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The releases of agrochemicals from radiation induced acrylamide/crotonic acid hydrogels

Dursun Saraydin[1,*], Erdener Karadağ [2], Olgun Güven[3]

[1] Chemistry Department, Cumhuriyet University, TR-58140 Sivas, Turkey
[2] Chemistry Department, Adnan Menderes University, TR-09010 Aydin, Turkey
[3] Chemistry Department, Hacettepe University, TR-06532 Beytepe Ankara, Turkey

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Summary

The aim of this work was to test the application of new copolymeric poly(acrylamide/ crotonic acid) (AAm/CA) hydrogels to agrochemicals (sodium 2,2 dichloropropionate (dalapon), ammonium nitrate, potassium nitrate and ammonium sulfate) releases. AAm/CA hydrogels containing agrochemicals is prepared by two different composition of crotonic acid and two different γ-rays doses. The herbiside such as sodium 2,2 dichloropropionate (dalapon) and fertilizers such as ammonium nitrate, potassium nitrate and ammonium sulfate were trapped in the gels by including it in the feed mixture of radiation polymerization. The equilibrium swelling degree in water was between 1020% and 1840%. The swelling kinetics of the hydrogels were studied at 25 °C, and the initial swelling rate, swelling rate constant, maximum swelling, diffusional exponent and diffusion coefficient of the process were obtained. The concentration of the released of agrochemicals from the hydrogels was determined by conductivity measurements. The initial releasing rate, release rate constant, maximum concentration of releasing agrochemicals were calculated. As a result, if AAm/CA hydrogels containing agrochemicals were swelled in water, release of agrochemicals was increased with the raising of crotonic acid quantities in the hydrogel and γ-rays doses.

Introduction

Hydrogels are polymers which will absorb and swell with a significant proportion of water without dissolution. The water-swollen hydrogels with high degrees of sweling can provide rate-controlling barriers of water soluble chemicals allowing highest attainable fluxes from polymers. Hydrogels have widespread applications in the biomedicine, bioengineering, pharmaceutical, vetenary, food industry, agriculture and related fields. It is used as controlled release systems of drugs and, a carrier of water and pesticides in agriculture field (1-3).

The use of chemicals such as pesticides and fertilizers in agriculture, and other environmental applications, is important part of plant and animal managements (4). These chemicals is incorporated into a polymeric carrier in a controlled release system (5,6). Acrylamide (AAm) hydrogels and its derivatives were used in agricultural fields as carriers of agrochemicals and soil conditioners (7,8). In previous study, radiation induced acrylamide/crotonic acid (AAm/CA) hydrogels were prepared with and without crosslinkers (9,10).

* Corresponding author

The purpose of this study is the use of a new radiation induced hydrogels based on copolymers of acrylamide (AAm) and crotonic acid (CA), with capacity of high water content, on agrochemicals releases. The agrochemicals used in this work were the herbicide such as sodium 2,2 dichloropropionate (dalapon) and the fertilizers such as ammonium nitrate, potassium nitrate (KNO_3) ammonium sulphate, which were included in these new hydrogels by trapping in the feed mixture of radiation polymerization.

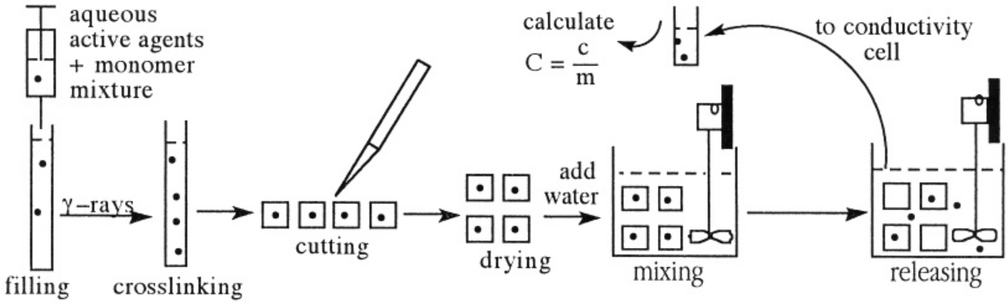
Experimental

For the preparation of hydrogels; 1 g of acrylamide (AAm) (BDH, Poole-UK) and 20 or 40 mg of crotonic acid (CA) (Sigma, St. Louis, US) were mixed with 1 ml water or 1 mol dm^{-3} 1 ml of the aqueous solution of sodium 2,2 dichloropropionate (dalapon) (Sigma, St. Louis, USA), or ammonium nitrate (NH_4NO_3) or potassium nitrate (KNO_3) or ammonium sulphate $(NH_4)_2SO_4$) (Merck, Darmstadt, Germany). These solutions were placed in PVC straws of 3 mm in diameter and irradiated at 2.6 and 5.2 kGy in air at ambient temperature in a ^{60}Co Gammacell 220 type γ irradiator at a fixed dose rate of 0.72 kGy hr^{-1}. The dose rate was determined by the conventional Fricke dosimeter. Fresh AAm/CA hydrogels obtained in long cylindrical shapes were cut into pieces of 5-7 mm in length. They were dried in air and a vacuum, and stored for swelling and releasing studies. After radiation polymerization process, the samples were optically transparent.

Dried hydrogels were left to swell in distilled water at 25±0.1°C to determine the parameters of swelling and diffusion. Swollen gels which were removed from the water bath at regular intervals were dried superficially with filter paper, weighed and placed in the same bath.

About 1 g AAm/CA hydrogel containing agrochemicals were transferred into 250 mL of triple distilled water and allowed to release of agrochemicals. Conductivity of the solutions were measured at the regular intervals at 25±0.1 °C in the water bath while the solutions were stirred by a mechanical mixer. Conductimetric measurements carried out using a JENWAY model conductivity meter cell. The concentrations of released agrochemicals were measured by means of precalibrated scales. The scheme of hydrogel experiment is shown in Scheme-1.

Also the release of dalapon in continuos system was investigated. AAm/CA hydrogel containing dalapon were put in 5 mL of tube and triple distilled water is treated with the hydrogel in the flow rate of 5 mL min^{-1} by the using of a peristaltic pomp. At the end of exit of the system, 250 mL of solution of dalapon was collected, the conductivity was measured for each collected solutions.



Scheme-1. The scheme of hydrogel experiments.

Results and Discussion

Ionizing radiation is very useful in producing polymers from monomeric units and in modifying the properties of preexisting polymers. Ionizing radiation provides a very clean method for the obtention and modification of polymers. No chemicals or catalysts have to be added to the reaction matrix. The polymerization achieved by free radicals (occasionally ions) created in the material at the end of process. Therefore, no chemicals or catalysts remain in the material by radiation (11).

The radiation technique seems to be promising for preparation of hydrogels because a polymer in aqueous solution or water-swollen state readily undergoes crosslinking on irradiation to yield a gel-like material. Since the hydrogel is not contaminated with foreign additives and crosslink is formed by stable C-C bonds, it is of interest to study the preparation of hydrogels by irradiation (12,13).

For preparation AAm/CA hydrogels containing agrochemicals along with ionizing radiation processing were used in this study. When monomers of AAm and CA are irradiated with ionization rays such as γ-rays, one of double bonds of –C=C– on the monomers breaks with the effect of ionization irradiation and free radicals are generated. Then these free radicals react with each other, and a copolymer ofAAm/CA is formed.

When irradiation dose is increased during ionising radiation of AAm and CA, the polymer chains crosslink and then gels are obtain. Gelation of AAm/CA copolymers occurs at a dose 2 kGy of γ ray irradiation doses at ambient temperature (12). So, dose of 2.6 kGy and 5.2 kGy of γ rays is the base for preparation of AAm/CA hydrogels containing agrochemicals. Dried gels are of glassy form and very hard, but swollen gels are soft. The hydrogels are obtained in the form of cylinders. Upon swelling, the hydrogels retained their shapes.

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. Swelling is one of the most important parameters about swelling studies. The swelling (S%) was calculated from the following relation (9,10):

$$\%S = ((m_t - m_o)/m_o) \times 100 \qquad 1$$

where m_t is the mass of the swollen gel at time t and m_o is the mass of the dry gel at time 0.

The water intake of initially dry hydrogels was followed for a long time. Swelling curves of AAm/CA hydrogels containing 20 mg CA and agrochemicals and irradiated to 2.6 kGy were plotted and, are shown in Figure 1. If Figure 1 is examined, it can be seen swelling is increased by time, however, awhile this becomes a constant swelling. This value of swelling may be named equilibrium of swelling. The values of equilibrium swelling of AAm/CA hydrogels are given in Table 1.

For extensive swelling of polymers, it can be written following relation (14,15);

$$\frac{t}{S} = A + B\,t \qquad 2$$

Where B = 1/Seq is the inverse of the maximum or equilibrium swelling, $A = 1/(k_S\, Seq^2)$ is the reciprocal of the initial swelling rate the gel, k_S is swelling rate constant. The relation represents second order kinetics (14).

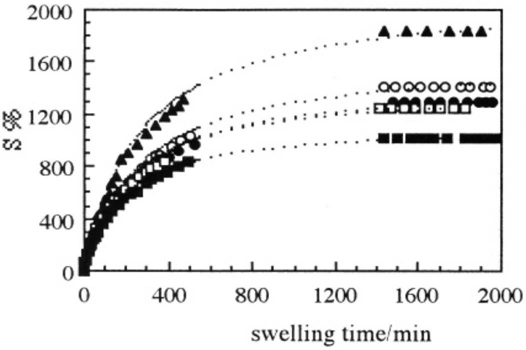


Figure 1. Time-depending swelling of AAm/CA hydrogels

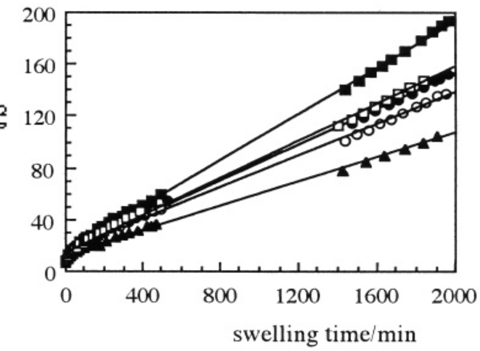


Figure 2. Swelling kinetcs curves of AAm/CA hydrogels

▲; no agrochemicals, ●; KNO_3, ○; NH_4NO_3, ■; $(NH_4)_2SO_4$, ❑; dalapon, ··· calculated.

Figure 2 shows the linear regression of the swelling curves obtained by means of equation 3. The initial swelling rate, swelling rate constant and theoretical equilibrium swelling of the hydrogels are calculated from the slope and intersection of the lines and, are presented in Table 1.

Table 1 shows that the values of theoretical equilibrium swelling of the hydrogels are parallel the results of equilibrium swelling of the gels. Swelling processes of AAm/CA without agrochemicals hydrogel is quicker than the swelling rate of AAm/CA hydrogels containing dalapon, NH_4NO_3, KNO_3 and $(NH_4)_2SO_4$. The swelling studies indicated that swelling degree of AAm/CA hydrogels in water were increased with following order; water >NH_4NO_3 > KNO_3 > dalapon > $(NH_4)_2SO_4$. The reason of these results is ionic groups on agrochemicals. These ions are caused by preventing the water into the hydrogels, thus, the swelling of the hydrogel containing agrochemical has decreased than AAm/CA hydrogel prepared in water.

Analysis of the mechanisms of water diffusion in swellable polymeric systems has received considerable attention in recent years because of the important applications of swellable polymers in the biomedical, pharmaceutical, environmental, and agricultural fields (2). The following equation was used to determine the nature of diffusion of water into hydrogels

$$F=k\,t^n \qquad 3$$

where F denote the fraction of solvent which diffused into the gel at time t, k is a constant related to the structure of the network, and the exponent, n, is a number to determine the type of diffusion. For cylindrical shapes, n=0.45-0.50 and corresponds to Fickian diffusion whereas $0.50<n<1.0$ indicates that diffusion is non-Fickian type. This equation is applied to the initial stages of swelling and plots of ln F versus In t yields straight lines up to almost a %60 increase in the mass of hydrogel (2). For the hydrogels, ln F versus ln t plots were drawn using the kinetics of swelling and, are shown in Figure 3.

The n and k were calculated from the slopes and intercepts of the lines, respectively. The values of diffusion constants and diffusional exponents of AAm/CA hydrogels containing agrochemicals are listed in Table 1.

Table-1. The values of swelling and diffusion of the AAm/CA hydrogels containing 20 mg of crotonic acid and agrochemicals. Total given doses are 2.6 kGy.

Agrochemicals	%S	r_i x 10^2	k_S x 10^4	S_{eq}	k x 10^2	n	D x 10^6/cm^2 s^{-1}
no agrochemicals	1840	4.74	1.80	21.12	1.41	0.66	2.22
ammonium nitrate	1420	6.14	2.34	16.28	1.38	0.67	2.10
potassium nitrate	1290	6.37	3.03	14.50	1.83	0.62	2.03
ammonium sulphate	1020	8.95	5.29	11.17	2.22	0.61	2.20
dalapon	1250	7.16	3.47	13.97	1.98	0.62	2.08

In Table 1, it is shown that the values of diffusional exponent are ranged between 0.61 and 0.67. In the experiments, the number to determine type of diffusion (n) was found to be over 0.50. Hence the diffusion of water into AAm/CA copolymers were taken as a *non-Fickian* character (2, 9, 10). This is generally explained as a consequence of slow relaxation of polymer matrix.

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behavior. For hydrogel characterization, diffusion coefficient can be calculated by various methods. The short time approximation method is used for calculation of diffusion coefficients of AAm/CA hydrogels (16). The short time approximation is valid for the first 60% of the swelling. The diffusion coefficients of the cylindirical AAm/CA hydrogels are calculated from the following relations:

$$F = 4\left[\frac{D\,t}{\pi r^2}\right]^{1/2} - \pi\left[\frac{D\,t}{\pi r^2}\right] - \frac{\pi}{3}\left[\frac{D\,t}{\pi r^2}\right]^{3/2} + \ldots\ldots \qquad 4$$

Where D in cm^2 s^{-1}, t in sec and r is the radius of cylindrical polymer sample. A graphical comparations of equations 3 and 4 shows the semi-emprical equation 3 with n=0.5 and $k=4(D/\pi r^2)^{1/2}$. For the hydrogels, F versus $t^{1/2}$ plots are plotted and, are shown in Fig. 4. The values of the diffusion coefficient of Aam/CA hydrogels containing agrochemicals are listed in Table 1.

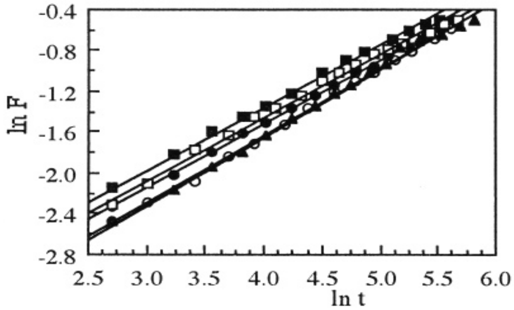


Figure 3. ln F-ln t curves of AAm/CA hydrogels containing agrochemicals.

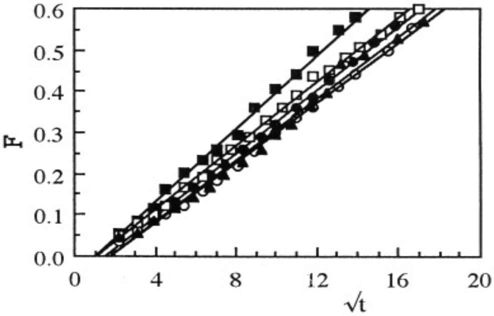


Figure 4. F-√t curves of AAm/CA hydrogels containing agrochemicals.

▲; no agrochemicals, ●; KNO_3, ○; NH_4NO_3, ■; $(NH_4)_2SO_4$, □; dalapon.

If Table 2 is examined, it is shown that the values of the diffusion coefficient of the hydrogels varied from $2.03x10^{-6}$ to $2.22x10^{-6}$ cm^2 s^{-1}. Diffusion of water to AAm/CA without agrochemicals hydrogel is quicker than the diffusion of water to AAm/CA hydrogels containing agrochemicals. This result is parallel to swelling result of the hydrogels..

To examine release of the agrochemicals from AAm/CA hydrogels, the released amount of the agrochemicals (C/ mM g $hydrogel^{-1}$) were plotted to release time, and a represantative release curves are shown in Figure 5.

For the release of agrochemicals from the hydrogel, it can be written following second order kinetics relation;

$$\frac{t}{C} = Q + W\,t \qquad 5$$

Where Q = 1/Cmax is the inverse of the maximum concentration of released agrochemicals, W = $1/(k_R Cmax^2)$ is the reciprocal of the initial release rate the gel, k_R is releasing rate constant.

Figure 6 shows the linear regression of the swelling curves obtained by means of equation 5. The initial release rate (mM g^{-1} min^{-1}), theoretical equilibrium concentration of released agrochemicals from the hydrogels (mM g^{-1}) and releasing rate constant (mM^{-1} g min^{-1}) were calculated from the slope an intersection of the lines and, are presented in Table 2.

Table 2 shows that the values of theoretical maximum concentration of releasing agrochemicals from the hydrogels are parallel the results of equilibrium concentration of releasing agrochemicals from the gels. On the other hand, the release of agrochemicals has increased when the quantity of crotonic acid in the hydrogels increases. With raising the irradiation doses, also the release of agrochemicals has generally increased.

The initial release rate and releasing rate constant of the AAm/CA hydrogels containing dalapon are higher than the other hydrogels containing ammonium nitrate, potassium nitrate and ammonium sulfate. So, release process of the herbicide from the AAm/CA hydrogels are quicker than the release of the fertilizers.

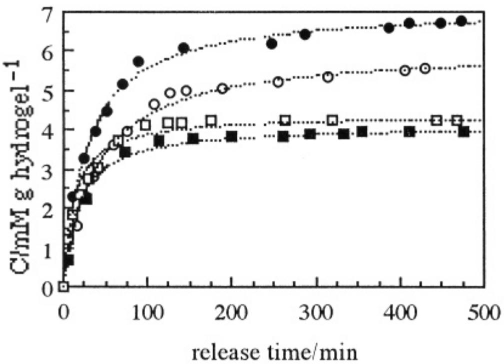


Figure 5. Time-depending release of agrochemicals from AAm/CA hydrogels.

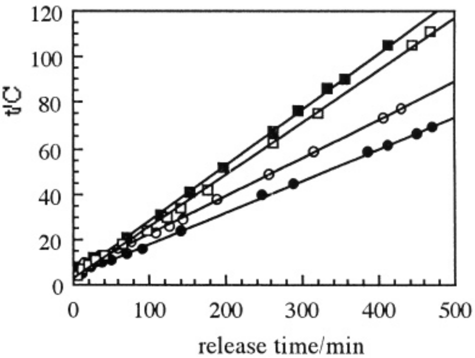


Figure 6. Second order release kinetics of agrochemicals from AAm/CA hydrogels.

●; KNO_3, ○; NH_4NO_3, ■; $(NH_4)_2SO_4$, □; dalapon ·····; calculated from eq.5.

Table 2. Changing of the release parameters of the agrochemicals from AAm/CA hydrogels with irradiation dose and content of CA in the hydrogels.

Agrochemicals	Dose, kGy	Mass of CA, mg	C, mM g gel^{-1}	Equilibrium time, min	$r_i \times 10^2$	$k_R \times 10^3$	C_{cal}, mM g gel^{-1}
ammonium nitrate	2.6	20	4.08	130	12.37	5.22	4.87
	2.6	40	5.21	255	15.79	4.31	6.05
	5.2	20	4.63	190	23.25	7.08	5.42
	5.2	40	6.15	220	20.77	4.73	7.01
potassium nitrate	2.6	20	2.71	140	7.72	6.01	3.59
	2.6	40	5.21	280	25.39	5.00	7.13
	5.2	20	6.15	250	19.52	5.94	5.73
	5.2	40	4.78	250	15.38	4.74	5.70
ammonium sulphate	2.6	20	3.42	130	17.27	12.81	3.67
	2.6	40	3.85	260	23.34	13.82	4.11
	5.2	20	2.84	170	19.52	13.99	3.14
	5.2	40	3.61	155	15.38	11.69	4.03
dalapon	2.6	20	4.13	100	49.75	27.69	4.24
	2.6	40	4.14	100	35.33	19.07	4.37
	5.2	20	4.35	110	40.98	18.46	4.63
	5.2	40	5.36	110	60.31	19.65	5.54

AAm/CA hydrogels containining agrochemicals can be defined as “swelling-controlled system” in controlled releases (17). In swelling-controlled polymeric system, the agrochemical is dissolved in monomer mixture. After the radiation polymerization process, a solvent-free, glassy polymeric matrix is obtained, with agrochemical uniformly dispersed it in.

Initially, there is no agrochemical diffusion through the solid polymer phase. However, as the water enters the matrix, the polymer swells, and swollen polymer allows the agrochemical to diffuse outward (17).

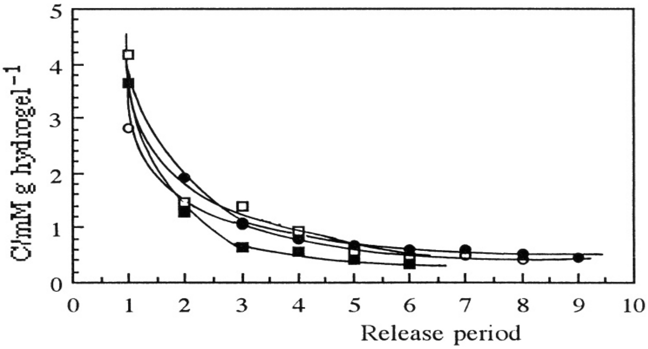


Figure 4. The release of dalapon from AAm/CA hydrogels in the continuos system. ○; 2.6 kGy/20 mg CA, ●; 2.6 kGy/40 mg CA, □; 5.2 kGy/20 mg CA, ■; 5.2 kGy/40 mg CA.

As it can be seen in Figure 4, the release of ammonium nitrate, potassium nitrate, ammonium sulphate and dalapon from AAm/CA hydrogels at continuous system were decreased by raising of release period number. After sixth release period, the released amount of the dalapon has arrived to the constant values of the concentration. This result was parallel to the released amount of the dalapon in the batch systems.

As a result, it is said that AAm/CA hydrogels containing agrochemicals can be used at the release of ammonium nitrate, potassium nitrate, ammonium sulphate and dalapon. At the same time, the hydrogel can be used as a soil conditioner due to the high water absorption capacity. However, the preparation conditions of AAm/CA hydrogels containing agrochemicals are not enough for long releasing periods. Because, irrigation in the agricultural applications could be made, if it is possible, for the longest releasing periods. For this, it must be used lower γ rays dose and higher content of crotonic acid in used the hydrogel systems for the controlled release of the agrochemicals.

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