Evaluation of nitrate controlled release systems based on (acrylamide-co-itaconic acid) hydrogels

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ABSTRACT

In order to mitigate the nitrate water pollution and nitrogenous gases emissions to the atmosphere, different types of highly swelling hydrogels based on acrylamide and itaconic acid have been prepared by using two different crosslinking agents: NMBA and EGDMA. Controlled release systems were evaluated by loading potassium nitrate into the hydrogels. The swelling and nitrate release kinetics were evaluated in Milli-Q water and saline medium, and various diffusion parameters were also calculated by applying the Ritger-Peppas equations, one of which modified by the authors for the diffusion process due to the innovative and non-described conical shape of the hydrogels used in this study. The hydrogels showed swelling and release characteristics highly dependent on their chemical composition and ionic strength of the medium, having the type of crosslinker the major impact on their behaviour, which can be related to the hydrophilic/hydrophobic characteristics of the crosslinkers. So, these hydrogels showed good potential applications for being used as soil conditioners and controlled release systems in agriculture.

1. Introduction

In recent years, the intense agricultural activity has caused an increase in nitrate pollution of the water environment due to the excessive or inadequate use of nitrogen fertilizers. In order to achieve a sustainable agriculture that maintains the balance between optimal agricultural production levels and environmental protection, it is necessary to apply preventive measures, such as intelligent systems that allow a continuous and controlled release of nitrogen fertilizers [1–7].

Controlled release systems are mostly applied in the field of biomedicine [8–10]. In these applications, the release generally adjusts to Fick's first law (first-order kinetic), according to which, the amount of released substance decreases continuously with time. In order to keep the amount of released substance constant (zero-order kinetic), it is necessary that the concentration of the active ingredient inside a deposit separated from the medium by a semipermeable membrane also remains constant. If in addition, a nitrogen compound is integrated into a macromolecule of natural or synthetic origin, either dissolved or chemically bound to it, its release will be controlled by diffusion or hydrolysis processes [11].

Hydrogels are physically or chemically crosslinked polymeric materials that can absorb large amounts of water without dissolving or losing their shape. Crossed hydrophilic polymeric chains form three-dimensional networks with intermediate properties between liquids and solids. This is, they swell in contact with water forming elastic and soft materials, retaining a significant fraction of it in their structure. These materials have special properties such as their biocompatibility, hydrophilic character, non-toxicity, biodegradability and water absorption and retention capacity, which depend on the nature of the monomers used in their synthesis and the crosslinking degree of the macromolecular network [12–15].

Intelligent systems based on hydrogels act as controlled release deposits and could regulate the contribution of nitrogen to the soil, allowing a lower concentration of it and minimizing its losses through leaching and evaporation. Furthermore, the use of hydrogels increases the water retention capacity of the soil, favouring water saving and better plants development. Although these factors are enough to improve the biological activity and increase the production, they also contribute to the improvement of the structure and the properties of the soil, as well as its aeration, with which, this type of materials help to the recovery of semiarid zones [5–7,16].

The development of this technology has focused fundamentally on maintaining an optimum concentration and an adequate release level of the active ingredient, achieving an increase in the effectiveness period of the fertilizers, as well as reducing costs and environmental damages. For this reason, the study of these systems is being extended more and

more towards the field of agriculture, since they are surmised as a potential solution to the processes of contamination derived from the use of pesticides and fertilizers [2,3,5,6,17].

In the last years, considerable research has been carried out on various kinds of polymeric systems where hydrogels have gained considerable interest and reviewed from different points of view. So, their swelling behaviour, sorption of contaminants, drugs release and pesticides controlled release systems have been and are a matter of actual interest. In particular, superabsorbent hydrogels based on acrylamide and/or itaconic acid prepared by different copolymerization methods have been widely described in literature [18–22].

However, the hydrogels containing nitrate as active ingredient and their use as controlled release systems is an area that could be improved. In this sense, the authors report in this paper the results obtained with an innovative non-described shape, conical geometry, for the preparation of nitrate controlled release systems based on hydrogels.

The aim of this study is the preparation, characterization and evaluation of controlled release systems of potassium nitrate based on hydrogels of itaconic acid, acrylamide and ethylenglycol dimethacrylate or N,N′-methylenbis(acrylamide) as crosslinking agents. So that these hydrogels are able to combine maximum effectiveness with minimum doses, their hydrophilia is adjusted by varying the type of crosslinker. Subsequently, the release kinetic of nitrate ions was analyzed in two media with different experimental conditions of ionic strength, and the dynamic behaviour of nitrate ions was modelled.

The obtained results, depending on the type of soil to which they are applied, could be used to design new strategies of agricultural practices that face the contamination of the environment, and simultaneously, improve the fertility of the agricultural model.

2. Materials and methods

2.1. Materials

The fertilizer used in release studies was potassium nitrate purchased from Panreac. Itaconic acid (minor monomer), acrylamide (major monomer), the crosslinkers ethylenglycol dimethacrylate (EGDMA) and N,N′-methylenbis(acrylamide) (NMBA), potassium peroxodisulfate and sodium bisulfite were all purchased from Sigma-Aldrich. The solvent used was distilled water. The media used in swelling and release studies were Milli-Q water and a saline solution 0.006M that contains sodium chloride 0.50M (Panreac), sodium carbonate 0.50M (Sigma-Aldrich) and decahydrated sodium sulphate 0.25 M (Sigma-Aldrich). All reagents were of analytical grade and used without further purification.

2.2. Hydrogels preparation

Four hydrogels of different composition were synthesized by varying the type of crosslinker (EGDMA or NMBA), with or without the fertilizer in the preparation (2.500 g of potassium nitrate). The amounts of itaconic acid (0.600 g), acrylamide (5.050 g), crosslinker (0.056 g), potassium peroxodisulfate (0.075 g) and sodium bisulfite (0.050 g) remained constant in all hydrogels. So, the hydrogels without nitrate are labelled as HEGDMA and HNMBA, and the ones containing nitrate, HEGDMA-N and HNMBA-N.

Aqueous solutions of the components were prepared by dissolving itaconic acid, acrylamide, the corresponding crosslinker and the redox initiators in distilled water under constant stirring at room temperature (no inert atmosphere was used). For those hydrogels that contain the fertilizer, potassium nitrate was dissolved in distilled water before adding the rest of the components to this aqueous solution. After five minutes of homogeneous mixing under ultrasonic treatment, the reaction mixture was degassed with nitrogen for five minutes without stirring. Aliquots of 0.20 mL were placed in Eppendorf tubes as

polymerization reactors and dried in stove at 60 °C for 24 h to obtain the dry hydrogel (xerogel).

2.3. Hydrogels swelling kinetics

Swelling studies were gravimetrically carried out in both Milli-Q water and saline solution.

Each xerogel was previously weighted and placed in 100 mL of the swelling medium in a thermostatic bath at 25 °C under constant stirring (150 rpm). After that, swollen hydrogels were removed from the medium at fixed time intervals, wiped with filter paper to eliminate the excess of liquid, weighted and placed into the same bath. This procedure was repeated until a constant weight was reached for each sample.

The swelling percentages of the hydrogels were calculated from the following equation:

$$Swelling\,(\%) = \frac{W_w - W_d}{W_d} \cdot 100 \tag{1}$$

where W_w is the wet weight of the hydrogel and W_d, the dry weight of the hydrogel before swelling (xerogel).

2.4. Hydrogels structural characterization

2.4.1. FTIR spectroscopy

Samples of all xerogels were pounded and completely mixed with FTIR grade potassium bromide (Sigma-Aldrich). The spectra of the pressed tablets were recorded with an Alpha I Bruker spectrometer.

2.4.2. SEM

Samples of all xerogels were adhered to an aluminium sample holder with double-sided carbon conductive tape. Afterwards, they were coated with gold, with a layer of approximately 15 nm thickness, by means of the sputtering technique with a SCD 005 Bal-Tec sputter coater and later, visualized with a S-3500N Hitachi scanning electron microscope with a thermionic cannon of the wolfram forked filament type.

2.5. Nitrate ions release kinetics

Nitrate release from hydrogels was determined by placing each xerogel in a flask containing 100 mL of the release medium (Milli-Q water and saline solution), at both constant stirring rate and temperature, 25 °C. After that, at different fixed time intervals, two aliquots of the release medium were taken for their further analysis by ionic chromatography. This procedure was repeated until a constant concentration was reached for each sample.

The concentration of nitrate ions was determined by ionic chromatography using a DX-120 Vertex Technics S.L. equipment (Barcelona, Spain). Separation was performed on an AS9-HC 4 × 250 mm Dionex IonPac analytical column. The mobile phase was a 9 mM solution of Na_2CO_3 and an ASRS ULTRA II-4 mm Dionex was used as suppressed column.

2.6. Diffusion mechanisms

To describe medium absorption and nitrate release behaviours from the hydrogels, diffusion mechanisms were analyzed by using the Ritger-Peppas equation for small molecules [23–27]:

$$\frac{M_t}{M_\infty} = k \cdot t^n \tag{2}$$

where M_t and M_∞ are the amounts of the absorbed medium or the released fertilizer at a time t and at equilibrium, respectively, n is the diffusion exponent which determines the type of mechanism and k, the constant of the fertilizer-polymer system that depends on the structural and geometric characteristics of the hydrogel. According to *Crank*

[28,29], the higher value for *k* parameter, the higher crosslinking degree. This degree describes not only the polymeric crosslinking but also the ionic one. The difference between them is that the first takes place between the C=C groups of the crosslinker and the monomers and the second, between the free functional groups of the polymeric chains and/or the external ions (from saline solution or fertilizer). It has been considered the first 4 h as the equilibrium time because is when diffusion takes place and the 60% of the fertilizer has been released.

According to the diffusion exponent values, the diffusion mechanism can be classified for a thin polymer film as quasi-Fickian (*n* < 0.5), Fickian (*n* = 0.5), non-Fickian or anomalous (0.5 < *n* < 1), case II (*n* = 1) or super-case II (*n* > 1) transports.

The diffusion coefficient *D* is another parameter derived from the Ritger-Peppas equation that also describes the diffusion process:

$$\frac{M_t}{M_\infty} = 4 \cdot \left(\frac{D}{\pi \cdot l^2}\right)^{0.5} \cdot t^{0.5} \tag{3}$$

where l^2 is the area of the xerogel. As the diffusion coefficient has only been described for a Fickian mechanism (*n* = 0.5) and for a thin polymer film (l^2), the Ritger-Peppas equation was adapted for any type of diffusion mechanism in hydrogels of conical geometry as follows:

$$\frac{M_t}{M_\infty} = 4 \cdot \left[\frac{D}{\pi^2 \cdot r \cdot (g + r)}\right]^n \cdot t^n \tag{4}$$

where *r* and *g* are the radius and the generatrix of the xerogel of conical geometry, respectively [9,30].

The values of the diffusion exponent (*n*) and the constant *k* are inversely related, as the constant *k* and the diffusion coefficient (*D*).

3. Results and discussion

3.1. Hydrogels morphology

The type of crosslinker was modified so that the hydrogels present different sorts of functional groups along the polymeric chains. This provides distinct active sites that interact with the nitrate ion and pore sizes that allow both its retention and its continuous and controlled release. So, EGDMA contributes with −COOR groups, NMBA with −CONHR groups, acrylamide with −CONH₂ groups and itaconic acid, with −COOH groups, which are directly responsible for the next results.

The chemical polymerization and therefore, the crosslinking of the polymeric network, is carried out between the C=C groups of the crosslinker agent and the monomers. Thus, the functional groups of the itaconic acid/acrylamide are free for other link types.

Hydrogels with potassium nitrate were obtained by polymerization in a medium that contains this fertilizer, so that the active ingredient is uniformly included in the whole structure when the polymers network has been formed.

All xerogels obtained were of conical geometry and glassy aspect, except for those synthesized with potassium nitrate, which presented a whitisher appearance.

3.2. Hydrogels swelling kinetics

In hydrogels swelling kinetics, two phases can be clearly distinguished: a first fast one in the interval of the first 4 h and a second slower one, until equilibrium is reached at 48 h.

Fig. 1a shows the swelling percentages of non-nitrate hydrogels in Milli-Q water and in saline solution at 25 °C in the first phase and Fig. 1b, the complete kinetics up to 48 h.

In both figures, it can be observed that hydrogels containing EGDMA present maximum rates and swelling percentages much higher than those formulated with NMBA. This different behaviour is justified taking into account, firstly, that EGDMA has a lower hydrophilic character than NMBA, which implies its lower reactivity with the active
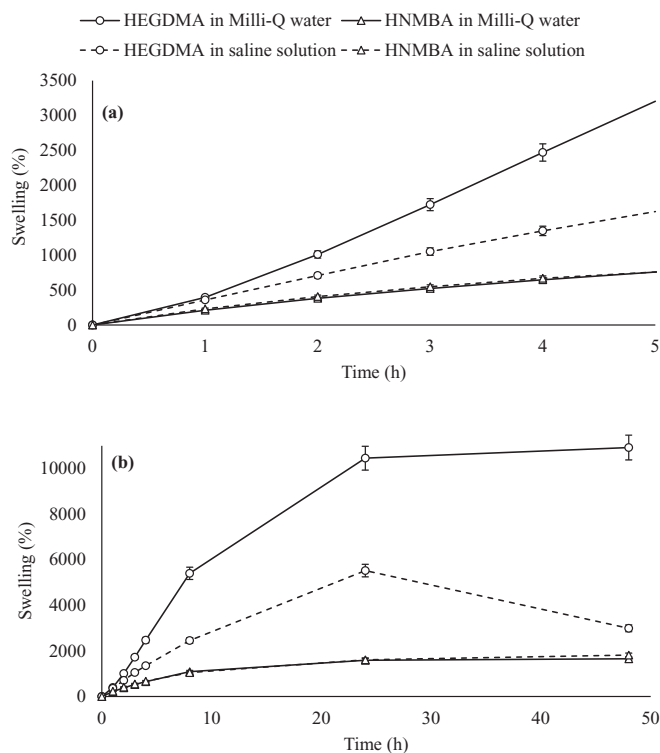

Fig. 1. Swelling kinetics of non-nitrate hydrogels in Milli-Q water and saline solution: (a) in the first phase and (b) up to 48 h.

groups of itaconic acid and acrylamide. This fact results in a more open structure of the polymer network, what reduces the crosslinking degree and allows a greater penetration of water molecules compared to NMBA [31]. Secondly, when comparing the chemical structures of the EGDMA and NMBA crosslinkers, both have the same number of available functional groups for the potential formation of hydrogen bonds, both being tetrafunctional. However, the presence of methyl groups as ramifications in the EGDMA is partly responsible for generating networks with greater free volume where water molecules could penetrate [32]. Thus, these two facts would justify the high swelling capacity of HEGDMA in relation to the hydrogel containing NMBA.

The study of the influence of ionic strength in the swelling process showed that it did not produce a significant change in the behaviour of the HNMBA until the first 24 h. The different behaviour of HNMBA in aqueous and saline medium can be explained on the fact that the structure of this hydrogel is quite rigid. At the same time, the NH groups from NMBA and CO groups from itaconic acid interact strongly between them, what could increase the ionic crosslinking degree of this network. Then, in saline medium, the external ions hardly affect the swelling behaviour because it is very difficult for them to penetrate into the structure of the hydrogel as well as the water molecules.

Comparing the HEGDMA kinetics in the two studied media, it was observed that, in the presence of salts, the initial slope of the kinetic decreased and the maximum swelling percentage was reduced practically by half. It should be mentioned that, from the first hour of contact of this hydrogel with the saline medium, a degradation process of the surface of the HEGDMA began to be observed, producing its total dissolution after 48 h, an effect known as *salting-in*. The salts concentration used to generate the ionic medium (0.006 M), the type of ions (Cl⁻, SO₄²⁻, CO₃²⁻, Na⁺) and the hydrophobic-hydrophilic character of the surface of the HEGDMA determined the chaotropic behaviour of the medium ions [33–35]. This resulted in the disorganization of the non-covalent intermolecular interactions of the polymeric chains, causing finally the complete dissolution of the hydrogel. All this would justify the decrease of the observed swelling degree from the beginning of the
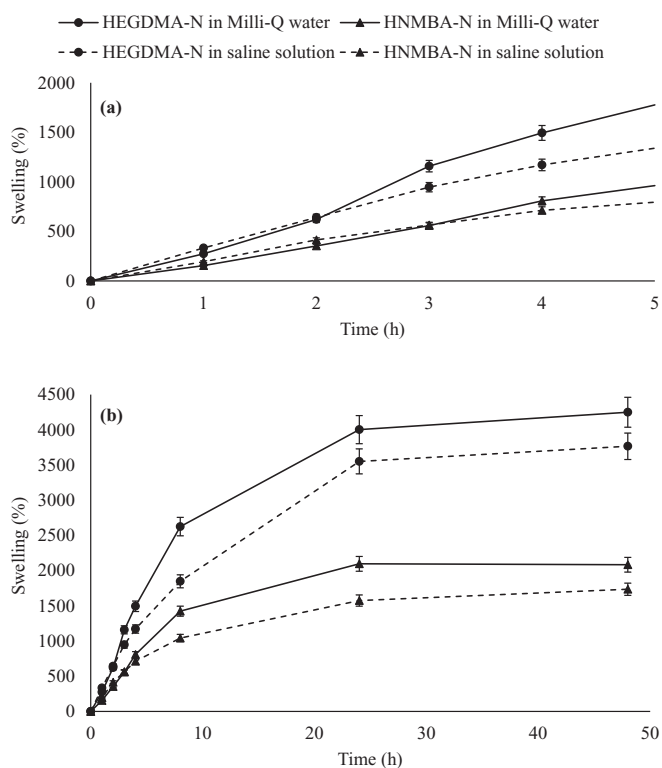
Fig. 2. Swelling kinetics of nitrate hydrogels in Milli-Q water and saline solution: (a) in the first phase and (b) up to 48 h.

kinetic study in saline medium.

The swelling kinetics in Milli-Q water and in saline medium at 25 °C, corresponding to the first phase and up to 48 h of the hydrogels containing nitrate (HEGDMA-N and HNMBA-N), can be observed in Fig. 2.

In view of the previous figures, it can be seen how the HEGDMA-N showed from the beginning of the kinetic study, higher swelling percentages than the HNMBA-N in the two studied media.

In relation to the influence of ionic strength, in the first phase of swelling (Fig. 2a), it is observed that the swelling degree of both HEGDMA-N and HNMBA-N until the second and third hours, respectively, was not practically altered by the presence of ions in the medium. After this time interval, the swelling percentages of both hydrogels in Milli-Q water are higher than those obtained in saline medium, with a very significant rate increase observed for HEGDMA-N in Milli-Q water compared to the HNMBA-N in the same medium.

In order to analyze and compare the behaviour of hydrogels with and without nitrate in the studied media, Figs. 3 and 4 show the swelling kinetics of the hydrogels with EGDMA and NMBA,
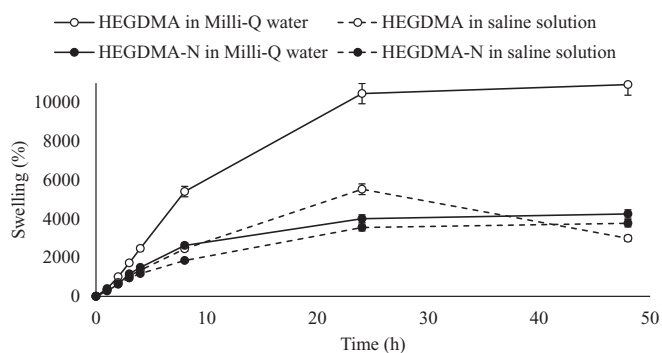

Fig. 3. Swelling kinetics of hydrogels with EGDMA in Milli-Q water and saline solution.
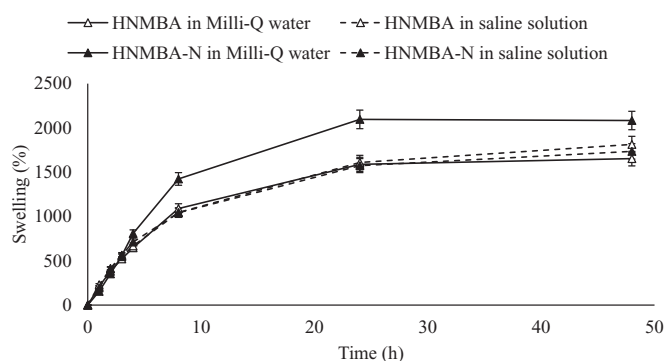

Fig. 4. Swelling kinetics of hydrogels with NMBA in Milli-Q water and saline solution.

respectively.

In this way, Fig. 3 shows that both the rate and the maximum swelling percentage of the HEGDMA-N in Milli-Q water (4249%) are much lower than the obtained with the HEGDMA in the same medium (10923%). On the other hand, it should be mentioned that the HEGDMA-N in saline medium did not dissolve although it showed a lower swelling degree in relation to the HEGDMA. In this case, the decrease in the volume of water inside the hydrogel produced by the presence of potassium nitrate plus the effect produced by the presence of salts in the medium, contribute to further reducing this inner volume of water [36]. The final result is such that the reduction in the number of water molecules prevents the *salting-in* effect from occurring.

As can be seen in Fig. 4, hydrogels containing NMBA showed a different behaviour. So, HNMBA-N in Milli-Q water showed the highest water molecule retention capacity, being the other swelling kinetics practically equal.

Fig. 5 shows a diagrammatic sketch proposed for the interaction of nitrate and potassium ions with the HNMBA structure.

3.3. Hydrogels structural characterization

3.3.1. FTIR spectroscopy

Fig. 6 shows the characteristic bands of the functional groups that exhibit all the xerogels.

All xerogels present a wide band located at $3450\,cm^{-1}$ that corresponds to O—H stretching and amide N—H stretching vibrations. At $2930\,cm^{-1}$ and $2860\,cm^{-1}$ there are two very low intensity bands corresponding to C—H stretching vibration for long alkylic chains, this is, CH_2 and aliphatic CH_3 groups. Between $1660\,cm^{-1}$ and $1640\,cm^{-1}$ there is a band that corresponds to carboxylic acid and amide C=O stretching vibration, and between $1120\,cm^{-1}$ and $1100\,cm^{-1}$, another of very low intensity for the C—N stretching one [4,6,37–44].

Non-nitrate loaded xerogels present a very low intensity band at $1390\,cm^{-1}$ corresponding to C—O stretching vibration [45].

Nitrate loaded xerogels present two narrow bands at $1380\,cm^{-1}$ and $830\,cm^{-1}$ assigned to the nitrate ion, which confirms its satisfactory incorporation to the xerogels [4,6,44].

3.3.2. SEM

Fig. 7 shows the topography of all xerogels, where each one presents a characteristic porous network.

All xerogels present interconnected pores in their structures, what confers them greater capillarity when absorbing the medium, converting them in superabsorbent materials [46,47].

Moreover, significant differences can be easily appreciated in the porosity of the microstructures when the xerogel changes from non-nitrate to nitrate loaded. Similarly, nitrate crystals adhered to the surface of the xerogels can be clearly observed (Fig. 7b and d).
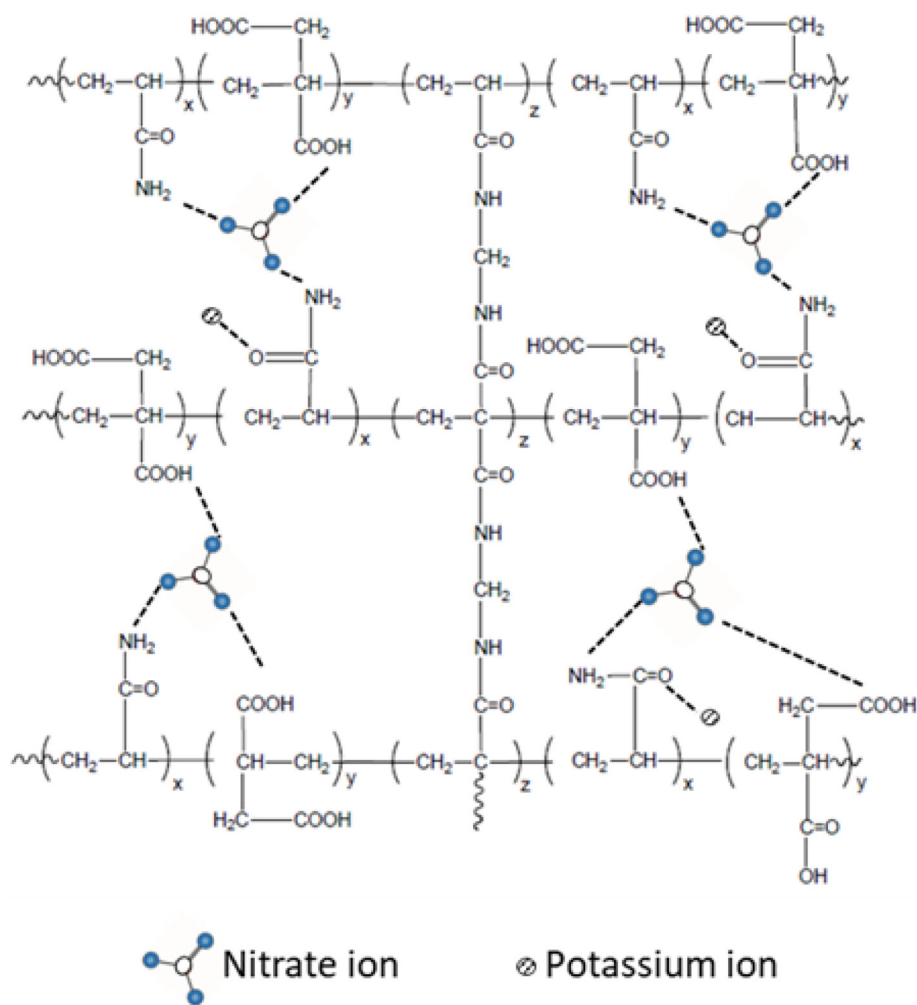
Fig. 5. Diagrammatic sketch proposed for the interaction of nitrate and potassium ions with the HNMBA structure.

3.4. Nitrate ions release kinetics

The monitoring of the nitrate ions release kinetics in Milli-Q water and in saline solution at 25 °C was carried out up to 48 h, when the systems reached the release equilibrium (Fig. 8a).

In view of the previous figure, it can be seen how, in all cases, there is a first phase characterized by a high release rate, corresponding to the dissolution of nitrate ions adhered to the surface of the hydrogels (Fig. 7b and d). After this first phase, the release was slower until equilibrium was reached at 48 h.

The presence of salts produced an increase in the release percentages of both hydrogels, a fact that is most evident in the first hours of the kinetic study. The greater release of nitrate ions in saline medium could be due to ionic exchange processes, especially between the SO_4^{2-} and CO_3^{2-} ions present in the medium, which would facilitate the exit of the nitrate ions. In general, the final release percentages were between 88% and 100%, corresponding to HNMBA-N and HEGDMA-N in saline solution, respectively.

Considering the possible use of the synthesized hydrogels as controlled release systems, the obtained results in the first hours of release are analyzed in greater detail (Fig. 8b).

The release percentages in the first hour were 47.2% for HNMBA-N and 65.8% for HEGDMA-N in Milli-Q water, increasing to 66% and 75%, respectively, in saline medium. In the second hour, both in Milli-Q water and saline solution, there was an increase of approximately 20% in the release of both hydrogels. In these first 2 h, it became clear that the hydrogel containing EGDMA as crosslinking agent showed a higher nitrate release percentage.

It is interesting to note that, in Milli-Q water, the HEGDMA-N experienced a 10% decrease in the release percentage when passing from the second to the third hour due to a process of reabsorption of the nitrate ions, which were again released until reaching a 93% at 48 h. This process of reabsorption could be explained taking into account that, as previously commented in the swelling study in Milli-Q water, the swelling rate of the HEGDMA-N increased significantly at the second hour caused by the penetration of a large amount of water molecules (Fig. 2a). These water molecules not only prevented the exit of nitrate ions from the inside of the network but also dragged with them nitrate ions present in the solution. From the third hour onwards, due to the concentration gradient, the nitrate ions present in the hydrogel structure slowly diffused into the aqueous medium.

Finally, and as a consequence of the above, from the third hour onwards the release percentages of nitrate ions presented by HNMBA-N in Milli-Q water were higher than those obtained for the HEGDMA-N in the same medium.

3.5. Diffusion mechanisms

The linearizations of the Ritger-Peppas equation (Eq. (2)) and the one proposed by the authors of this paper (Eq. (4)), have allowed the determination of the parameters indicated in Tables 1 and 2 corresponding to the diffusion of the medium and the nitrate ions, respectively, for the first 4 h. As can be observed, the determination coefficients, in general, were higher than 98.90%, which indicates a very
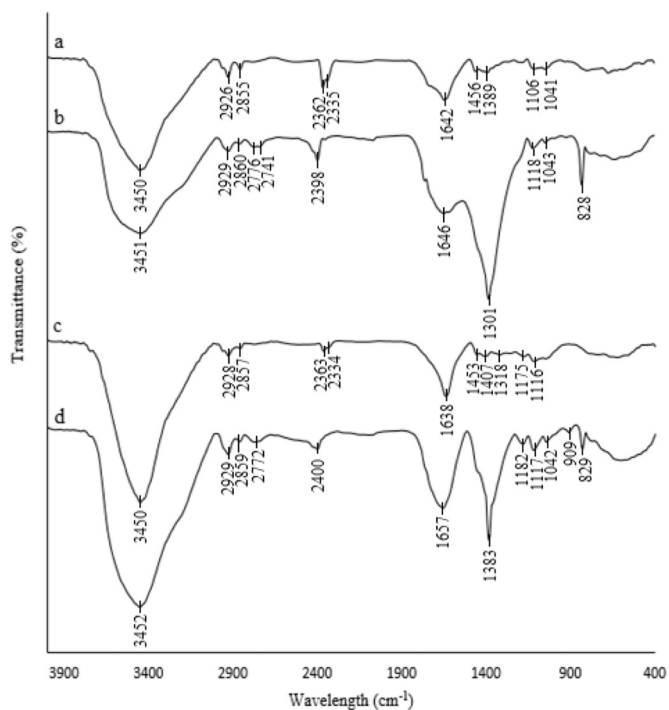
Fig. 6. FTIR spectra of: (a/b) EGDMA/EGDMA-N xerogels and (c/d) NMBA/NMBA-N xerogels.
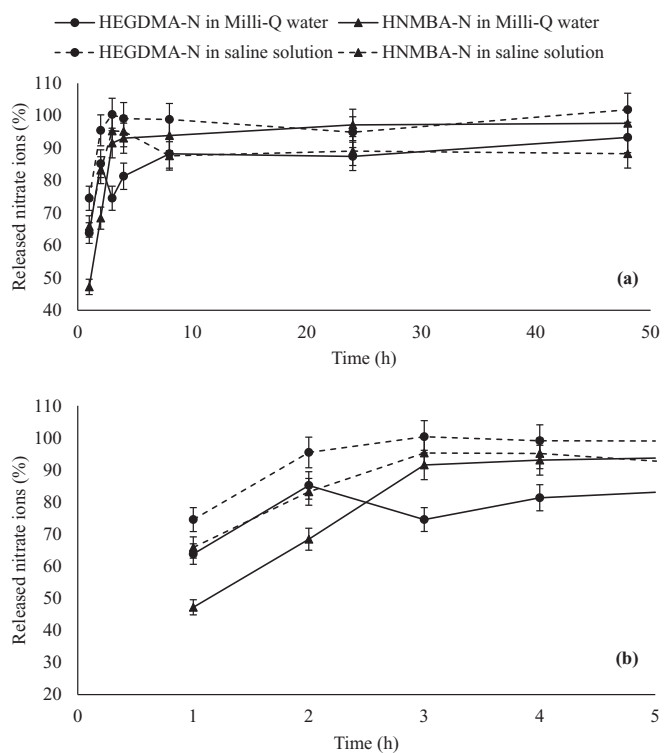

Fig. 8. Nitrate ions release kinetics of hydrogels in Milli-Q water and saline solution: (a) up to 48 h and (b) in the first phase.
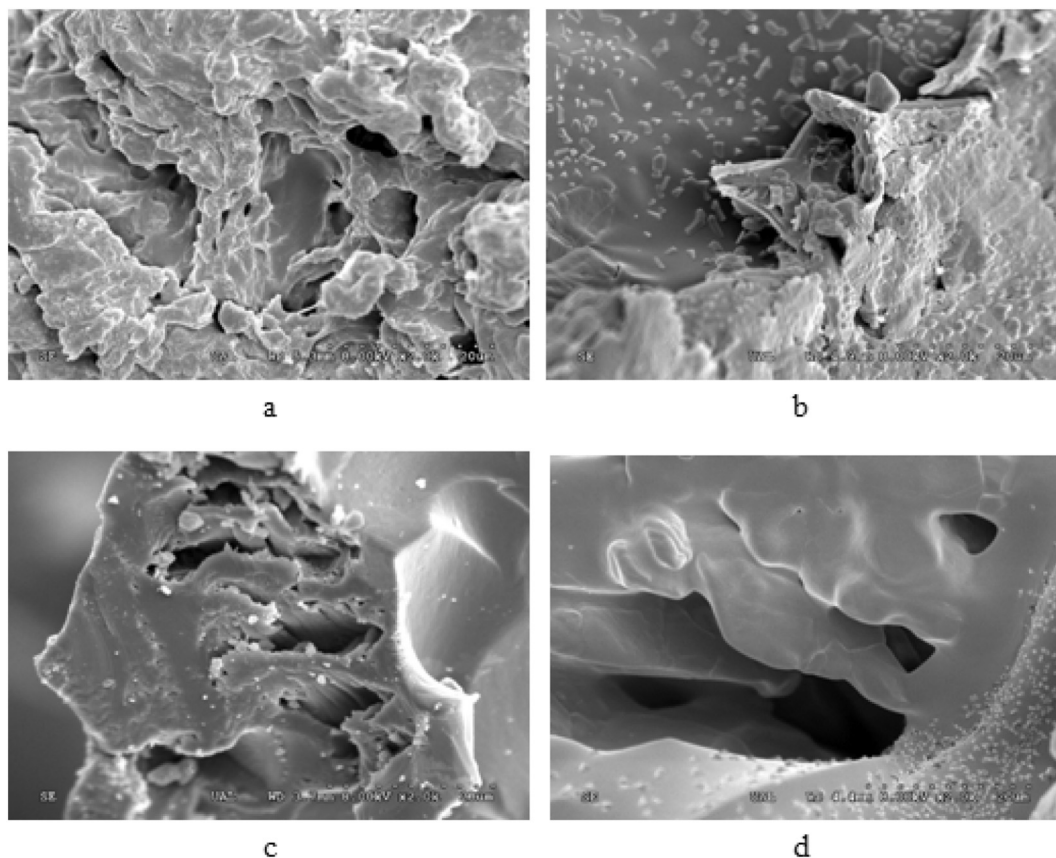

Fig. 7. SEM images of: (a/b) EGDMA/EGDMA-N xerogels and (c/d) NMBA/NMBA-N xerogels.

Table 1
Parameters related to diffusion mechanism of the medium contained in hydrogels in presence or absence of the agrochemical fertilizer.

Hydrogel	Medium	n	k	R^2 (%)	D (cm^2/s)	R^2 (%)	Diffusion mechanism
HEGDMA	Milli-Q water	1.33	0.16	99.98	0.19	99.96	Super-Case II
	Saline solution	0.96	0.27	99.95	0.13	99.90	Non-Fickian
HEGDMA-N	Milli-Q water	1.26	0.18	99.52	0.28	98.90	Super-Case II
	Saline solution	0.92	0.29	99.83	0.18	99.66	Non-Fickian
HNMBA	Milli-Q water	0.81	0.33	99.88	0.09	99.87	Non-Fickian
	Saline solution	0.77	0.35	99.84	0.08	99.81	Non-Fickian
HNMBA-N	Milli-Q water	1.18	0.19	99.97	0.19	99.93	Super-Case II
	Saline solution	0.94	0.28	99.19	0.14	99.17	Non-Fickian

good reliability of the transport models, except for the diffusion of nitrate ions in the HEGDMA-N in Milli-Q water. In this case, the low value obtained of R^2 (44.10%) is justified, as indicated above, by the drop in the nitrate release percentage in the second hour due to a reabsorption process as a consequence of the massive penetration of water.

3.5.1. Medium diffusion

The analysis of the results shown in Table 1 for the parameter n revealed two types of transport depending on the type of hydrogel and medium used. In this way, all the hydrogels in saline solution, as well as the HNMBA in Milli-Q water, presented a non-Fickian or anomalous transport ($0.5 < n < 1$), showing that the rates of medium diffusion and relaxation of the polymer chains are similar. On the other hand, the type of transport for HEGDMA, HEGDMA-N and HNMBA-N in Milli-Q water was super-case II, characterized by $n > 1$. This mechanism is an extreme case of case II diffusion ($n = 1$), where the diffusion of the medium is faster than the relaxation of the polymeric chains when it penetrates the hydrogel.

About the constant k, it presented values between 0.16 and 0.35, being higher in saline solution. The swelling behaviour of HNMBA in both media can be justified taking into account the higher and similar values of the k parameter (0.33 and 0.35 for Milli-Q water and saline medium, respectively). Additionally, the diffusion coefficient presented high values between $0.08\,cm^2/s < D < 0.28\,cm^2/s$, being higher in Milli-Q water than in saline solution. All the above indicated means that, the penetration rate of the medium is low due to the irregular and sinuous configuration of the hydrogel, being slower in saline solution than in Milli-Q water.

The effect of the ionic strength can also be clearly appreciated for those hydrogels whose diffusion mechanism has changed from super-case II to non-Fickian transport. According to some authors [25,48], in saline solution the pore size of hydrogels decreases compared to Milli-Q water, which slows down the diffusion mechanism and justifies this change of mechanism.

3.5.2. Nitrate ions diffusion

The values of n corresponding to the diffusion of nitrate ions (Table 2) were lower than those obtained for the medium diffusion (Table 1), both in HEGDMA and HNMBA and in those loaded with nitrate (HEGDMA-N and HNMBA-N). With the exception of the value of n obtained for HNMBA-N in Milli-Q water ($n = 0.52$), the rest presented values lower than 0.5, indicating that the diffusion of nitrate ions through the hydrogel structure takes place through a quasi-Fickian transport. In this extreme case, the diffusion of the nitrate ions occurs

more slowly than the relaxation of the polymeric chains when the medium penetrates into the hydrogel.

About the constant k, it can be observed that this parameter has values between $0.51 < k < 0.83$, indicating an uncontrolled release phenomenon of nitrate ions known as *burst effect* [2,3,11]. So, part of the nitrate ions contained in the hydrogels are immediately released in the first 4 h (Fig. 8). Most of these nitrate ions are placed on the surface of the hydrogels (Fig. 7b and d), being their values higher in Milli-Q water than in saline solution, except for HNMBA-N. The diffusion coefficient (D) presented values between $5.32{\cdot}10^{-5}\,cm^2/s < D < 0.04\,cm^2/s$. All the above indicates that the diffusion of nitrate ions from the inside of the hydrogels is more prevented and not uniform, existing a strong interaction between the nitrate ions and the hydrogel due to their preferential passage through the interconnected pores.

Finally, it should be noticed that in the presence of ionic strength, both hydrogels presented similar values of the parameter n showing a quasi-Fickian transport.

4. Conclusions

The results show that both the hydrogels composition and the ionic strength of the medium affect the swelling and nitrate release kinetics, as well as their diffusion mechanisms. Additionally, IR spectroscopy and SEM confirm the incorporation of the agrochemical fertilizer into the hydrogels and their characteristic porous network.

In this way, when varying the type of crosslinker, it was observed that hydrogels containing EGDMA presented rates and swelling percentages much higher than those formulated with NMBA, which is justified due to the lower hydrophilic character of this compound, presenting the hydrogel a more open structure given the lower crosslinking degree that exists between its polymeric chains. Therefore, the different behaviour observed by using EGDMA or NMBA is due to firstly, their different functional groups and how they interact with the monomers, and secondly, the way they link with the monomers allows the polymeric network to have a different free volume, what confers them different crosslinking degrees.

The study of the influence of the ionic strength on the swelling process showed that it did not produce any change in the behaviour of the hydrogels containing NMBA. However, the presence of salts produced a drastic reduction in swelling in those containing EGDMA, followed by a degradation process that finally led to the complete dissolution of the hydrogel.

On the other hand, the incorporation of nitrate into the hydrogel structure affected the swelling kinetics of the studied hydrogels in

Table 2
Parameters related to diffusion mechanism of the agrochemical fertilizer loaded in the hydrogels.

Hydrogel	Medium	n	k	R^2 (%)	D (cm^2/s)	R^2 (%)	Diffusion mechanism
HEGDMA-N	Milli-Q water	0.15	0.83	49.65	$5.32{\cdot}10^{-5}$	44.10	Quasi-Fickian
	Saline solution	0.22	0.78	85.93	$1.33{\cdot}10^{-3}$	83.68	Quasi-Fickian
HNMBA-N	Milli-Q water	0.52	0.51	96.94	0.04	94.73	Non-Fickian
	Saline solution	0.28	0.70	95.43	$4.78{\cdot}10^{-3}$	94.00	Quasi-Fickian

different ways, although in all cases, it was again observed that the HEGDMA-N showed swelling percentages higher than the HNMBA-N in the two studied media, not being observed in this case dissolution of the HEGDMA-N in the presence of salts. Thus, in Milli-Q water, both the rate and the maximum swelling percentage of the HEGDMA-N were much lower than the obtained with the HEGDMA, which could be due to the presence of nitrate ions that decrease the available inner volume of water in these hydrogels. However, the presence of nitrate for the HNMBA-N slightly decreased the swelling regarding HNMBA in this medium.

The influence of the ionic strength in this case showed that, except in the first 3 h where the swelling degree was not practically altered by the presence of ions in the medium for both HEGDMA-N and HNMBA-N, the swelling degree in the hydrogels decreased with respect to that observed in Milli-Q water after this time.

In relation to the release of nitrate ions, it was observed that hydrogels containing EGDMA had the highest release percentage in saline solution, which is justified given its lower hydrophilic character compared to NMBA. However, the obtained release profiles indicate that using the synthesized systems, release percentages higher than 80% are reached at least in the experimental conditions used in this study, producing the highest release rate in the first 4 h.

The diffusion mechanism in swelling kinetics varies between non-Fickian and super-case II transports, whereas in nitrate release kinetics, between quasi-Fickian and non-Fickian transports.

Taking into account the conditions under which the experiences of this study have been carried out, it is clear that varying the composition of the hydrogels can be achieved a slower, continuous and controlled release of nitrate ions. However, it is necessary to continue with this work and study the application of these hydrogels in similar conditions to those found in agricultural soils, experiences that will be presented in future works.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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