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Relationship between the swelling process and the releases of water soluble agrochemicals from radiation crosslinked acrylamide/itaconic acid copolymers

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Summary

An attempt was made in this study to relate the releases of water soluble herbicide (sodium 2,2 dichloropropionate (Dowpon)) and model fertilizers (ammonium nitrate, potassium nitrate and ammonium sulfate) from the cylindrical devices of radiation crosslinked poly(acrylamide/itaconic acid) (AAm/IA) copolymers with the swelling that may effect the release behaviour. AAm/IA copolymers containing agrochemicals are prepared by two different composition of itaconic acid and two different γ-rays doses. The agrochemicals were trapped in the gels by including it in the feed mixture of radiation polymerization. The equilibrium swelling, diffusional exponent, and diffusion and intrinsic diffusion coefficients of the process were obtained. The agrochemical dissolution was determined by conductimetric method. The maximum concentrations of releasing agrochemicals and initial releasing rates were calculated by using of second order kinetics equation. The agrochemical releases appeared to be controlled by swelling. As a result, if AAm/IA hydrogels containing agrochemicals were swelled in water, release of agrochemicals was decreased with the raising of γ-rays doses and itaconic acid quantities in the hydrogel.

Introduction

Hydrogels are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining possibly huge volume in the swollen state. The water-swollen hydrogels with high degrees of swelling 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 (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 are incorporated into a polymeric carrier in a controlled release system. Acrylamide hydrogels and its derivatives were used in agriculture as carriers of agrochemicals and soil conditioners (5-13). In our previous studies, some radiation crosslinked acrylamide based

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hydrogels were used swelling, adsorption separation and release studies (1, 2, 14-16). The purpose of this study is the use of a new radiation crosslinked hydrogels based on copolymers of acrylamide (AAm) and itaconic acid (IA), with capacity of high water content (1), on agrochemicals releases. The agrochemicals used in this work were the herbicide such as sodium 2,2 dichloropropionate (Dowpon) and the model fertilizers such as ammonium nitrate (NH_4NO_3), potassium nitrate (KNO_3) ammonium sulfate ($((NH_4)_2SO_4)$), which were included in these new hydrogels by trapping in the feed mixture of radiation polymerization. The model fertilizers such as NH_4NO_3, KNO_3 and $(NH_4)_2SO_4$) are the nutrient for agricultural soils as the sources of potassium, nitrogen and ammonia. Dowpon is an organochlorine herbicide and plant growth regulator used to control specific annual and perennial grasses, such as quarkgrasses, Bermuda grass, Johnson grass, as well cattails and rushes. The major food crop use of Dowpon is on sugarcane and sugar beets. It is also used on various fruits, potatoes, carrots, asparagus, alfaalfa, and flax, as well as in forestry, home gardening, and in or near water to control reed and sedge growth.

Experimental

For the preparation of copolymers; 1 g of acrylamide (AAm) (BDH, Poole-UK) and 40 or 60 mg of itaconic acid (IA) (Sigma, St. Louis, US) were mixed with 1 mL water or 1 mol dm^{-3} 1 mL of the aqueous solution of ammonium nitrate (NH_4NO_3) or potassium nitrate (KNO_3) or ammonium sulfate $NH_4)_2SO_4$) (Merck, Darmstadt, Germany) and, 1 or 0.2 mol dm^{-3} 1 mL of the aqueous solution of Dowpon (Sigma, St. Louis, US). 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/IA 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 bath.

About 1 g AAm/IA copolymer 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.

Results and Discussion

Preparation of radiation crosslinked AAm/IA copolymers containing agrochemicals

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)

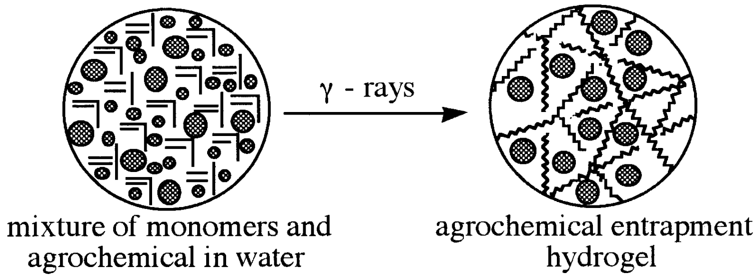

Fig. 1. Schematic presentation of hydrogel preparation, ∼∼∼ ; crosslinked polymer chain, ⌉ ; acrylamide monomer, ⫤ ; itaconic acid monomer, ● ; agrochemical, ⊗ ; water.

created in the material at the end of process. Therefore, no chemicals or catalysts remain in the material by radiation (17).

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 (18,19).

For preparation radiation crosslinked AAm/IA copolymers 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 of AAm/IA is formed. When irradiation dose is increased during ionising radiation of AAm and IA, the polymer chains crosslink and then gels are obtain. Gelation of AAm/IA copolymers occurs at a dose 2 kGy of γ ray irradiation doses at ambient temperature (18). So, dose of 2.6 kGy and 5.2 kGy of γ rays is the base for preparation of radiation crosslinked AAm/IA copolymers 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. Schematic representation of the release system is shown in Fig. 1.

Swelling of the radiation crosslinked AAm/IA copolymers

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 (1, 2):

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

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. Time-depending swelling curves of radiation crosslinked AAm/IA copolymers containing 40 mg IA and agrochemicals and irradiated to 2.6 kGy were plotted and, are shown in Fig. 2.

If Fig. 2 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 (S_{eq}). The values of equilibrium swelling of AAm/IA hydrogels are given in Table 1.

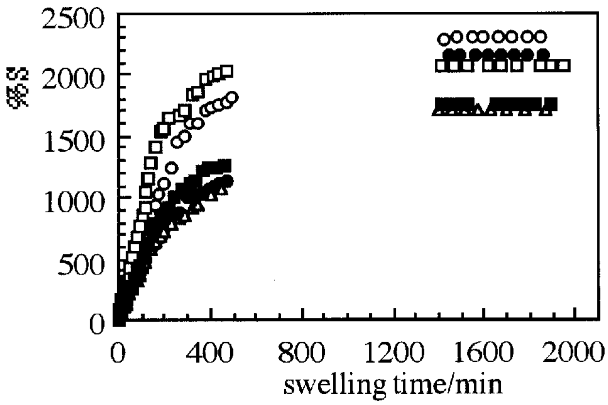

Fig. 2. Time-depending swelling of AAm/IA hydrogels containing agrochemicals.
●; KNO_3, ○; NH_4NO_3, ■; $(NH_4)_2SO_4$, □; Dowpon (0.2 M), ▲; Dowpon (1 M).

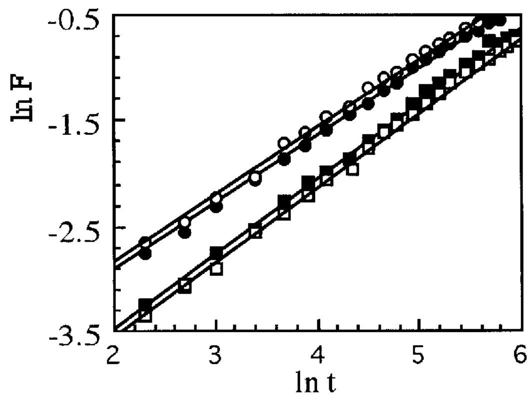

Fig. 3. ln F-ln t curves of AAm/IA hydrogels containing 1 M Dowpon.
■; 40 mg IA/2.6 kGy, □; 60 mg IA/2.6 kGy, ●; 40 mg IA/5.2 kGy, ○; 60 mg IA/5.2 kGy.

Table 1. The values of swelling and diffusion of radiation crosslinked AAm/IA copolymers

Agrochemical	dose, kGy	mass, mg	S_{eq}	n	$D \times 10^6$ $cm^2\ s^{-1}$	$\mathcal{D} \times 10^6$ $cm^2\ s^{-1}$
no agrochemical	2.6	40	19.17	0.56	5.44	9.68
	2.6	60	20.61	0.64	8.58	13.72
	5.2	40	13.95	0.59	9.35	11.29
	5.2	60	15.21	0.54	5.93	8.41
ammonium nitrate	2.6	40	20.81	0.82	2.94	5.07
	2.6	60	27.12	0.62	2.80	5.23
	5.2	40	14.00	0.78	2.14	3.63
	5.2	60	18.86	0.75	2.06	3.98
potassium nitrate	2.6	40	17.56	0.78	2.08	4.37
	2.6	60	24.16	0.78	2.11	4.60
	5.2	40	13.43	0.67	1.29	2.41
	5.2	60	18.78	0.81	1.92	3.98
ammonium sulfate	2.6	40	17.14	0.78	1.61	3.80
	2.6	60	18.04	0.77	1.49	3.19
	5.2	40	13.18	0.72	2.39	3.82
	5.2	60	15.18	0.83	1.83	6.18
Dowpon 0.2 M	2.6	40	23.15	0.80	2.21	4.85
	2.6	60	23.94	0.89	2.16	4.26
	5.2	40	14.50	0.91	3.81	5.25
	5.2	60	19.00	0.73	3.55	5.62
Dowpon 1.0 M	2.6	40	21.56	0.71	1.11	2.85
	2.6	60	26.00	0.71	1.29	3.74
	5.2	40	14.14	0.64	1.08	1.79
	5.2	60	14.11	0.64	1.36	2.09

The swelling studies indicated that swelling degree of AAm/IA hydrogels in water were generally increased with following order; Dowpon >NH_4NO_3 > KNO_3 > $(NH_4)_2SO_4$. The reason of these results is ionic groups on agrochemicals. These ions are caused by preventing the water into the hydrogels, thus, the swelling degree of the hydrogel containing agrochemical was varied between % 1320 and %2710. On the other hand, the swelling of the hydrogels was increased with the increase of IA content, while this process was decreased with the increase of the irradiation dose. Increasing of hydrophilic groups (i.e. IA) in the hydrogel is caused to the increase of the swelling. But, increasing of radiation dose is caused to the decrease of the pore size in the hydrogel. So, the swelling of the hydrogel was increased with IA content, while it was decreased with the radiation dose.

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 (1, 2). The following equation was used to determine the nature of diffusion of water into hydrogels

$$F = k\,t^n \qquad 2$$

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 ln 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. The plots of swelling kinetics of radiation crosslinked AAm/IA copolymers containing Dowpon are shown in Fig. 3.

The values of diffusional exponents of radiation crosslinked AAm/IA copolymers were calculated from the slopes of the lines, and they are listed in Table 1.

In Table 1, it is shown that the values of diffusional exponent are ranged between 0.54 and 0.91. In the experiments, the number to determine type of diffusion (n) was found to be over 0.50. Hence the diffusion of water into the copolymers was taken as a *non-Fickian* character (1, 2). This is generally explained as a consequence of slow relaxation of polymer matrix.

The study of diffusion phenomena in hydrogels and water is valuable since it clarifies the polymer behaviour. The complete swelling-time curves for hydrogels in water are used to calculated the diffusion and the intrinsic diffusion coefficients (20). For the hydrogel characterization, diffusion coefficient D in $cm^2\,s^{-1}$ are calculated by following equation.

$$D = 0.049 / (t / 4r^2)_{1/2} \qquad 3$$

Where t (in sec) is the time at which the swelling is one half the equilibrium value (V/V_0) and r is the radius of cylindrical polymer sample. The intrinsic diffusion coefficient, *D*, may be expressed as

$$D = \mathrm{D}\,(1 - \mathrm{V})^{-3} \qquad 4$$

where V volume of fraction of solvent penetrating the polymer in the time t defined above. The values of the diffusion coefficients of the hydrogels are listed in Table 1.

If Table 1 is examined, it is found that the values of intrinsic diffusion coefficient of the radiation crosslinked copolymers are bigger than the values of the diffusion coefficient. Eq 3 gives a measure not only diffusion but also of the mass flow the whole system. Eq. 4 gives the intrinsic diffusion coefficient for cases where no mass action effects enter.

Release of agrochemicals from hydrogel

To examine the release of the agrochemicals from the radiation crosslinked copolymers, the effect of following factor on the rate of the agricultural release were investigated: (i) agrochemical type, (ii) IA content in the copolymer and (iii) irradiation dose.

The released amount of the agrochemicals (C/mM g hydrogel^{-1}) were plotted to release time, and a representative release curves are shown in Figure 4.

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

$$\frac{t}{C} = A + B\,t \qquad 5$$

Where $B=1/C_{max}$ is the inverse of the maximum concentration of released agrochemicals, and $A=1/r_i$ is the reciprocal of the initial release rate the gel (16).

Fig. 5 shows the linear regression of the release curves of Dowpon obtained by means of eq. 5. The initial release rate (mM g^{-1} s^{-1}) and theoretical equilibrium concentration of released agrochemicals from the hydrogels (mM g^{-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

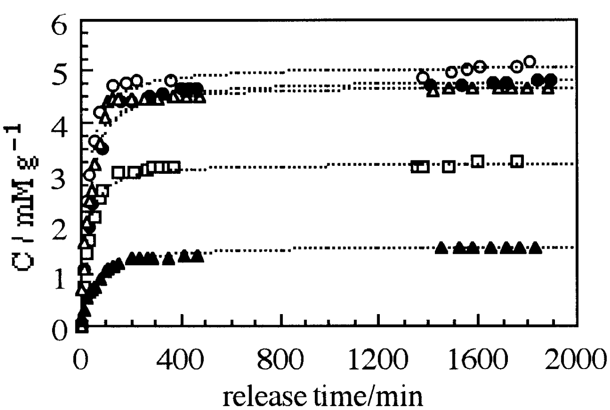

Figure 4. Time-depending release of agrochemicals from AAm/IA copolymer.
●; NH_4NO_3, ○; KNO_3, □; $(NH_4)_2SO_4$, ▲; Dowpon (0.2 M), Δ; Dowpon (1 M), ...; simulated curve

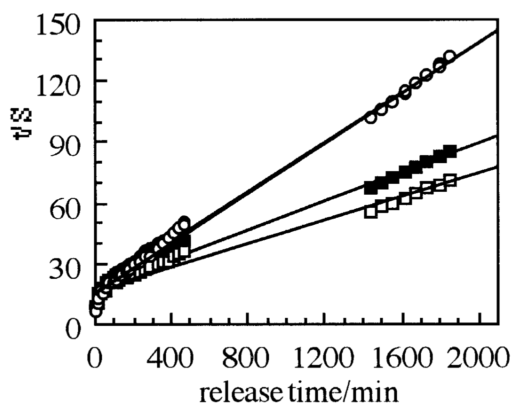

Figure 5. Second order release kinetics of Dowpon from AAm/IA copolymers.
■; 40 mg IA/2.6 kGy, □; 60 mg IA/2.6 kGy, ●; 40 mg IA/5.2 kGy, ○; 60 mg IA/5.2 kGy.

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

Agrochemical	Dose, kGy	mass, mg	$C_{max, exp}$, mM g gel^{-1}	$t_{equilibrium}$, min	r_i, mM g^{-1} s^{-1}	$C_{max, cal}$, mM g gel^{-1}
ammonium nitrate	2.6	40	4.31	160	10.27	4.87
	2.6	60	3.00	100	7.46	3.52
	5.2	40	3.83	160	9.43	4.40
	5.2	60	2.68	145	4.76	3.25
potassium nitrate	2.6	40	4.72	125	15.32	5.12
	2.6	60	3.96	190	8.87	4.24
	5.2	40	3.84	125	11.30	4.30
	5.2	60	2.83	190	5.46	3.13
ammonium sulfate	2.6	40	3.03	145	10.54	3.21
	2.6	60	3.01	135	11.26	3.20
	5.2	40	2.91	145	10.17	2.97
	5.2	60	2.91	135	9.43	3.07
Dowpon 0.2 M	2.6	40	1.56	130	1.88	1.60
	2.6	60	1.82	150	2.32	1.83
	5.2	40	1.50	130	1.60	1.54
	5.2	60	1.63	150	1.86	1.66
Dowpon 1.0 M	2.6	40	3.67	110	13.87	4.73
	2.6	60	3.47	150	13.10	4.60
	5.2	40	3.22	170	10.02	3.59
	5.2	60	2.98	170	9.52	3.47

decreased when the quantity of itaconic acid in the hydrogels increases. With raising the irradiation doses, also the release of agrochemicals has generally decreased.

The initial release rate of the AAm/IA hydrogels containing 1 M Dowpon are higher than the other hydrogels containing ammonium nitrate, potassium nitrate and ammonium sulfate. So, release process of the herbicide from the AAm/IA hydrogels are quicker than the release of the fertilizers.

Radiation crosslinked AAm/IA copolymers containing agrochemicals can be defined as "swelling-controlled system" in controlled releases (21). 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.

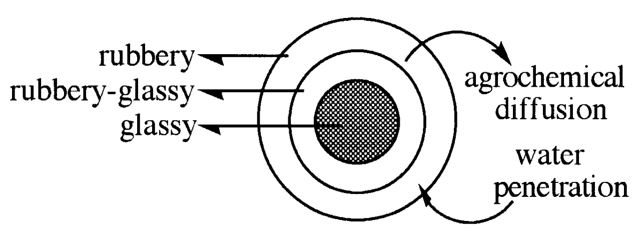

Fig. 6. The schematic representation of the swelling-release process.

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 (21). The schematic representation of the swelling-release process is shown in Fig. 6.

As a result, it is said that radiation crosslinked AAm/IA copolymers containing agrochemicals can be used at the release of ammonium nitrate, potassium nitrate, ammonium sulfate and Dowpon. 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/IA 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 the content of itaconic acid in used the hydrogel systems for the controlled release of the agrochemicals.

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