Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Radiation Synthesis of Superabsorbent Hydrogels Based on Chitosan and Acrylic Acid for Controlled Drug Release

Sahar A. Ismail[a]; El-Sayed A. Hegazy[a]; Nihal O. Shaker[b]; Entsar E. Badr[b]; Noha M. Deghiedy[a]
[a] National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt [b] Chemistry Department, Faculty of Science, Al Azhar University, Cairo, Egypt

To cite this Article Ismail, Sahar A. , Hegazy, El-Sayed A. , Shaker, Nihal O. , Badr, Entsar E. and Deghiedy, Noha M.(2009) 'Radiation Synthesis of Superabsorbent Hydrogels Based on Chitosan and Acrylic Acid for Controlled Drug Release', Journal of Macromolecular Science, Part A, 46: 10, 967 — 974
To link to this Article: DOI: 10.1080/10601320903158560
URL: http://dx.doi.org/10.1080/10601320903158560

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2009) **46**, 967–974

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903158560

Taylor & Francis
Taylor & Francis Group

Radiation Synthesis of Superabsorbent Hydrogels Based on Chitosan and Acrylic Acid for Controlled Drug Release

SAHAR A. ISMAIL[1], EL-SAYED A. HEGAZY[1], NIHAL O. SHAKER[2], ENTSAR E. BADR[2] and NOHA M. DEGHIEDY[1,*]

[1]*National Center for Radiation Research and Technology, P. O. Box 29, Nasr City, Cairo, Egypt*
[2]*Chemistry Department, Faculty of Science, Al Azhar University, Cairo, Egypt*

Received April 2009, Accepted May 2009

Superabsorbent hydrogels based on the natural polymer chitosan and acrylic acid (CS/AAc) was prepared using ^{60}Co gamma radiation as a source of initiation and crosslinking. The factors, which affect the preparation of CS/AAc hydrogels such as irradiation dose, CS/AAc ratios, and acrylic acid monomer concentrations, to get the best optimum conditions, were investigated. The kinetic studies of the swelling of CS/AAc hydrogel showed that it follows a Fickian type of water diffusion. The Fickian constant value *'n'* was more than 0.5 with a high swelling capacity of 300 g/g as superabsorbent hydrogel. In addition, the suitability of CS/AAc hydrogel as carrier material for the drug Chlortetracycline-HCl has been investigated by adsorption isotherm studies. The performance of drug release from hydrogel systems, influenced by acrylic acid ratio and the effect of pH of the medium was studied.

Keywords: Acrylic acid, chitosan, hydrogel, drug carriers, swelling, release

1 Introduction

Hydrogels are water-swollen, crosslinked polymeric structures produced by the simple reaction of one or more monomers, which find an extremely wide range of applications in the fields of medicine, pharmacy, biotechnology, agriculture, and controlled release of drugs. In recent years, hydrogels have been used for the immobilization of enzymes, proteins, antibodies, and antigens. They find these considerable applications and have been extensively studied, because they combine glassy behavior (in their dry state) with elasticity (when sufficient water is adsorbed). The key in the preparation of hydrogels is the formation of crosslinking structure, which maintains their stability in aqueous medium (1–3). Recently, many investigators have prepared hydrogels with additional functions, such as the ability to swell or shrink in response to a signal. These hydrogels are often called 'intelligent' or 'smart' hydrogels. The most widely known smart hydrogels are those which respond (i.e., swell, shrink, bend, or degrade) to changes the environmental change in pH, temperature, ionic strength, electric field and magnetic field (4–7).

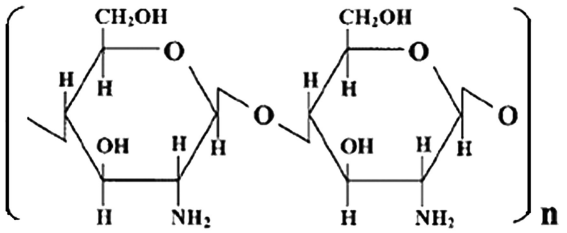
Biomaterials for tissue engineering or drug delivery have seen numerous advances in recent years as researchers continue to develop and modify polymeric materials to meet the demanding needs of these biomedical applications. As an important class of biomaterials, hydrogels have been paid a great deal of attention especially as site specific or controlled-release drug delivery systems (8–12).

Superabsorbent hydrogels are loosely crosslinked networks of hydrophilic polymers that can absorb and retain aqueous solutions up to hundreds of times their own weight and the absorbed water is hardly removable even under some pressure. Compared with traditional absorbing materials, superabsorents have many excellent properties and are widely used in many fields, such as hygienic products, horticulture, gel actuators, drug-delivery systems and coal dewatering (13–15). Superabsorbent hydrogels prepared with natural materials, such as cellulose (16), starch (17), dextran, guar gum (18) and chitosan (19), have attracted great attention (20) because of their abundant resources, low production-cost and biodegradability However, most of the superabsorbents are acrylic acid and acrylamide based products and cannot be biodegraded in nature. Thus, the superabsorbents and hydrogels with eco-friendly property and biodegradability are finding increasing interest in the academic and industrial field (21).

Chitosan (CS), poly-ß-(1-4)-2-amino-2-deoxy-D-glucose, is a naturally occurring biodegradable and biocompatible cationic polysaccharide derived from the N-deacetylation of chitin, which is the most abundant natural structural polysaccharide after cellulose. It can

*Address correspondence to: Noha M. Deghiedy, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt. E-mail: n_deghiedy@hotmail.com

be found in insects, exoskeleton of crustaceans, in fungal cell walls. As a natural renewable resource, chitosan has a number of unique properties such as antimicrobial activity, non-toxicity, biocompatibility and biodegradability, which attract scientific and industrial interest in such fields as biotechnology, pharmaceutics, wastewater treatment, cosmetics, agriculture, food science and textiles (22–25). In recent decades, considerable interest has been focused on modification by grafting synthetic polymers onto the most abundant naturally occurring polysaccharides. Many works have been reported on the preparation of chitosan hydrogels via grafting of various hydrophilic monomers. Graft polymerization of hydrophilic monomers onto chitosan enhances hydrophilicity and water uptake capacity of the backbone (26).



Chitosan

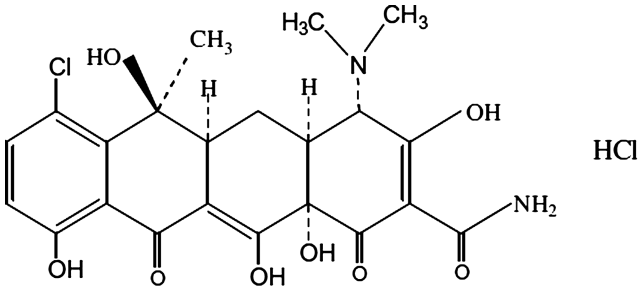
Poly (acrylic acid) (PAAc) has carboxylic acid groups, which could develop different intermolecular interaction like electrostatic interaction, hydrogen bonds, and dipole ion with other polymers. Many investigations have shown that these interactions exert strong influence on the swelling behavior of hydrogels and there is a great potential for their application in pharmaceutical preparations, particularly in drug delivery systems (5). PAAc is one of the pH-sensitive synthetic polymers with the potential use in the area of the site-specific drug delivery to specific regions of the gastrointestinal tract, especially in the colon-specific delivery of low molecular weight protein drugs (18).

Radiation processing has many advantages over other conventional methods. In radiation processing, no catalysts or additives are needed to initiate the reaction. The advantages of radiation methods are that they are relatively simple, and the degree of crosslinking, which strongly determines the extent of swelling of hydrogels, can be controlled easily by varying the radiation dose. In addition, the radiation process can join hydrogel formation and sterilization in one technological step. Therefore, these methods are found to be very useful in preparing hydrogels for medical applications, where even a small contamination is undesirable (27–31). The objective of this paper is to prepare polymeric hydrogels composed of chitosan and acrylic acid by using γ-irradiation as a source of initiation and crosslinking and investigate the swelling properties at different conditions. In addition, the suitability of chitosan/acrylic hydrogel as carrier material for the controlled release of drug Chlortetracycline HCl is investigated. The influence of acrylic ratio and pH of the medium on the hydrogel release properties were examined.

2 Experimental

2.1 Materials

Chitosan (CS) powder was supplied by Fluka Chemical. The degree of deacetylation and molecular weight were determined as 14% and 50,000, respectively. Acrylic acid (AAc) was purchased from Acros Chemical Company, USA. Other chemicals, such as citrate, phosphate buffer salts of analytical reagents, were purchased from El-Nasr Co. for Chemical Industries, Egypt. Chlortetracycline HCl (Sigma Chemical Co., USA); mainly used in the treatment of Chlamydia, Vibrocholera, Acne vulgaris, Gonorrhea, Syphilis, Prostitis and Sinusitis with a dosage 250 and 500 mg (three times per day). Structure of drug is shown below:



Chlortetracycline Hydrochloride

2.2 Preparation of Chitosan/Acrylic Acid Hydrogels

0.5 g of CS was dissolved in 50 ml of 1 wt% acetic acid solution. CS/AAc hydrogels were obtained by gamma irradiation-induced polymerization and crosslinking of aqueous solutions of CS and AAc mixtures with different volume ratios in glass tubes using ^{60}Co gamma rays with different doses, at a dose rate 1.8 Gy/s. After completion of the reaction, the tubes were broken; the formed hydrogels in the cylinder form were removed and cut into discs of 2 mm thickness. All samples were washed in excess water to remove the unreacted components and then air dried at room temperature.

2.3 Swelling Studies

Analysis of the dynamic swelling characteristics of all hydrogels was performed in double distilled water. The dried gel disks were left to swell in the distilled water until the swelling equilibrium was reached. The swollen gels were withdrawn at regular time intervals from the water, and weighed after removal of excess surface water by light blotting with a filter paper. Thus, absorbency of water was calculated as gram of water per gram of polymer (g/g).

The equilibrium swelling (ES) was calculated using the following equation:

$$ES\ (g/g) = (W_s - W_d) / W_d$$

Where W_s and W_d are the weights of the swollen gel and dry sample, respectively.

2.4 Adsorption of Chlortetracycline HCl-on Hydrogel

Polymer-drug conjugate was prepared by dissolving 5.0 mg of Chlortetracycline HCl in 20 ml phosphate buffer of pH 8. The dry hydrogels were soaked in the drug solution at room temperature until complete absorption.

2.5 Release of Chlortetracycline HCl from Loaded Hydrogel

Release experiments were performed by placing the CS/AAc hydrogels loaded with Chlortetracycline HCl into buffer solution of pH 1 and 7.5 at 37°C. At first, the loaded gels were put in 25 ml of 0.2 M HCl (pH 2) for 3.5 h, and then transferred to 50 ml 0.2 M phosphate buffer (pH 8) for 24 h. One milliliter sample was withdrawn on time intervals to follow the release process. The concentration of Chlortetracycline HCl was measured by UV spectroscopy (UNICAM UV/Vis Spectrometer. 1000 Model).

3 Results and Discussion

3.1 Swelling Studies

3.1.1. *Effect of CS/AAc feed concentration*

The effect of CS/AAc feed solution concentration on the hydrogel equilibrium swelling is shown in Figure 1. It can be seen that the highest swelling (296 g/g) was observed at CS/AAc concentration of 50%, while the other factors were kept constant. Swelling capacity was increased by increasing the concentration from 20 to 50% from 276 to 296 g/g. As the concentration was increased up to 50%, the active sites can react easily with monomers. Increasing the concentration more than 50% results in a high viscosity of the medium and a decrease in the diffusion of monomers to active sites to produce crosslinked hydrogels (32).

3.1.2. *Effect of AAc/CS ratio*

The relationship between the CS/AAc ratio and equilibrium swelling values was studied by varying the AAc content in Figure 2. It is observed that the swelling is substantially increased with increasing the AAc ratio and then it is decreased. The initial increment in swelling values can be attributed to the higher hydrophilicity of the hydrogel and the greater availability of AAc molecules in the vicinity of chitosan macroradicals. This is because the dense crosslinking network formation (19).

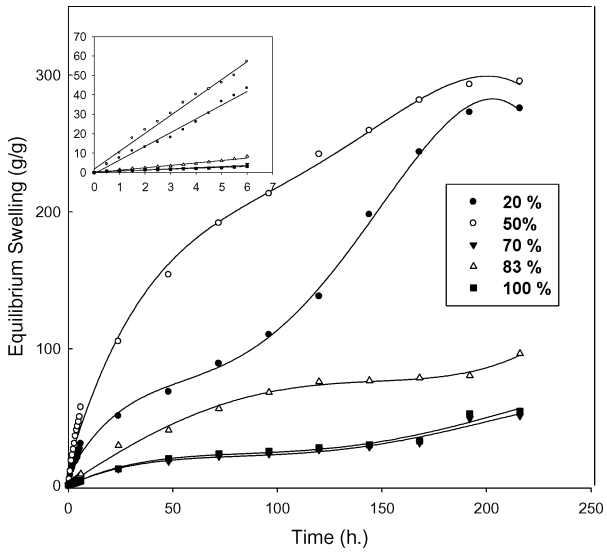


Fig. 1. Effect of time (h) on the equilibrium swelling for different CS/AAc concentrations formed at 5 kGy. AAc:CS ratio is 50:50 vol%.

The type of water diffusion mechanism in the hydrogels has a great deal of relevance due to the unique applications of the hydrogels. The following equation can be used to determine the nature of water diffusion into the hydrogels:

$$F = \frac{M_t}{M_\infty} = kt^n \qquad (1)$$

Where **F** is the fractional uptake at time **t**, $\mathbf{M}_t$ and $\mathbf{M}_\infty$ represent the amount of water absorbed by the hydrogel at time t and at equilibrium, **k** is a constant incorporating characteristic of the polymer network and the solvent, **n** is the diffusion exponent, which is indicative of the transport mechanism.

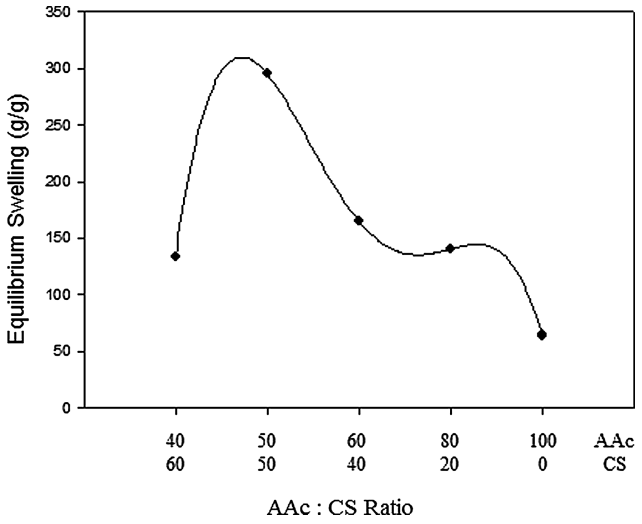


Fig. 2. Effect of AAc/CS ratio on the equilibrium swelling at conc. 50% at dose 5 kGy.

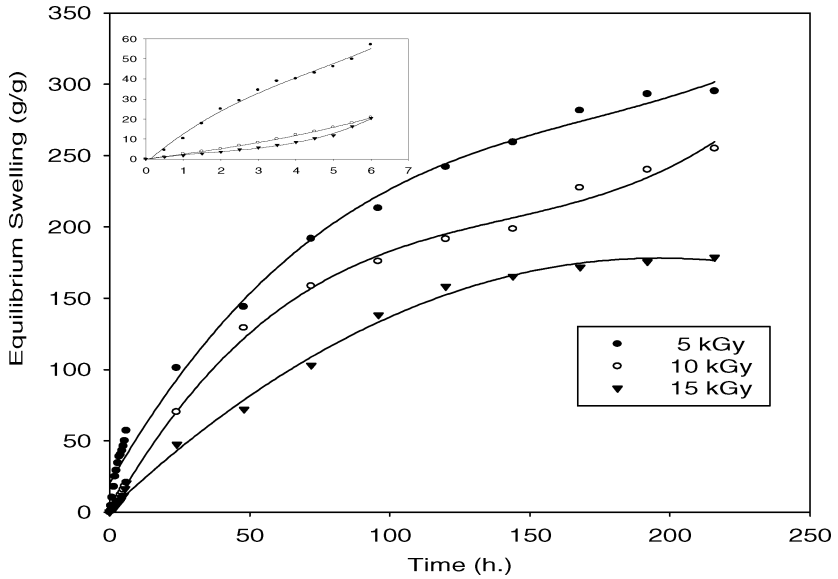


Fig. 3. Effect of time (h) on the equilibrium swelling for different doses at conc. 50% and AAc:CS ratio 50: 50 vol%.

The values of '**n**' and '**k**' can be calculated from the slope and intercept of the plot of ln F against ln t. A value of $n \leq 0.5$ indicates a Fickian diffusion mechanism, while value of $0.5 < n < 1$ indicates that the diffusion is anomalous or non-Fickian (intermediate situation). In this situation the penetrate mobility and segmental relaxation are on a comparable time scale. Equation 1 was applied to the initial stages of swelling and plots of ln F vs. ln t yields straight lines up to almost 60% increase in the mass of hydrogel (not shown). The values of diffusion exponent and gel characteristics constant 'k' are presented in Table 1. No variation of the diffusion exponent is observed, and the values are higher than 0.5, indicating that the diffusion of water to the interior of all the hydrogels follows an anomalous mechanism and reveals the existence of certain coupling between molecular diffusion and tension relaxation developed during swelling of the hydrogels.

3.1.3. *Effect of irradiation dose*

Figure 3 shows the equilibrium swelling ratio of CS/AAc hydrogels prepared at different doses. The degree of swelling decreases with increasing dose. It can be assumed that the degree of swelling is controlled by changes in the crosslinking density (33). Higher irradiation dose increases the number of intermolecular crosslinks, which leads to the decreasing of the degree of swelling.

Table 1. Swelling kinetic parameters for CS/AAc hydrogels (synthesized at 5 kGy)

AAc/CS ratio (vol%)	*n*	$K \times 10^2$	R^2
40/60	0.610	4.03	0.97
50/50	0.605	4.70	0.99
60/40	0.628	3.70	0.97
80/20	0.615	4.40	0.98
100/0	0.631	4.30	0.96

3.1.4. *Effect of pH*

To investigate the sensitivity of the hydrogel to pH, firstly the equilibrium swelling of the hydrogel was studied at various pH's. No additional ions (through buffer solution) were added to the medium for setting pH because swelling of a superabsorbent is strongly affected by ionic strength. Therefore, stock NaOH (pH 13.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. According to Figure 4, the two sharp swelling capacity changes can be attributed to high repulsion of $-NH_3^+$ groups in acidic media

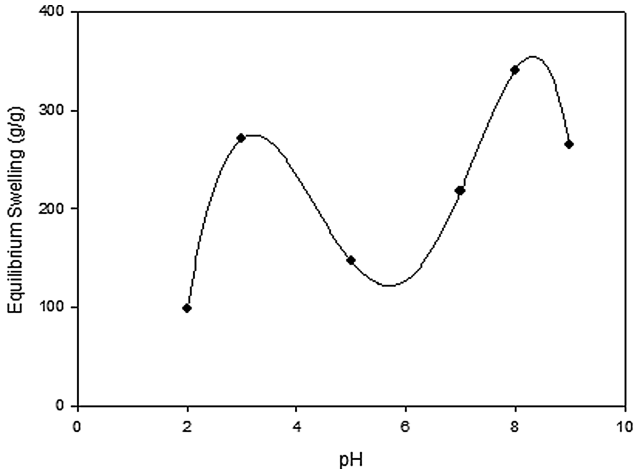


Fig. 4. Effect of pH on the equilibrium swelling at CS/AAc ratio 50:50 vol% and dose 5 kGy.

and $-COO^-$ groups in basic media. However, at very acidic conditions (pH $\geq$ 2), a screening effect of the counter ions, i.e. Cl^- , shields the charge of the ammonium cations and prevents an efficient repulsion **(34)**. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). Around pH 5, the carboxylic acid component comes into action as well. Since the pK_a of the weak polyacid is about 6.4, its ionization occurring above this value, may favor enhanced swelling. But under pH 6.4, at a certain pH range 4–6, the majority of the base and acid groups are in non-ionized forms, so hydrogen bonding between amine and carboxylic acid may lead to a kind of crosslinking followed by a decrease in swelling. At higher pHs, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling. Again, a screening effect of the counter ions (Na^+) limits the swelling at pH above 8.

3.1.5. *Effect of ionic strength*

Figure 5 shows the effect of NaCl solution concentration on the swelling behavior of the hydrogels. The increase of ionic strength in the solution leads to a decrease in the swelling ratio of the hydrogels. This behavior can be explained on the basis of osmotic pressure developed due to unequal distribution of ions in the medium and the polymer network. The ions attached to the polymer network are immobile and considered to be separated from the external solution by a semi-permeable membrane. When the hydrogels are placed in water, there is maximum osmotic pressure developed and hence the maximum swelling is attained. When the polymer is placed in NaCl solution, the osmotic pressure developed is much lower because the external solution contains Na^+ and Cl^- . So the swelling is drastically reduced. This behavior can be attributed to a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, leading to a decreased osmotic pressure (ionic pressure) between the hydrogel network and the external solution (32).

3.1.6. *Effect of different salt cation solutions on equilibrium swelling of hydrogels*

According to Figure 6, the ultimate swelling capacities of hydrogels in different salt solutions are decreased compared with the value measured in distilled water. This undesired swelling loss can be attributed to the "charge screening effect" of the cations leading to the reduction of osmotic pressure; the driving force for swelling between the gel and the aqueous phases. An additional reason may be the increased electrostatic attraction between anionic sites of chains and multi-valent cations (Ca^{2+} and Al^{3+}) resulting in an increase in the "ionic crosslinking" degree and subsequent loss of swelling. The effect of charge of cations on swelling can be concluded. As shown in Figure 6, the swelling of the hydrogels in the studied salt solution, from high to low is monovalent > divalent > trivalent cations. It was clear that increasing the charge of the cation, the degree

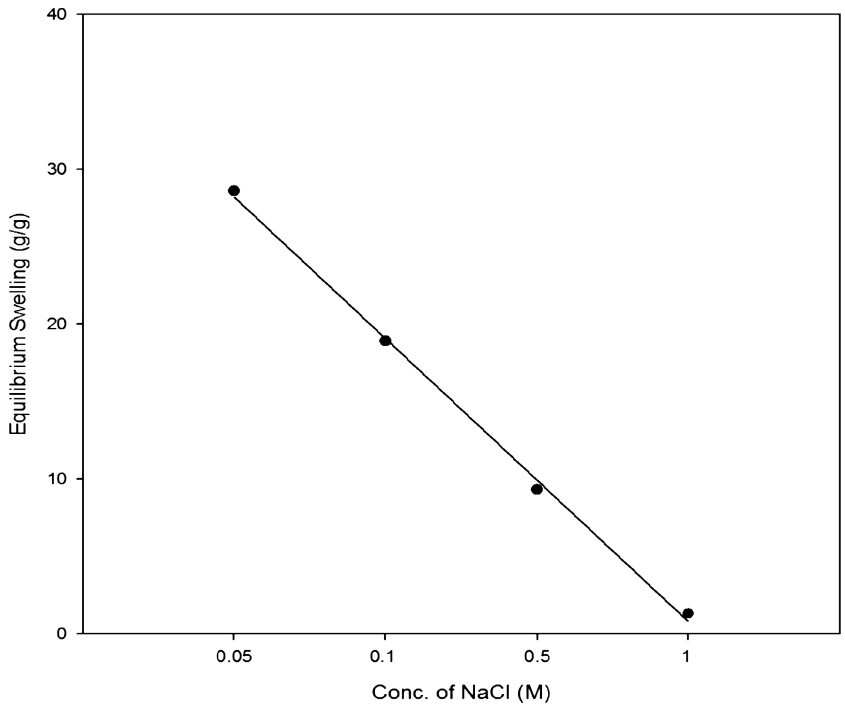


Fig. 5. Effect of sodium chloride concentration on the equilibrium swelling of hydrogels at a dose of 5 kGy and the AAc : CS ratio is 50:50 vol%.

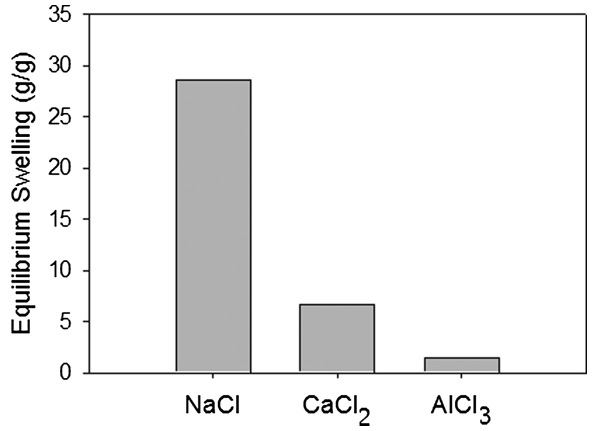


Fig. 6. Effect of different salt cation solutions on equilibrium swelling of hydrogels at a dose of 5 kGy and the AAc: CS ratio is 50:50 vol%.

of crosslinking is increased and swelling is consequently decreased. This dramatic decrease of water absorbency in multivalent cationic solutions could be due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increase in the crosslinking density of network.

3.1.7. *Effect of drug concentration*

The equilibrium swelling of CS/AAc hydrogels loaded with different amounts of drug was investigated at different hydrogel compositions. Equilibrium swelling values of hydrogels in Chlortetracycline HCl solution at pH 8 are given in Figure 7. It was seen from this figure that the increase of sorption Chlortetracycline HCl shows a decrease in hydrogel swelling. When the concentration of drug increases from 0.3 to 0.8 mg/ml, a slight decrease in the swelling values was observed.

3.1.8. *Adsorption of Chlortetracycline HCl*

For investigation, the cationic drug adsorption behavior of CS/AAc hydrogels prepared in this study, hydrogels were initially swollen in Chlortetracycline HCl solution at concentrations 0.3, 0.5 and 0.8 mg/ml. In order to obtain adsorption isotherms of hydrogels, the mass of adsorbate per unit mass of adsorbent (q_e) was plotted vs. the equilibrium concentration of drug (C). q_e values are calculated from the following equation:

$$q_e = [(C_i - C) / m] \times V_t$$

Where q_e is in mg adsorbate per gram of dry adsorbent, C_i and C are the initial and equilibrium concentrations of adsorbate solution (mg/ml), V_t is the volume of solution treated in (ml), and m is the mass of dry adsorbent (g).

As can be seen from Figure 8, adsorptions of the drug by CS/AAc hydrogels correspond to type 'S' adsorption isotherms in the Giles classification system for adsorption of a solute from its solution. In the 'S' curves in the Giles classification system, initial direction of curvature shows that adsorption easier as concentration rises.

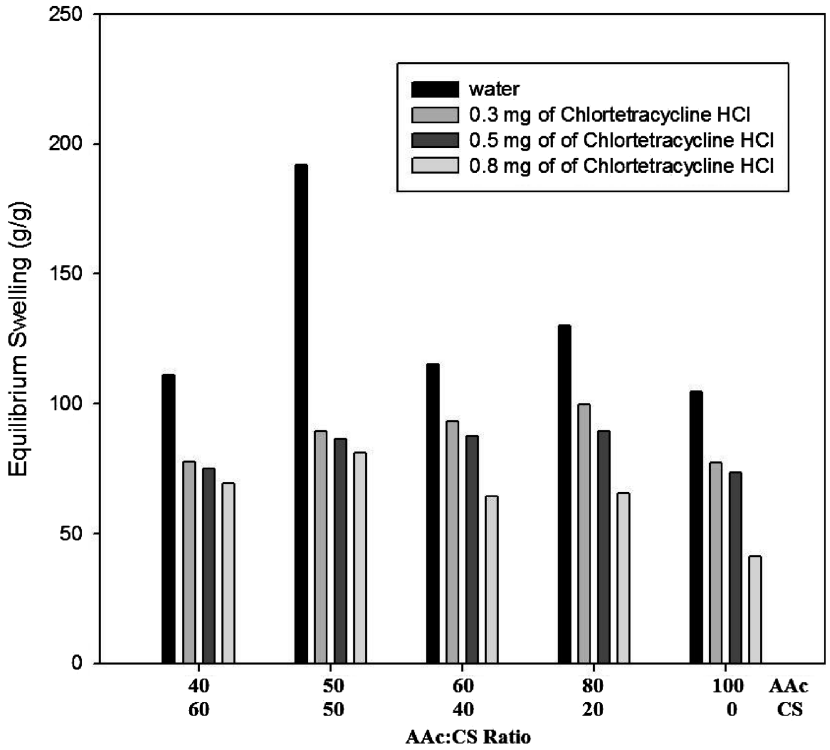


Fig. 7. Effect of AAc: CS ratios on the equilibrium swelling at different concentration of Chlortetracycline HCl.

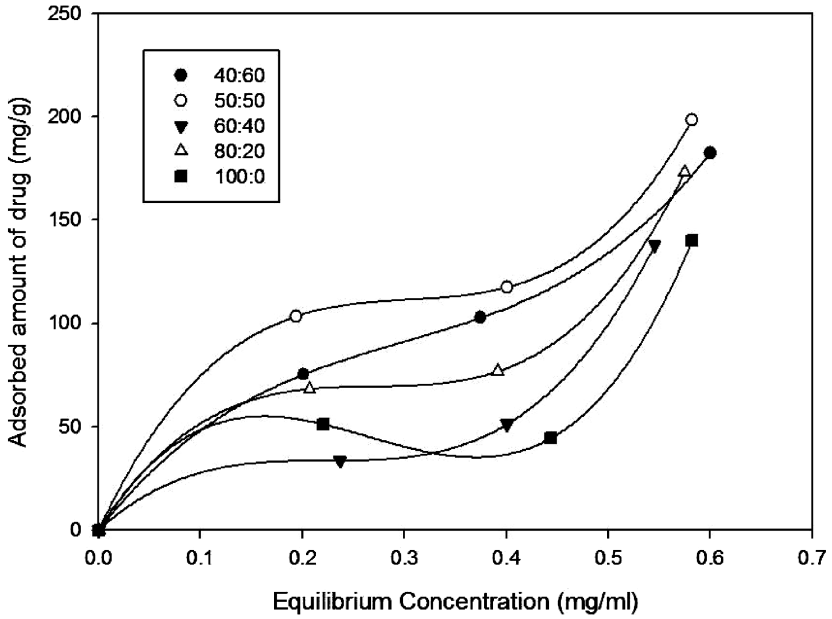


Fig. 8. Relationship between equilibrium concentration (C) of Chlortetracycline HCl and its amount adsorption (mg/g) for different (CS/AAc) compositions.

In practice, the 'S' curve usually appear when three conditions are fulfilled: the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition, for substrate sites, from molecules of the solvent or of another absorbed species. The hydrogel is covered with a layer of adsorbed water, however, the adsorbent–adsorbate interaction would be virtually reduce to the weak dispersion energy of water with drug, so that a type S isotherm should results. In system that give rise to a type S isotherm, however, the multilayer is being built up on some parts of the surface whilst the monolayer is still incomplete on other parts (35).

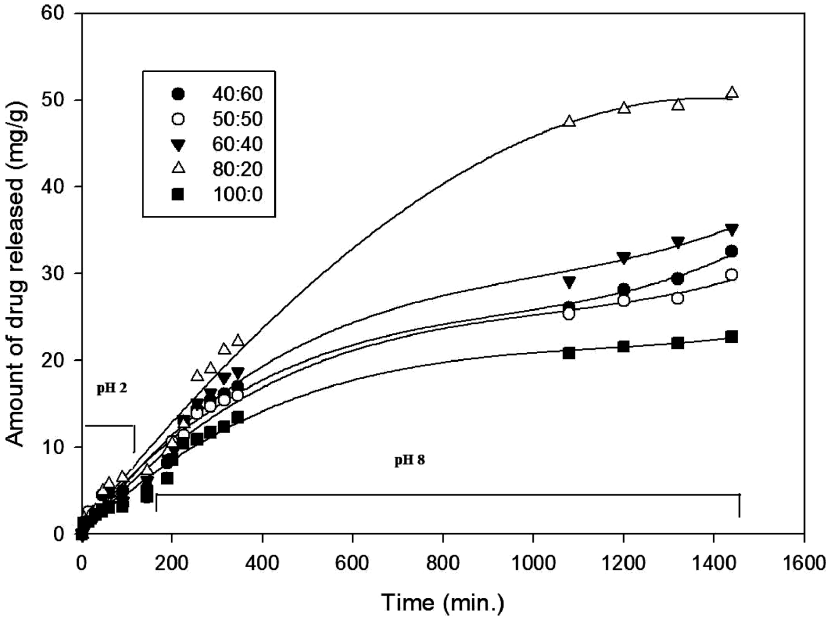


Fig. 9. Chlortetracycline HCl released from different (CS/AAc) composition as a function of time; at two pH values (pH 2 at time up to 180 min and pH 8 at a time above 180 min) and at a constant concentration of drug 0.8 mg/ml.

3.1.9. *Release of Chlortetracycline HCl*

The release experiments was carried out at a buffer solution of pH 2, which is almost similar to that of stomach medium for 3.5 h and at buffer solution of pH 8, which is similar to that of the intestine medium. Figure 9 shows the drug release behavior of CS/AAc hydrogels of different compositions as a function of time at pH 2 and 8. The figure shows that there is no significant drug release at pH 2, whereas the drug release occurs as soon as the copolymer transferred to buffer solution of pH 8. The results show that the drug release is not only pH dependent but also shows the influence of the copolymer composition on the release rate and total released drug.

4 Conclusions

A pH-responsive hydrogel based on AAc/chitosan was developed for oral drug delivery. The preparation of these hydrogels was carried out using the radical polymerization technique by gamma irradiation. Variations in the reaction parameters affecting the ultimate swelling capacity of the final product optimized the synthesis of superabsorbent hydrogel. The release of Chlortetracycline HCl from the CS/AAc hydrogels, as studied at the physiological temperature of 37°C, exhibits a strong pH-dependent release behavior, thus offering minimum release at pH 2 and maximum release at pH 8. The pH-dependent release behavior is totally governed by the presence of –COOH groups along the macromolecular chains, which ionize at higher pH, while providing hydrophobicity to the gels at lower pH. The hydrogels prepared in this study can be considered as potential carriers for the drug-delivery systems.

References

1. Shin, M.S., Sun, I.K., Kim, I.Y., Kim, N.G., Song, C.G. and Seon, J.K. (2002) *J. of Appl. Polym. Sci*., 84, 2591–2596.
2. Dilek, S.O., Sibel, D. and Murat, T. (2008) *Radiat. Phys. Chem*., 77, 447–452.
3. Sergey, A.D. and Grigoriy, A.M. (2009) *Radiat. Phys. and Chem*., 78, 65–68.
4. Mani, P. and Joa, F.M. (2006) *Macromol. Biosci*., 6, 991–1008.
5. Yihua, Y., Xingmin, J., Hui, D., Yi, Y. and Hua, Z. (2008) *Carbohydr. Polym*., 71, 682–689.
6. Bajpai, A., Sandeep, K., Smitha, B. and Sanjana, K. (2008) *Prog. Polym. Sci.,* 33, 1088–1118.
7. Luke, M.G., Ciaran, C.C., John, G.L., James, E.K., Michael, J.D., Sinead, D. and Clement, L.H. (2008) *Europ. J. Pharm. and Biopharm*., 69, 1147–1159.
8. Ezequiel, S., Edel, F.B., Alexandra, A.P., Mansur, W.V. and Herman, S.M. (2008) *Carbohydr. Polym*., 76, 472–481.
9. Sokker, H.H., Abdel Ghaffar, A.M., Gad, Y.H. and Aly, A.S. (2009) *Carbohydr. Polym*., 75, 222–229.
10. Zonghua, L., Yanpeng, J. and Ziyong, Z. (2007) *J. Appl. Polym. Sci.,* 103, 3164–3168.
11. Huiqun, Y., Jun, L. and Chaobo, X. (2007) *Macromol. Biosci*., 7, 1100–1111.
12. Santos, D.E.S., Neto, C.G.T., Fonseca, J.L.C. and Pereira, M.R. (2008) *J. Membr. Sci*., 325, 362–370.
13. Kabiri, K., Omidian, H., Hashemi, S.A. and Zohuriaan-Mehr, M.J. (2003) *Europ. Polym. J*., 39, 1341–1348.
14. Jianghua, L., Qin, W. and Aiqin, W. (2007) *Carbohydr. Polym.,* 70, 166–17.
15. Lichen, Y., Ziming, Z., Yizhe, H., Jieying, D., Fuying, C., Cui, T. and Chunhua, Y. (2008) *J. Appl. Polym. Sci*., 108, 1238–1248.
16. Farag, S. and Al-Afaleq, E.I. (2002) *Carbohydr Polym.,* 48, 1–5.
17. Zhang, A. and Wang, J.P. (2007) *Bioresource Technol*., 98, 327–332.
18. Xiuyu, L., Wenhui, W., Jianquan, W. and Yufeng, D. (2006) *Carbohydr. Polym*., 66, 473–479.
19. Xiaomin, Y., Qi, L., Xiliang, C. and Zhiyong, Z. (2008) *J. Appl. Polym. Sci*., 108, 1365–1372.
20. Jae, W.S. and Young, C.N. (2003) *J. Appl. Polym. Sci*., 90, 3270–3277.
21. Nguyen, Q.H., Dang, V.P., Nguyen, N.D. and Ha, T.H. (2005) *Nucl. Instrum. Methods Phys. Res. B*, 236, 606–610.
22. Khelil, S., Laurence, M., Caroline, A.C., Alexandre, L., Denis, L. and Najet, Y. (2009) *Polym. Degrad. Stabi*., 94, 584–590.
23. Andrzej, G.C., Mohammad, H.S. and Shamshad, A. (2005) *Methods in Phys. Res. B*, 236, 44–54.
24. Ge, H. C., Pang, W. and Luo, D.K. (2006) *Carbohydr. Polym*., 66, 372–378.
25. Shuibo, H. and Aiqin, W. (2009) *Carbohydr. Polym.,* 75, 79–84.
26. Lionetto, F., Sannino, A. and Maffezzoli, A. (2005) *Polym.,* 46, 1796–1803.
27. Ping, D., Huang, K.L., Li, G.Y. and Liu, Y.F. (2007) *Internat. J. Biolog. Macromol*., 41, 125–131.
28. Francisco, P., Thierry, V. and Eric, G. (2008) *J. Appl. Polym. Sci*., 107, 3568–3578.
29. Elzatahry, A.A., Mohy Eldin, M.S., Soliman, E.A. and Hassan, E.A. (2009) *J. Appl. Polym. Sci*., 111, 2452–2459.
30. Hiroki, K., Weihua, K. and Yoshio, I. (2008) *J. Appl. Polym. Sci.,* 107, 3823–3830.
31. Mahdavinia, G.R., Pourjavadi, A. and Zohuriaan-Mehr, M.J. (2006) *J. Appl. Polym. Sci*., 99, 1615–1619.
32. Pourjavadi, A., Barzegar, Sh. and Zeidabadi, F. (2007) *React. Funct. Polym*., 67, 644–654.
33. Fumio, Y., Long, Z., Radoslaw, A.W., Naotsugu, N., Hiroshi, M. and Tamikazu, K. (2003) *Nucl. Instrum. Methods Phys. Res. B*, 208, 320–324.
34. Chen, Y. and Tan, H. (2006) *Carbohydr Res*., 341, 887–896.
35. Manal, F.A., Samia, E.A., Nabil, A.E. and El-Sayed, A.H. (2007) *Europ. Polym. J.,* 43, 468–477.