Swelling dynamics of Poly (N, N- Dimethylacrylamide - co- Crotonic acid) Hydrogel and Evaluation of its Potential for Controlled Release of Fertilizers

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ABSTRACT

Poly(N,N-dimethymethylacrylamide -co-crotonic acid) (P(DMA-CAx)) hydrogels were prepared by free radical polymerization, using N,N- methylenebisacrylamide (NMBA) as cross-linking agent. The synthesized hydrogels were characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The effects of comonomer composition and pH of the medium on the swelling behavior of hydrogels were investigated. The obtained results showed that the swelling capabilities of hydrogels increased as crotonic acid content and pH increased. In order to evaluate the controlled release potential of the polymeric matrix, it was loaded with potassium nitrate and ammonium nitrate as fertilizers and the release kinetics was studied as a function of the chemical composition of the hydrogel and the content of the fertilizer. Various kinetic parameters such as the diffusion exponent and diffusion coefficient were also determined. These pH sensitive copolymer hydrogels present a promising approach for controlled release of fertilizers.

KEYWORDS: *Hydrogel, N,N- dimethymethylacrylamide /crotonic acid, pH- sensitivity, Swelling, Fertilizer release.*

1. INTRODUCTION

The usage of fertilizer has a critical impact on agriculture, either directly or indirectly, by altering the cost of growing and the relative profitability of crops. The main problem with the conventional application of fertilizers is the use a greater quantity of fertilizers over a long period that actually needed, which lead to

environmental pollution such as the eutrophication of estuaries and other coastal regions. Controlled release polymer matrix systems can keep the amount of fertilizer at effective levels in the soil solution and release the fertilizer when the plant most needs it. As a result, it has been observed a maximal utilization of the fertilizer from plant systems, a remarkable decrease with respect to fertilizer application rate, the least possible losses of the fertilizer trough volatilization or leaching, a reduction of the requirements in irrigation and pollution environmental agricultural. In addition, controlled release formulations offer possibilities of reduction of costs significant to the agricultural companies and improve production of crops.

Hydrogels are three-dimensional, crosslinked hydrophilic polymer networks capable of swelling and retaining possibly huge volume of water in the swollen state. The water imbibing property of hydrogels is responsive to the surrounding conditions such as pH [1-3], temperature [4-6], ionic strength [7], magnetic field [8] and ultra violet light [9]. These systems are the focus of considerable scientific research due to their potential technological application in large number of areas such as the biomedicine production [10-12], tissue engineering technology [13], agricultural soil conditioners [14,15] and other fields. Specifically, they are also used as controlled release systems of drugs [16-18], pesticides and fertilizers [19-21].

Poly (N,N-dimethylacrylamide) (PDMA), due to its remarkable properties such as water solubility and biocompatibility, is extensively used in the biomedical applications including polymer supports for protein synthesis, two-phase catalysts and controlled drug delivery [22,23]. The hydrogels prepared from chitosan derivative/ polyethylene glycol dimethacrylate/ N,N-dimethylacrylamide are promised for the applications in the biomaterials area as bone tissue engineering matrix [24]. Moreover, grafting of the N,N-dimethylacrylamide monomer onto k-carrageenan produces a material which may be used as super absorbent, coating materials and flocculant to remove impurities from coalmine waste water [25].

The current work focuses on the elaboration and swelling behavior of pH- responsive copolymer hydrogel based on N, N-dimethylacrylamide (DMA) combined with an anionic monomer such as crotonic acid (CA). On the other hand, fertilizers such as ammonium nitrate and potassium nitrate were entrapped in a hydrogel structure from DMA and CA by free radical polymerization. The release dynamics of ammonium nitrate and potassium nitrate from hydrogels have been discussed, for the evaluation of the release mechanism and diffusion coefficients.

2. EXPERIMENTAL

2.1. Materials

N, N-dimethylacrylamide (DMA; Merck) and crotonic acid (CA; Fluka) are employed as monomers. N,N-methylenebisacrylamide (NMBA; Fluka), as a cross-linking agent, potassium persulfate (KPS; Merck), as an initiator, potassium nitrate (KNO_3; Merck) and ammonium nitrate (NH_4NO_3; Merck), as fertilizers, were used as received. Distilled water was used for the polymerization reactions and swelling studies.

The following pH-buffered solutions were used in order to examine the swelling behavior [26]: pH = 4, citric acid/phosphate, I = 0.23 M; pH = 6, citric acid/phosphate, I = 0.38 M;

pH = 7, citric acid/phosphate, I = 0.49 M; pH = 9, boric acid/NaOH, I = 0.02 M.; pH = 10, boric acid/NaOH, I = 0.14 M.

The ionic strength is calculated from the following equation:

$I = 0.5 \Sigma(c_i z_i^2)$, where I, c_i and z_i are the ionic strength, the ionic concentration, and charge on each individual ion, respectively.

2.2. Synthesis of non-loading hydrogels

Poly (N,N-dimethylacrylamide) (PDMA) and poly (N,N-dimethylacrylamide -co-crotonic acid) (P(DMA-CAx)) containing 22, 43, 54 and 63 mol % of crotonic acid were synthesized by free-radical polymerization using NMBA (0.32 mol % of the total mole number of monomers) as cross-linking agent and KPS (0.036 mol % of the total mole number of monomers) as initiator.

Polymerization reactions were performed in a 50 ml three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer. DMA and CA monomers with different molar ratios and crosslinker NMBA were dissolved in 4 ml of distilled water. After nitrogen bubbling for 20 min through the solution, the initiator KPS was added. Then, the polymerization was carried out at 56 °C for 15 min. The resultant crosslinked polymers were immersed in distilled water for 5 days, and the water was changed every 24 hours in order to remove any residual monomers. The resulting swollen gels were dried at room temperature for several days and then in a vacuum oven at 60 °C until constant weight. The dry disks were polished to achieve a smooth and uniform surface of 5 mm thickness. The copolymerization reaction is illustrated in Scheme 1.
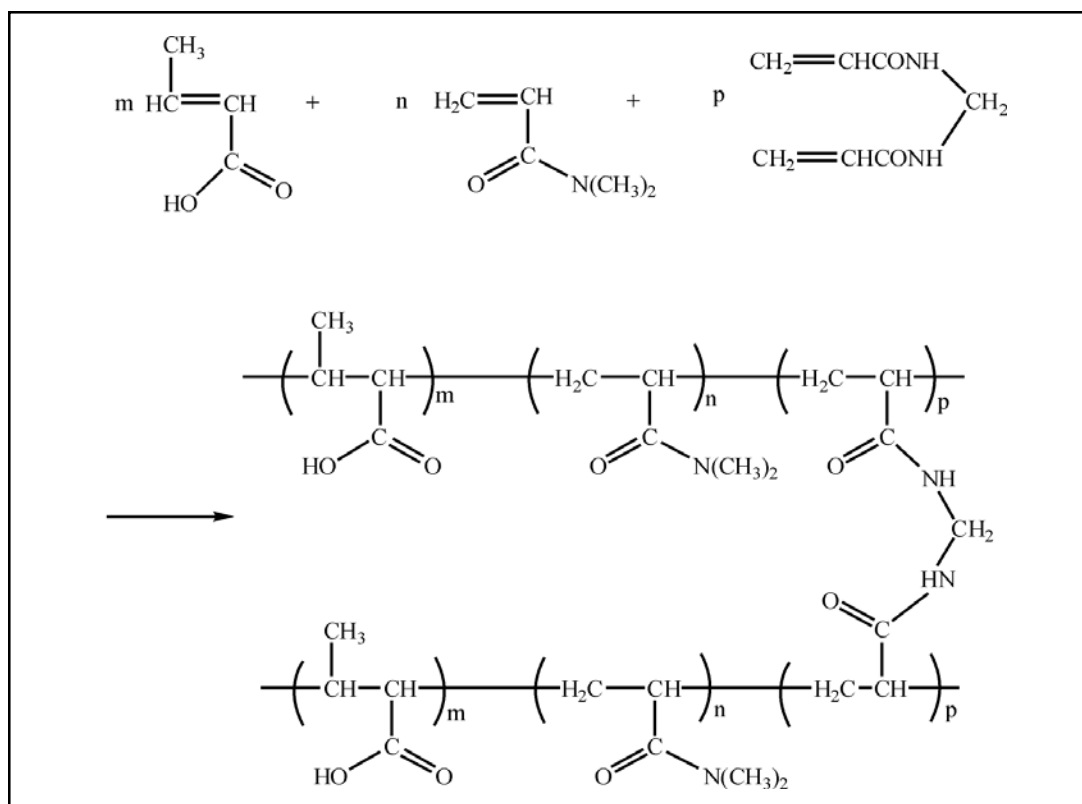
Scheme 1: Schematic representation of copolymerization reaction of crotonic acid with N,N-dimethylacrylamide in the presence of N,N-methylenebisacrylamide at 56 °C.

2.3. Synthesis of fertilizer loading hydrogels

KNO_3 or NH_4NO_3 loading hydrogels were prepared by following the method of non-loading hydrogels preparation and using KNO_3 or NH_4NO_3 solution instead of distilled water. With a one-step in situ copolymerization method, KNO_3 or NH_4NO_3 was loaded within the gel matrix. The resulting hydrogels were dried in a vacuum oven at 60 °C until constant weight without washing them. The polymerization recipes are listed in Table 1.

TABLE 1: Feed composition of the loaded P (DMA-CAx) hydrogels.

DMA/CA mole ratio in feed	DMA (mmol)	CA (mmol)	Fertilizer[a] (wt %)		KPS[b] (mol %)	NMBA[b] (mol %)
			KNO_3	NH_4NO_3		
100/0	41.00	0.00	10	-	0.036	0.32
100/0	41.00	0.00	-	10	0.036	0.32
78/22	32.30	9.30	10	-	0.036	0.32
78/22	32.30	9.30	-	10	0.036	0.32
57/43	24.20	18.60	10	-	0.036	0.32
57/43	24.20	18.60	-	10	0.036	0.32
46/54	20.20	23.67	10	-	0.036	0.32
46/54	20.20	23.67	-	10	0.036	0.32
37/63	16.16	27.27	10	-	0.036	0.32
37/63	16.16	27.27	20	-	0.036	0.32
37/63	16.16	27.27	25	-	0.036	0.32
37/63	16.16	27.27	-	10	0.036	0.32
37/63	16.16	27.27	-	20	0.036	0.32
37/63	16.16	27.27	-	30	0.036	0.32
37/63	16.16	27.27	-	40	0.036	0.32

[a] wt% of the total weight of monomers.
[b] mol % of the total mole number of monomers.

2.4. Characterization

2.4.1. FTIR measurements

Hydrogel samples were prepared by grinding the dry hydrogels with KBr and compressing the mixture to form disks and then dried in vacuum oven at 70 °C for several days. FTIR spectra of these hydrogels were recorded on a model Perkin Elmer spectrophotometer at room temperature with a resolution of 2 cm-1 and were averaged over 60 scans.

2.4.2. Thermogravimetric analysis

Thermogravimetric analysis of the hydrogels was carried out on a TA instrument Q500 under nitrogen atmosphere from 25 °C to 580 °C at a heating rate of 10 °C/ min.

2.5. Swelling measurements

Dried hydrogels were allowed to hydrate in buffer solutions with different pH values 4, 6, 7, 9 and 10 at 25°C. After being fully hydrated, the samples were taken out and the excess water on their surface was gently removed by filter paper.

The weights of the hydrating samples were measured at timed intervals. The swelling ratio (SR) and equilibrium swelling ratio (SRe) are calculated by the following equations [18]:

$$SR\ (\%)\ =\ [(m_t - m_0)/\ m_0] \times 100 \qquad (1)$$

$$SRe\ (\%) = [(m_\infty - m_0)/\ m_0] \times 100 \qquad (2)$$

where m_0 is the mass of the dry gel, m_t is the mass of the swollen gel at time t and m_∞ denotes the mass of

the gel at equilibrium swelling.

2.6. Release of fertilizer

To study the release of KNO_3 and NH_4NO_3, the loaded gels of known weights (0.1 g) were placed in measured volume (100 ml) of distilled water (release medium) under stirred condition. The released amount of KNO_3 and NH_4NO_3 at different time intervals was determined by measuring the conductivity of the release medium using a conductivity meter (INOLAB COND 730) at desired time intervals. This was related to the amount of KNO_3 and NH_4NO_3 using a calibration plot.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

Figure 1a shows the scale - expanded infrared spectra of PDMA and P (DMA-CAx) recorded at room temperature in the 3900-2400 cm^{-1}

region. The spectrum of pure PDMA shows a band at 3503 cm^{-1}, corresponded to hydrogen bonding between carbonyl groups of amide and hydroxyl groups of water. When the CA groups are introduced into PDMA matrix, this latter broadens and gradually shifts to lower wave numbers 3460 cm^{-1}, indicating the presence of hydrogen bonding interactions between carboxylic group of CA and carbonyl of amide.

In the carbonyl stretching 1780-1560 cm^{-1} region, the infrared spectrum of PDMA recorded at room temperature shows a band at 1640 cm-1, assigned to the free carbonyl groups of the amide. With the incorporation of the CA groups within PDMA chain, this band broadens and shifts to lower wavenumbers 1627 cm^{-1}, corresponding to the DMA carbonyl group
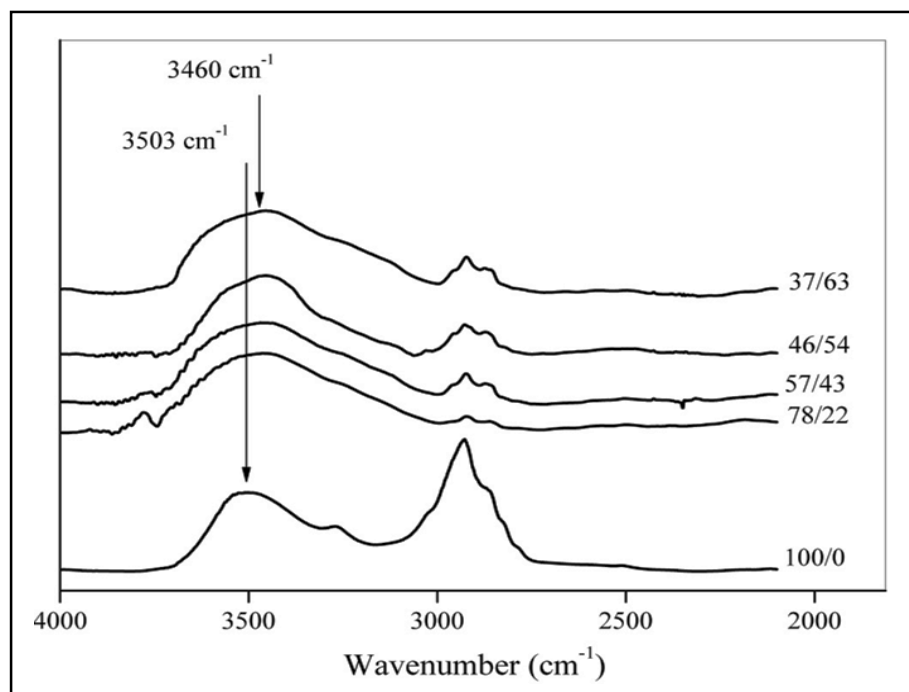

Fig. 1a. Scale-expanded infrared spectra of P(DMA-CAx) hydrogels in the hydroxyl region.

that is directly hydrogen bonded to the CA hydroxyl group. In addition, the shoulder appeared at 1730 cm^{-1} is attributed to free carboxyl groups (Figure 1b).
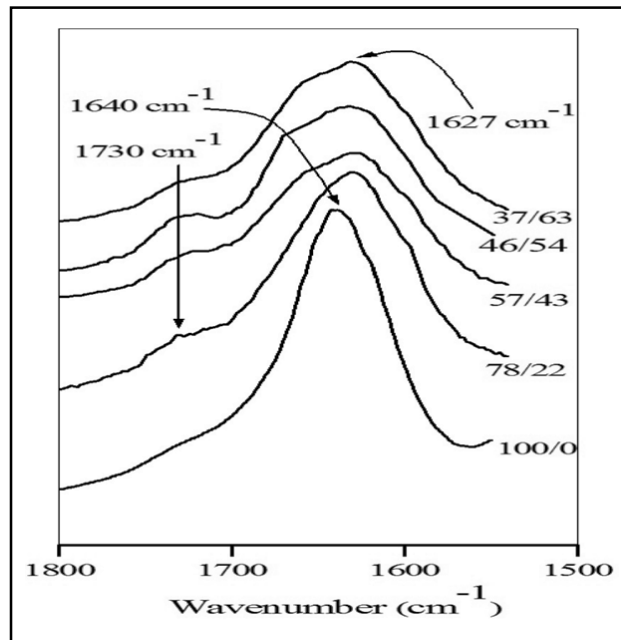

Fig. 1b. Scale-expanded infrared spectra of P(DMA-CAx) hydrogels in the carbonyl Region

The infrared spectra of unloaded and loaded P(DMA-CA63) recorded at room temperature in the 1800-1000 cm^{-1} region are illustrated in Figure 1c. With the incorporation of KNO_3 and NH_4NO_3 into P (DMA-CA63) matrix, we observe a shift of the characteristic band of the carboxyl-carbonyl amide interactions (1627 cm-1) to lower wavenumbers 1616 cm-1 and 1607 cm^{-1}, respectively. In addition, the carbonyl band probably associated with the copolymer/ fertilizer interaction is a free carbonyl band, at 1716 cm^{-1}, which is caused by the liberation of the CA carbonyl group when the CA hydroxyl group forms a hydrogen bond with the unpaired electrons on oxygen atoms of KNO_3 and NH_4NO_3 [27]. The small peak at 1400 cm^{-1} corresponds to the nitrate ion. All these bands indicate the entrapment of KNO_3 and NH_4NO_3 in the hydrogel matrix.

3.2. Thermogravimetric analysis

The thermogravimetric (TGA) and derivative thermogravimetric (DTGA) curves for PDMA and P(DMA-CAx) hydrogels are represented in Figure 2. It is seen that all studied hydrogels, in contrast to PDMA, degrade in two main stages. Parameters, such as temperature of maximum degradation (determined considering the derivative curves) and percentage of mass loss in each stage of degradation for all studied
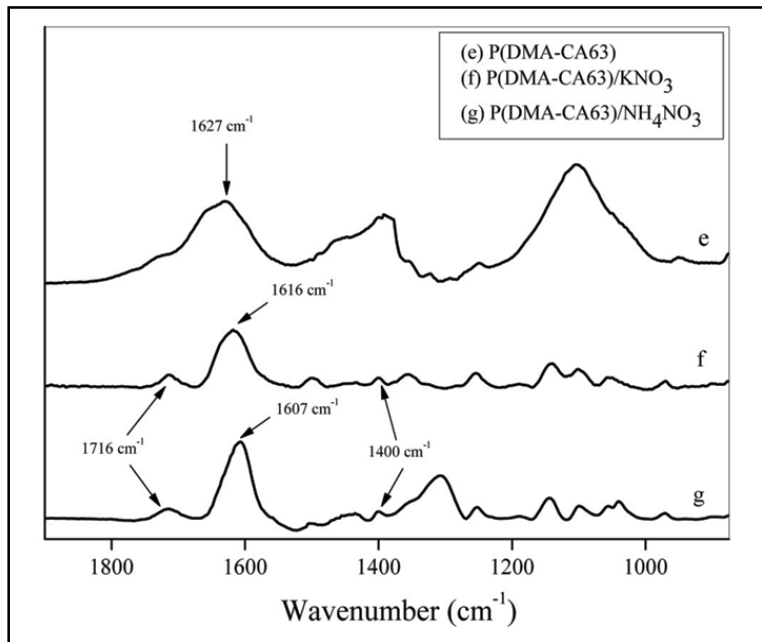
Fig. 1c. Scale-expanded infrared spectra of unloaded and loaded P(DMA-CA63) hydrogels. The content of both KNO_3 and NH_4NO_3 is 20 wt % of the total weight of monomers.
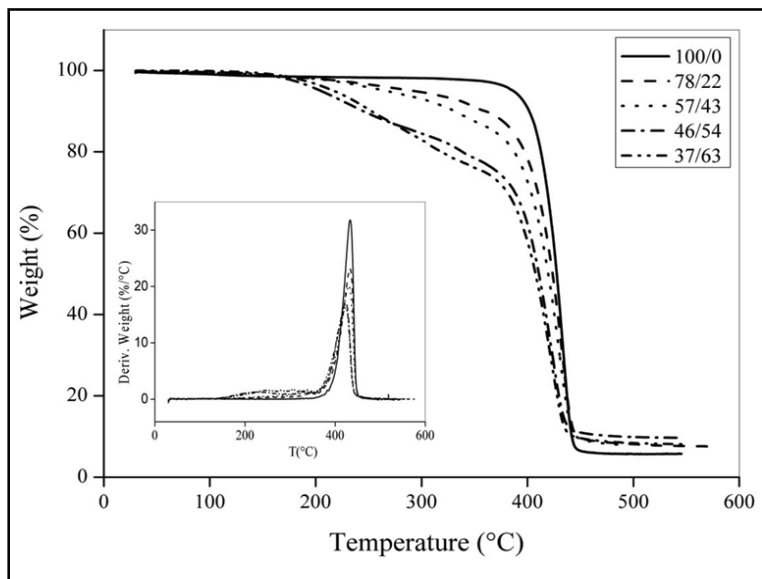

Fig. 2. TGA thermograms and DTGA curves of P(DMA-CAx) hydrogels.

systems, are summarized in Table 2. As observed, the percentage of mass loss for PDMA is 93 % in the temperature range 354-472°C, corresponding to the degradation of the polymer.

For P(DMA-CAx), the percentage of mass loss at the range 8-18 % in stage 1 is assigned to the loss of water absorbed by the hydrophilic groups and water molecules elimination through the formation of cyclic anhydride [28]. In the second stage, at higher temperatures decomposition of anhydride rings takes place

and it is overlapped with degradation of the main chain. The onset temperature of the second main degradation stage as well as temperature of maximum degradation for copolymers decreases with increasing the content of crotonic acid. The amount of residual weight at the end temperature of degradation is in the range 6-10 % for P(DMA-CAx). The reason for incomplete degradation of copolymers is probably the thermal cross-linking induced by heating the sample during thermogravimetric analysis.

TABLE 2. Thermogravimetric parameters for P (DMA-CAx) hydrogels with different compositions of CA.

Hydrogels	Stage 1		Stage 2			Char residue at 500 °C (wt%)
	ΔT^a (°C)	Δm^b (wt%)	ΔT^a (°C)	Δm^b (wt%)	T^c_{max} (°C)	
PDMA	57-132	0.67	354-472	93	433	6
P (DMA-CA22)	146-345	8	359-487	83	432	8
P (DMA-CA43)	164-337	10	354-473	77	430	8
P (DMA-CA54)	145-315	16	348-477	68	423	10
P (DMA-CA63)	159-307	18	338-487	68	422	8

[a]Temperature range.
[b]Total weight loss percentage at the end of the step.
[c]Temperature maximum values of DTGA curves.

3.3. Swelling behavior

3.3.1. Effect of crotonic acid content

The effect of crotonic acid composition on the swelling of the prepared P (DMA-CAx) hydrogels at different pHs (4, 6, 7, 9 and 10) and at 25 °C was investigated. For instance, the swelling curves of P (DMA-CAx) hydrogels with different compositions of CA at pH 7 are given in Figure 3. It is seen that the water uptake by the hydrogels increases with time

and reaches equilibrium state named equilibrium swelling. It is well known that the swelling is induced by the electrostatic repulsion of ionic charges present within the network. Thus, as the number of carboxylic groups increases on going from PDMA to P(DMA-CAx), the swelling increases too. On the other hand, in each pH medium, the hydrophilic nature of the copolymer hydrogel is enhanced by increasing the amount of crotonic acid [29].
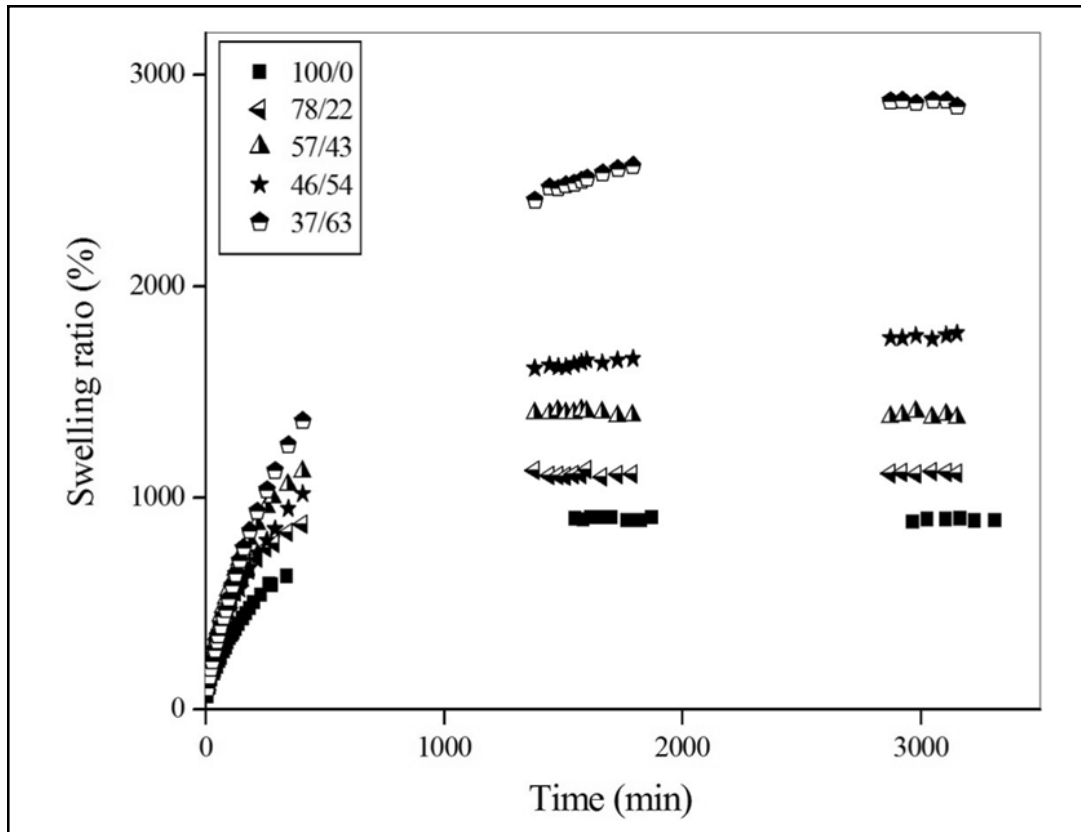
Fig. 3. Effect of crotonic acid content on the dynamic swelling behavior of P(DMA-CAx)
hydrogels in the media of pH 7 at 25 °C.

3.3.2. Effect of pH

Figure 4 represents pH dependence of the equilibrium swelling ratio for P(DMA-CAx) hydrogels at 25 °C in buffer solution from pH 4 to 10. As shown in figure 4, the pure PDMA has not ionic-groups, and as expected it is not responsive to pH. The swelling ratios of P(DMA-CAx) hydrogels are enhanced as the pH values of buffer solutions are increased, and the maximum extent of swelling is reached at pH 9. The hydrogels exhibit lower swelling capability in an acid medium and higher swelling degree

in a basic medium. This is related to the fact that the carboxyl groups could accept or release protons in response to various pH aqueous media. Under acidic conditions, anionic carboxylate groups are protonated. As a result, a compact copolymeric network is formed, leading to a lower swelling ratio. At high pH values, the ionization of the carboxylic acid groups of the gel occurred, consequently, an electrostatic repulsion is generated among polymer networks, so a higher swelling ratio is observed [30,31]. However, beyond pH value 9 a drop in the swelling ratios is noticed. This is

attributed to a shielding effect, in which the high ionic strength of the buffered solution caused fewer acidic side groups to become ionized, decreasing the electrostatic repulsion and the swelling ratio [32]. Indeed, an increase in ionic strength reduces the mobile ion concentration difference between the gel and external medium, causing a shrinking of the gel [33].
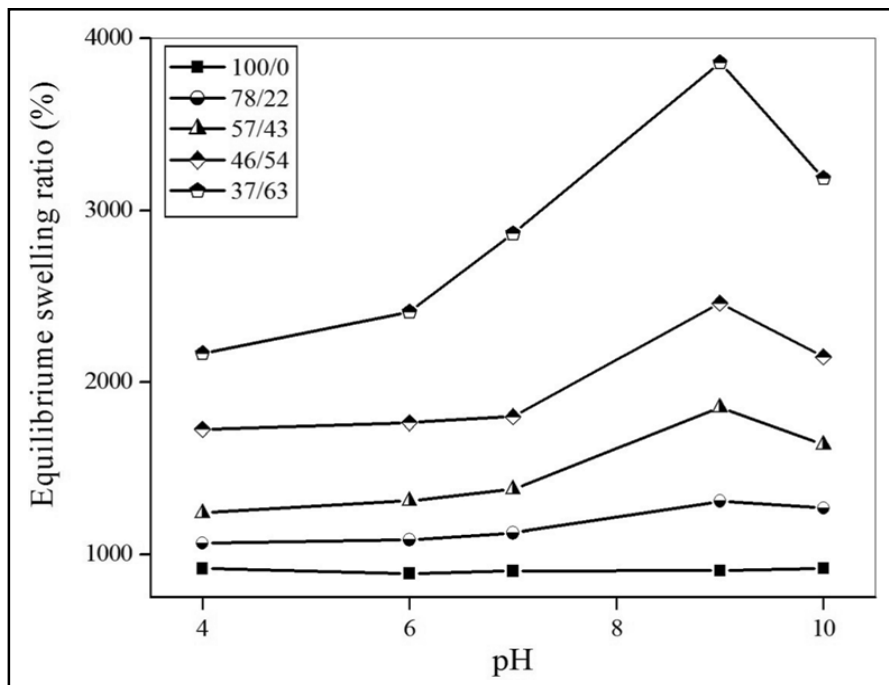

Fig. 4. Effect of pH on the equilibrium swelling ratio of P (DMA-CAx) hydrogels for different CA concentrations at 25 °C.

3.3.3. Diffusion process at different pH

Analysis of the mechanisms of water diffusion in swelling polymeric systems has received considerable attention in recent years, because of the important applications in biomedical, pharmaceutical, environmental, and agricultural engineering fields.

To determine the nature of water diffusion into hydrogel, kinetic modelling was conducted based on Fickian diffusion law for the onset stage of swelling (the model is valid only for the first 60% of the swelling) [34, 35].

$$M_t / M_\infty = kt^n \qquad (3)$$

where M_t is the total amount of water intake at time t, M_∞ is the total amount of water intake at an equilibrium state which is determined by a gravimetric method, k is a swelling coefficient which is a parameter correlated with the polymeric network structures, and n is an exponent characteristic of the swelling which

represents solvent diffusion modes inside hydrogels. Normal Fickian diffusion is characterized by n = 0.5, while case II diffusion by n = 1. A value of n between 0.5 and 1 indicates non-Fickian or anomalous diffusion.

For example, in the representation on ln (M_t/ M_∞) versus ln t for hydrogels with different contents of CA at pH = 7 (Figure 5a), a linearity must be observed until values of the swelling fraction $M_t/M_\infty \leq 0.6$, and n and k are got from the slope and the intercept, respectively. The values of kinetic parameters k and n in different buffer solutions are listed in Table 3. The results indicate that the values of diffusional exponent range generally between 0.49 and 0.75. Hence, non-Fickian or anomalous diffusion occurs and the rate of diffusion of water and the rate of relaxation polymeric chains are comparable.

Initial diffusion coefficient (D_I), average diffusion coefficient (D_A) and late diffusion coefficient (D_L) of water into the hydrogel can be calculated from the equations (4)-(6) [34, 35].

$$\frac{Mt}{M\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{0.5} \qquad (4)$$

$$D_A = \frac{0.049l^2}{t_{1/2}} \qquad (5)$$

$$\frac{Mt}{M\infty} = 1 - \left(\frac{8}{\pi^2}\right) exp\left[\frac{(-\pi^2 Dt)}{l^2}\right] \qquad (6)$$

where M_t and M_∞ denote the amount of water diffused into the hydrogel at time t and infinite time, respectively, D is the diffusion coefficient, t the time and l the thickness of the sample. $t_{1/2}$ is the time at which the swelling is one-half the equilibrium value ($M_t/M_\infty = 0.5$).
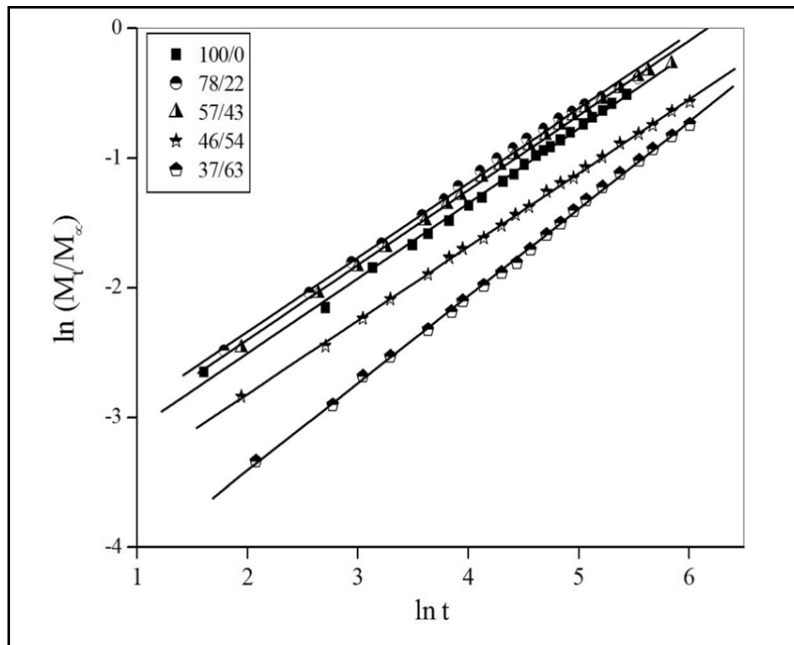

Fig. 5a. Plots of ln (M_t/M_∞) versus ln t for the swelling kinetics of P (DMA-CAx) hydrogels with different compositions of CA in the media of pH 7 at 25 °C.

TABLE 3. Values of n, k, and diffusion coefficients, D, of P (DMA-CAx) hydrogels with various compositions of CA at different pH media.

pH medium	Hydrogels	n	k x 10^2	Diffusion coefficients (cm²/min)		
				DI x 10^5	DA x 10^5	DL x 10^5
4	PDMA	0.55	4.90	1.00	8.87	8.51
	P (DMA-CA22)	0.58	2.44	0.73	6.56	6.57
	P (DMA-CA43)	0.61	2.43	1.36	11.6	10.73
	P (DMA-CA54)	0.61	1.76	0.61	5.11	6.29
	P (DMA-CA63)	0.62	1.48	0.46	3.72	4.44
6	PDMA	0.49	5.04	1.16	11.52	9.73
	P (DMA-CA22)	0.57	2.95	1.23	8.03	7.84
	P (DMA-CA43)	0.70	1.60	1.02	8.08	12.42
	P (DMA-CA54)	0.62	1.92	0.69	5.91	6.54
	P (DMA-CA63)	0.62	1.32	0.39	3.31	4.23
7	PDMA	0,57	2.56	1.44	14.79	12.58
	P (DMA-CA22)	0.59	2.90	1.07	9.41	7.94
	P (DMA-CA43)	0.59	2.70	0.95	8.37	9.20
	P (DMA-CA54)	0.64	1.44	0.46	4.04	4.26
	P (DMA-CA63)	0.67	0.86	0.19	1.78	3.04
9	PDMA	0.49	6.38	5.51	16.69	14.45
	P (DMA-CA22)	0.54	3.07	0.75	6.88	8.90
	P (DMA-CA43)	0.59	3.04	1.29	10.86	13.34
	P (DMA-CA54)	0.64	2.62	0.87	7.21	8.03
	P (DMA-CA63)	0.75	0.56	0.32	4.18	5.73
10	PDMA	0.53	4.31	2.27	20.26	24.90
	P (DMA-CA22)	0.61	3.69	2.01	17.20	16.28
	P (DMA-CA43)	0.62	3.00	1.79	12.85	13.64
	P (DMA-CA54)	0.63	1.60	0.77	6.61	6.50
	P (DMA-CA63)	0.68	1.01	0.48	3.59	3.27

For instance, from the plots M_t/M_∞ versus $t^{1/2}$ (Figure 5b) and ln $(1- M_t/M_\infty)$ versus t (Figure 5c) for P (DMA-CAx) hydogels at pH = 7, straight lines were obtained, and the diffusion coefficients, D_I and D_L, were calculated from the slope of them, respectively. The values of diffusion coefficients for the swelling of the hydrogels at different pH values are reported in Table 3. It is observed from the table that the values for the average and late time diffusion coefficients are higher than the values of initial diffusion coefficients. Indeed, in general, the expansion of the polymer network by the water is slower at the earlier stages of the process, since the gel goes from xerogel (glass state) to hydrogel form [36]. In addition, the low values of diffusion coefficients observed at high contents of CA can be attributed to the fact that the diffusion of water molecules into P (DMA-CA63) is quite slower as compared to the other hydrogel samples.
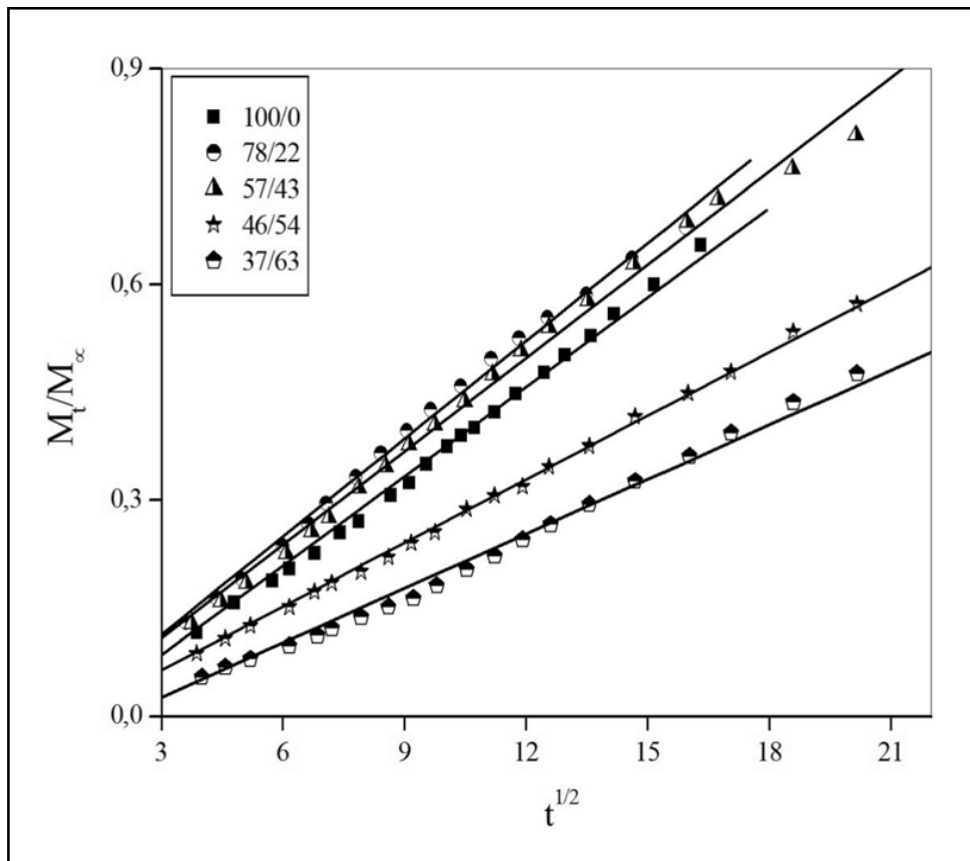

Fig. 5b. Plots of M_t/M_∞ versus $t^{1/2}$ for the swelling kinetics of P (DMA-CAx) hydrogels
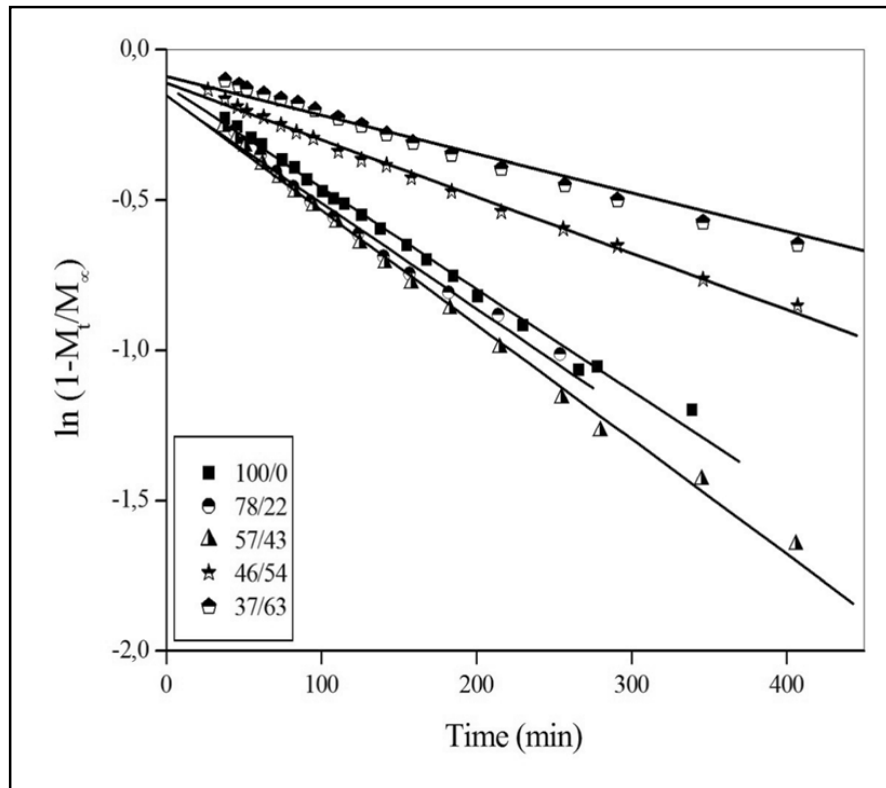with different compositions of CA in the media of pH 7 at 25 °C.

Fig. 5c. Plots of ln $(1-M_t/M_\infty)$ versus time for the swelling kinetics of P (DMA-CAx) hydrogels with different compositions of CA in the media of pH 7 at 25°C.

3.4. Release study of fertilizer

The release of fertilizer from hydrogels occurs as following : penetration of water into the polymeric network, dissolution of the dispersed fertilizer and release of the solute from the hydrogel under swelling conditions. The release of agrochemicals from hydrogel is closely related to its water sorption [37-39]. The highly swelled hydrogel should release a greater amount of solute trapped within the gel. In the present study, we will discuss the effects of fertilizer content and crotonic acid composition on the release kinetics.

3.4.1. Effect of content of fertilizer on the release

KNO$_3$

The effect of KNO$_3$ content of the loaded P(DMA-CA63) hydrogel on the release profile of KNO$_3$ has been investigated by varying the amount of KNO$_3$ in the range 10-25 wt %. The results are depicted in Figure 6a, which reveal that the amount of released KNO$_3$ increases with increasing KNO$_3$ content in the hydrogel. This is attributed to the larger amount of loading. The larger initial load, the faster the

movement of the solvent front penetrating the surface of the loaded hydrogel[40]. A larger loading of the hydrogel may also facilitate the

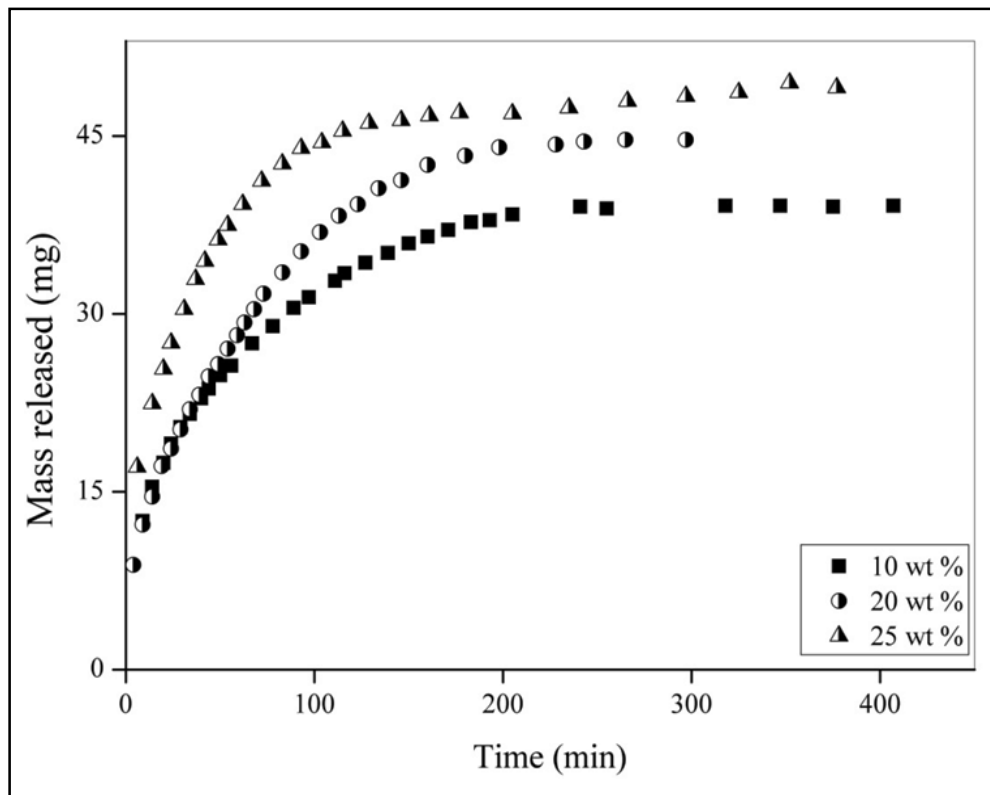relaxation of macromolecular chains of the hydrogel network.

Fig. 6a: Effect of potassium nitrate content on the released amount of potassium nitrate
from the loaded P (DMA-CA63) hydrogel in distilled water at 25°C.

NH_4NO_3

The effect of increasing the amount of NH_4NO_3 in the loaded P(DMA-CA63) hydrogel, on the release profiles of NH_4NO_3 has been investigated by varying the amount of NH_4NO_3 in the range 10-40 wt %. As seen in Figure 6b, the released amount of NH_4NO_3 increases up to 30 wt % and, thereafter, a decrease is observed with further increase in the amount of

NH_4NO_3. The results are attributed to the fact that with increasing NH_4NO_3 content in the hydrogel (from 10 to 30 wt %), the movement of the solvent front penetrating the surface of the loaded hydrogel becomes faster, thus leading to a higher released amount of NH_4NO_3. However, beyond 30 wt % of ammonium nitrate, the structure of copolymer hydrogel could become dense due to hydrogen bonding

between NH_4NO_3 and carboxylic groups of CA, thus reducing the relaxation of macromolecular chains. This results in slow diffusion of water into the hydrogel, and consequently the release of NH_4NO_3 amount decreases.
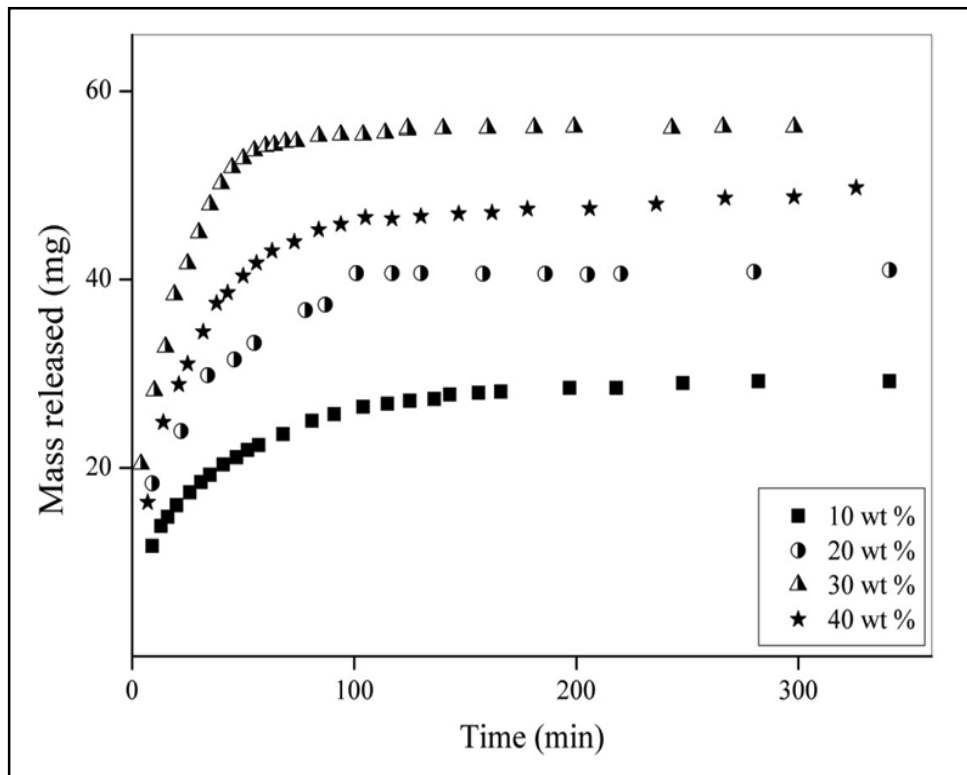

Fig. 6b : Effect of ammonium nitrate content on the released amount of ammonium nitrate from the loaded P (DMA-CA63) hydrogel in distilled water at 25°C.

3.4.2. Effect of crotonic acid content on the release

The effect of crotonic acid content of the loaded P(DMA-CAx) hydrogels on the release profiles of KNO_3 and NH_4NO_3 has been investigated by varying the concentration of crotonic acid in the range 22-63 mol%, and the results are depicted in the Figures 7a and 7b, respectively. It is noticed that the released amounts of KNO_3 and NH_4NO_3 are increased with increasing crotonic acid content. This can be explained by the fact that increasing the hydrophilic groups in the polymer matrix increases the affinity for water, thus resulting in a greater release of fertilizer amount. In other words, the fast release of fertilizer is due to the higher swelling behavior of hydrogel with high concentration of CA. The release results correlate well with the swelling results.
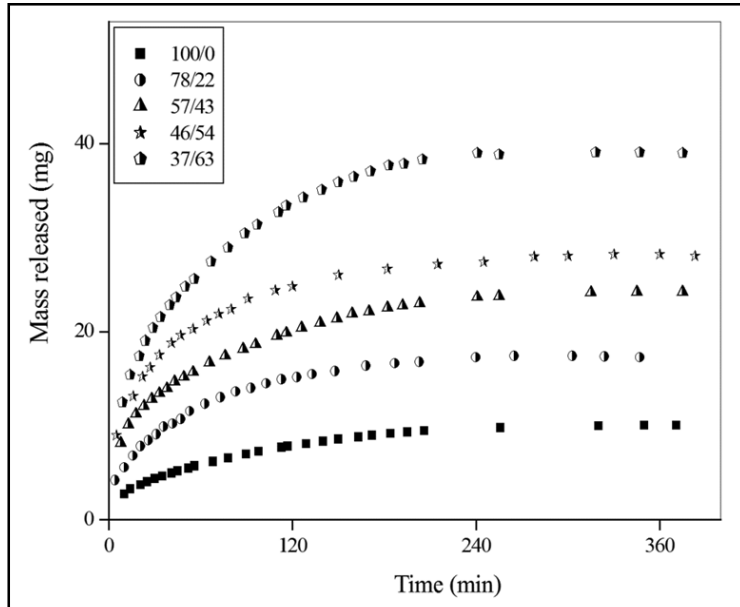
Fig. 7a: Effect of crotonic acid content on the release dynamics of potassium nitrate from the P(DMA-CAx) hydrogels loaded with 10 wt% of potassium nitrate in distilled water at 25°C.
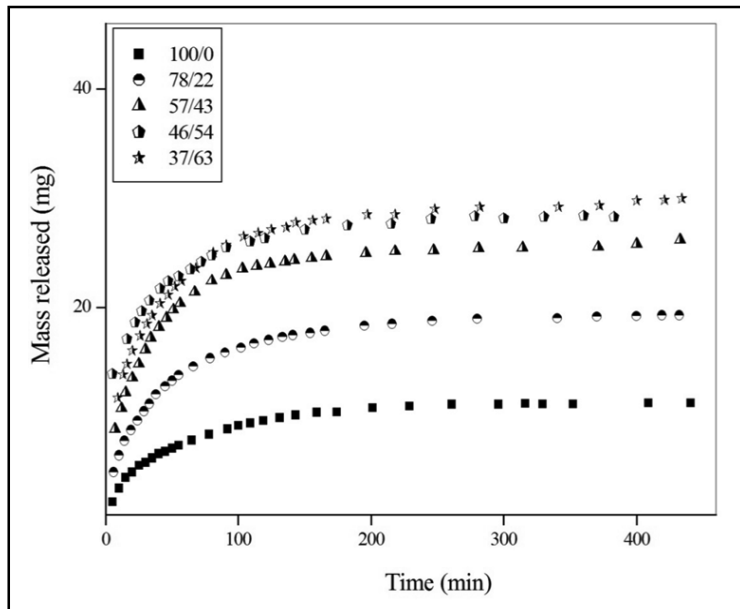

Fig. 7b: Effect of crotonic acid content on the release dynamics of ammonium nitrate from the P (DMA-CAx) hydrogels loaded with 10 wt% of ammonium nitrate in distilled water at 25°C.

3.4.3. Release dynamics fertilizer from polymer matrix

To obtain a more quantitative understanding of the release kinetics of fertilizer from P(DMA-CAx), the release data are also analyzed using the equation (3), where in this case, M_t/M_∞ is the fractional release of fertilizer in time t; k, a kinetic constant characteristic of the fertilizer/polymer system; and n, a characteristic exponent of the fertilizer release mechanism.

For example, Figure 8a can be used to elucidate dependence of ln (M_t/M_∞) on ln t for potassium nitrate release from hydrogels containing different crotonic acid compositions. After having been fitted, the obtained values of k, and n, for the release studies of KNO_3 and NH_4NO_3, are tabulated in Tables 4a and 4b, respectively. It is clearly seen from the tables that the value of exponent n is less than 0.5. This suggests that the release process tends to a Fickian nature.
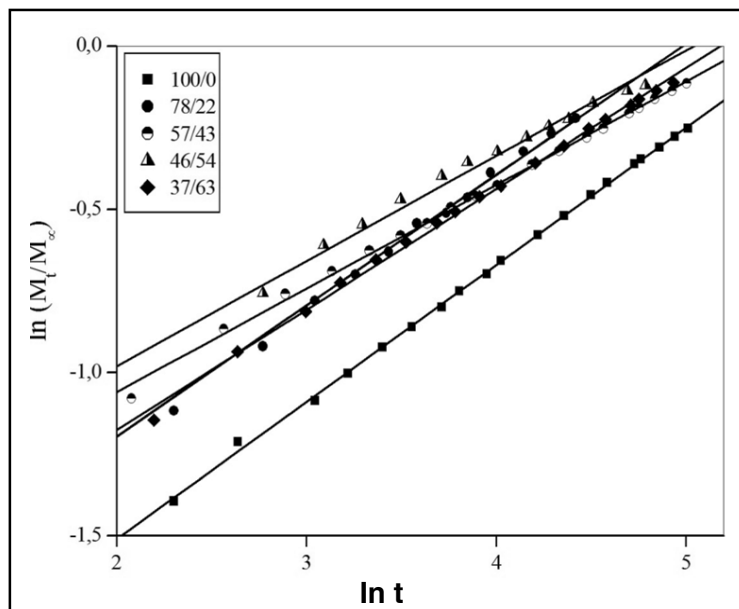

Fig. 8a.   Plots of ln (M_t/M_∞) versus ln t for the se dynamics of potassium nitrate from the P (DMA-CAx) hydrogels loaded with 10 wt% of potassium nitrate in distilled water at 25°C.

Initial diffusion coefficient (D_I), average diffusion coefficient (D_A) and late diffusion coefficient (D_L) of the fertilizer release from the hydrogels can be calculated from the equations (4) - (6). In this case, M_t and M_∞ are the masses of released fertilizer at time t and equilibrium time, respectively. For instance, initial diffusion coefficient DI and late diffusion coefficient DL for potassium nitrate release from hydrogel samples with different crotonic acid contents were evaluated, respectively, from the slope of the plots M_t/M_∞ versus $t^{1/2}$ (Figure 8b) and ln (1 - M_t/M_∞) versus t (Figure 8c). The values of diffusion coefficients for the release studies of KNO_3 and NH_4NO_3 are summarized in Tables 4a and

TABLE 4 a: Values of n, k, and diffusion coefficients, D, for the release of potassium nitrate from loaded hydrogel samples of P (DMA-CAx).

Hydrogels	KNO_3 (wt.%)	n	k x 10^1	Diffusion coefficients (cm^2/min)		
				D_I x 10^4	D_A x 10^4	D_L x 10^4
PDMA	10	0.42	0.96	0.36	4.10	4.17
P (DMA-CA22)	10	0.39	1.42	0.56	6.55	5.84
P (DMA-CA43)	10	0.32	1.84	0.59	6.01	4.89
P (DMA-CA54)	10	0.35	1.83	0.56	7.98	6.10
P (DMA-CA63)	10	0.37	1.47	0.57	6.35	5.56
P (DMA-CA63)	20	0.45	1.04	0.46	5.10	5.60
P (DMA-CA63)	25	0.36	1.80	0.73	9.07	7.32

TABLE 4 b: Values of n, k, and diffusion coefficients, D, for the release of ammonium nitrate from loaded hydrogel samples of P (DMA-CAx).

Hydrogels	NH_4NO_3 (wt%)	n	k x 10^1	Diffusion coefficients (cm^2/min)		
				D_I x 10^4	D_A x 10^4	D_L x 10^4
PDMA	10	0.43	1.12	0.54	6.06	5.77
P (DMA-CA22)	10	0.39	1.45	0.68	7.29	5.49
P (DMA-CA43)	10	0.34	1.97	0.86	9.82	8.89
P (DMA-CA54)	10	0.21	3.46	0.94	14.48	6.75
P (DMA-CA63)	10	0.33	1.99	0.89	10.30	6.98
P (DMA-CA63)	20	0.32	2.22	0.94	10.84	8.58
P (DMA-CA63)	30	0.40	1.99	1.49	16.20	18.64
P (DMA-CA63)	40	0.44	1.49	1.06	11.14	9.57

4b, respectively. It is observed from the tables that the values for initial diffusion coefficients are lower than the values of average and late diffusion coefficients. It reflects that in the initial stages, the rate of release of KNO_3 and NH_4NO_3 from polymer matrix is lower as compared to the average and late stages.

Moreover, the high values of initial, average and late diffusion coefficients for the loaded P(DMA-CA63) hydrogel with 30 wt% of NH_4NO_3 can be assigned to the fact that the release of NH_4NO_3 is faster than the other hydrogel samples.
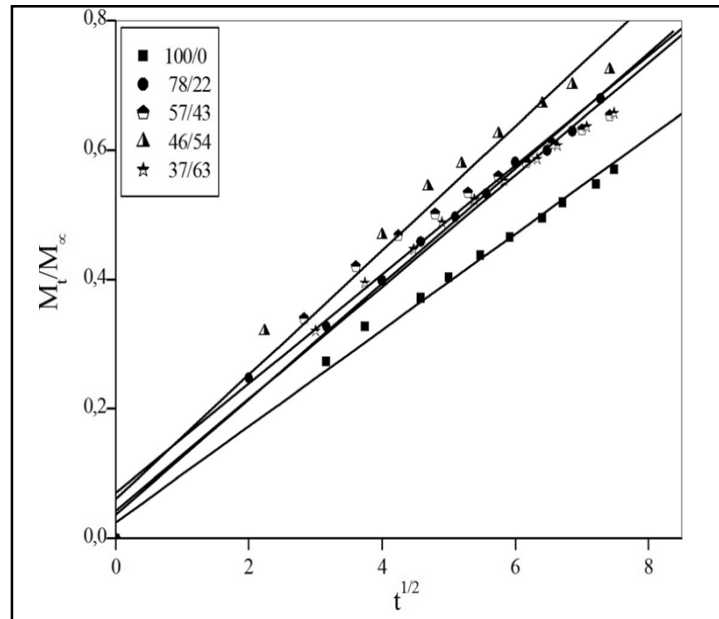
Fig. 8b: Plots of M_t/M_∞ versus $t^{1/2}$ for the release dynamics of potassium nitrate from the P(DMA-CAx) hydrogels loaded with10 wt% of potassium nitrate in distilled water at 25°C.

Fig. 8c: Plots of ln (1- M_t/M_∞) versus time for the release dynamics of potassium nitrate from the P (DMA-CAx) hydrogels loaded with 10 wt% of potassium nitrate in distilled water at 25°C.
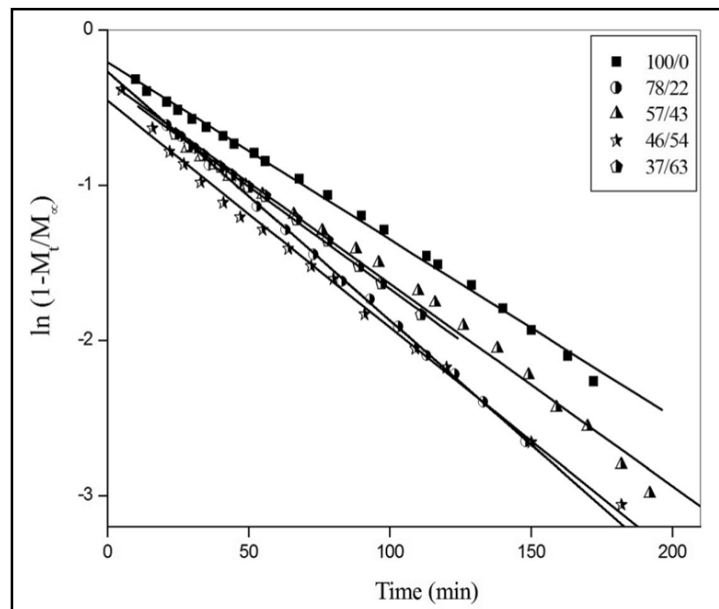
4. CONCLUSION

In this study, poly(N,N- dimethylacrylamide -co- crotonic acid) hydrogels were prepared by free radical polymerization in water using NMBA as crosslinker. As the crotonic acid content in the hydrogel increases its swelling is higher, because of the hydrophilic character of that monomer. The swelling studies of P(DMA-CAx) hydrogels showed that pH of swelling medium is the basic parameter affecting the equilibrium swelling of the hydrogels. From the values of the diffusion exponent n, it is concluded that the non-Fickian diffusion mechanism has occurred for the diffusion of water molecules into polymeric matrix. In each pH medium, the values for the average and late time diffusion coefficients are higher than the values of initial diffusion coefficients. It means that the water molecule slowly infiltrates into hydrogels at the earlier stages of the process.

The second part of this study has shown that the release of KNO_3 and NH_4NO_3 from the hydrogel could maintain a slow rate, and the release rate was closely related to the compositions of crotonic acid, KNO_3 and NH_4NO_3. The values of the diffusion exponent are less than 0.5, indicating that the release of KNO_3 and NH_4NO_3 from P(DMA-CAx) hydrogels fits a fickian behavior. The values for average and late time diffusion coefficient have been observed higher than those of initial diffusion coefficient. It means that in the start, the rate of release of fertilizer from the polymer matrix has been lower than the latter stages.

As a result, these hydrogels show a potentiality to act as a carrier for controlled release of fertilizers and may help to prevent environmental pollution.

REFERENCES

1. Y. Huang, H. Yu and C. Xiao, *Carbohydr. Polym.* 69 (2007) 774.

2. D.S. Bag, S. Alam and G.N. Mathur, *Smart Mater. Struct.* 13 (2004) 1258.

3. D.S. Bag and S. Alam, *Chirality.* 24 (2012) 506.

4. S.P. Zhao, M.J. Cao, L.Y. Li and L.W. Xu, *Polym. Degrad. Stab.* 95 (2010) 719.

5. D.S. Bag and A.K. Saxena, in "Kirk-Othmer Encyclopedia of Chemical Technology," John Wiley & Sons, Inc. New York, 2014, pp.1.

6. R. Katiyar, D.S. Bag and I. Nigam, *J. Polym. Mater.* 30 (2013) 15.

7. M. Şen, Ö. Kantoglu and O. Güven, *Polymer.* 40 (1999) 913.

8. T. Tanaka, I. Nishio, S.T. Sun and S. Ueno-Nishio, *Science.* 218 (1982) 467.

9. A. Suzuki and T. Tanaka, Nature. 346 (1990) 345.

10. A. S. Hoffman, *Macromol. Symp.* 98 (1995) 645.

11. A. S. Hoffman, *Adv. Drug. Deliv.* 43 (2002) 3.

12. J. Kopeček, *Biomaterials.* 28 (2007) 5185.

13. K.Y. Lee and D.J. Mooney, *Chem. Rev.* 101 (2001) 1869.

14. B. Azeem, K. Kushaari, B. Z. Man, A. Basit and H.T. Thanh, *J. Control. Release.* 181 (2014) 11.

15. A. M. Senna, J.B. Do Carmo, J.M.S. Da Silva and V. R. Botaro, *J. Environ. Chem. Eng.* 3 (2015) 996.

16. B. Singh and V. Sharma, Carbohydr. Polym. 101 (2014) 928.

17. Y. Qiu and K. Park, Adv. Drug . *Deliv. Rev.* 64 (2012) 49.

18.   Y. Luo, K. Zhang, Q. Wei, Z. Liu and Y. Chen, Acta. *Biomater.* 5 (2009) 316.

19.   B. Tyliszczak, J. Polaczek and K. Pielichowski, Polish. *J. Environ. Stud.* 18 (2009) 475.

20.   A. Pourjavadi, M. Doulabi, R. Soleyman, S. Sharif and S.A. Eghtesadi, React. Funct. *Polym.* 72 (2012) 667.

21.   K. Zhong, X.L. Zheng, X.Y. Mao, Z.T. Lin and G.B. Jiang, Carbohydr. *Polym.* 90 (2012) 820.

22.   S. Kondo, N. Nakashima, H. Hado and K. Tsuoa, *J. Polym. Sci., Part A: Polym. Chem.* 28 (1990) 2229.

23.   A. Valdebenito and M.V. Encinas, *Polym. Int.* 59 (2010) 1246.

24.   G. Ma, D. Yang, Q. Li, K. Wang, B. Chen. , J.F. Kennedy and J. Nie, Carbohydr. *Polym.* 79 (2010) 620.

25.   D.K. Mishra, J. Tripathy and K. Behari, Carbohydr. *Polym.* 71 (2008) 524.

26.   Alexeev. : "Analyse Qualitative", 4ème édition, 1980.

27.   E. Karadağ, D. Saraydin, Y. Çaldiran and O.Güven, Polym. Adv. Technol. 11 (2000) 59.

28.   M. Ś. Żeliazkow *Polym. Degrad. Stab.* 91 (2006) 1233.

29.   H. El-Hamshary, *Eur. Polym. J.* 43 (2007) 4830

30.   S. Bennour and F. Louzri, *Adv. Chem.* (2014) 1.

31.   M. Pulat and M. Çetin, *J. Bioact. Compat. Polym.* 23 (2008) 305.

32.   C.S. Brazel and N.A. Peppas, *Macromolecules.* 28 (1995) 8016.

33.   R. Katiyar, D.S. Bag and I. Nigam, *Adv. Mat. Lett.* 5 (2014) 214.

34.   P.L. Ritger and N.A. Peppas, *J. Control. Release.* 5 (1987a) 23.

35.   P.L. Ritger and N.A. Peppas, *J. Control. Release.* 5 (1987b) 37.

36.   D.M. Garcıa , J.L. Escobar , Y. Noa , N. Bada, E. Hernáez and I. Katime, *Eur. Polym. J.* 40 (2004) 1683.

37.   P. Colombo, R. Bettini and N. A. Peppas, *J. Control. Release.* 61 (1999) 83.

38.   A. K. Bajpai and A. Giri, Carbohydr. *Polym.* 53 (2003) 271.

39.   S.M. Ma, M.Z. Liu and Z.B. Chen, *J. Appl. Polym. Sci.* 93 (2004) 2532.

40.   A. K. Bajpai and A. Giri, React. Funct. *Polym.* 53