

Research Article

Synthesis of Potato Starch-Acrylic-Acid Hydrogels by Gamma Radiation and Their Application in Dye Adsorption

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Several kinds of acrylic-acid-grafted-starch (starch/AAC) hydrogels were prepared at room temperature (27°C) by applying 5, 10, 15, 20, and 25 kGy of gamma radiation to 15% AAC aqueous solutions containing 5, 7.5, and 15% of starch. With increment of the radiation dose, gel fraction became higher and attained the maximum (96.5%) at 15 kGy, above which the fraction got lowered. On the other hand, the gel fraction monotonically increased with the starch content. Swelling ratios were lower for the starch/AAC hydrogels prepared with higher gamma-ray doses and so with larger starch contents. Significant promotions of the swelling ratios were demonstrated by hydrolysis with NaOH: $13632 \pm 10\%$ for 15 kGy radiation-dosed [5% starch/15% AAC] hydrogel, while the maximum swelling ratio was $\sim 200\%$ for those without the treatment. The authors further investigated the availability of the starch/AAC hydrogel as an adsorbent recovering dye waste from the industrial effluents by adopting methylene blue as a model material; the hydrogels showed high dye-capturing coefficients which increase with the starch ratio. The optimum dye adsorption was found to be 576 mg per g of the hydrogel having 7.5 starch and 15% AAC composition. Two kinetic models, (i) pseudo-first-order and (ii) pseudo-second-order kinetic models, were applied to test the experimental data. The latter provided the best correlation of the experimental data compared to the pseudo-first-order model.

1. Introduction

Hydrogels can be defined as hydrophilic polymer networks that can retain a significant amount of water within their structures and can swell without dissolving in water. The hydrogels which can absorb very large amount of water and hold it even under pressure are called superabsorbent hydrogels [1]. So far, two general classes of hydrogel are mentioned in the literature. One is physical gels or pseudo gels and the other is chemical gels. Physical gels are nonpermanent and possible to convert in polymer solution by heating, while chemical gels are permanent and usually composed of covalently bonded cross-linking network. Many applications

of hydrogels are already mentioned in the literature. The most successful and promising use is in the field of medicine, pharmacy, and tissue engineering [2, 3]. Due to their high water absorption capacity and biocompatibility properties, they have been used in wound dressing, drug delivery, agriculture, and dye adsorption, as well as a number of commercially available products: contact sanitary pads, transdermal systems, dental materials, implants, injectable polymeric systems, ophthalmic applications, and hybrid-type organs (encapsulated living cells) [4–7]. Recently, many researchers have focused on modifying hydrogels with a view to enhance their water absorbency, network strength, and absorption rate [8, 9]. Starch, a specimen in the present study, can be a good

natural-polymer superabsorbent because of containing a large number of hydrophilic groups ($-\text{OH}$) and having adequate properties for practical use (such as renewable, very cheap, and biodegradable) [10].

Radiation-induced processes, in which radiation-energy-absorbed backbone polymer generally initiates a free radical process, have many advantages over other conventional methods [2, 9]. In the radiation synthesis of hydrogel from polymer solution, there is no necessity to add catalysts, initiators, cross-linkers, and so forth which are possibly harmful and difficult to remove. In addition, these processes discharge almost no waste and can be carried out with relatively low costs. Swelling behavior of acrylic-acid-grafted hydrogel can be improved by treatment with alkaline solution [11]. By these reasons, the authors adopted an irradiation synthesis method for synthesizing hydrogels in the present study. So far, the radiation grafting of acrylamide, acrylonitrile, methacrylonitrile, alkyl methacrylate, and vinyl ketones 2-dimethylaminoethylmethacrylate onto starch was investigated intensively [12]; however, there are almost no investigations on starch's property change by the grafting of acrylic acid (AAc) by low-dose gamma radiation.

Water pollution is a serious problem nowadays. Different bioadsorbents are being used to remove the water soluble dyes from water [13]. Hydrogel is one of the best candidates for removing soluble dyes from water.

In the first part of the present study, the authors investigated how the gel fraction is influenced by the gamma-radiation dose and starch concentration in the preparation process of AAc-grafted starch (starch/AAc) hydrogels initiated by applying low-dose gamma radiation. Secondly, the swelling properties of the starch/AAc hydrogels were examined including the effect of the hydrolysis with sodium hydroxide (NaOH). Thirdly, the authors also investigated the methylene blue (MB) adsorption efficiency of NaOH -treated starch/AAc hydrogel in order to explore the possibility of the hydrogels' application for removing dyes from aqueous solution. The pseudo-first-order and pseudo-second-order models are used to correlate the adsorption kinetics data of MB onto synthesized hydrogels.

MB is a cationic dye and is most commonly used for coloring paper, dyeing cottons, wools, and so forth. In addition, this dye is generally used to test the adsorption capacity of various adsorbents, which permits quantitative comparisons between the adsorption capacities of various adsorbents [14]. Other than these, adsorption of MB is still important from an environmental point of view because acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in human.

2. Experimental

2.1. Materials. Potato starch was obtained from Sigma Aldrich and methylene blue (MB, C.I. number 52015) and acrylic acid were obtained from Merk. Chemical formula of methylene blue is $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ (molecular weight: 319.85, λ_{max} : 663 nm). Distilled water was used as a solvent.

2.2. Preparation of Starch/AAc Hydrogel. An aqueous solution of potato starch was prepared by dissolving it in the distilled water in a three-neck flask under vigorous stirring at 200 rpm and with heating at 80°C for 30 minutes. After the dissolution, the starch solution was left at room temperature for a while for cooling. Then, AAc was added to the cooled solution with stirring. The composition of three starch/AAc solutions was After becoming homogeneous, the starch/AAc solution was taken in several test tubes, which were sealed and allowed to be irradiated with 5, 10, 15, 20, and 25 kGy of ^{60}Co gamma-ray-radiation dose at 6.8 kGy/h of radiation-dose rate. Finally, after being cut into small pieces, the starch/AAc hydrogels were dried in the air and then in an oven until becoming of constant weights.

2.3. Determination of Gel Fraction. For 24 hrs, the dried gel samples had been kept in beakers containing 50°C distilled water in order to remove soluble fraction. Then, the gel samples were taken out from the beakers and dried to constant weights in an oven at 60°C . The gel fractions of samples were calculated as follows:

$$\text{Gel fraction [\%]} = \frac{W_1}{W_0} \times 100, \quad (1)$$

where W_0 and W_1 are the dried gel weights before and after the rinsing, respectively.

2.4. Determination of Swelling Properties. After immersing the rinsed-and-dried hydrogel samples in distilled water at room temperature, the samples were periodically weighed with blotting excess surface water with filter papers. The water absorption of the samples was calculated as follows:

$$\text{Water absorption [\%]} = \frac{W_t - W_1}{W_1} \times 100, \quad (2)$$

where W_1 and W_t are the gel weights before and after immersing in the water, respectively.

2.5. Improvement of Swelling Properties. After the immersion of rinsed-and-dried hydrogel samples in 0.45 M NaOH aqueous solutions for 24 hrs, the swollen samples were dried in the air and then in an oven (60°C) until becoming of constant weights. The swelling properties of the NaOH -treated hydrogels were investigated and analyzed in the same way as described in Section 2.4.

2.6. Determination of FTIR Spectroscopy. The FTIR spectra of the several pellets of the powder mixture of the rinsed-and-dried starch/AAc gels and KBr were obtained from a Fourier Transform Infrared Spectrometer (IP Prestige-21, Shimadzu).

2.7. Differential Scanning Calorimetry. By utilizing a differential scanning calorimeter (Q100, TA Instruments), thermograms of untreated and NaOH -treated dried hydrogels having composition 5% starch/15% AAc were obtained with elevating temperature at $10^\circ\text{C}/\text{min}$ in a range from 30 to 580°C and sample weight 28.400 mg. During the DSC measurements, inert atmosphere was maintained by purging nitrogen

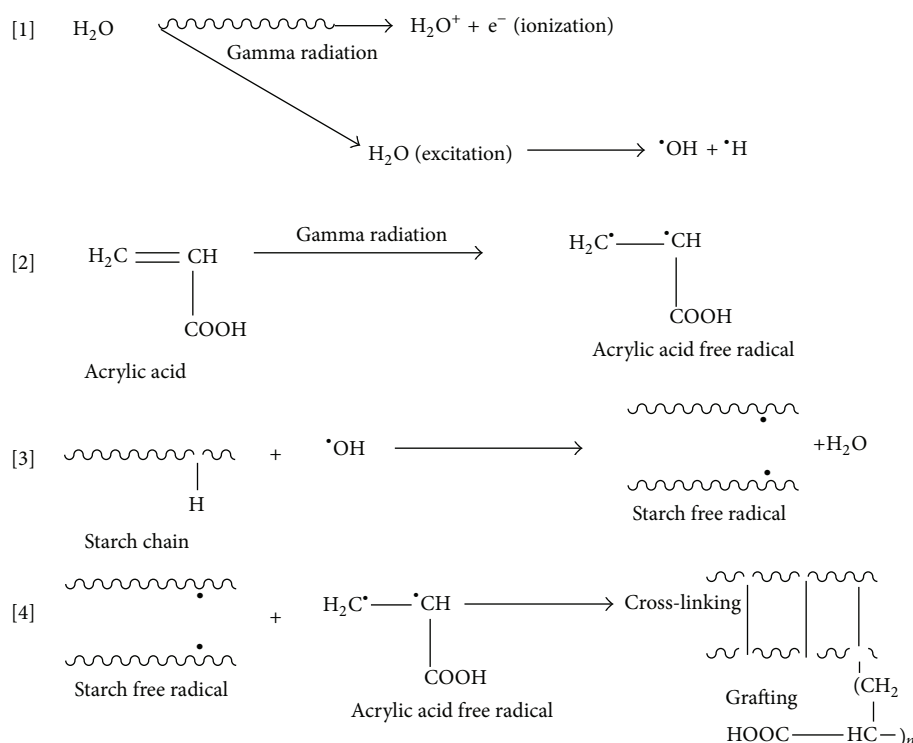


FIGURE 1: Possible grafting and cross-linking reaction mechanism of starch and acrylic acid.

at 50 mL/min of flow rate. An empty pan was used as a reference.

2.8. SEM Photograph. The SEM micrograph of the untreated and NaOH-treated dried hydrogels having composition 5% starch/15% AAc was observed by using an electron microscope (JSM-6490, JEOL) operated at 20 kV.

2.9. Determination of Dye Adsorption. The hydrogels of different composition of starch and AAC synthesized by applying 15 kGy gamma radiation were immersed in aqueous MB solutions (250 mL, initial dye concentration: 80 mg/L), and the dye-concentration evolution of the surrounding solutions was measured with utilizing a UV-visible spectrometer (UV-1800 Series, Shimadzu). The adsorption capacity after certain period t during the treatment, q_t (mg/g), is given by [12]

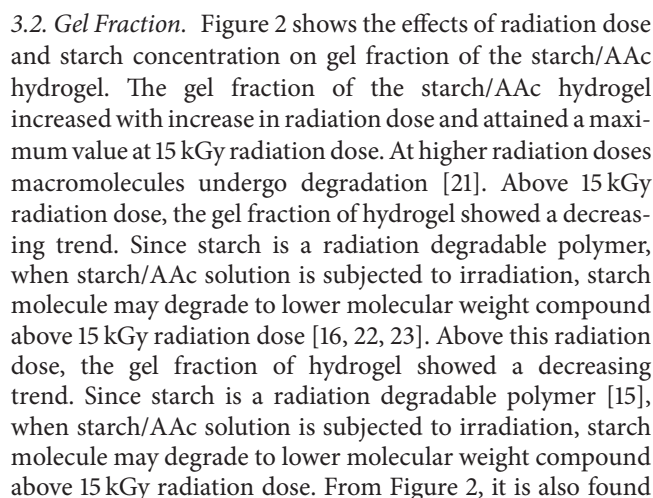
$$q_t = \frac{(C_0 - C_t)V}{W}, \quad (3)$$

where C_0 and C_t are the dye concentration (mg/L) of the initial solution and that at t , respectively, while V is the volume of the solution (L) and W is the dry weight of the hydrogel (g).

3. Result and Discussion

3.1. The Mechanism of the Reaction. The cross-linking mechanism of polymers in a solution by gamma irradiation was reported in [2, 15–19]. There are three main reactive species formed in water upon irradiation: hydrated electron,

hydroxyl radicals, and hydrogen radicals. Electrons exhibit low reactivity toward simple, hydrophilic hydrogel-forming polymers. This is an expected behavior since they do not contain functional groups being efficient scavengers of hydrated electrons. Reaction of hydrogen radicals with polymers is rarely studied in detail. In acidic media, their contribution to the total yield of macroradicals does not exceed 20%. Two hydrogen radicals can recombine causing the evolution of hydrogen gas. When the aqueous blend of starch and AAC is irradiated by gamma radiation, the hydroxyl radicals are produced from water. The hydroxyl radicals abstract hydrogen atoms from macromolecules and thus macroradicals are formed (Figure 1) [2, 20].



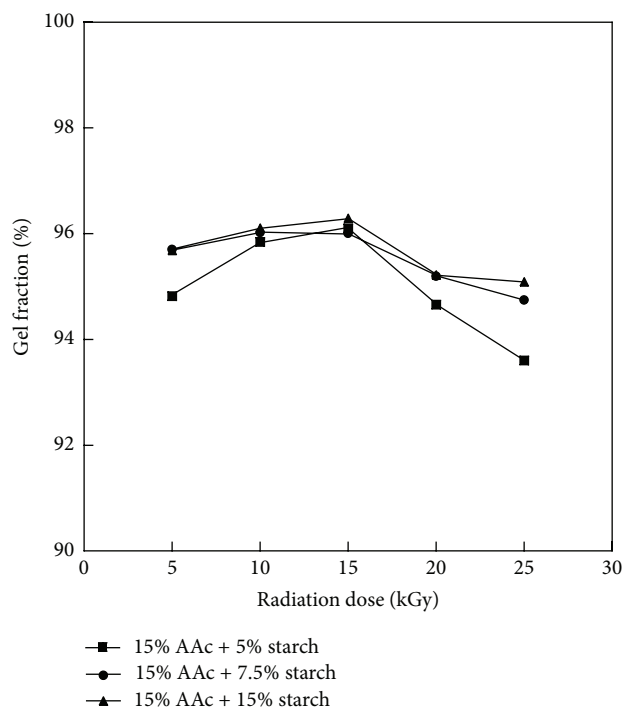


FIGURE 2: Effects of radiation dose and starch concentration on gel fraction of starch/AAC hydrogel.

that, in a broad way, the gel fraction of hydrogel increased with increased concentration of starch in starch/AAC solution. When the aqueous solution of starch/AAC is subjected to irradiation with gamma ray, free radicals are generated on starch and AAC. Random reactions of these radicals lead to formation of the graft copolymer of starch and AAC. When the radiation dose has been increased beyond a certain value, the polymer chains cross-link and then a gel-like material is obtained. For the formation of cross-linked macromolecules, the subsistence of two radicals on neighboring chains and their subsequent combination are required. At the higher concentration of polymer, the macromolecules come close and that makes it easy to form cross-linking.

3.3. Swelling Properties. Swelling properties of the hydrogels are influenced by the network cross-linking feature. With the increment of cross-linkage density, the swelling ratio usually decreases because of the decrement of the slack in the network polymer necessary for expanding the network on the swelling of the hydrogels. Figures 3(a)–3(e) show the effects of starch concentration and gamma-radiation dose on the water absorption of the starch/AAC hydrogel. The water content reached equilibrium around 24 hrs. It was observed that the water absorption capacity decreases with the starch content, which indicates the cross-link-density increase with the starch content.

3.4. Swelling Properties after Treatment of NaOH. Figure 4 shows the effects of starch concentration and gamma-radiation doses on the water absorption of the NaOH-treated

starch/AAC hydrogels. It was found that the water absorption capacities of NaOH-treated starch/AAC hydrogels are higher than those of the corresponding starch/AAC hydrogels without NaOH treatment (Figure 3). This may come from the transformation of AAC in the starch/AAC hydrogel into sodium carboxylate caused by NaOH. The hydrophilicity of carboxylate may be higher than that of carboxylic group. The maximum water absorbance capacity was found for 5% starch/15% AAC composite with 15 kGy gamma-radiation dose. Figure 5 shows an NaOH-treated hydrogel before and after swelling in water.

3.5. FTIR Analysis. Figure 6 presents the infrared spectra of potato starch and the starch/AAC gel. The peaks observed at 3423 cm^{-1} and $1022\text{--}1161\text{ cm}^{-1}$ can be ascribed to the O–H stretching and C–O–C skeletal vibration of starch. The absorption peak at 2945 cm^{-1} corresponds to C–H stretching of the acrylate unit and starch, while the bands at 1412 and at 1321 cm^{-1} correspond to the angular deformation of C–H. The peak at 1714 cm^{-1} can be assigned to the C=O stretching of carbonyl group of AAC, which is absent in the spectra of starch. This result indicates that AAC interacts with/entraps starch.

3.6. Thermal Analysis of Untreated and NaOH-Treated Hydrogel. Figure 7 shows the DSC thermal properties of the untreated and NaOH-treated hydrogels with 5% starch and 15% AAC composition measured at $10^\circ\text{C}/\text{min}$ of heating rate under the flow of nitrogen gas.

The DSC curves were obtained for starch-acrylic-acid hydrogels before and after alkali (NaOH) treatment. The thermogram of starch-acrylic-acid hydrogel before alkali treatment reveals endothermic glass transition temperature at $\sim 225^\circ\text{C}$ and exothermic peak at $\sim 276^\circ\text{C}$ due to decomposition of hydrogel. Thermogram of alkali treated starch-acrylic-acid hydrogel reveals glass transition temperature at $\sim 135^\circ\text{C}$ and decomposition temperature at $\sim 256^\circ\text{C}$. It can be concluded that the glass transition temperature and decomposition temperature of starch-acrylic acid hydrogel decrease due to alkali treatment.

3.7. Scanning Electron Microscopy (SEM). SEM micrographs of the starch/AAC hydrogels before and after the NaOH treatment are shown in Figure 8. As can be seen in the figure, the NaOH treatment also induces a significant change in the surface structure of the starch/AAC hydrogel. Before the NaOH treatment, the surface shows a compact structure in SEM image (Figure 8(a)) which may be due to hydrogen-bond attraction between the grafted $-\text{COOH}$ chains. On the other hand, the surface shows a more expanded structure after the NaOH treatment (Figure 8(b)), which is thought to come from the repulsion between the grafted chains with the larger electrostatic force among $-\text{COO}^-$ groups. This expansion can facilitate the NaOH-treated hydrogel to MB adsorption.

3.8. Application of Prepared Hydrogels in Dye Removal from Wastewater. Other than the above-described basic properties, the important purpose in the present study was to investigate the availability of the starch/AAC hydrogels for

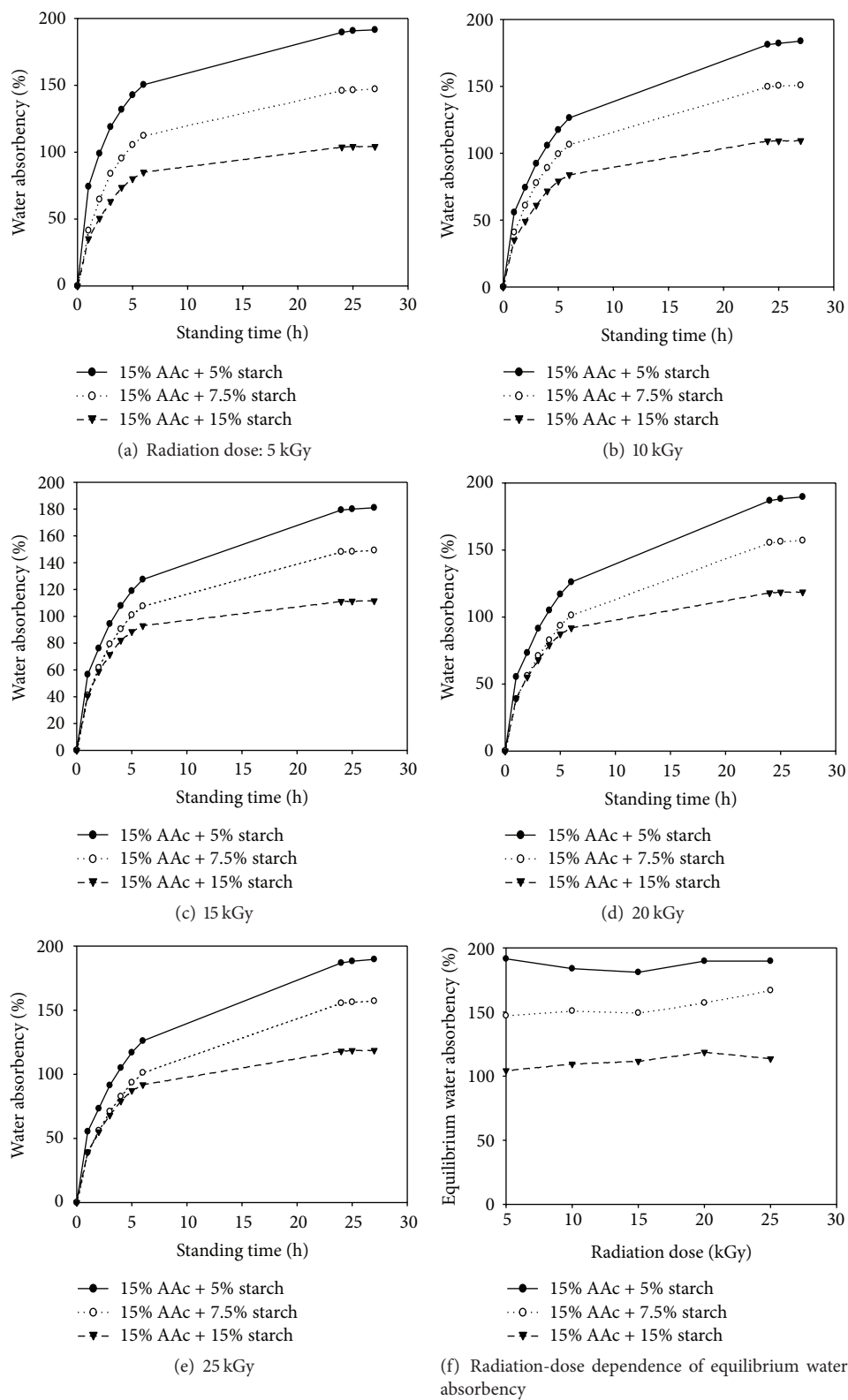


FIGURE 3: Effects of radiation dose and starch concentration on the swelling behavior of starch/AAC hydrogel.

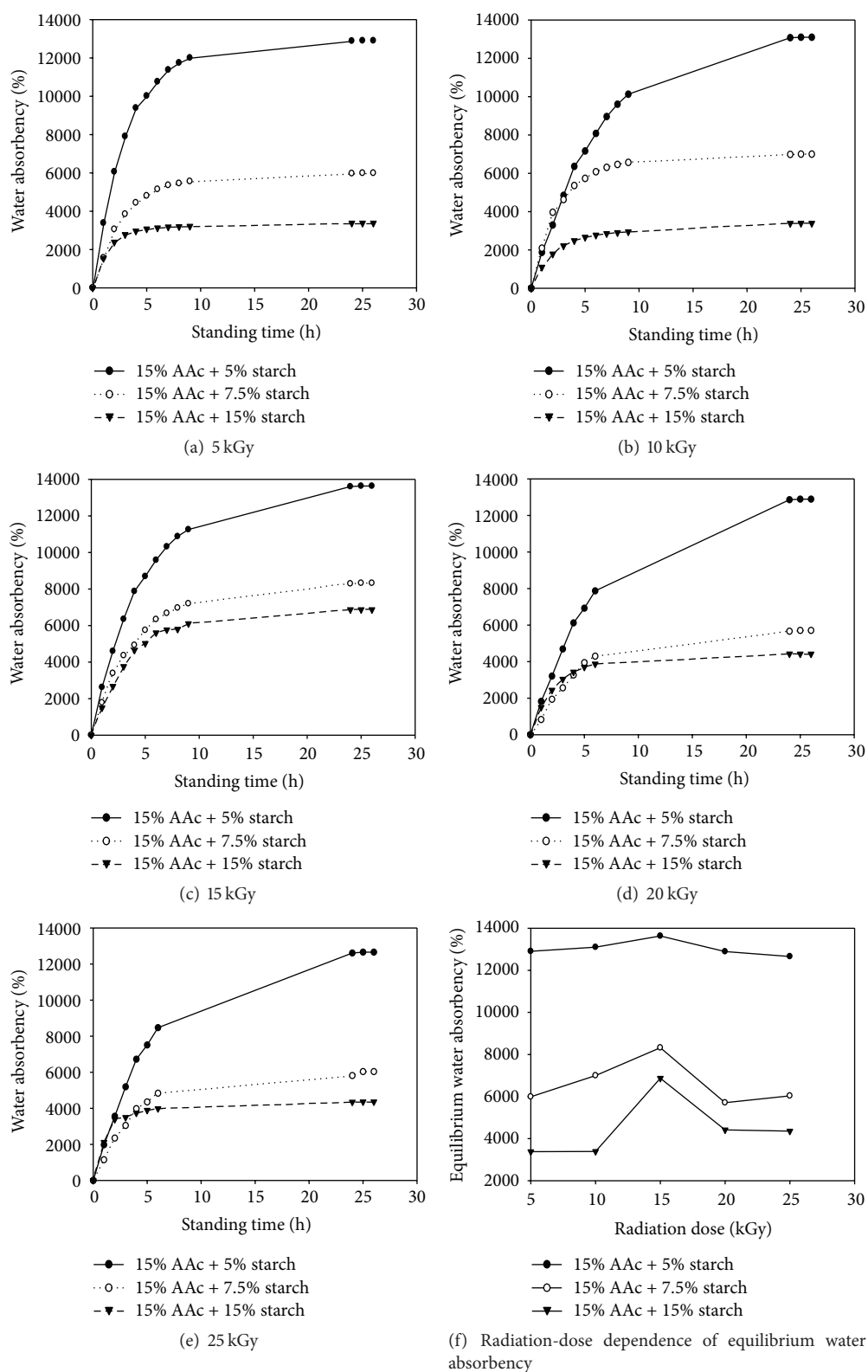


FIGURE 4: Effects of radiation dose and starch concentration on water absorption of starch/AAc hydrogel after being treated with NaOH.

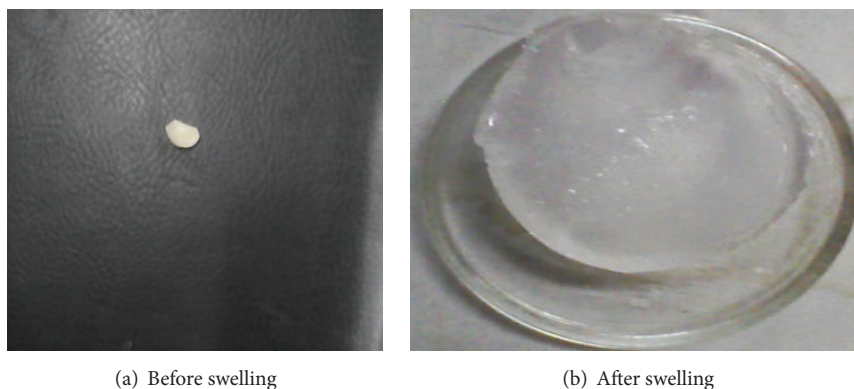


FIGURE 5: Volume change of an NaOH-treated starch/AAC hydrogel before and after swelling.

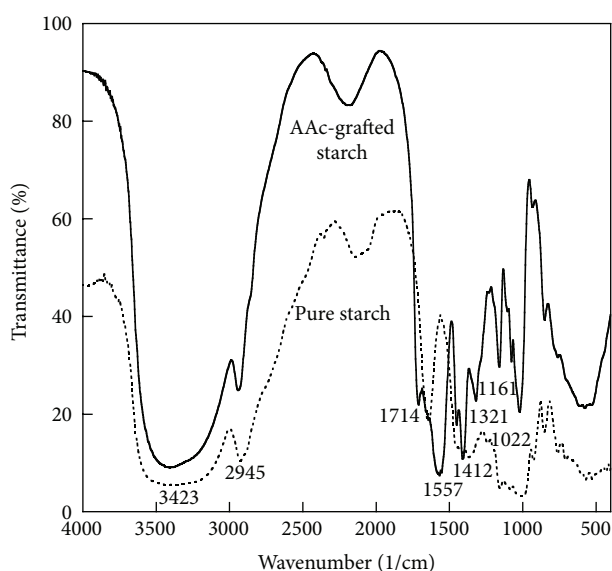


FIGURE 6: FT-IR spectra of potato starch and starch/AAC gel.

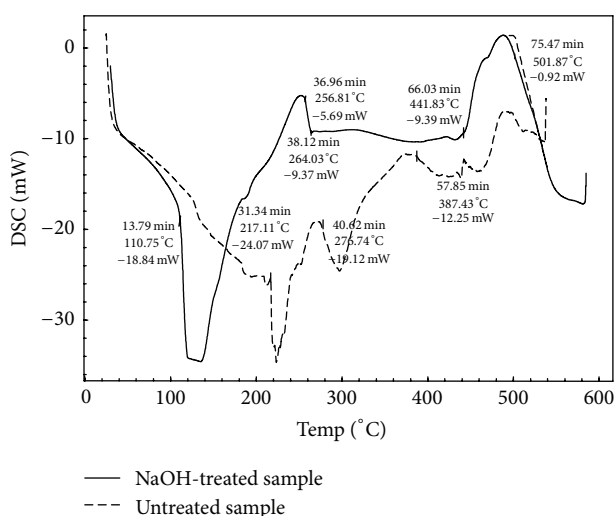


FIGURE 7: Thermal analysis of untreated and NaOH-treated starch/AAC hydrogel.

the removal of hazardous dyes from the waste fluids (adopting MB as a model material). In the MB-capturing experiments, the starch/AAC hydrogels prepared by 15 kGy gamma-radiation dose were utilized because their gel fractions showed maxima at this dose as shown in Figure 2, indicating the most preferable condition for forming gel network.

Figure 9 shows MB-adsorption evolution by the starch/AAC hydrogels with different compositions prepared by irradiating 15 kGy gamma-radiation dose. Their MB adsorptions increased with time and, at 72 hrs, attained their respective maximum values around 449, 576, and 360 mg/g for 5% starch, 7.5% starch, and 15% starch/15% AAC hydrogels, respectively. The capturing mechanism of MB by the starch/AAC hydrogel is forming an ionic complex between the imine group of MB and the ionized carboxyl group of starch/AAC hydrogel. As shown in Figure 9, 7.5% starch/15% AAC hydrogel shows the highest MB-capturing efficiency, which may come from more beneficial conditions than those of other starch/AAC hydrogels for forming the complex between the end groups of MB and starch/AAC hydrogel.

Someone can notice, from Figure 9, that MB-capturing rates of all the starch/AAC hydrogels are higher in the beginning than in the later stage. These features can be explained by two mechanisms with the MB-adsorption progress: one can be the decrease in unoccupied -COO^- end groups in starch/AAC hydrogel and the other will be stiffening of the hydrogel network preventing the -COO^- swinging for searching for the MB's imine group to form their complex.

3.9. Adsorption Kinetics of MB Adsorption. Two simplified kinetic models were applied to fit the adsorption by the alkali-modified AAC-starch hydrogels. The pseudo-first-order and pseudo-second-order equations [24] are expressed as follows:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t, \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e}, \quad (5)$$

where q_t and q_e are the amount of MB adsorbed (mg/g) at time t and equilibrium time, respectively, k_1 was the rate constant (hr^{-1}) of first-order adsorption, and k_2 is the rate

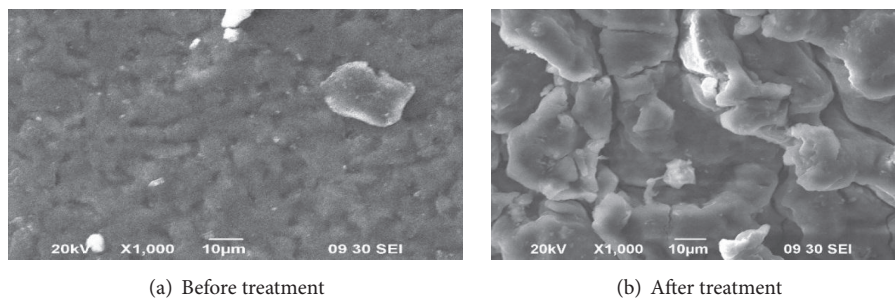


FIGURE 8: SEM micrographs of (a) untreated and (b) NaOH-treated starch/AAc hydrogel.

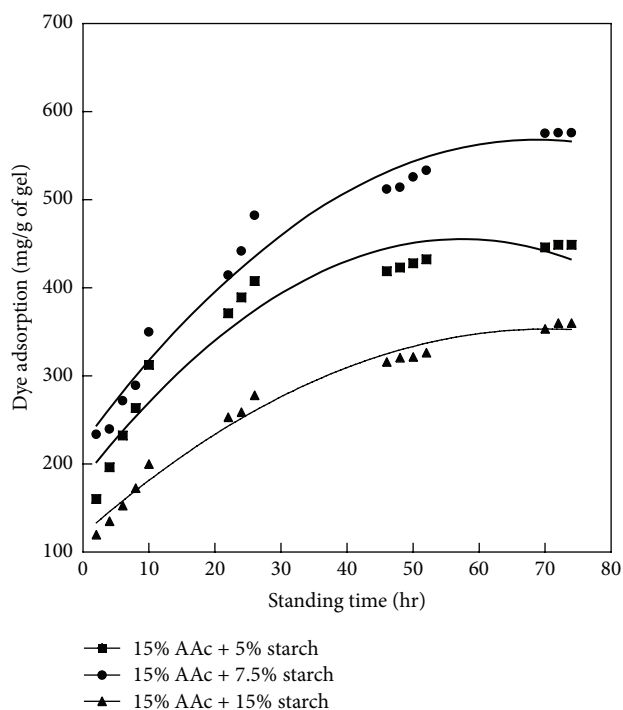


FIGURE 9: Effect of standing time and concentration of starch/AAc hydrogel on dye adsorption.

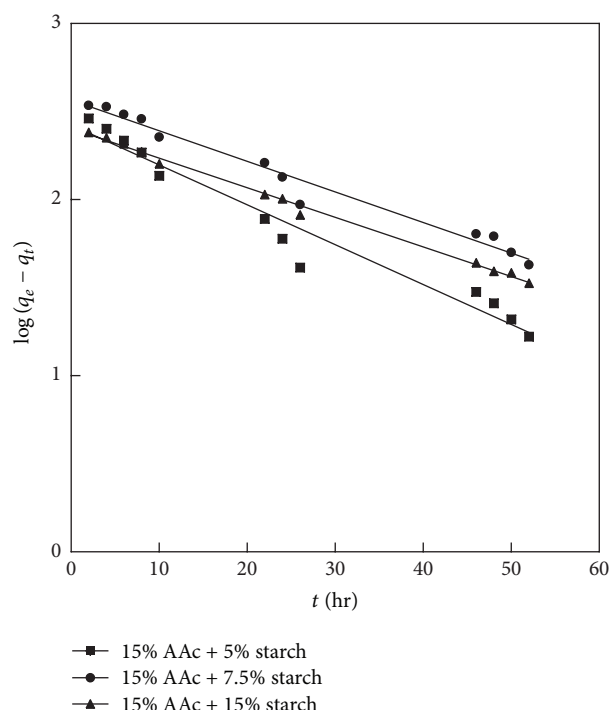


FIGURE 10: Pseudo-first-order kinetic model for adsorption of MB on starch-acrylic-acid hydrogel.

constant ($\text{g hr}^{-1} \text{mg}^{-1}$) of second-order adsorption. Figure 10 shows $\log(q_e - q_t)$ versus t straight line plots for the adsorption of MB on hydrogels of different starch composition. The k_1 , $q_{e,\text{cal}}$ (calculated equilibrium concentration), and correlation coefficients R^2 were calculated for these plots and listed in Table 1 along with experimental q_e values. The correlation coefficients R^2 listed in Table 1 for first-order kinetic model were 0.958, 0.976, and 0.996 for 5%, 7.5%, and 15% starch concentrations, respectively.

Figure 11 shows plots of t/q_t versus t for second-order kinetic model. The k_2 and $q_{e,\text{cal}}$ values from (5) and correlation coefficient R^2 values from the plots of second-order kinetic model were also listed in Table 1. R^2 values for this model were 0.999, 0.994, and 0.992 for 5%, 7.5%, and 15% starch concentrations, respectively, which were higher than the R^2 values obtained for the pseudo-first-order model. It can be seen that the difference between the experimental q_e

values and the q_e values calculated from first-order kinetic model was very high, while the difference was lower for second-order kinetic model.

It can be seen that the difference between the experimental q_e and calculated values for pseudo-first-order kinetic model was very high while the difference was lower for pseudo-second-order kinetic model.

Based on the intraparticle diffusion model, the diffusion rate of the dye molecule in particle, k_i , can be calculated by the following equation [25, 26]:

$$q_t = k_i t^{1/2} + c, \quad (6)$$

where q_t is the amount of dye adsorbed in time t (mg/g), k_i is the intraparticle diffusion rate constant, and c (mg/g) is a constant that characterizes boundary layer thickness. In Figure 12, the plots of q_t against $t^{1/2}$ represented multilinearity

TABLE 1: Adsorption kinetic parameters for the adsorption of MB on hydrogels.

Hydrogel composition	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			Intraparticle diffusion (mg g ⁻¹ hr ⁻¹)			
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	Rate constant k_1 (hr ⁻¹)	R^2	$q_{e,cal}$ (mg/g)	Rate constant k_2 (hr ⁻¹)	R^2	R^2	k_{i1}	k_{i2}	k_{i3}
15% AAc + 5% starch	449	263.94	0.0521	0.958	476.19	0.00036	0.999	0.8718	94.37	74.51	44.46
15% AAc + 7.5% starch	576	365.94	0.0399	0.976	624.22	0.00019	0.994	0.9304	101.09	81.67	44.46
15% AAc + 15% starch	360	251.83	0.0386	0.996	395.96	0.00025	0.992	0.96	59.76	49.62	37.41

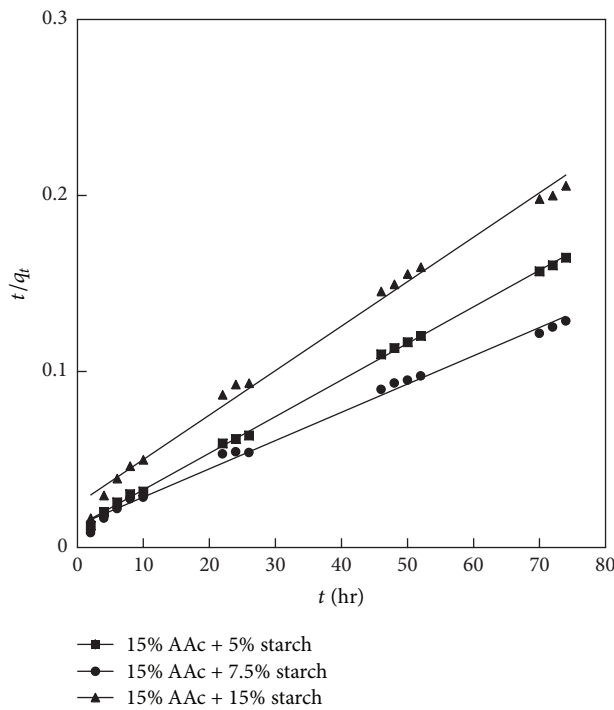


FIGURE 11: Pseudo-second-order kinetic model for adsorption of MB on starch-acrylic-acid hydrogel.

containing at least three linear segments. It can be seen that the order of adsorption rate was $k_{i1} > k_{i2} > k_{i3}$ and the diffusion rate constant was the highest for 7.5% starch composition. The first stage was attributed to the rapid transfer of adsorbate onto the adsorbent surface by diffusion through the boundary layer. In the second stage, the MB molecules diffused from the external surface into the pores of the hydrogel adsorbent and this was the rate determining stage which actually represents adsorption due to intraparticle diffusion. The third stage was the final stage where the MB molecules were adsorbed on the active sites on the internal surface of the pores and the equilibrium was attained. Therefore, the change of diffusion rate constant values can be considered to the adsorption stages of the external surface, internal surface, and equilibrium, respectively.

So, the pseudo-second-order kinetic model fits with the experimental kinetic data which indicates that intraparticle diffusion process was the rate limiting step of the adsorption.

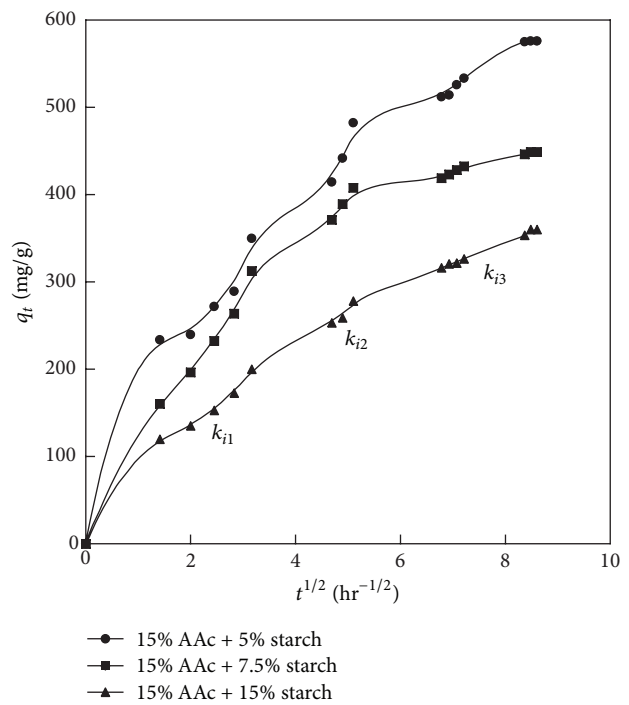


FIGURE 12: Intraparticle diffusion plots for the hydrogels.

3.10. UV-Visible Spectroscopic Analysis of Dye Adsorption. By using Beer-Lambert law, concentration of methylene blue (MB) was calculated at 663 nm [27].

Figure 13 shows the UV-visible absorbance spectrum of the initial MB solution (80 mg/L) and three UV spectra of the aqueous phases surrounding the respective starch/AAc hydrogels after attaining the equilibrium MB adsorptions (at 72 hrs). This result indicates that the methylene blue is absorbed by hydrogel.

3.11. Conclusion. From the present investigations, it can be concluded that the preparation of starch/AAc hydrogel can be satisfactorily performed by utilizing ⁶⁰Co gamma radiation. With respect to the gel fraction, 15 kGy radiation dose is considered as a required radiation dose for the preparation of the starch/AAc hydrogel. Swelling behaviors of the starch/AAc hydrogel can be improved by the treatment with NaOH. The highest swelling ratio of the 5% starch/15% AAc hydrogel

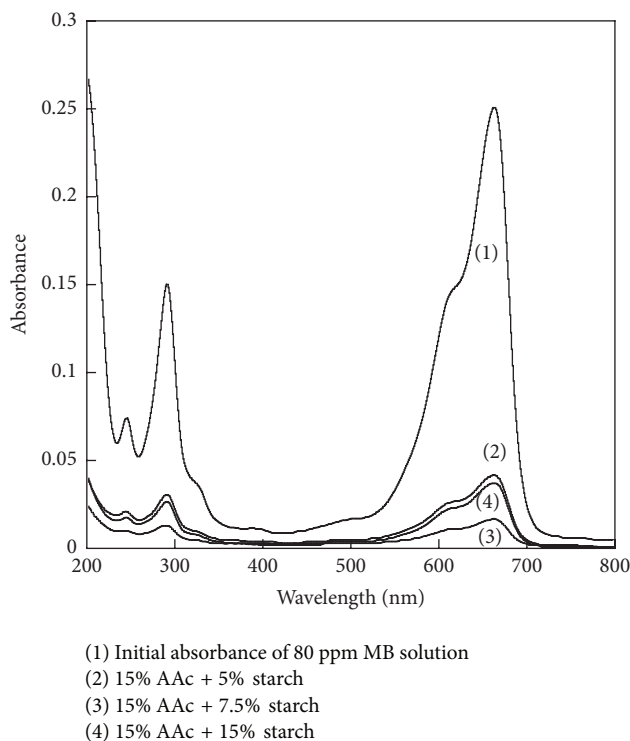


FIGURE 13: UV-visible spectra of MB.

increased from 200% to $13632 \pm 10\%$ by the hydrolysis with NaOH. From FTIR spectroscopic measurements, it is found that AAc interacts with starch and forms hydrogel. Differential scanning calorimetry shows the decreasing trend of glass transition temperature and decomposition temperature with alkali treatment. Scanning electron microscopy reveals that treating the hydrogel with NaOH solution facilitates the expansion of surface followed by the greater dye adsorption. The adsorption of MB was carried out by varying the concentration of starch in starch/AAc hydrogel. The value of adsorbed MB is found ~ 576 mg/g of dry gel with 7.5% starch containing starch/AAc hydrogel indicating the possibilities for the application in pharmacy, agriculture, and environmental technology. Between the pseudo-first-order and second-order kinetic model, the latter can be used to interpret the kinetics of adsorption data.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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