Preparation and Swelling Behavior of Macroporous Poly(acrylamide-*co*-sodium methacrylate) Superabsorbent Hydrogels

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ABSTRACT: Macroporous superabsorbent hydrogels (SAHs) composed of acrylamide (AAm) and sodium methacrylate (NMA) were prepared by aqueous solution polymerization in the presence of a glucose solution. Their swelling capacity was investigated as a function of the concentrations of the glucose solution, sodium methacrylate, crosslinker, initiator, and activator. The porosity of the poly(acrylamide-*co*-sodium methacrylate) superabsorbent hydrogels was confirmed using scanning electron microscopy. The SAHs were characterized by IR spectroscopy. To estimate the effect on the swelling behavior, three types of crosslinkers were employed: *N*,*N*′-methylenebisacrylamide, 1,4-butanediol diacrylate, and diallyl phthalate. Network structural parameters such as initial swelling rate, swelling rate constant, and maximum equilibrium swelling were evaluated by water absorption measurement. The equilibrium water content (EWC%) of the AAm–NMA macroporous SAHs was found to be in the range of 93.31–99.68, indicating that these SAHs may have applications as biomaterials in the medicinal, pharmaceutical, and veterinary fields. Most of the SAHs prepared in this investigation followed non-Fickian-type diffusion, and few followed a case II– or super–case II-type diffusion. The diffusion coefficients of these macroporous SAHs were investigated. Further, the swelling behavior of these SAHs also was investigated at different pHs and in different salt solutions and simulated biological fluids. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3202–3214, 2006

Key words: macroporous polymers; swelling; hydrogels; crosslinking

INTRODUCTION

Superabsorbent polymers (SAPs), or hydrogels, are a special class of hydrophilic water-insoluble polymers that can swell in water and hold a huge amount of water while maintaining their structure even under pressure.[1,2] These materials were first developed in the United States for use in agriculture as water-retention materials. In the 1970s these materials were developed for hygienic and personal care products, such as diapers, sanitary napkins, and surgical pads. Because of their excellent properties they are utilized in agricultural, horticultural, biomedical, and pharmaceutical applications.[3–11] They can also be used in controlled drug delivery, metal extraction, and separation applications.[12–19] The desired properties of any superabsorbent are high swelling capacity, high swelling rate, and good mechanical strength of the swollen gel.

Recently, porous superabsorbent hydrogels have gained much attention because of their improved swelling and absorption rate.[20–27] The swelling rate of superabsorbent hydrogels can be enhanced through the creation of porosity in the hydrogel structure. The pores in the hydrogel generate a large surface area in order to accommodate large amount of water in a short time. Porous hydrogels are classified as microporous, mesoporous, macroporous, or superporous, depending on the pore size.[21] Several methods are available for use in creating porosity in hydrogels. In the phase separation method, a well-known technique for obtaining porous hydrogels, the hydrogels are prepared at a temperature higher than the lower critical solution temperature (LCST) of the base polymer.[28–30] Temperature-sensitive hydrogels such as porous poly(*N*-isopropyl acrylamide) can be obtained by use of this method.[28–30] A second method is the porogen technique, in which pore generators such as sodium chloride or polyethylene glycol or sucrose are dispersed in the polymerization mixture and subsequently are extracted with the appropriate solvent.[31–33] These materials should not have reacted with other reactants present in the polymerization system, and they must be easily extractable after polymerization. A third method is the foam formation technique. In this method, two types of foaming

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agents are used for porosity generation. Carbonate compounds such as sodium bicarbonate, potassium carbonate, magnesium carbonate, and calcium carbonate and organic solvents such as pentane, hexane, methanol, and acetone can be used as porosity generators.[20,25,26,34–38] In addition to these methods, freeze-drying methods also are considered effective.[39]

In the present article, we report the preparation of macroporous superabsorbent hydrogels (SAHs) based on acrylamide and sodium methacrylate in the presence of a porogen (glucose) solution in normal atmospheric conditions with an ammonium persulfate (APS)/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) redox system. The effects of variables such as the concentrations of monomer, crosslinker, initiator, and activator on the swelling behavior of macroporous superabsorbent hydrogels were studied. The stimuli-responsive behavior of the hydrogel also is reported. Swelling and diffusion characteristics were evaluated in detail.

EXPERIMENTAL

Materials

Acrylamide (AAm), glucose, and *N,N*-methylenebisacrylamide (MBA) were received from S.D. Fine-Chem Ltd. (Mumbai, India); 1,4-butanediol diacrylate (BDDA), diallyl phthalate (DP), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI). The remaining chemicals and reagents were purchased from Sigma Aldrich Pvt. Ltd. (Secunderabad, India). All the monomers and chemicals were used as received. Sodium methacrylate was prepared by neutralization of methacrylic acid with sodium hydroxide in methanol.[3]

Synthesis of macroporous poly(AAm–NMA) superabsorbent hydrogels

Macroporous superabsorbent hydrogels were synthesized by free-radical polymerization of AAm, NMA, and crosslinker with an APS/TMEDA redox pair initiating system in the presence of 2 mL of pore-generating (glucose) solution.[22] In a typical reaction, 10.55 m*M* acrylamide, 2.77 m*M* sodium acrylate, and 0.064 m*M* MBA were dissolved in 2 mL of a 1*M* aqueous glucose solution. Then 0.043 m*M* APS and 0.086 m*M* TMEDA were added sequentially to the reaction mixture, and the total reaction mixture was then transferred to a poly(vinyl chloride) (PVC) straw 3 mm in diameter as a polymerization reactor. The reactions were carried out by varying the reaction parameters such as the concentrations of sodium methacrylate, crosslinker, APS, and TMEDA. The complete experimental details are presented in Table I. The polymerizations were conducted for 10 h at room temperature. The gels were obtained within 1 h in all cases. The synthesized SAPs were transferred into a 1-L beaker containing distilled water and left for 24 h while changing the water every 2 h in order to remove the unreacted monomers and other chemicals. The structures of the monomers, crosslinkers, initiator, and activator are shown Scheme 1.

Characterization of hydrogels

After completely drying, the macroporous AAm–NMA SAP hydrogel samples were coated with a thin layer of palladium gold alloy. The structural and morphological variations were observed by using a JOEL JSM 840A (Japan) scanning electron microscope (SEM).

IR spectra

The IR spectra of dry superabsorbent hydrogels were carried out on a Perkin–Elmer Spectrophotometer ASCII (Perkin–Elmer Cetus Instruments, Norwalk, CT).

Swelling studies

The degree of swelling[40,41] (swelling ratio, *S*) and equilibrium water content[40,41] (EWC%) of the macroporous superabsorbent hydrogels were determined by a conventional gravimetric method. About 50 mg of superabsorbent hydrogel was immersed in a beaker containing 100 mL of distilled water and allowed to swell until it reached equilibrium. The completely swollen gel was taken out, and the excess water was removed superficially by filter paper and then weighed accurately. The swelling ratio and equilibrium water content of SAP were calculated using eqs. (1) and (2), respectively, as shown below:

$$S = \frac{[\text{Weight of swollen gel}(W_s) - \text{Weight of dry gel}(W_d)]}{[\text{Weight of dry gel}(W_d)]} \quad (1)$$

$$EWC\% = \frac{[\text{Weight of swollen gel}(W_{eq}) - \text{Weight of dry gel}(W_d)]}{[\text{Weight of swollen gel}(W_{eq})]} \times 100 \quad (2)$$

pH solutions preparation

Buffer solution I was prepared by mixing 12.3 g of anhydrous boric acid (0.20*M*) and 10.51 g of citric acid (0.05*M*) in 1000 mL of distilled water, and buffer solution II was prepared by dissolving 38.01 g of trisodium phosphate (*M*) in 1000 mL of distilled water. To prepare a specific buffer solution, the two pH solu-

TABLE I
Composition, Swelling Ratio, Equilibrium Water Content, and Selling/Diffusion Characteristics of Macroporous Poly (AAm-*co*-NMA) Superabsorbent Hydrogels (AAm = 10.55 mM and Glucose Solution = 2 mL of 1*M* solution)

Polymer code	NMA (m*M*)	Crosslinker (m*M*)	APS (m*M*)	TMEDA (m*M*)	Swelling ratio or equilibrium swelling ratio (S_{eq}) (g water/g gel)	EWC (%)	Theoretical equilibrium swelling ratio (TS_{eq})(g water/g gel)	Initial swelling rate (r_i) [(g water/g gel) min)]	Swelling rate constant (k_s) [(g gel/g water)/min]	Swelling exponent (n)	Diffusion coefficient (D) (cm^2/s^{-1})
NMA1	0.92	0.064	0.043	0.086	13.67	93.31	14.56	0.46	0.068	0.79	5.722
NMA2	1.38	0.064	0.043	0.086	34.35	97.71	38.13	0.46	0.026	0.76	3.646
NMA3	1.85	0.064	0.043	0.086	53.89	98.17	65.27	0.34	0.015	0.76	3.655
NMA4	2.77	0.064	0.043	0.086	66.01	98.50	81.16	0.38	0.012	0.72	3.962
NMA5	4.62	0.064	0.043	0.086	72.02	98.63	78.86	1.08	0.012	0.71	3.522
MBA1	2.31	0.016	0.043	0.086	251.25	99.60	495.04	0.37	1.49×10^{-6}	1.00	0.702
MBA2	2.31	0.032	0.043	0.086	144.58	99.31	223.21	0.25	5.11×10^{-6}	0.86	1.586
MBA3	2.31	0.048	0.043	0.086	102.20	99.03	166.66	0.19	7.15×10^{-6}	0.95	1.043
MBA4	2.31	0.097	0.043	0.086	52.87	98.14	62.735	0.27	7.10×10^{-5}	0.82	1.442
MBA5	2.31	0.129	0.043	0.086	41.07	97.62	45.97	0.37	1.79×10^{-5}	0.89	1.476
BDDA1	2.31	0.012	0.043	0.086	103.86	99.04	149.03	0.37	1.70×10^{-5}	0.96	4.071
BDDA2	2.31	0.037	0.043	0.086	110.66	99.10	157.72	0.47	1.90×10^{-5}	1.05	4.153
BDDA3	2.31	0.050	0.043	0.086	90.68	98.90	134.77	0.22	1.22×10^{-5}	0.87	3.154
BDDA4	2.31	0.075	0.043	0.086	75.39	98.60	101.93	0.30	2.92×10^{-5}	0.94	4.153
DP1	2.31	0.009	0.043	0.086	187.55	99.47	198.01	5.41	1.38×10^{-5}	1.77	8.212
DP2	2.31	0.018	0.043	0.086	221.86	99.55	268.81	1.79	2.48×10^{-5}	1.49	5.798
DP3	2.31	0.028	0.043	0.086	318.24	99.68	429.18	1.69	9.18×10^{-6}	1.44	4.903
DP4	2.31	0.056	0.043	0.086	204.23	99.51	228.83	2.43	4.64×10^{-5}	0.91	6.014
APS1	2.31	0.064	0.010	0.086	34.20	97.13	36.15	0.78	6.02×10^{-5}	0.75	6.685
APS2	2.31	0.064	0.021	0.086	45.94	97.86	49.11	0.46	1.91×10^{-5}	0.82	5.421
APS3	2.31	0.064	0.032	0.086	53.40	98.16	62.61	0.40	1.03×10^{-5}	0.79	4.812
APS4	2.31	0.064	0.065	0.086	56.41	98.25	78.80	0.15	2.51×10^{-5}	0.86	3.465
APS5	2.31	0.064	0.087	0.086	61.38	98.39	78.06	0.19	3.17×10^{-5}	0.81	3.409
TMEDA1	2.31	0.064	0.043	0.021	35.51	97.26	38.94	0.39	2.62×10^{-5}	1.04	7.161
TMEDA2	2.31	0.064	0.043	0.043	53.92	98.17	69.10	0.20	4.3×10^{-5}	0.81	5.343
TMEDA3	2.31	0.064	0.043	0.064	60.42	98.37	75.52	0.21	3.82×10^{-5}	0.83	4.509
TMEDA4	2.31	0.064	0.043	0.129	83.25	98.81	104.38	0.34	3.14×10^{-5}	0.86	4.403
TMEDA5	2.31	0.064	0.043	0.172	92.95	98.93	129.19	0.26	1.61×10^{-5}	0.92	5.864

Swelling ratio or equilibrium swelling ratio (g of water/g of gel) determined experimentally; theoretical equilibrium swelling ratio (g of water/g of gel) calculated from graph.

tions (solutions I and II) were mixed at different volumes as described by Shugar and Dean.[42]

Physiological fluids preparation

To study the water uptake and water transport phenomena of macroporous superabsorbent hydrogels in biological media, different fluids were made for 100 mL of distilled water. These solutions were saline water (0.9 g NaCl/100 mL), synthetic urine [(0.8 g of NaCl + 0.10 g of $MgSO_4$ + 2.0 g of urea + 0.06 g of $CaCl_2$)/100 mL], KI (15 g/100 mL), urea (5 g/100 mL), and D-glucose (5 g/100 mL).

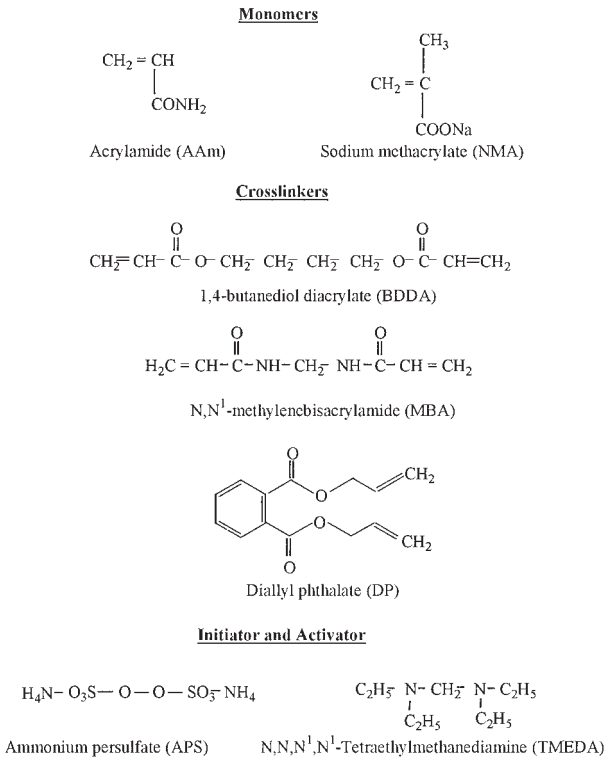
RESULTS AND DISCUSSION

IR spectra

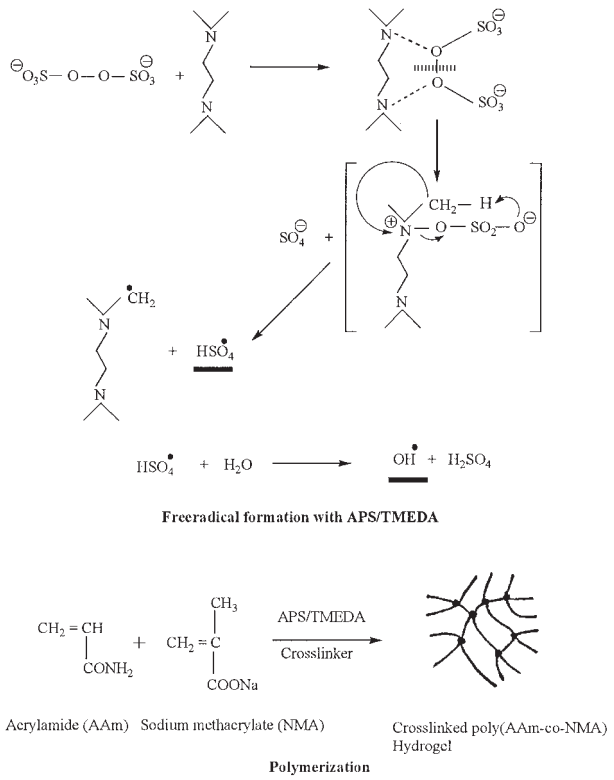
The IR spectra of the macroporous AAm–NMA hydrogels showed peaks corresponding to the functional groups of the monomers in the polymeric chains. The observed peaks—at 3340 cm^{+1}, corresponding to hydrogen-bonded (bridged) N—H stretching because of acrylamide and MBA; 1735 cm^{+1}, corresponding to the νC═O of the acrylate unit of the sodium methacrylate; 1658 cm^{+1}, corresponding to the νC═O group of the acrylamide and MBA units; and 1239 and 1172 cm^{+1}, corresponding to the C—O—C stretching coupling interactions of the ester groups. From the IR analysis, it was clearly confirmed that acrylamide, sodium acrylate, and MBA units were incorporated into the copolymer chain.

Preparation of macroporous superabsorbent hydrogels

It has been proved that macroporosity can be attained in gels by employing small amounts of a glucose solution instead of low-boiling-point solvents in the



Scheme 1 Structure of the monomers, crosslinkers, initiator and activator.



Scheme 2 Schematic representation of free-radical formation and preparation of crosslinked poly(AAm-co-NMA) Hydrogel.

polymerization reactions.[20,25,34–38] In the present investigation, the polymerization reactions of AAm and NMA with the MBA crosslinker were conducted in the presence of APS/TMEDA in 2 mL of a glucose solution of different molar concentrations, and a blank (without glucose solution) polymerization also was performed in order to compare the properties as well as the morphology of the AAm–NMA superabsorbent hydrogels. The polymerization process started with the reaction between APS and TMEDA to form an activated TMEDA molecule containing unpaired valence electrons. The unpaired valence electrons could form free radicals, which might interact with AAm, NMA, and/or the crosslinker, thereby initiating the polymerization, copolymerization, and crosslinking processes. Free-radical formation and the polymerization process are depicted in Scheme 2.

Morphology observations

The structural morphology of AAm–NMA hydrogels was studied by SEM analysis. The SEM micrograph of the hydrogel prepared in distilled water, presented in Figure 1, shows no porosity. In contrast, the SEM micrographs of the hydrogels prepared in different concentrations of the glucose (porogen) solution, given in Figure 2, show pore channels and layers instead of pores in the cross-sectional views of the hydrogels. Further, the concentration of the glucose solution had a synergistic effect on the obtaining of pore channels or connecting layers. Thus, the number of pore channels increased with an increase in the concentration of the porogen solution used for the polymerization reactions.

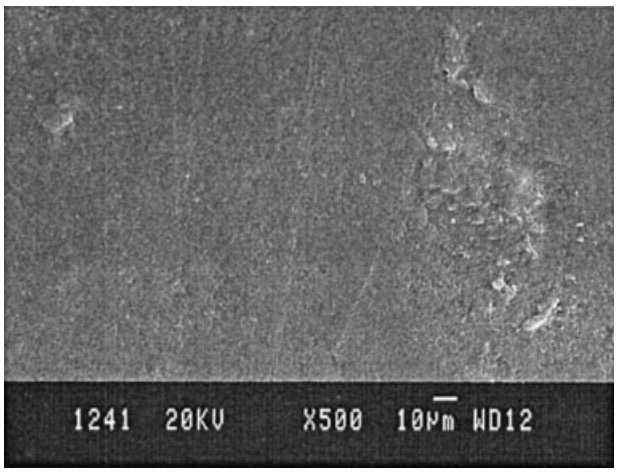


Figure 1 SEM micrograph of conventional AAm–NMA superabsorbent hydrogel prepared in water.

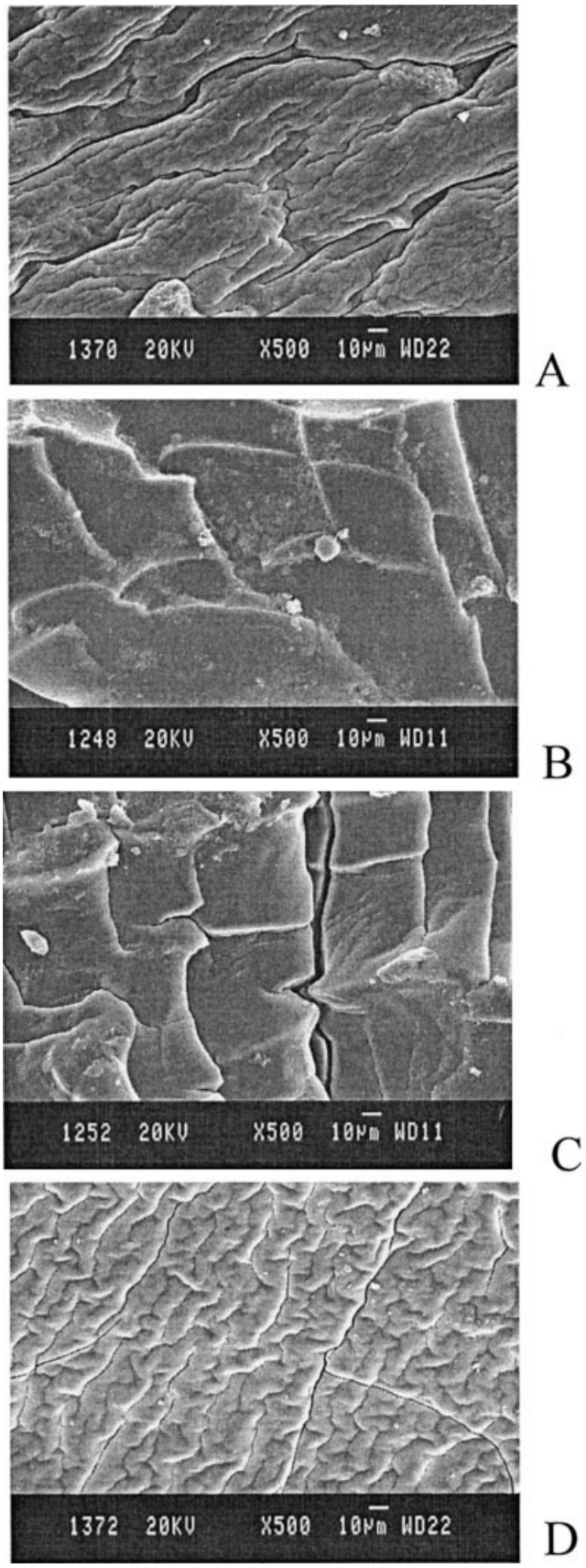


Figure 2 SEM micrographs of AAm–NMA superabsorbent hydrogels prepared in (A) 0.25*M* (B) 0.50*M* (C) 1.00*M*, and (D) 1.50*M* glucose solutions.

Properties of macroporous poly(AAm-*co*-NMA) hydrogels

The key property of the hydrogels was their swelling behavior, which could be measured from its absorption mechanism, which in turn was caused by the diffusion process. The diffusion process represents the affinity between the polymeric networks and external solution. Therefore, swelling behavior depends on the nature of the polymer network involving the strength of hydrophilic groups, crosslinking density, and elasticity of polymer network. Further, swelling behavior also depends on the type of external solution and the characteristics of the external solution. Three main forces will determine the swelling behavior of a hydrogel[43]: (1) the free energy between the chain networks of the polymers and external solvent, (2) the electrostatic repulsion (donnan effect), and (3) the elastic retractile response of the networks. The first two forces promote the swelling behavior and the latter suppress the swelling phenomena of the hydrogel.

Our macroporous AAm–NMA superabsorbent hydrogel network structure could be altered by changing the reaction parameters, including the concentrations of sodium methacrylate (hydrophilic monomer), crosslinker, initiator, and activator, leading to variation in the swelling behavior of AAm–NMA superabsorbent hydrogel.

Effect of NMA concentration

The swelling ratio of a hydrogel or superabsorbent polymer can be determined quantitatively by Flory's equation:[44]

$$Q^{5/3} = \frac{[(i/2V_uS^{1/2})^2 + (1/2 - X_i)/v_1]}{[V_e/V_0]} \qquad (6)$$

where Q, V_e/V_o, $[(1/2) - X_i]$, $V_{u,}$ i/V_u, and S are the water absorption, the crosslinking density of polymer, the affinity between polymer and external solution, the volume of the structural unit, the fixed charge per volume of polymer, and the ionic strength of the external solution, respectively. In the present study, the effect of the ionic monomer, sodium methacrylate, on the swelling behavior was studied by varying the concentration of sodium methacrylate from 0.92 to 4.62 m*M* in the feed mixture of the AAm–NMA hydrogel. The complete details about the swelling behavior of hydrogels are presented in Figure 3, from which it can be clearly observed that the swelling ratio of SAP increased constantly with increasing concentration of NMA in the feed mixture. The increased swelling ratio of superabsorbent hydrogel can be explained in two ways. One explanation is that with the increase in the number of carboxylate ions along the main

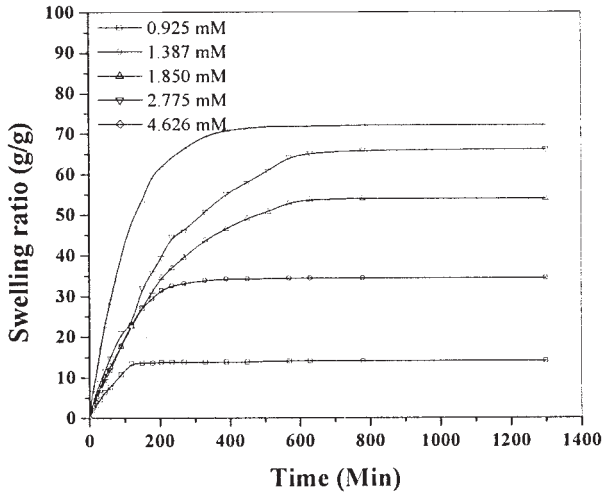


Figure 3 Swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different NMA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.064 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

chain of poly(acrylamide), the electrostatic repulsive forces among the COO^- groups became operative, resulting in loosening of the network chains and causing an increase in swelling.[3–6] According to Flory's equation, with an increased concentration of NMA in the copolymer, the concentration of fixed charges, that is, i/V_u, increased within the hydrogel, thereby increasing the swelling ratio.

Effect of crosslinker

The crosslinking agent contained two or more double bonds, which were able to participate in the free-radical polymerization of the acrylic monomers and to form permanent crosslinking networks between the polymeric chains. The nature of the crosslinking agent and the concentration of crosslinker were able to directly affect and also to considerably change the swelling behavior of the hydrogel.

A hydrophilic crosslinker, *N,N′*-methylenebisacrylamide, was employed to evaluate the swelling behavior of the AAm–NMA macroporous superabsorbent hydrogel at different concentrations. The MBA concentration was varied in the reaction in the range of 0.016–0.129 m*M*. The results are depicted in Figure 4, which clearly shows that at lower concentrations of MBA, the swelling ratio was high with increased concentration of the crosslinker, leading to drastic decrements in the swelling behavior. This behavior can be explained by formation of networks in the copolymer chains. At lower crosslinker concentrations the formed copolymer had a lower crosslink density, whereas at higher crosslinker concentrations, its crosslink density was higher, causing a decrease in the space between the polymer chains and thereby suppressing the swelling ratio of the AAm–NMA macroporous superabsorbent hydrogel.[5,6]

To investigate the effect of the different types of crosslinker on the swelling behavior of the macroporous AAm–NMA hydrogel, two more crosslinkers were employed: BDDA and DP. As BDDA concentration varied, the swelling ratio of the copolymers also varied, that is, there was a slight increase in the swelling ratio from 103 to 110 g/g as the concentration of BDDA varied from 0.012 to 0.037 m*M*. Further increases in the BDDA concentration from 0.050 to 0.075 m*M* decreased the swelling ratio from 90 to 75 g/g (Fig. 5). The DP-crosslinked AAm–NMA hydrogels showed similar behavior. The DP-crosslinked copolymer showed an increase in the swelling ratio from 187 to 318 g/g as the concentration of DP varied from 0.009 to 0.028 m*M* and then decreased to 204 g/g at a crosslinker concentration of 0.056 m*M* (Fig. 6). This type of behavior in the nature of swelling with change in the concentration of crosslinker was observed in our earlier studies[3,4] and also has been reported by many other authors.[40,41] Further, it has been observed that the order of the increase in the swelling ratio of the hydrogel was DP > MBA > BDDA. DP-crosslinked copolymers have shown higher swelling ratios than BDDA- and MBA-crosslinked copolymers. DP crosslinker reacts slowly (30–150 min) compared to BDDA and MBA (< 10 min), and therefore it is possible to obtain a lower crosslink density for the hydrogel with DP-crosslinked hydrogels. So, their swelling capacity is higher.

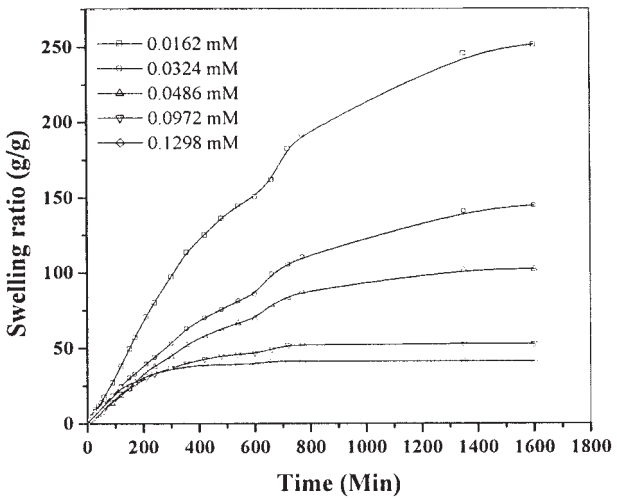


Figure 4 Swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different MBA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

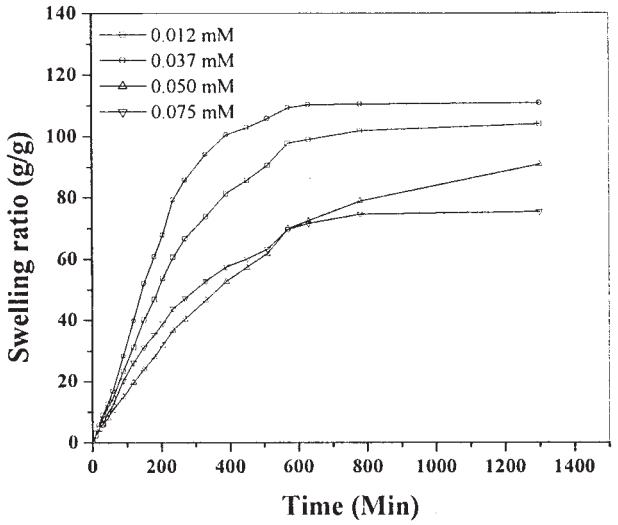


Figure 5 Swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different BDDA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

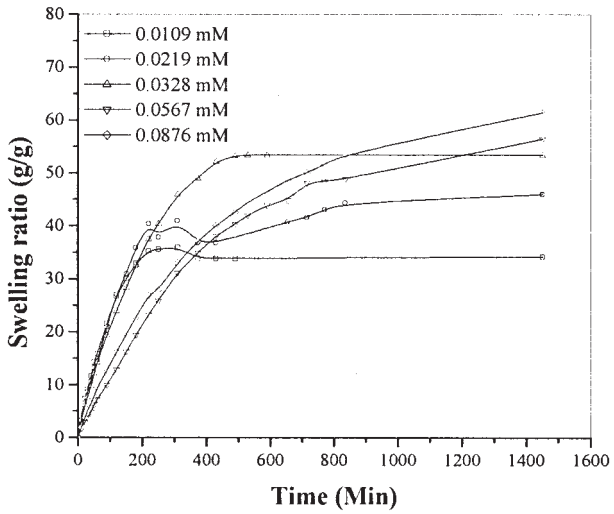


Figure 7 Swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different APS concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.064 m*M*, and [TMEDA] = 0.086 m*M*.

Effect of initiator

It is well known that an initiator or initiating system directly influences the physical properties of superabsorbent because it affects the crosslinking network structure as well as phase behavior. The concentrations of initiator and activator have a great impact on the molecular weight of the end SAP. Further, they are also responsible for the inhomogeneity of the SAP system. In the present study, APS and TMEDA were employed as initiator and activator, respectively. The effects of their concentrations on the swelling ratio of AAm–NMA superabsorbent hydrogel were studied, which are shown in Figures 7 and 8. As the concentration of APS and TMEDA increased in the polymerization reactions, the swelling ratio of superabsorbent hydrogel also increased. This can be explained by the different chain lengths obtained by varying the APS and TMEDA concentrations. At lower concentrations of APS, the number of free radicals produced were comparatively fewer in number and were responsible

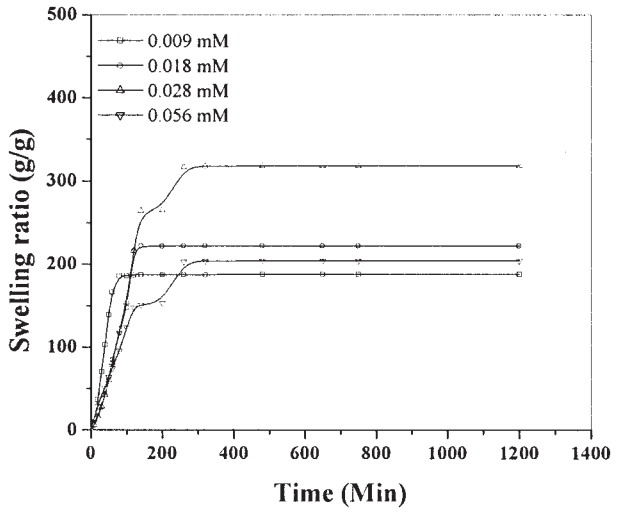


Figure 6 Swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different DP concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

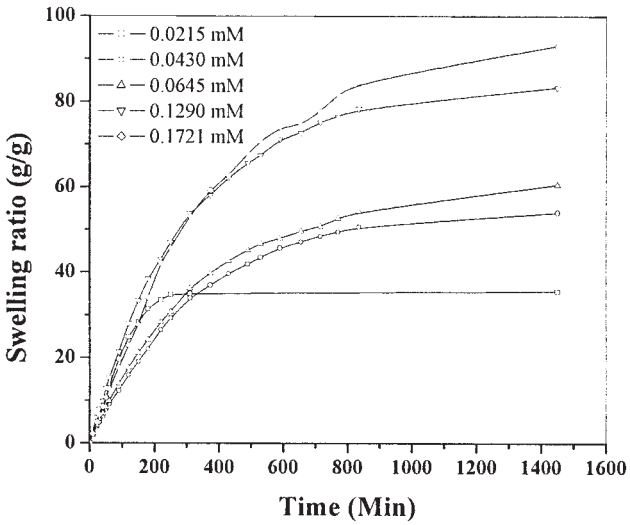


Figure 8 Swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different TMEDA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.064 m*M*, and [APS] = 0.043 m*M*.

for long polymeric chain lengths and lower crosslinking networks, thereby causing a low swelling capacity of the hydrogel. This changed as the APS concentration increased, producing a considerable number of three-dimensional networks that made the hydrogels more highly absorbent. The SAHs showed higher swelling ratios of 0.087 m*M* APS and 0.172 m*M* TMEDA.

Influence of external stimuli on swelling behavior

Over the last two decades it has been noted that important physical characteristics of hydrogels are linked to changes in specific environmental parameters such as temperature, pH, electric field, solvent quality, light intensity and wavelength, pressure, ionic strength, nature of ions in the swelling medium, and specific chemical triggers like glucose and biological fluids.

Effect of salts

Salt concentration and charge valence significantly affect the swelling behavior of hydrogels. The presence of salts in the swelling medium is very important in biomedical applications. The great effect of salt on swelling behavior is a result of changes in the mechanical properties and matrix of the gel, which are responsible for different diffusion coefficients of drug release.

A possible consequence of salt ions in the swelling medium is a change in osmotic pressure as a result the difference between the ionic concentration of the interior of the macroporous SAP and the external solution. Donnan equilibrium theory contributes to the determination of osmotic pressure (π_{ion}), which reveals the extent of swelling, as shown in the following equation:[45]

$$\pi_{ion} = RT \Sigma_i (C_i^g - C_i^s) \quad (7)$$

where C_i *is* the mobile ion concentration of species I and superscripts g and s represent the gel and solution phases, respectively.

Effect of sodium chloride concentration

The effect of the concentration of sodium chloride solution on the swelling behavior of AAm–NMA superabsorbent hydrogels was investigated. Figure 9 illustrates the swelling ratios of macroporous AAm–NMA hydrogels as a function of crosslinker concentration in different concentrations of sodium chloride solution. Figure 9 shows that the swelling ratio of hydrogel decreased in salt solution as the ionic concentration of the salt solution increased. This was a result of the decrease in the expansion of the gel network because of repulsive forces of counter-ions acting on the polymeric chain shielded by the bound ionic charges. Therefore, the difference in the osmotic pressure between the gel network and the external solution decreased with an increase in the ionic strength of the saline concentration. Similar results were found in other copolymer hydrogels.

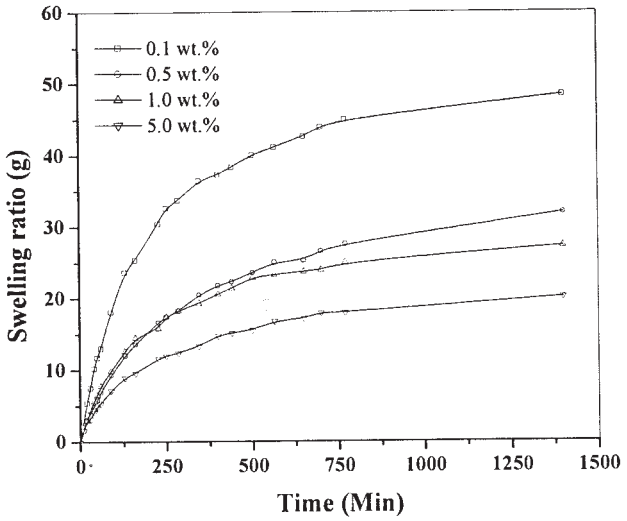


Figure 9 Effect of the weight percent of sodium chloride solution concentration on the swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.032 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

Effect of anions

Halide anions of potassium were added to the swelling medium, and their effect on the swelling behavior of macroporous SAP was investigated. The results are depicted in Figure 10, which clearly demonstrates that the swelling ratio of macroporous superabsorbent hydrogels decreased with an increasing ionic concentration in the following order: $I^- > Br^- > Cl^-$. A higher swelling ratio was a result of the presence of I^- ions, and a very low swelling ratio was caused by Cl^- ions. This behavior can be explained by the size of the ions, with I^- ions greater in size than the other halides, preventing diffusion into the interior of the gel and resulting in a decrease in ionic concentration, C_i^g, which in turn resulted in a higher swelling ratio than that of the other ions in the medium.

Effect of cations

To investigate the influence of cations on the swelling behavior of macroporous SAP, chloride salts of K^+, Ca^{2+}, and Fe^{3+} were used in an aqueous medium in the concentration range of 0.005*M*–0.1*M*. The results

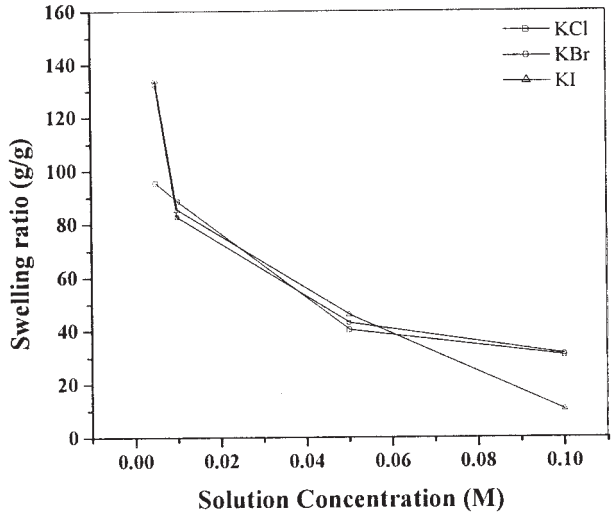


Figure 10 Effect of the addition of anions of potassium on the swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.032 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

obtained are presented in Figure 11. The results indicate that for all the ions, the swelling ratio decreased as the concentration of added salts increased. It was found that aqueous Ca^{2+} and Fe^{3+} media had lower swelling ratios than did K^+ ionic media. Ca^{2+} and Fe^{3+} ions can form complexes with carboxylate groups in hydrogels, leading to deswelling or contraction. K^+ ions were not able to form any complexes and showed normal swelling capacity.

The sensitivity of polyelectrolyte superabsorbents toward absorption by the addition of small amounts of

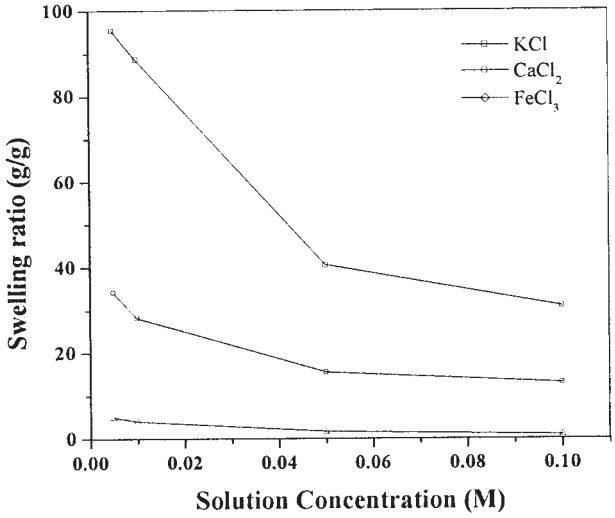


Figure 11 Effect of the addition of cations of chloride on the swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.032 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

TABLE II
Dependence of Dimensionless Swelling Factor (α) of AAm–NMA Superabsorbent Hydrogel Prepared for a Defined Composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.032 m*M*, [APS] = 0.043 m*M*, [TMEDA] = 0.086 m*M*

Salts used	Dimensionless factor (α)			
	$\alpha_{0.1}$	$\alpha_{0.05}$	$\alpha_{0.01}$	$\alpha_{0.005}$
KCl	0.122	0.161	0.353	0.220
KBr	0.124	0.171	0.329	0.527
KI	0.041	0.183	0.340	0.526
$CaCl_2$	0.051	0.061	0.112	0.136
$BaCl_2$	0.054	0.058	0.099	0.116
$FeCl_3$	0.007	0.002	0.016	0.019

ionic species to water is well known. The effect of increasing salinity on the swelling ratio of macroporous superabsorbent hydrogel is presented in Table II. This salt sensitivity was evaluated by calculating the dimensionless factor (α), which is the ratio of absorption of salt-free water at a given salinity.[46] The α values for different saline concentrations are given in Table II.

Effect of pH

SAPs/hydrogels that are pH responsive have found enormous applications in the drug delivery systems. The principle involved in drug delivery is the pH-controlled swelling of gel, which normally results in variation in the relaxation rate of network chains of the gel by changing the pH of the medium. In the present study, to verify the effect of the pH of the medium on the swelling capacity of macroporous SAHs, swelling media with different pHs (pH from 2 to 12) were employed. The detailed results (Fig. 12), showed that the swelling ratio increased with an increasing pH of the medium in the range 2–7 and that the pH increased further, from 7 to 11, resulting in a fall in the swelling ratio.

The increased swelling behavior of macroporous SAH in pH 2–7 can be explained by the increase in the ionization of the carboxylic groups of the sodium methacrylate units as the pH of the medium increased. The resulting anionic charged species in the hydrogel network repelled each other, leading to relaxation of the hydrogel networks, responsible for easy penetration of water molecules into the hydrogel three-dimensional networks. At pH = 7, the swelling behavior of SAH increased rapidly after 400 min because of a higher degree of repulsions in the hydrogel networks. As the alkaline medium increased beyond pH = 7, the swelling behavior decreases because of the greater charge density in the hydrogel networks, which in turn prevented the entrance of water molecules. However, at pH = 12, a higher swelling capacity relative to

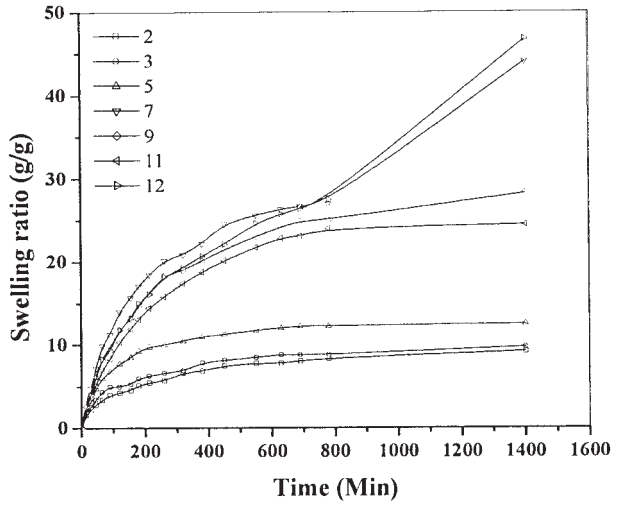


Figure 12 Effect of pH of swelling medium on swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.032 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

other alkaline media was attained as a result of the lessening of the hydrogel network structure because of its low crosslink density. But the dissolved gel in the above medium remained more than 1 day, whereas similar behavior was not observed in all other pH media.

Effect of simulated biological fluids

It is well accepted theoretically as well as experimentally that the swelling is the result of osmotic and the restoring elastic pressure.

It is widely accepted both theoretically and experimentally that swelling results from osmotic pressure and restoring elastic pressure. Solute in the surrounding aqueous medium is capable of tilting this balance, resulting in variation in swelling behavior.[47] To study the influence of simulated biological fluids on the swelling behavior of macroporous superabsorbent hydrogel, five biological fluids were employed. The results, shown in Figure 13, demonstrate that the swelling ratios observed in all biological fluids were lower than those in water as the swelling medium. This can be explained by the increase in the concentrations of various ionic species in the swelling medium. It was further observed that of the five simulated biological fluids, the D-glucose solution had the highest swelling ratio, whereas the potassium iodide solution had a very low swelling ratio. A higher swelling ratio was obtained for the hydrogel in D-glucose within a short period (200 min) because of the formation of hydrogen bonds between copolymeric chains of the hydrogel and the D-glucose unit. After some time, more hydrogen bonds between the copolymeric chains and glucose units may lead to a dense three-dimensional network structure in the hydrogel, thereby causing deswelling.

Swelling and diffusion characteristics

To examine the mechanism of the swelling process, several kinetic models were used to test the experimental data. A simple kinetic analysis was performed with the following second-order equation:

$$\frac{dS}{dt} = k_s(S_{eq} - S)^2 \tag{3}$$

where S_{eq} and k_S are the degree of swelling at equilibrium and the swelling rate constant, respectively. The integration of the above equation over the limits $S = S_0$ at $t = t_0$ and $S = S$ at $t = t$ gave the following equation:[48]

$$\frac{t}{S} = A + Bt \tag{4}$$

where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = (1/k_S S_{eq}^2)$ is the reciprocal of the initial swelling rate of the SAP, and k_s is the swelling rate constant. This relation represents second-order kinetics.[49] To examine swelling kinetic parameters such as initial swelling rate (r_i), maximum equilibrium swelling ratio (S_{eq}), and swelling rate constant (k_s) for superabsorbent hydrogels, graphs of t/S versus t were drawn, which, along with a representative graph, are shown in Figure 14. These parameters

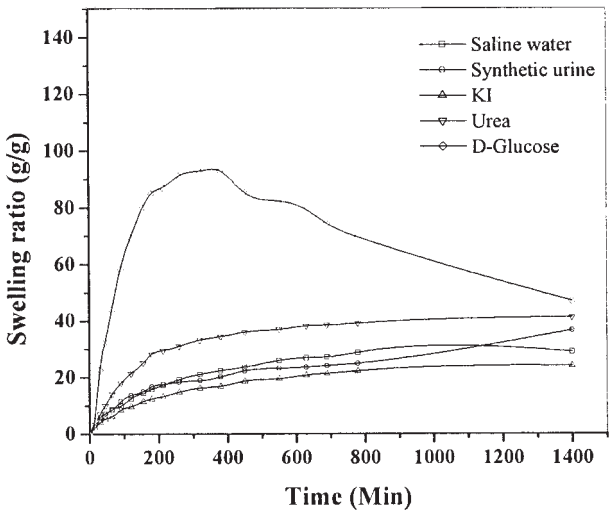


Figure 13 Effect of simulated biological fluids on swelling behavior of macroporous AAm–NMA superabsorbent hydrogels prepared for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.032 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

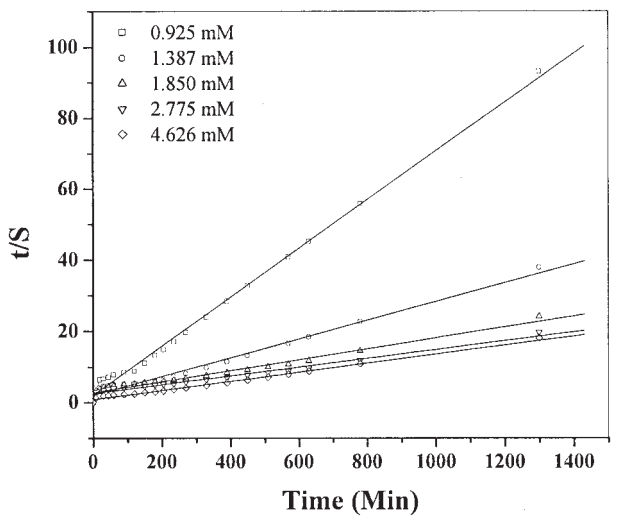


Figure 14 Swelling isotherms of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different NMA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.064 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

were calculated as per the equations used in the literature.[40,41] They were calculated for all the superabsorbent copolymers for different reaction parameters and are presented in Table I, which indicates that the swelling parameters varied as the concentration of the reaction parameters varied. However, in most of the macroporous polymers, the maximum equilibrium swelling ratio and the initial swelling rate were observed for the macroporous poly(AAm-*co*-NMA) hydrogel, which had both a higher swelling capacity and lower swelling constants.

Swellable polymers are considered important materials in the agricultural engineering, biotechnology, biomedicine, environmental, and other fields, and analysis of the mechanism of water diffusion in SAPs has gained attention. Generally, SAP brings contact with water, and water diffuses into the SAP and causes it to swell. The diffusion process involves migration of water molecules into the free spaces between the polymeric chains and leads to the swelling of SAP. This results in increased segmental mobility of the polymeric chains and therefore increases the distance between the polymeric chains.

The dynamics of the water sorption process were investigated by monitoring the change in the amounts of water imbibed by SAPs at various intervals. The present study also followed the swelling method described previously. For the kinetic analysis, the swelling results were utilized only up to 60% of the swelling curves.[50]

$$F = \frac{W_s - W_d}{W_d} = \mathrm{k}t^n \qquad (5)$$

where F, W_s, and W_d are the fraction of water uptake at time t, the weight of swollen hydrogel at time t, and the weight of dried hydrogel at time $t = 0$, respectively; k is a swelling constant related to the structure of the network; and n is the swelling exponent, which indicates the water transport mechanism.

When the penetrant solvent (water) invaded the AAm–NMA gel surface, a moving front was observed that clearly separated the unsolvated glassy copolymer region ahead in front from the swollen and rubbery gel phase behind.[51] Just ahead of the front, the presence of solvent plasticized the polymer and caused it to undergo a glassy to rubbery transition.[52] Therefore, there are two possibilities as to what may occur. (1) If the glass-transition temperature (T_g) of the copolymer was well below the swelling medium temperature, the copolymer would be in the rubbery state, possessing higher copolymer chain mobility and allowing easier penetration of the water molecules. This would result in Fickian diffusion (case I), which is represented as the solvent diffusion rate, $R_{\mathrm{diff}} <$ copolymer relaxation rate, R_{relax}. (2) If the experimental temperature was below the T_g of the copolymer, the copolymer chains may not have had sufficient flexibility to create free volume of different meshes that are responsible for immediate penetration of the solvent into the copolymer matrix. Therefore, it may follow a non-Fickian diffusion process that includes Case II diffusion ($R_{\mathrm{diff}} > R_{\mathrm{relax}}$) and anomalous diffusion ($R_{\mathrm{diff}} - R_{\mathrm{relax}}$). For a better understanding of the diffusion process, a hypothetical model describing the diffusion phenomena of SAP is shown in Figure 15.

To estimate the swelling exponent (n) by using the above equation up to 60% of the swelling ratio values, the graphs were plotted ln S versus ln t, and a repre-

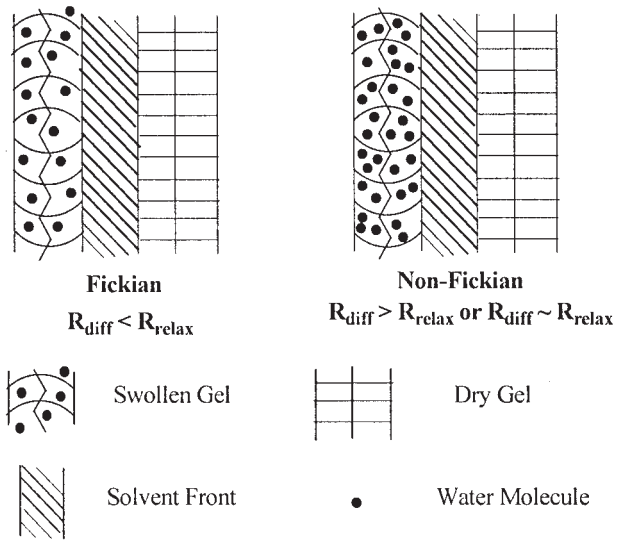


Figure 15 A hypothetical model describing diffusion of the superabsorbent hydrogel.

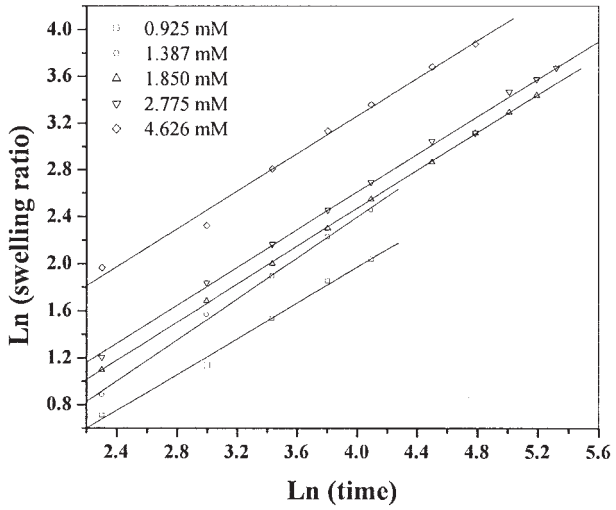


Figure 16 Swelling kinetic curves of macroporous AAm–NMA superabsorbent hydrogels prepared in 1*M* glucose solution with different NMA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.064 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

sentative graph is shown in Figure 16. The swelling exponent was calculated from the slope of the lines of the ln S − ln t plots. In the present investigation, for AAm–NMA hydrogels prepared under various reaction conditions, such as varying the concentration of NMA, crosslinker MBA, APS, and TMEDA, the n values obtained fluctuated between 0.5 and 1.0, indicating an anomalous type of swelling. This characterizes the rate of diffusion of water as equal to chain relaxation, $R_{diff} - R_{relax}$ (anomalous). But a few of the hydrogels prepared with different concentrations of BDDA or DP crosslinkers showed higher values of n, representing Case II ($R_{diff} > R_{relax}$) and super Case II behavior (close to 1 or > 1).

The phenomenon of diffusion of water into SAP is of greater value in many areas of applications, indicating the behavior of the polymer. To analyze this characteristic, the swelling curves of the SAPs were utilized to calculate the diffusion coefficient by different methods. Among these is the short time approximation method, which is valid only for the first 60% of swelling.[53,54] The diffusion coefficients of these SAPs were calculated with the following equation:

$$F = 4[D/\pi r^2]^{1/2} (t)^{1/2} \quad (6)$$

where D, F, and r are the diffusion coefficient of the SAP, the fractional uptake of water at time t, and the radius of the SAP, respectively. To evaluate the diffusion coefficient, F versus $t^{1/2}$ graphs were plotted, and a representative graph is shown in Figure 17. From these graphs, the diffusion coefficient of the SAPs was calculated from the slope of the lines, whose results are listed in Table I, which shows that the diffusion coefficients for the macroporous superabsorbent hydrogels varied according to the reaction conditions. However, it was observed that the hydrogels that had a lower swelling capacity in their respective series had higher diffusion coefficients. In contrast, lower diffusion coefficients were observed for hydrogels with a higher swelling capacity. For examples, for macroporous superabsorbent hydrogels prepared with different concentrations of NMA (polymer codes NMA1–NMA5), it was clearly confirmed that the diffusion coefficients varied from 3.522 to 5.722 cm^2/s. The highest diffusion coefficient, 5.722 cm^2/s, was observed for NMA1 (swelling ratio, 13.67 g/g) and the lowest diffusion coefficient, 3.522 cm^2/s, for NMA5 (swelling ratio, 72.20 g/g). Similar diffusion coefficient results were identified for the other series of macroporous superabsorbent hydrogels, as can be clearly observed in Table I.

CONCLUSIONS

Macroporous hydrogels consisting of acrylamide and sodium methacrylate crosslinked with *N,N′*-methylenebisacrylamide were found to be ionizable, hydrophilic, and stimuli responsive (salt, pH, temperature, and biological fluids). The water sorption capacity, swelling kinetics, and diffusion characteristics of these superabsorbent hydrogels were greatly influenced by the chemical architecture of the hydrogel network structure. The effect of the concentration of the glucose solution, NMA, MBA, APS, and TEMDA in the polymerization, on the swelling ratio of the hydrogels was

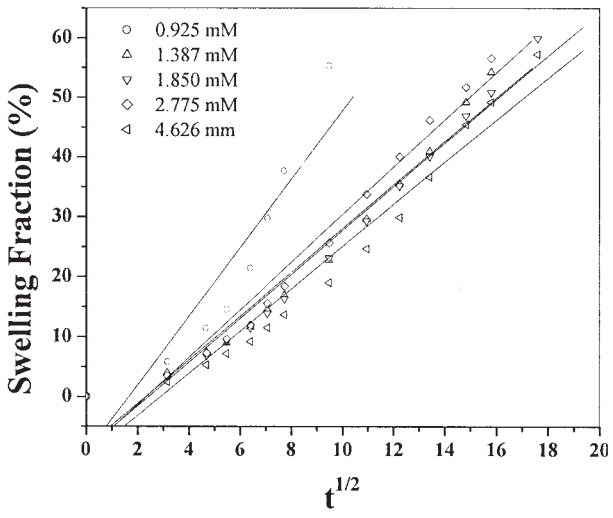


Figure 17 Diffusion curves of macroporous AAm–NMA superabsorbent hydrogels prepared in a 1*M* glucose solution with different NMA concentrations for a defined composition of [AAm] = 10.55 m*M*, [NMA] = 2.31 m*M*, [MBA] = 0.064 m*M*, [APS] = 0.043 m*M*, and [TMEDA] = 0.086 m*M*.

investigated in detail. The influence of the nature of various crosslinkers on the swelling behavior of the hydrogels was evaluated using three crosslinkers, namely, MBA, BDDA, and DP. The salt sensitivity of the porous hydrogels was investigated, and the results indicated that with an increased ion concentration, swelling capacity decreased. The influence of different halide anions of potassium and chloride salts of cations on swelling behavior was discussed. These hydrogels showed a pH-dependent swelling property. Optimum swelling was obtained at pH 11, whereas the hydrogel dissolved after being at pH 12 for 1 day. The macroporous hydrogels showed reduced swelling behavior in simulated biological fluids such as saline water, artificial urine, and KI, urea, and glucose solutions. The AAm–NMA porous hydrogels also exhibited temperature-dependent water absorbency. These macroporous superabsorbent hydrogels followed non-Fickian diffusion (anomalous and case II) and also super–case II diffusion.

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