Investigation of Sorption/Swelling Characteristics of Chemically Crosslinked AAm/SMA Hydrogels as Biopotential Sorbent

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ABSTRACT: The aim of this study was to investigate the equilibrium swelling and sorption properties of chemically crosslinked copolymeric hydrogels as biopotential sorbent consisting of acrylamide (AAm) and sodium methacrylate (SMA). Highly swollen AAm/SMA hydrogels were prepared by free-radical polymerization in aqueous solution of AAm with SMA as comonomer and three multifunctional crosslinkers such as 1,4-butanediol dimethacrylate, ethylene glycol dimethacrylate, and trimethylolpropane triacrylate. Swelling experiments were performed in aqueous urea solutions and safranin T at 25°C, gravimetrically. The hydrogels showed enormous swelling in aqueous (urea/water or dye/water) medium and displayed swelling characteristics that were highly depended on the chemical composition of the hydrogels. Some parameters related swelling and diffusion behavior were investigated. The values of the equilibrium percentage swelling values of AAm/SMA hydrogels were between 585 and 19,900%. The numbers determining the type of diffusion (n) are between 0.54 and 0.99. Hence, the diffusion type was found to be non-Fickian in character for the hydrogels. Chemically crosslinked AAm/SMA hydrogels were used in experiments on sorption of water-soluble monovalent cationic dye such as safranin T (Basic red 2, ST). For sorption of cationic dye, ST into the hydrogels was studied by batch sorption technique at 25°C. The sorption capacity of AAm/SMA hydrogels was investigated. At the end of the experiments, 17.91–83.78 ST% adsorptions were determined. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1787–1797, 2010

Key words: swelling; urea; acrylamide/sodium methacrylate; hydrogel; sorption; safranin T

INTRODUCTION

The use of polymer hydrogels as biopotential sorbent or carriers for the removal of the model molecules from aqueous solutions or controlled release studies of them has been continued to attract considerable attention in recent years. Hydrogels are polymers in three-dimensional network arrangement, which are able to retain large amount of water. To keep the spatial structure, the polymer chains are usually physically or chemically crosslinked. Because of their swelling capacity, hydrogels can be easily rinsed to remove reagents residues. On the other hand, the big water content that makes hydrogels such a special class of materials. The importance of hydrogels in the biomaterial field is justified by some unique characteristics: the elastomeric and soft nature of the hydrogels.[1–6]

Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, and food industry and water purification and separation process. Because of characteristic properties such as swell ability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical, and environmental applications. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility.[1–10]

Hydrogels can be used as a composite membrane for various enzymes. For example, for immobilization of urease enzyme, various composite hydrogel membranes can be used. Urease is a highly specific enzyme. It catalyzes the hydrolysis of urea to ammonium and carbon dioxide. It has been immobilized for analytical and biomedical purposes. One of the major applications of immobilized urease is the direct removal from blood for detoxification, or in the dialysis regeneration systems of artificial kidney machines. Other applications of immobilized urease will be in a bioreactor for the conversation of urea present in fertilizer wastewater effluents to ammonia and carbon dioxide or in the food industry for the removal of urea from beverages and foods.[9] Urea is

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one of the main toxic wastes in the dialysate solution from hemodialysis. The most effective way of removing urea from aqueous solutions is the utilization of immobilized urease as no efficient adsorbent is available for urea. On the other hand, urea has a great importance in biological systems.

Adsorption or ion exchange using different polymeric materials and synthetic resins is the method of choice in many wastewater treatment processes for removing dyes from chemical process industries in certain developed countries. Studies have been reported on the use of hydrogels or hydrophilic characteristic crosslinked polymers or copolymers as adsorbents for the removal of dyes, for the recovery of metals, for removal of toxic or radioactive elements from various effluents, and for metal preconcentration for environmental sample analysis from aqueous solutions.[11–16] Adsorption of some species such as enzyme and amino acids, desalination of sea water, ultrafiltration and purification of aqueous solutions containing colloids, micro- and macroparticles, or other biochemical/physiological species in aqueous media has been studied for use industrial and/or biotechnological processes.[11–16]

AAm based highly swollen crosslinked copolymers have received much considerable attention for use as "water sorbent material" at many applications such as purification of wastewater and metal extraction.[10–13]

This article reports that swelling study in urea solutions and sorption study of safranin T by a novel type of hydrogel prepared acrylamide hydrogels with vinyl functional groups containing chemical reagents such as sodium methacrylate (SMA) via free-radical solution polymerization method. It was of interest to swelling properties of AAm/SMA hydrogels in urea solutions for new hydrogels synthesis for urea treatment as new membranes or crosslinked polymeric carriers, or dye sorption capacity of AAm/SMA hydrogels adsorption. Then, swelling and sorption properties of these hydrogels were studied.

MATERIALS AND METHODS

Raw materials

Acrylamide (AAm), ethylene glycol dimethacrylate (EGDMA), the initiator, ammonium persulphate (APS), and the activator *N,N,N′,N′*-tetramethylethylenediamine (TEMED) were supplied by Merck, Darmstad, Germany, and anionic comonomer, SMA was supplied by Aldrich Chemical, Steinhelm, Germany and other crosslinkers, 1,4-butanediol dimethacrylate (BDMA) and trimethylolpropane triacrylate (TMPTA) were supplied by Aldrich Chemical, Milwaukee, US. All chemicals were used as received.

Urea was provided from Merck, Darmstadt, Germany. Cationic dye, safranin T (Basic red 2, ST) used in sorption studies, was purchased from Riedel De Haen, Darmstadt, Germany.

Preparation of AAm/SMA hydrogels

Acrylamide/sodium methacrylate (AAm/SMA) hydrogels were prepared by free-radical crosslinking copolymerization of AAm monomer with addition of SMA and some multifunctional crosslinkers such as BDMA, EGDMA, and TMPTA.

To prepare highly swollen AAm/SMA hydrogel systems, AAm weighing 1.0 g/14.07 mmol was dissolved in 1 mL of water. Then, 0 mg, 10 mg/0.09 mmol, 20 mg/0.18 mmol, 30 mg/0.28 mmol, 40 mg/0.37 mmol, 50 mg/0.46 mmol, 60 mg/0.55 mmol, 70 mg/0.65 mmol, and 80 mg/0.74 mmol of SMA was added to aqueous AAm solution. For the synthesis, 0.25 mL of 1.0% concentration crosslinker solution (0.011 mmol of BDMA, 0.013 mmol of EGDMA, or 0.009 mmol of TMPTA) was added this aqueous solution. A total of 0.20 mL/0.044 mmol of APS (5 g/100 mL water) and 0.25 mL/0.017 mmol of TEMED (1/100 mL water) were then added to the solution. The solutions were placed in PVC straws of 3-mm diameter. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm in length. They were washed and thoroughly rinsed with distilled water, blotted dry with filter paper, dried in air and vacuum, and stored for swelling studies.

FTIR analysis of AAm/SMA hydrogels

For structural characterization, FTIR analysis was made. Spectra were taken on KBr disks by using VARIAN FTS 800 FTIR spectrophotometer.

Measurement of swelling in water, aqueous urea, and aqueous ST solutions

Equilibrium swelling experiments were used to investigate the swelling properties of AAm/SMA hydrogels. Dry gels were weighed and then immersed in distilled water, or aqueous 0.01*M* urea solutions, and aqueous $10.0 \times 10^{-5} M$ ST solutions at $25 \pm 0.1^{\circ}C$. Swollen gels were removed from water or aqueous solutions at predetermined times, blotted dry, and weighed in air.

Sorption equilibrium experimental

Batch studies were proceeding in all sorption experiments. For the sorption, equilibrium sorption isotherms of the hydrogel/dye system, the sorption

capacity (q), removal efficiency (RE%), and partition coefficient (K_d) were investigated.

Solutions of the cationic dye, "safranin T," (Basic red 2, ST) concentration range 1.0×10^{-5} to $15.0 \times 10^{-5} M$ in distilled water were prepared. For concentration effect of the cationic dye, AAm/SMA hydrogels containing 60 mg SMA was used in a known volume of dye solution until equilibrium was reached. For content of SMA effect on the dye sorption, aqueous solution of concentration of aqueous $10.0 \times 10^{-5} M$ ST solutions was used.

After sorption, dye solution was separated by decantation from the hydrogels. Spectrophotometric method was applied to dye solutions. Spectrophotometric measurements were carried out using a Shimadzu UV 1601 model UV–Vis spectrophotometer at ambient temperature. The absorbances of these solutions were read at 530 nm for ST.[17] Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales.

RESULTS AND DISCUSSION

Highly swollen AAm/SMA hydrogels were prepared by free-radical solution polymerization. Molecular formulas of AAm, SMA, and repeating unit of AAm/SMA copolymeric system have been presented at Figure 1. The crosslinked copolymers are obtained in the form of cylindrical shape. On swelling, the hydrogels were strong enough to retain their shape.

FTIR analysis

To understand binding and crosslinking of AAm/SMA hydrogels during polymerization, FTIR spectra

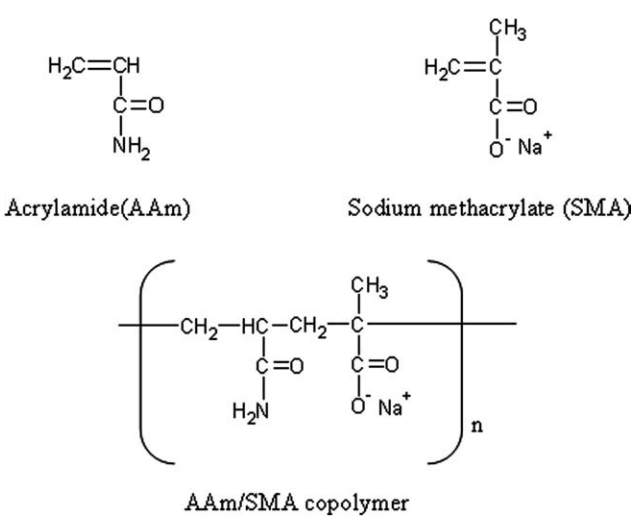


Figure 1 Chemical structures of AAm and SMA monomers and possible repeating unit of AAm/SMA copolymer.

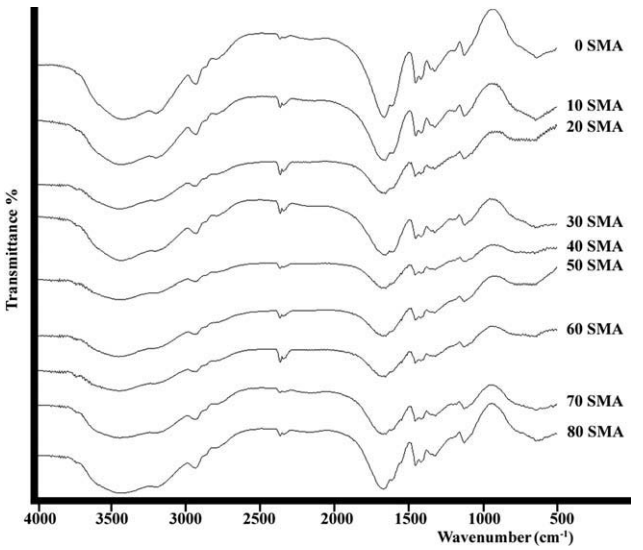


Figure 2 FTIR spectrum of AAm/SMA hydrogels crosslinked by BDMA including of various contents of SMA.

of all the hydrogels were evaluated and three spectra are presented in Figures 2–4. In the FTIR spectra of the hydrogels, the bands at about 1700 and 3100–3500 cm^{-1} are important. The peak at 1650–1660 cm^{-1} is the carbonyl group and related to amide groups and at 1500–1600 cm^{-1} is the N—H bonding vibration. The peak at 1700 cm^{-1} can be described as COO^- group in SMA molecules.[18] The bands at 1600–1700 cm^{-1} could be attributed to a shift in stretching vibration associated with hydrogen that is bonded directly to an overtone of the strong carbonyl absorption. The much broader absorption peaks in the regions of 3100 cm^{-1} and 3500 cm^{-1} are N—H bands and related to "polymeric" bands. The broad peak 3500 cm^{-1} is characteristic peak of

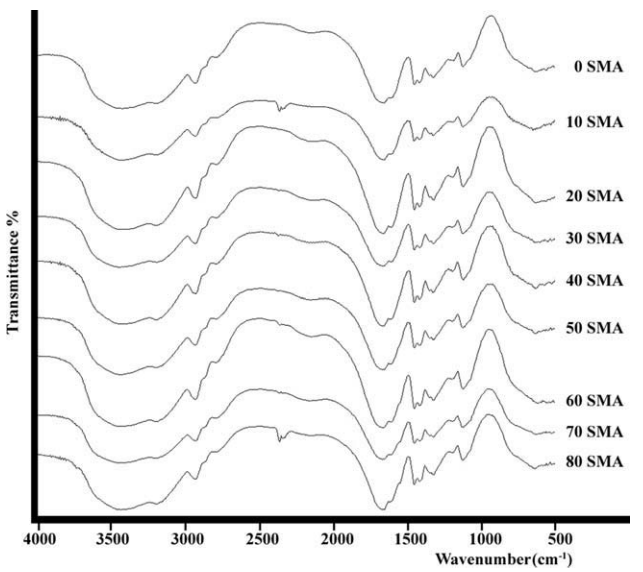


Figure 3 FTIR spectrum of AAm/SMA hydrogels crosslinked by EGDMA including of various contents of SMA.

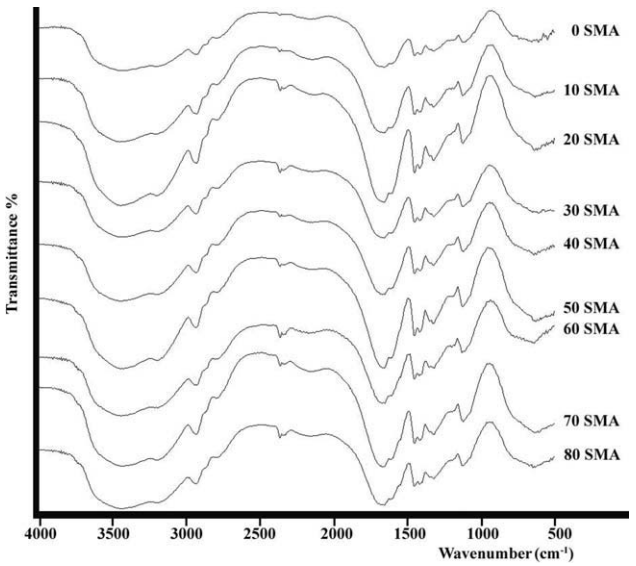


Figure 4 FTIR spectrum of AAm/SMA hydrogels crosslinked by TMPTA including of various contents of SMA.

primary amine. On the other hand, it is thought that the peaks at 1200 cm^{-1} are C—N bands, and the peaks at 2850 cm^{-1} and 1400 cm^{-1} show —CH_2— groups on the polymeric chain. Again, it is thought that the peaks at 1170–1240 cm^{-1} are ester bands.[18] The peaks observed in the FTIR spectra confirm the presence of AAm and SMA.

Equilibrium swelling studies

A fundamental relationship exists between the swelling of a polymer in a swelling medium and the nature of the polymer and the swelling medium. In dynamic swelling studies, the percentage swelling ($S\%$) of the hydrogels in distilled water or aqueous solutions was calculated from the following relation,

$$S\% = \frac{m_t - m_0}{m_0} \times 100 \quad (1)$$

where m_t is the mass of the swollen gel at time t and m_0 is the mass of the dry gel at time 0.

The water intake of initially AAm/SMA hydrogels was followed for a period of time, gravimetrically. Swelling isotherms of AAm/SMA hydrogels were constructed and representative swelling curves are shown in Figure 5 for water, Figure 6 for aqueous 0.01M urea solutions, and Figure 7 for aqueous $10.0 \times 10^{-5}M$ ST solutions.

Figures 5–7 show that swelling increase with time up to certain level, and then levels off. This value of swelling may be called the "equilibrium percentage swelling," ($S_{eq}\%$). The values of $S_{eq}\%$ of AAm/SMA hydrogels are used for the calculation of network characterization parameters. The values of $S_{eq}\%$ of AAm/SMA hydrogels are given Tables I–III.

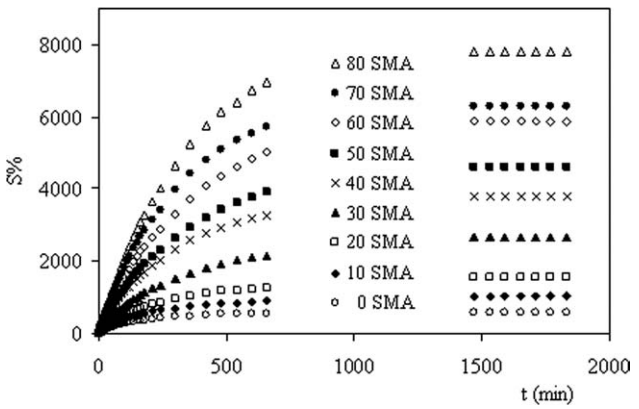


Figure 5 Swelling isotherms of AAm/SMA hydrogels crosslinked by TMPTA in water.

Table I shows that the values of $S_{eq}\%$ of AAm hydrogels is 585–765%, but $S_{eq}\%$ of AAm/SMA hydrogels are 995–19,900% with the incorporation of SMA groups into AAm chains crosslinked by BDMA, EGDMA, and TMPTA for water. Table II shows that the values of $S_{eq}\%$ of AAm hydrogels is 725–1045%, but $S_{eq}\%$ of AAm/SMA hydrogels are 980–8805% with the incorporation of SMA groups into AAm chains crosslinked by BDMA, EGDMA, and TMPTA for aqueous 0.01M urea solutions. On the other hand, Table III shows that the values of $S_{eq}\%$ of AAm hydrogels is 570–835%, but $S_{eq}\%$ of AAm/SMA hydrogels are 860–6070% with the incorporation of SMA groups into AAm chains crosslinked by BDMA, EGDMA, and TMPTA for $10.0 \times 10^{-5}M$ of aqueous ST solutions.

For understanding the effect of SMA content on the swelling behavior, $S_{eq}\%$ of the hydrogels versus the content of SMA monomer is plotted in Figure 8 for water, Figure 9 for aqueous 0.01M urea solutions, and Figure 10 for aqueous $10.0 \times 10^{-5}M$ ST solutions. In Figures 8–10, $S_{eq}\%$ of the hydrogels generally has increased with the monomer content in the copolymers. $S_{eq}\%$ of AAm/SMA is higher than $S_{eq}\%$

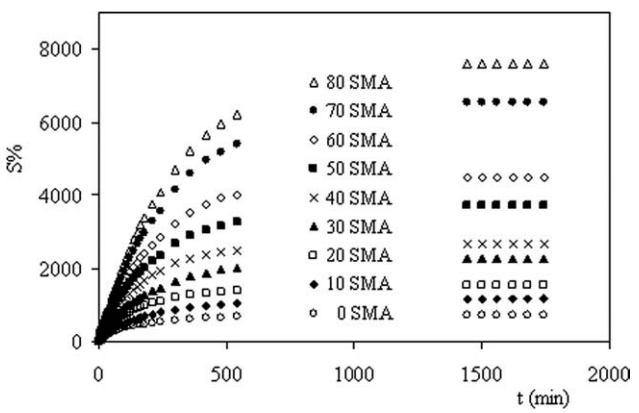


Figure 6 Swelling isotherms of AAm/SMA hydrogels crosslinked by BDMA in aqueous 0.01M urea solutions.

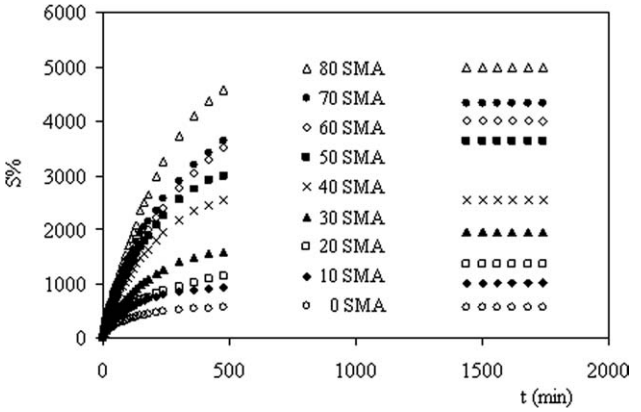


Figure 7 Swelling isotherms of AAm/SMA hydrogels crosslinked by BDMA in aqueous $10.0 \times 10^{-5}M$ ST solution.

of AAm hydrogels. The reason of this is the hydrophilic groups on SMA. The ionic charge content in the polymeric structure is important. SMA groups contain many ionic units. The swelling degree of the hydrogels increases due to increase of the hydrophilic units on hydrogel structure. The more hydrophilic groups in the SMA get the more the swelling of the AAm/SMA hydrogels. Hydrophilicity of SMA molecules becomes greater than that of AAm, so the swelling of AAm/SMA hydrogels is greater than the swelling of AAm hydrogels.

On the other hand, the values of S_{eq}% of AAm/SMA hydrogels swollen in water are bigger than the hydrogels swollen in urea solutions. The reason of this different behavior is the hydrophilic character of urea molecules. Urea molecule has got more hydrophilic sites, as NH_2 and C=O. When, urea molecules have interacted with polymer chains, so there has been less swelling than swelling values in water, also. When urea molecules have been interacted with the polymeric groups such as —COO groups in methacrylate molecules, less swelling values could

TABLE I
Equilibrium Percentage Swelling (S_{eq}%) and Equilibrium Water Content (EWC) of AAm/SMA Hydrogel Systems in Water

SMA/mg	BDMA	EGDMA	TMPTA
Equilibrium percentage swelling (S_{eq}%)			
0	675	765	585
10	995	1110	1040
20	2205	2250	1545
30	4340	4035	2670
40	6075	6890	3805
50	10270	9430	4620
60	12040	11430	5885
70	16170	13015	6300
80	19900	14180	7810
Equilibrium water content (EWC)			
0	0.8790	0.8840	0.8540
10	0.9085	0.9175	0.9125
20	0.9565	0.9575	0.9390
30	0.9775	0.9760	0.9640
40	0.9840	0.9860	0.9745
50	0.9905	0.9895	0.9790
60	0.9920	0.9915	0.9835
70	0.9940	0.9925	0.9845
80	0.9950	0.9930	0.9875

TABLE II
Equilibrium Percentage Swelling (S_{eq}%) and Equilibrium Urea/Water Content (EUWC) of AAm/SMA Hydrogel Systems in Aqueous 0.01*M* Urea Solutions

SMA/mg	BDMA	EGDMA	TMPTA
Equilibrium percentage swelling (S_{eq}%)			
0	725	1045	880
10	1170	1190	980
20	1535	1750	1105
30	2270	1955	2010
40	2670	2810	2930
50	3725	4425	3365
60	4470	6200	4435
70	6550	8255	5015
80	7600	8805	5895
Equilibrium urea/water content (EUWC)			
0	0.8983	0.9012	0.8879
10	0.9155	0.9381	0.9125
20	0.9458	0.9529	0.9427
30	0.9692	0.9648	0.9577
40	0.9779	0.9741	0.9667
50	0.9828	0.9791	0.9719
60	0.9845	0.9817	0.9744
70	0.9863	0.9843	0.9763
80	0.9884	0.9870	0.9805

TABLE III
Equilibrium Percentage Swelling (S_{eq}%) and Equilibrium ST/Water Content (ESTWC) of AAm/SMA Hydrogel Systems in Aqueous $10.0 \times 10^{-5}M$ ST Solutions

SMA/mg	BDMA	EGDMA	TMPTA
Equilibrium percentage swelling (S_{eq}%)			
0	570	835	690
10	1000	1055	860
20	1350	1290	955
30	1960	2060	1450
40	2545	2340	2130
50	3640	3690	3100
60	4010	4870	3470
70	4325	5815	3695
80	4995	6070	4500
Equilibrium ST/water content (ESTWC)			
0	0.8504	0.8930	0.8735
10	0.9093	0.9133	0.8960
20	0.9309	0.9367	0.9274
30	0.9515	0.9537	0.9355
40	0.9622	0.9655	0.9552
50	0.9732	0.9736	0.9687
60	0.9757	0.9799	0.9720
70	0.9774	0.9831	0.9736
80	0.9804	0.9838	0.9782

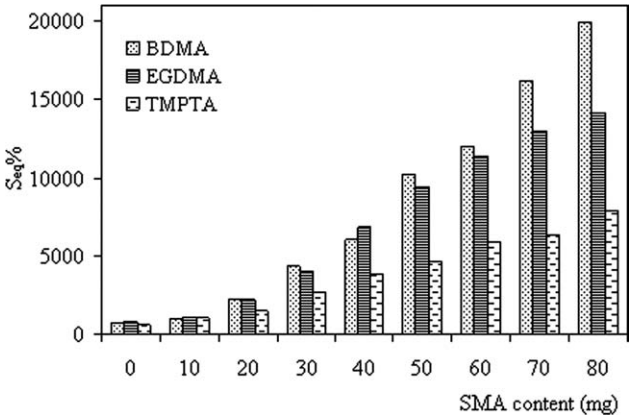


Figure 8 Effect of the content of SMA and crosslinker onto swelling of AAm/SMA hydrogels in water.

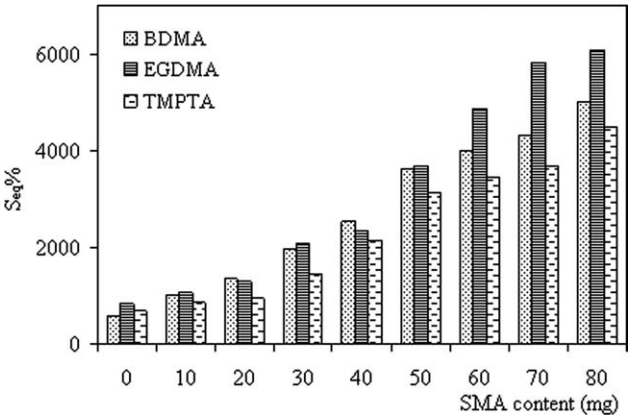


Figure 10 Effect of the content of SMA and crosslinker onto swelling of AAm/SMA hydrogels in aqueous $10.0 \times 10^{-5}M$ ST solution.

have been observed when the hydrogels swollen in aqueous urea solutions. Here, main characteristic effect is the hydrophilic character of urea molecules.

In Table III, it was seen that the values of S_{eq}% of AAm/SMA hydrogels swollen in water are bigger than the hydrogels swollen in aqueous $10.0 \times 10^{-5}M$ ST solutions. Again, it will be expected that the same swelling results for swelling characteristics of swollen AAm/SMA hydrogels in aqueous urea solutions. When ST molecules having charged sites have been interacted with the polymeric groups such as —COO groups in methacrylate molecules, less swelling values could have been observed when the hydrogels swollen in aqueous $10.0 \times 10^{-5}M$ ST solutions (Table III). It would be expected that dye molecules can be interacted with hydrophilic groups on the polymeric chains in stead of water molecules (Table IV).

On the other hand, if it is investigated that all swelling results (Tables I and III), it was seen that the values of S_{eq}% of AAm/SMA crosslinked by BDMA and EGDMA are generally higher than values of S_{eq}% of AAm/SMA crosslinked by TMPTA hydrogels.

The reason for this arrangement may be the molecular structure and mass of used crosslinkers. First, BDMA and EGDMA have got two end group functionalities for crosslinking, but TMPTA has got three end group functionalities. On the other hand, used crosslinker contents were different for preparing hydrogel systems. For the synthesis, the molar numbers of the crosslinkers were different (0.009 mmol of TMPTA, 0.011 mmol of BDMA, or 0.013 mmol of EGDMA). It can be said that TMPTA and EGDMA have got bigger molecular structure than BDMA. Then, there can be a lot of porous for water sorption and swelling.

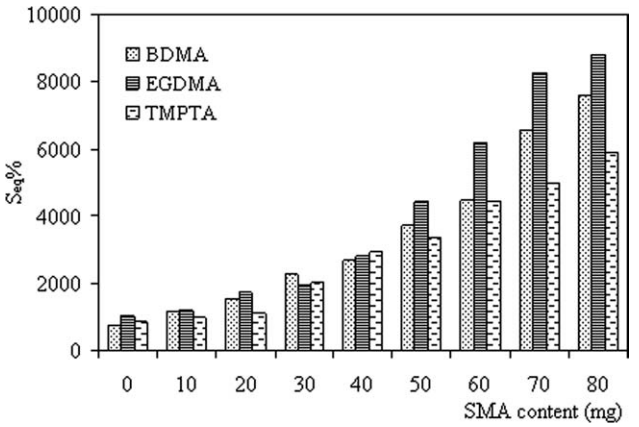


Figure 9 Effect of the content of SMA and crosslinker onto swelling of AAm/SMA hydrogels in aqueous 0.01*M* urea solutions.

Equilibrium water or urea/water or ST/water content

The water (or with together urea, or with together safranin T) absorbed by AAm/SMA hydrogels is quantitatively represented by equilibrium water content (EWC), equilibrium urea/water content (EUWC), or equilibrium safranin T/water content (ESWC),[19,20] by using below equation

$$\mathrm{EWC} = \frac{m_s - m_o}{m_s} \tag{2}$$

Here, m_s is the mass of the swollen gel at time t (equilibrium) and m_0 is the mass of the dry gel at time 0. The EWC (or EUWC or ESWC) values of AAm/SMA hydrogels were calculated. The EWC (or EUWC or ESWC) values of the hydrogels are tabulated in Tables I and III. Generally, it was seen that the EWC (or EUWC or ESWC) values of the hydrogels are increased by the adding of SMA molecules. Here, the main effect is the hydrophilic character of SMA.

Diffusion of water

When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the network expands resulting in swelling of the hydrogel. Diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger segmental motion resulting, ultimately, in increased separation between hydrogel chains.

Analysis of the mechanisms of water diffusion into swellable polymeric systems has received considerable attention in recent years, because of important applications of swellable polymers in biomedical, pharmaceutical, environmental, and agricultural engineering.

The following equation is used to determine the nature of diffusion of water into hydrogels:[20–22]

$$F = \frac{M_t}{M_s} = kt^n \tag{3}$$

where F is the fractional uptake at time t. Here, M_t and M_s are the mass uptake of the water at time t and the equilibrium, respectively. Equation (3) is valid for the first 60% of the fractional uptake. Fickian diffusion and case II transport are defined by n values of 0.5 and 1.0, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and case II. That is reflected by n between (0.5) and (1.0).[20–22] The values of diffusion exponents (n) and diffusion constants (k) were calculated from the slope and the intercept of the plot of ln$F$ against ln$t$, respectively.

For chemically crosslinked hydrogels, ln$F$ versus ln$t$ graphs are plotted and representative results are shown in Figure 11 for water, Figure 12 for aqueous 0.01M urea solutions, and Figure 13 for aqueous $10.0 \times 10^{-5}M$ ST solutions. Diffusion exponents (n) and diffusion constants (k) are calculated and are listed in Tables V–VII.

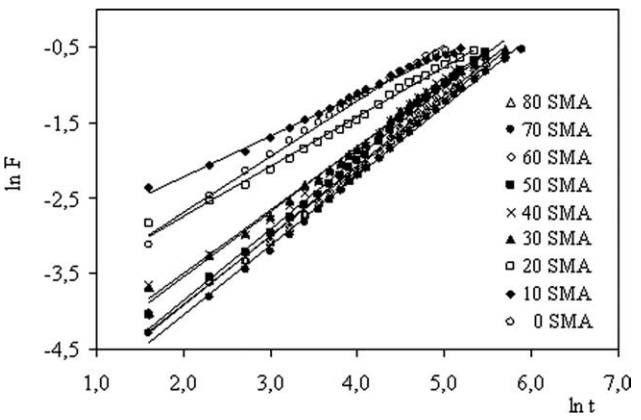


Figure 11 Plots of ln$F$ versus ln$t$ for AAm/SMA hydrogels crosslinked by EGDMA in water.

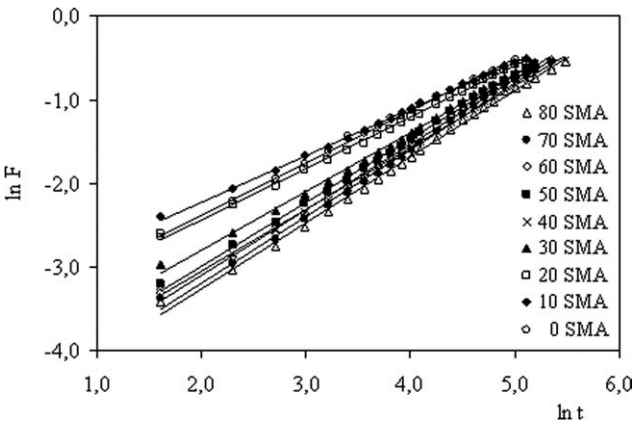


Figure 12 Plots of ln$F$ versus ln$t$ for AAm/SMA hydrogels crosslinked by TMPTA in aqueous 0.01M urea solutions.

Tables V–VII show that the number determining the type of diffusion, n is over 0.50. Hence, the diffusion of water into the super water-retainer hydrogels is generally found to have a non-Fickian character.[22] When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. As water or other penetrates diffuses into the hydrogel, rearrangement of chains does not occur immediately.[22]

The study of diffusion phenomena of water or other penetrates in hydrogels is of value in that it clarifies polymer behavior. For hydrogel characterization, the diffusion coefficients can be calculated by various methods. The diffusion coefficient, D of the water was calculated using the following equation:[23]

$$D = \pi r^2 \left(\frac{k}{4}\right)^{1/n} \tag{4}$$

where D is in cm^2 min^{-1}, r is the radius of a cylindrical polymer sample, n is the diffusional exponent,

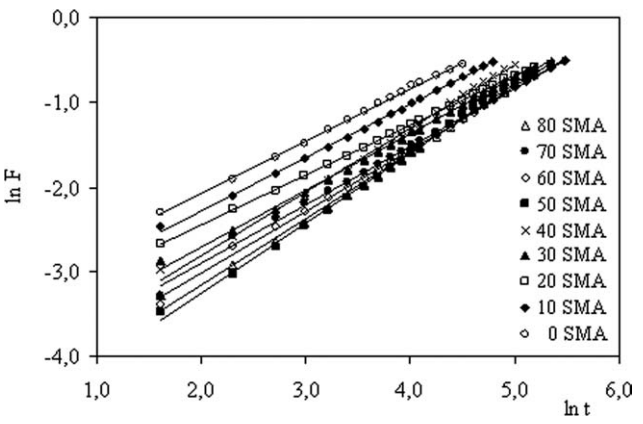
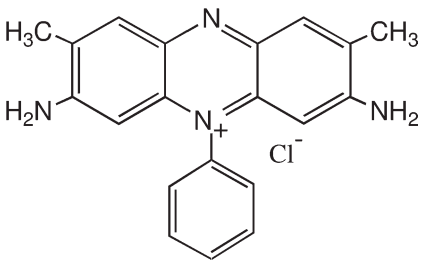


Figure 13 Plots of ln$F$ versus ln$t$ for AAm/SMA hydrogels crosslinked by BDMA in aqueous $10.0 \times 10^{-5}M$ ST solution.

TABLE IV
Some Properties of Safranin T

Name(s)	Chemical formula	Molar mass (g mol^{-1})	λ_{mak}(nm)	CI No.
Safranin T (Basic red 2) (BR 2)		350,85	530	50240

and k is a constant incorporating characteristic of the macromolecular network system and the penetrant.

The values of diffusion coefficient determined for the hydrogels are listed in Tables V–VII. Tables V–VII show that the values of the diffusion coefficient of AAm/SMA hydrogels vary from 0.96×10^{-4} cm^2 min^{-1} to 24.32×10^{-4} cm^2 min^{-1}. Diffusion coefficients, generally, increase with the increasing of SMA in water, in aqueous 0.01M urea solutions, and in aqueous $10.0 \times 10^{-5}M$ ST solutions. The reason of these effects can be the hydrophilic characteristics of SMA.

Equilibrium sorption studies

To observe the sorption of ST, AAm/SMA hydrogels were placed in aqueous solutions of ST and allowed to equilibrate for 4 days at 25°C. At the end of this

TABLE V
Diffusion Exponents (n), Diffusion Constants (k), and Diffusion Coefficient (D) of AAm/SMA Hydrogel Systems in Water

SMA/mg	BDMA	EGDMA	TMPTA
Diffusion exponent (n)			
0	0.81	0.74	0.78
10	0.62	0.54	0.60
20	0.74	0.66	0.68
30	0.88	0.84	0.73
40	0.97	0.86	0.79
50	0.94	0.95	0.80
60	0.95	0.93	0.84
70	0.99	0.93	0.81
80	0.92	0.91	0.84
Diffusion constant ($k \times 10^3$)			
0	10.84	15.35	14.19
10	27.24	36.89	25.18
20	10.94	17.21	14.57
30	5.62	5.68	9.27
40	3.90	5.15	7.78
50	2.89	3.17	6.59
60	2.68	3.11	5.26
70	2.14	2.71	6.80
80	2.70	3.28	5.35
Diffusion coefficient ($D \times 10^4$)			
0	5.32	6.14	5.67
10	2.03	1.08	2.04
20	4.56	2.47	2.93
30	16.25	4.60	4.94
40	22.30	9.88	6.54
50	15.76	18.84	6.67
60	12.92	17.23	8.43
70	24.32	19.19	8.64
80	17.55	19.92	9.65

TABLE VI
Diffusion Exponents (n), Diffusion Constants (k), and Diffusion Coefficient (D) of AAm/SMA Hydrogel Systems in Aqueous 0.01M Urea Solutions

SMA/mg	BDMA	EGDMA	TMPTA
Diffusion exponent (n)			
0	0.77	0.68	0.62
10	0.61	0.59	0.55
20	0.66	0.67	0.61
30	0.78	0.63	0.70
40	0.74	0.67	0.74
50	0.64	0.86	0.76
60	0.75	0.93	0.78
70	0.79	0.84	0.80
80	0.93	0.85	0.79
Diffusion constant ($k \times 10^3$)			
0	16.18	19.20	26.72
10	25.20	28.62	35.67
20	22.02	17.01	25.55
30	10.60	24.01	14.99
40	14.71	15.35	10.91
50	19.17	5.73	11.07
60	10.96	4.93	9.40
70	7.41	6.50	8.38
80	3.64	6.59	7.97
Diffusion coefficient ($D \times 10^4$)			
0	4.96	2.47	2.43
10	1.94	3.07	1.47
20	3.59	3.27	2.85
30	6.59	2.83	5.26
40	4.87	4.38	6.88
50	3.66	11.19	8.66
60	7.70	23.37	14.75
70	8.85	12.16	10.17
80	15.22	15.07	10.81

TABLE VII
Diffusion Exponents (*n*), Diffusion Constants (*k*), and Diffusion Coefficient (*D*) of AAm/SMA Hydrogel Systems in Aqueous 10.0 × 10^{-5}*M* ST Solutions

SMA/mg	BDMA	EGDMA	TMPTA
Diffusion exponent (*n*)			
10	0.63	0.57	0.60
20	0.59	0.58	0.56
30	0.67	0.70	0.77
40	0.75	0.65	0.74
50	0.82	0.80	0.79
60	0.72	0.86	0.78
70	0.69	0.79	0.82
80	0.78	0.73	0.80
Diffusion constant ($k \times 10^3$)			
10	29.20	28.68	24.21
20	26.43	27.80	34.22
30	17.56	11.80	15.43
40	13.62	15.85	11.71
50	7.46	8.33	9.56
60	11.58	6.16	9.08
70	14.05	7.73	8.33
80	8.90	10.51	7.97
Diffusion coefficient ($D \times 10^4$)			
10	2.04	1.36	1.58
20	1.01	0.96	1.93
30	1.93	2.75	5.76
40	6.80	1.91	4.26
50	6.23	10.09	5.43
60	4.59	12.17	6.27
70	2.18	8.33	9.48
80	7.02	5.15	8.46

period, AAm/SMA hydrogels in ST solutions showed the dark-red coloration.

There can be many reasons for noncovalent interactions in the binding of ST by AAm/SMA hydrogels. The main interactions between the hydrogel systems and the cationic dye, ST, may be hydrophobic and hydrogen bonding. Specially, hydrogen bonding will be expected to occur between amine groups and nitrogen atoms on the dye molecules and the amine and carbonyl groups on the monomer unit of crosslinked polymer. Hydrophobic effects are especially aqueous solutions interactions, which in the present case will involve that aromatic ring on the dye molecules and the methine and methyl groups on the gel. There can be some other interactions such as dipole–dipole and dipole-induced dipole interactions between the dye molecules and the hydrogel chains.

For equilibrium sorption studies, the sorption capacity (q), removal efficiency (RE%), and partition coefficient (K_d) can be investigated. The sorption capacity of AAm/SMA hydrogels were evaluated by using the following equation:

$$q = \frac{(C_0 - C)v}{m} \quad (5)$$

where q is the sorption capacity (the amount (mol) of dyes sorbed onto unit dry mass) of AAm/SMA hydrogels (mol g^{-1}), C_0 and C are the concentration of ST in the initial solution and the aqueous phase after treatment for a certain period time, respectively (mol L^{-1}), v is the volume of the aqueous phase (L), and m is the amount of dry AAm/SMA hydrogels (g).

The sorption capacity of AAm/SMA hydrogels was calculated for uptake of dye within the hydrogel in 10.0 × 10^{-5} mol ST in liters of aqueous solutions, and presented in Table VIII. Table VIII presents that the sorption capacity of AAm/SMA hydrogels were changed between 0.45 × 10^{-5} and 2.59 × 10^{-5} mol g^{-1} for AAm/SMA hydrogels. The sorption capacity of the AAm/SMA hydrogels gradually increased with the increase of content of SMA in the hydrogels.

SMA groups contain many ionic units. The swelling degree of the hydrogels increases due to increase of the hydrophilic units on hydrogel structure. Therefore, AAm/SMA hydrogels have many ionic groups that can increase interaction between the dye molecules and anionic groups of hydrogels.

Equilibrium ST sorption isotherms of AAm/SMA hydrogels crosslinked by BDMA, EGDMA, and TMPTA are presented in Figures 14–16. To Figures 14–16, the sorption capacity of the hydrogel systems

TABLE VIII
Some Adsorption Parameters of AAm/SMA Hydrogel Systems in Aqueous 10.0 × 10^{-5}*M* ST Solutions

SMA/mg	BDMA	EGDMA	TMPTA
Sorption capacity ($q \times 10^5$)			
10	0.68	0.45	0.61
20	1.51	1.18	1.54
30	1.80	1.76	2.16
40	1.97	1.66	2.24
50	1.80	2.17	2.06
60	2.17	2.04	2.26
70	2.07	2.03	2.31
80	2.59	2.25	1.98
Removal efficiency (RE%)			
10	22.58	17.91	22.64
20	53.27	51.72	58.98
30	62.53	58.32	71.22
40	65.80	68.59	74.74
50	71.86	73.19	78.52
60	75.66	73.54	80.23
70	76.30	75.35	83.72
80	81.12	78.90	83.08
K_d			
10	0.29	0.22	0.29
20	1.14	1.07	1.44
30	1.67	1.40	2.48
40	1.92	2.18	2.96
50	2.55	2.73	3.66
60	3.11	2.78	4.06
70	3.22	3.06	5.14
80	4.30	3.74	4.91

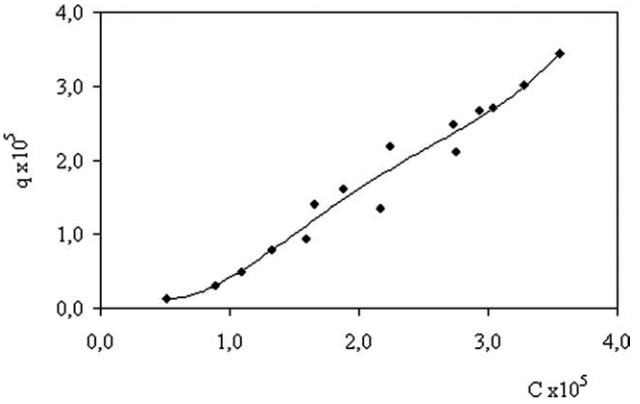


Figure 14 Equilibrium sorption isotherms of AAm/SMA hydrogels crosslinked by BDMA in aqueous ST solutions.

is increased with the increasing concentration of ST. This is expected result.

Removal efficiency (RE%) of AAm/SMA hydrogels can be calculated by following equation:

$$\mathrm{RE\%} = \frac{C_0 - C}{C_0} \times 100 \tag{6}$$

Removal efficiency (RE%) of AAm/SMA hydrogels is changed among 17.91–83.72% (Table VIII).

Partitioning of dissolved constituents between an aqueous phase and adsorbents in waters and sediments has commonly been described by an empirical partition coefficient that simply relates the total concentration of a dissolved species to the total concentration of the adsorbed species[24,25]:

$$K_d = \frac{(C_0 - C)}{C} \tag{7}$$

where K_d is empirical partition coefficient at equilibrium. C_0 and C were defined earlier. Partition coefficients of ST between dye solution and hydrogels were calculated and are shown in Table VIII.

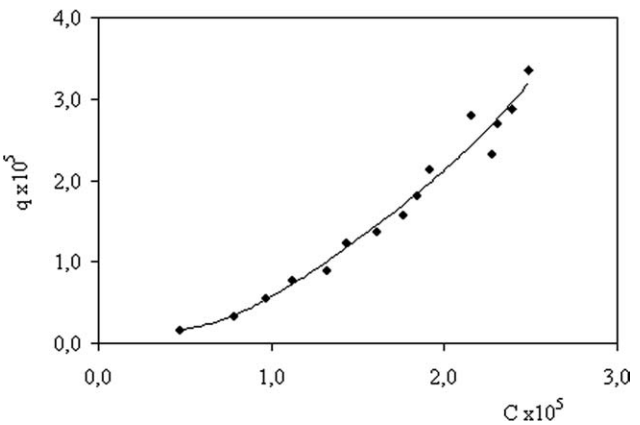


Figure 15 Equilibrium sorption isotherms of AAm/SMA hydrogels crosslinked by EGDMA in aqueous ST solutions.

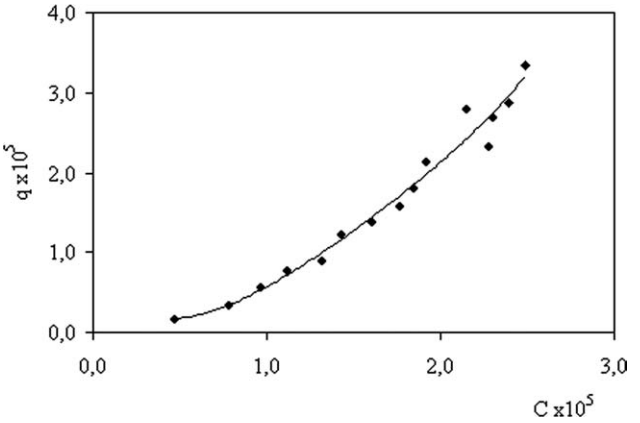


Figure 16 Equilibrium sorption isotherms of AAm/SMA hydrogels crosslinked by TMPTA in aqueous ST solutions.

In Table VIII, it is shown that the values of partition ratio of AAm/SMA hydrogels containing of 10 mg SMA are small than 1.0. For the other AAm/SMA hydrogel systems, the values of partition ratio are bigger than 1.0. So, it can be said that AAm/SMA hydrogels are good adsorbent for ST.

CONCLUSION

In this study, incorporation of hydrophilic groups containing chemicals such as SMA in AAm hydrogels can be obtained successively by free-radical solution polymerization method. Multifunctional crosslinkers such as BDMA, EGDMA, and TMPTA have been used at the polymerization process. The hydrogels showed high water, or urea, or cationic dye such as safranin T absorbency. It was seen that swelling of AAm/SMA hydrogels increased with the increasing of content of SMA.

It can be concluded from the data presented in this article that the AAm/SMA hydrogels are appropriate matrix for pharmaceutical formulations and for biotechnological applications due to its favorable physicochemical properties. The AAm/SMA hydrogels reported can be used to carry substances in an aquatic, urea/water field for pharmaceutical, agricultural, environmental, and biomedical applications.

On the other hand, this work has given the quantitative information on the sorption characteristic of a cationic dye such as ST with AAm/SMA hydrogels. In this study, it has shown that AAm/SMA hydrogels have sorbed the cationic dye, ST while AAm do not. Some sorption parameters are increased with the content of SMA in AAm/SMA hydrogels. So, it can be said that AAm/SMA hydrogels having high content of SMA is good adsorbent for ST.

At the end of this study, it is seen that chemically crosslinked AAm/SMA hydrogels may be used a sorbent in water, or in aqueous systems including mixing of water/urea and for removal of some dye molecules such as ST. The utilization of these types of hydrogels, in biotechnology, environment, sorption, separation, purification, immobilization, and enrichment of some species makes hydrogel more popular.

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