table 2. n and k values for Carra series. |
|-----|-----|-----|-----|-----|-----|
| Car0 | Car7 | Car14 | Car20 | Car24 |
| N    | 0.46 | 0.58 | 0.67 | 0.73 | 0.78 |
| K    | 3.56 | 4.39 | 5.06 | 5.6  | 5.93 |
| $R^2$| 0.99 | 0.99 | 0.98 | 0.99 | 0.99 |

| Table 3. n and k values for MBA series. |
|-----|-----|-----|-----|-----|-----|
| no  | MBA | MBA | MBA | MBA | MBA |
| 4   | 8   | 12  | 16  | 4   | 20  |
| N   | 0.69 | 0.66 | 0.6  | 0.6 | 0.58 |
| K   | 5.25 | 5.06 | 4.5  | 4.5 | 4.36 |
| $R^2$| 0.98 | 0.98 | 0.98 | 0.98 | 0.99 |
Table 4. $n$ and $k$ values for Carra series.

<table>
<thead>
<tr>
<th>no.</th>
<th>Clay0</th>
<th>Clay1.5</th>
<th>Clay5</th>
<th>Clay12</th>
<th>Clay17</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>0.66</td>
<td>0.58</td>
<td>0.66</td>
<td>0.68</td>
<td>0.63</td>
</tr>
<tr>
<td>$k$</td>
<td>5.08</td>
<td>4.64</td>
<td>5.06</td>
<td>5.27</td>
<td>4.9</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99</td>
<td>0.98</td>
<td>0.98</td>
<td>0.97</td>
<td>0.98</td>
</tr>
</tbody>
</table>

$M_t/M_\infty \leq 0.6$ (Rittger and Peppas 1987). The $n$ values for samples can be achieved from plotting of $Ln \left( \frac{M_t}{M_\infty} \right)$ against $Ln t$ that the $n$ values will be the slope of these curves (Fig. 11).

The $n$ values are illustrated in Tables 2, 3, and 4 for Carra, MBA, and Clay series, respectively. According to these data, the release mechanism is non-Fickian. But Carra0 sample showed Fickian mechanism.

CONCLUSION

Carrageenan-based Semi-IPN nanocomposite hydrogels were synthesized using in situ polymerization of AAm and MBA in the presence of Na-MMt clay. XRD pattern of nanocomposite containing 5 %wt of clay showed that clay layers are completely exfoliated.

-DSC study of nanocomposites depicted that introducing of clay into hydrogel composition causes an increase in $T_g$ point.

-While the rate of swelling for nanocomposites with various content of MBA was higher for the sample with high content of MBA, in the Carra series, it was higher for nanocomposite with low content of carrageenan. The rate of swelling for nanocomposites containing various amount of clay was close to each others only for Clay17.

-the study of swelling kinetics of all nanocomposite revealed that all samples obey second order kinetic.

-Release of Sq from nanocomposites with various content of MBA was fast for hydrogel with low content of MBA. In the Carra series, the rate of release was approximately similar only for Carra24 that was lower than that of other Carra series. Releasing of Sq from nanocomposite containing various content of clay was similar.

-the release rate of Sq in salt solution was low.

-while the release mechanism for Carr0 was Fickian, for all nanocomposite samples was non-Fickian.

-a part of loaded Sq in nanocomposite was not released. The XRD patterns revealed interaction between clay and Sq.

REFERENCES


