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Application of AAm/APTAC hydrogels and semi-interpenetrating polymer networks including of PVA in uptake of anionic dye from aqueous solutions

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ABSTRACT

A series of novel hydrogels acrylamide(AAm)/(3-acrylamidopropyl) trimethyl ammonium chloride (APTAC) and semi-interpenetrating polymer networks (semi-IPNs) composed of poly(vinyl alcohol) (PVA) and random copolymers AAm/APTAC were prepared by free radical polymerization in aqueous solution. Ammonium persulfate/*N,N,N′,N′*-tetramethylethylenediamine was used in polymerization as redox initiating pair in presence of 1,4 butanediol dimethacrylate and ethylene glycol dimethacrylate as crosslinkers. Fourier Transform Infrared Spectroscopy was used to identify the presence of different repeating units in the hydrogels and semi-IPNs. Scanning Electron Microscopy images were taken for determination of surface porosity of hydrogels and semi-IPNs. Swelling experiments were performed in water at 25°C, gravimetrically. The hydrogel systems that synthesized in this study were showed high water absorbency. Water and dye adsorption properties of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs were investigated as a function of chemical composition of the hydrogels. An anionic dye, calconcarboxylic acid was used in sorption studies. This study also gives the quantitative information on the swelling and sorption characteristic of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs for many potential applications.

Keywords: Acrylamide; Adsorption; Cationic hydrogel; Interpenetrating polymer networks; Swelling

1. Introduction

Hydrogels are three-dimensional polymeric networks that have a solid-like appearance, formed by two or more components, one of which is a liquid present in high quantity. The capability of hydrogels to swell in water is due to the hydrophilic groups present in the polymer chains, while its mechanical resistance is due in part to the physical or chemical network crosslinking. Hydrogels have gained popularity as scaffolds for tissue engineering due to their high water content, good biocompatibility, and consistency similar to soft tissue [1–4]. Water sorption property of hydrogels accounts for a great number of biomedical and technological applications such as drug delivery systems, artificial implants, contact lens, enzyme immobilization, catheters, wound dressings, biosensors, superabsorbents, and etc. [5–7]. With the ability of carrying charges on their backbone, hydrogels are very useful materials for biological and environmental applications. For example, negatively charged polymers are generally used for the removal of oppositely charged metal ions and dyes in environmental applications. Positively charged polymers, on the other hand, are generally used in biological applications, i.e., they can neutralize the negative charges of DNA and can be used for delivery purposes in gene therapy, and separation, purification, and/or pre-concentration of rare species. Positively charged polymer networks can also be used for environmental applications [8–12].

An effective role to develop mechanically strong polymeric materials has been through the preparation of interpenetrating polymer networks (IPNs), which are defined as

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a combination of two polymers, in network form, of which at least one is synthesized and/or crosslinked in the immediate presence of the other without any covalent bonds between them [13, 14]. Some physical properties of hydrogels may be improved by preparing semi-interpenetrating polymer networks (semi-IPNs), when the hydrogel network is prepared in the presence of a previously made linear polymers such as poly(ethylene glycol), polyacrylamide (PAAm), poly(*N*-isopropyl acrylamide), poly(vinyl pyrrolidione), poly(vinyl alcohol) (PVA), or poly(acrylic acid), poly(vinylsulfonic acid) sodium salt, etc. [13–16].

PVA is a common and well-known polymer that possesses salient features such as water solubility, ease-of-use, film-forming property and biodegradability. In recent years, several research groups have succeeded in preparing hydrogels from PVA in various methods such as polymerization of multifunctional monomer systems, end-linking reaction, or freeze-thawing method to observe some of important properties of the PVA hydrogels. Because of their inherent non-toxicity, good biocompatibility, non-carcinogenicity, and desirable physical properties, PVA hydrogels have been used in biomedical applications such as implants, embolic materials, soft contact lenses and artificial organs [17–20].

PAAm based hydrogels have received considerable attention because of their use in many applications. In our previous study, copolymeric hydrogels of acrylamide with some acidic monomers were prepared by free radical solution polymerization and used in separation and adsorption of some dye molecules [21–25].

In this study, we tried to increase the water absorption capacity of AAm hydrogels by using APTAC and PVA which contain highly hydrophilic functional groups. Some crosslinked polymers and/or copolymers containing APTAC or PVA has been synthesized by some different research groups as well [3, 11, 26–33]. The main purpose of this study was to combine both monomers and a polymer in a new polymeric system via free radical solution polymerization method. In this respect, a series of copolymeric hydrogels were synthesized by changing the content of APTAC and PVA. Then, some swelling, and some diffusional properties of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs were studied in water for swelling characterization. Water uptake, dye sorption properties of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs were investigated as a function of chemical composition of the hydrogels.

2. Experimental

2.1. Materials

Chemically crosslinked highly swollen AAm/APTAC hydrogels were prepared by free radical crosslinking copolymerization of acrylamide (AAm) (Merck, Darmstad, Germany) monomer with addition of a cationic comonomer such as (3-acrylamidopropyl) trimethyl ammonium chloride (APTAC) (Aldrich, Steinheim, Germany) and two multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA) (Merck, Schuchardt, Germany) and 1,4 butanediol dimethacrylate (BDMA) (Aldrich, Steinheim, Germany). A linear polymer such as PVA (M_w = 13,000–23,000) was supplied from Aldrich, Steinheim, Germany. The initiator, ammonium persulfate (APS) Merck, Darmstadt, Germany and the activator *N,N,N′,N′*-tetramethylethylenediamine (TEMED) was purchased from Merck Schuchardt, Germany. The anionic dye, calconcarboxylic acid (CCA, Aldrich, Steinheim, Germany) was used in sorption studies. All chemicals were used as received.

2.2. Preparation of AAm/APTAC hydrogels

To prepare highly swollen AAm/APTAC hydrogel systems, AAm weighing 1.0 g (14.07 mmol) was dissolved in 1,000 μL water. Then, 10 μL (0.0537 mmol), 20 μL (0.1074 mmol), 30 μL (0.1611 mmol), 40 μL (0.2148 mmol), 50 μL (0.2685 mmol), 60 μL (0.3222 mmol), 70 μL (0.3759 mmol) and 80 μL (0.4296 mmol) of APTAC were added to each AAm solutions, respectively. After these additions, for the synthesis, 250 μL (0.0226 mmol) of 2.0% concentration of BDMA in methanol and 200 μL (0.0438 mmol) aqueous solutions of APS (5.0 g APS/0.022 mol/100 mL water) and 250 μL (0.0167 mmol) 1.0% of concentration of TEMED were added into these aqueous solutions. The solutions were placed in PVC straws of 3 mm diameter. After gelation, fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm in length. They were placed in distilled water for 4 d to remove unreacted materials, dried blotting with filter paper, and finally dried in air and vacuum for swelling studies. Schematic representation of the preparation, swelling and sorption studies of the hydrogel systems were presented in Fig. 1.

For the synthesis of AAm/APTAC hydrogels crosslinked by EGDMA, 250 μL (0.0265 mmol) of 2.0% concentration of EGDMA in methanol was used as crosslinker.

2.3. Preparation of AAm/APTAC/PVA semi-IPNs

Firstly, 20.0% concentration of aqueous PVA solutions was prepared at 80°C. Then, this solution was used for the synthesis of the semi-IPN systems.

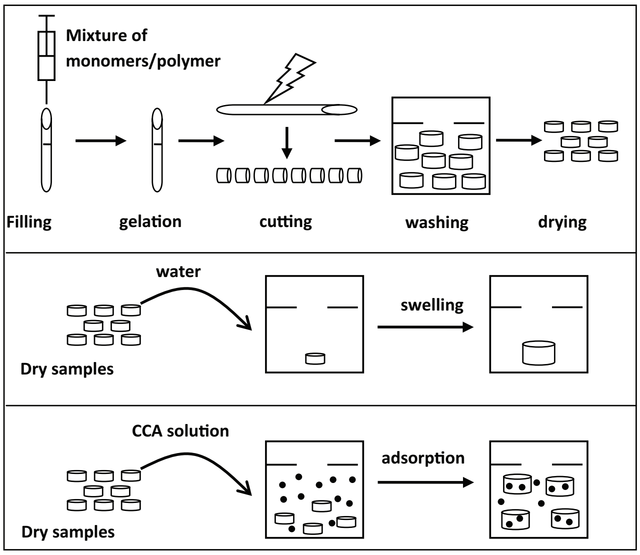


Fig. 1. Schematic representation of the preparation, swelling and sorption studies of the hydrogel systems.

For the preparation of AAm/APTAC/PVA semi-IPN systems (containing fixed content of PVA), AAm weighing 1.0 g (14.07 mmol) was dissolved in aqueous mixture of 250 μL (0.0028 mmol) 20.0% concentration of aqueous PVA solutions with 750 μL of water. Then, 10 μL (0.0537 mmol), 20 μL (0.1074 mmol), 30 μL (0.1611 mmol), 40 μL (0.2148 mmol), 50 μL (0.2685 mmol), 60 μL (0.3222 mmol), 70 μL (0.3759 mmol) and 80 μL (0.4296 mmol) of APTAC were added to each AAm solutions, respectively. Then, the other experimental details were applied as previously given.

For the preparation of AAm/APTAC/PVA semi-IPN systems (containing different contents of PVA), the same method was used as mentioned above with addition of 125 μL (0.0014 mmol), 375 μL (0.0042 mmol) and 500 μL (0.0053 mmol) of aqueous 20.0% concentration of PVA solutions to 875 μL, 625 μL and 500 μL of water containing of 1.0 g of AAm and 60 μL of APTAC.

For synthesis of all used samples in this study, the quantities of AAm, APTAC and PVA were presented in Table 1.

For dynamic swelling studies, AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs were accurately weighted and transferred into water. Water uptake with respect to time was obtained by removing the samples from water, quickly blot drying and reweighing periodically. The measurements were conducted at 25 ± 0.1°C in a water bath (Fig. 1).

2.4. FT-IR analysis of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs

For structural characterization, FT-IR analysis was made. Spectra were taken on KBr discs by using VARIAN FTS 800 FT-IR spectrophotometer (United States of America).

2.5. SEM studies of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs

The surface morphology of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems was visualized by a scanning electronic microscope PHILLIPS XL-30S FEG (Netherlands) [31, 34].

2.6. Dye sorption equilibrium experimental

Batch sorption studies were conducted in all sorption experiments. The anionic dye, CCA was used in sorption studies and some properties of CCA were given in Table 2 [35].

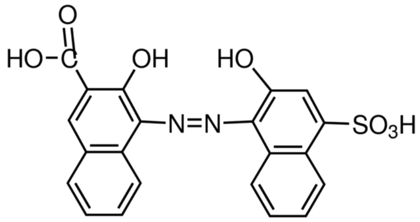
CCA solutions were prepared in distilled water. To investigate the effect of solution concentration onto dye sorption, CCA concentrations were changed from 0.40 × 10^{-3} M to 4.20 × 10^{-3} M. AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems containing 60 μL of APTAC were interacted with known volume of dye solution until equilibrium was reached. On the other hand, to detect the effect of APTAC on the dye sorption 2.00 × 10^{-3} M of CCA solution 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 (Australia) at ambient temperature. The absorbances of related solutions were read at 560 nm for CCA [35]. Distilled water was chosen as the reference. The equilibrium concentrations of the dye solutions were determined by means of pre-calibrated scales.

Table 1
Compositions of the hydrogel systems containing APTAC and PVA

BDMA	Co-monomer, APTAC (μL)	20% of aqueous PVA solution (μL)	Water (μL)
AAm/APTAC	0, 10, 20, 30, 40, 50, 60, 70, 80	—	1,000
AAm/APTAC/PVA	0, 10, 20, 30, 40, 50, 60, 70, 80	250	750
AAm/APTAC/PVA (for PVA changing)	60	125; 250; 375; 500	875; 750; 625; 500
EGDMA	Co-monomer, APTAC (μL)	20% of aqueous PVA solution (μL)	Water (μL)
AAm/APTAC	0, 10, 20, 30, 40, 50, 60, 70, 80	—	1,000
AAm/APTAC/PVA	0, 10, 20, 30, 40, 50, 60, 70, 80	250	750
AAm/APTAC/PVA (for PVA changing)	60	125; 250; 375; 500	875; 750; 625; 500

Table 2
Some properties of calconcarboxylic acid (CCA)

Name	Chemical formula	Molar mass (g mol^{-1})	CAS number	λ_{max} (nm)
Calconcarboxylic acid (CCA)		438.41	3737-95-9	560

3. Results and discussion

3.1. Preparation

AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems were prepared by free radical solution polymerization. Chemical structures of monomers and possible binding mechanism between AAm and APTAC for crosslinked AAm/APTAC copolymers are presented in Fig. 2. Dried AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems are glassy and very hard, but swollen gels are soft. The synthesis of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems via radical chain polymerization is a well-established procedure. Upon swelling, the hydrogels were strong enough to retain their shape. The photographs of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems are presented in Figs. 3 and 4 as dry state or swollen state. The swelling capacity of the hydrogels can be seen from Figs. 3 and 4 [28, 29, 36, 37].

3.2. FT-IR analysis

FT-IR spectra of the hydrogel systems were evaluated to confirm the functional groups in copolymeric hydrogels and to understand binding and crosslinking of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs during polymerization. Representative spectrums are presented in Figs. 5 and 6. In the FT-IR spectra of the hydrogels, the broad bands observed between 3,000 and 3,600 cm^{-1} correspond to hydrogen bonded O-H and N-H stretching vibrations of the amide group of AAm/APTAC and AAm/APTAC/PVA units. The peaks can be observed between 1,500 and 1,700 cm^{-1} corresponding to the C=O stretching of the unit of APTAC monomeric groups. The peaks observed this region also corresponding to the C=O group of AAm. On the other hand, it is thought that the peaks at 1250 cm^{-1} are C-N bands, and the peaks at 2,800–3,000 cm^{-1} were assigned to the stretching vibration of CH_3 and CH_2, which were echoed by the peaks at 1,200–1,450 cm^{-1} assigned to the bending vibration of CH_3 and CH_2. The peaks around 3,500 and 1,100 cm^{-1} are assigned to the terminal hydroxyl group and C–O stretching of polyether, respectively. The peak for N-H bending appeared around 1,450 cm^{-1} and 1,550 cm^{-1} clearly shows the existence of an ammonium ion [18, 30–33].

3.3. Scanning electron microscopy (SEM) analysis

Scanning electron microscopy (SEM) analysis is the most used technique to investigate the shape, size, morphology, crosslink and porosity of hydrogels, or other related materials. SEM images of hydrogels and semi-IPNs containing 60 μL APTAC are presented in Fig. 7 as representative. With the incorporation of APTAC groups

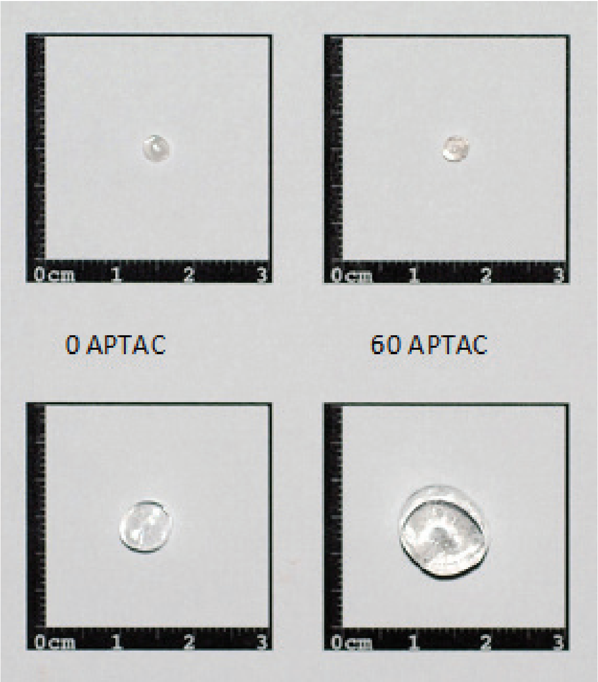


Fig. 3. The photographs of AAm/APTAC hydrogels crosslinked by BDMA (as dry state or swollen state).

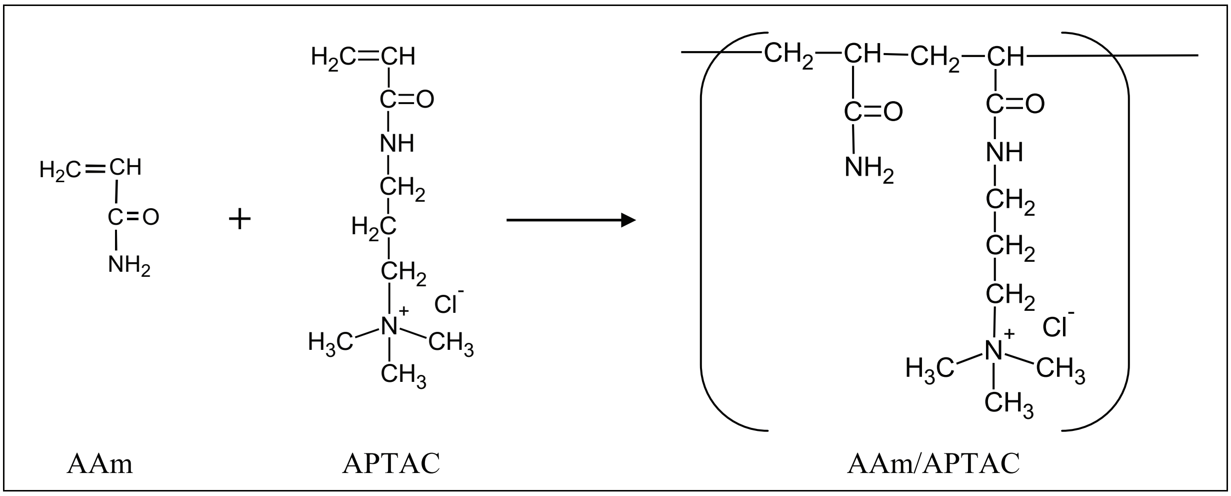


Fig. 2. Chemical structures of monomers and the probable binding mechanism of AAm/APTAC copolymers.

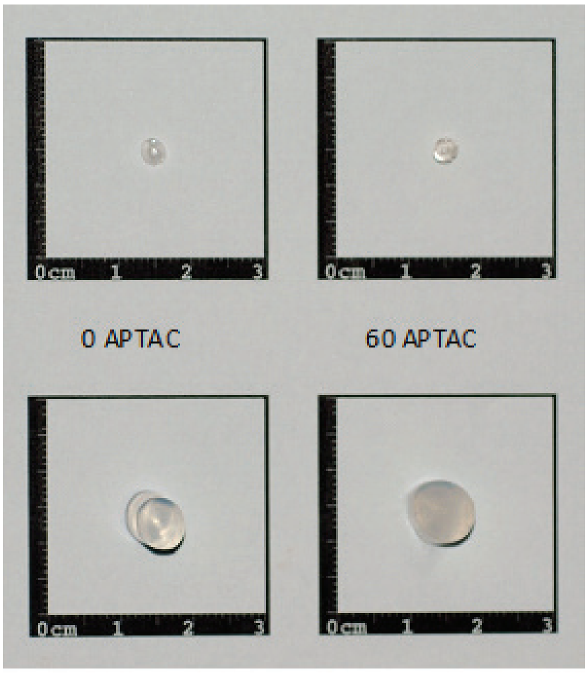


Fig. 4. The photographs of AAm/APTAC/PVA semi-IPNs crosslinked by EGDMA (as dry state or swollen state).

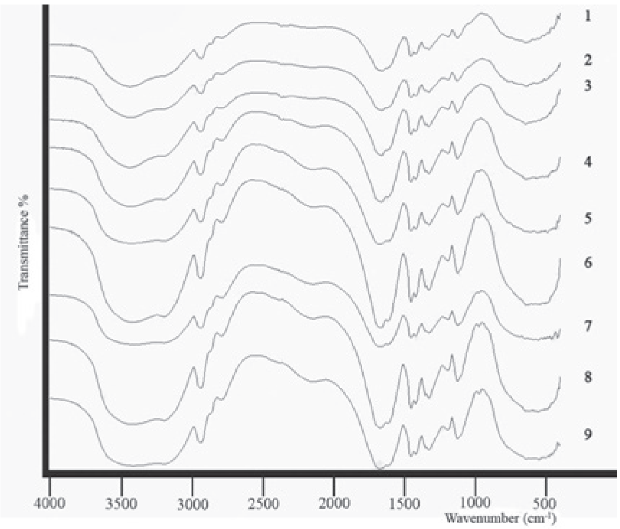


Fig. 5. FT-IR spectra of AAm/APTAC/PVAsemi-IPNs crosslinked by BDMA.
Notes: 1 – 0 APTAC/PVA; 2 – 10 APTAC/PVA; 3 – 20 APTAC/PVA; 4 – 30 APTAC/PVA; 5 – 40 APTAC/PVA; 6 – 50 APTAC/PVA; 7 – 60 APTAC/PVA; 8 – 70 APTAC/PVA; 9 – 80 APTAC/PVA.

into chemically crosslinked AAm copolymers, it would be expected that a lot of number of porous. The synthesized AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPN systems have a large number of porous and their sizes are varying with the range of a few micrometers to tens of micrometer [29, 31, 38].

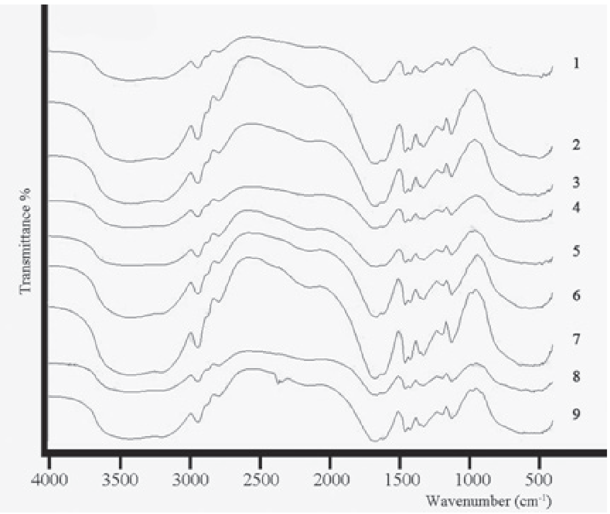


Fig. 6. FT-IR spectra of AAm/APTAC hydrogels crosslinked by EGDMA.
Notes: 1 – 0 APTAC; 2 – 10 APTAC; 3 – 20 APTAC; 4 – 30 APTAC; 5 – 40 APTAC; 6 – 50 APTAC; 7 – 60 APTAC; 8 – 70 APTAC; 9 – 80 APTAC.

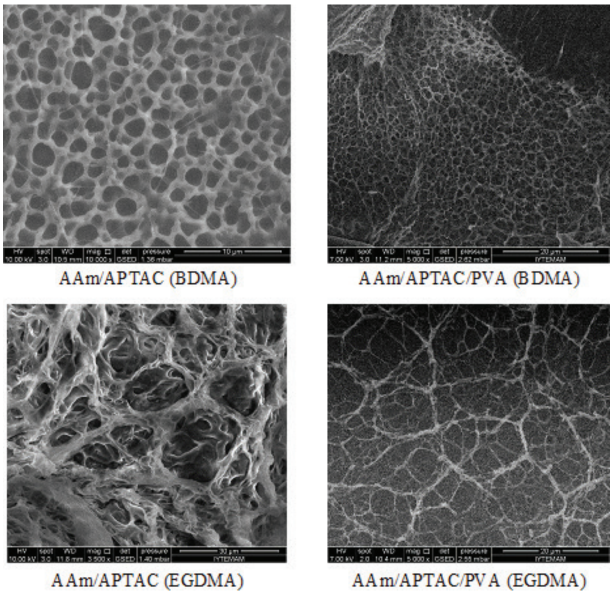

AAm/APTAC (BDMA)
AAm/APTAC/PVA (BDMA)
AAm/APTAC (EGDMA)
AAm/APTAC/PVA (EGDMA)

Fig. 7. SEM images of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs containing 60 μL APTAC crosslinked by BDMA, or EGDMA.

3.4. Equilibrium swelling studies

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. When a glassy hydrogel is brought into contact with water, water diffuses into the hydrogel and the hydrogel swells. Diffusion involves migration of water into preexisting or dynamically formed spaces between hydrogel chains. Swelling of the hydrogel involves larger scale segmental motion resulting, ultimately, in an increased distance of separation between hydrogel chains. The percentage swelling ratio (S%) of the hydrogels in distilled water (pH 7.00) was calculated from the following relation [21, 22]:

$$S\% = \frac{m_t - m_o}{m_o} \times 100 \tag{1}$$

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

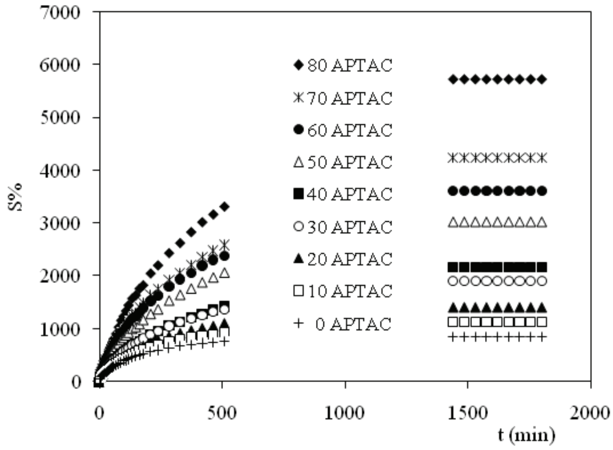


Fig. 8. Swelling isotherms of AAm/APTAC hydrogels crosslinked by BDMA.

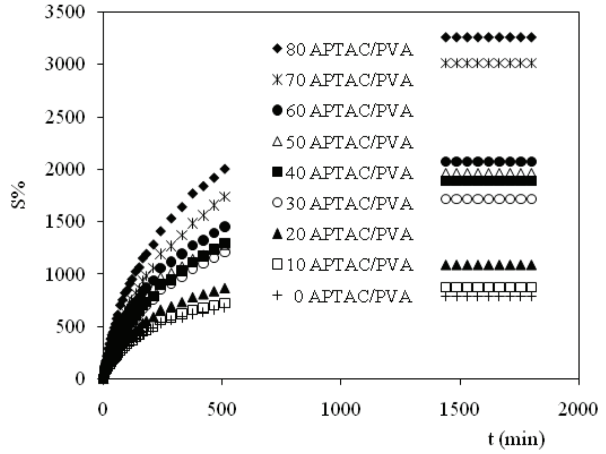


Fig. 9. Swelling isotherms of AAm/APTAC/PVA semi-IPNs crosslinked by EGDMA.

The water intake of initially dry hydrogels was followed for AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs crosslinked by BDMA, or EGDMA in water, and swelling isotherms of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs are shown in Figs. 8 and 9 as representative.

Figs. 8 and 9 show that swelling increases with time up to certain level, then levels off. This value of "swelling" can be called as the equilibrium percentage swelling ratio (S_{eq}%). S_{eq}% values of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs are given in Table 3.

Table 3 shows that S_{eq}% values of AAm hydrogels is 850% for samples crosslinked by BDMA and is 1187% for samples crosslinked by EGDMA, but S_{eq}% of AAm/APTAC hydrogels are 1,135%–7,633% with the incorporation of APTAC groups into AAm hydrogels, and S_{eq}% of AAm/APTAC/PVA semi-IPNs are 871%–3,257% with the incorporation of PVA groups into AAm/APTAC hydrogels, while equilibrium swelling percent value of AAm/PVA hydrogels is 856% for samples crosslinked by BDMA and is 782% for samples crosslinked by EGDMA. In Table 3, S_{eq}% values of the hydrogels increased with the APTAC contents in the copolymers. S_{eq}% values of AAm/APTAC hydrogels is higher than S_{eq}% of AAm hydrogels. Table 3 also shows that S_{eq}% values of AAm/APTAC/PVA semi-IPNs are lower than S_{eq}% values of AAm/APTAC hydrogels. One of the reasons of these results is decreasing of hydrophilic character at crosslinked polymeric systems. There is no interaction of PVA with AAm and APTAC. PVA chains are placed into the crosslinked copolymeric system by tangling. Because of the located PVA chains in the free space of crosslinked polymer networks, water diffusion is prevented [28]. For understanding the effect of APTAC content on the swelling behavior, S_{eq}% values of the hydrogels versus the content of APTAC are plotted in Figs. 10 and 11. It is clearly seen that S_{eq}% values of the hydrogels gradually increased with increasing of APTAC content in the hydrogels in Figs. 10 and 11.

As it can be seen in Table 3, S_{eq}% values of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs increased in the following order:

S_{eq}% values (crosslinked by EGDMA) > S_{eq}% values (crosslinked by BDMA)

Table 3
Values of the equilibrium percentage swelling ratio of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs

APTAC/μL	0	10	20	30	40	50	60	70	80
	Equilibrium percentage swelling ratio (S_{eq}%)								
BDMA	850	1,135	1,418	1,913	2,174	3,031	3,622	4,230	5,719
PVA/BDMA	856	1,163	1,247	1,319	1,355	1,426	1,687	2,102	2,565
EGDMA	1,187	1,670	2,187	2,734	4,198	5,414	6,229	6,661	7,633
PVA/EGDMA	782	871	1086	1,708	1,884	1,963	2,064	3,002	3,257

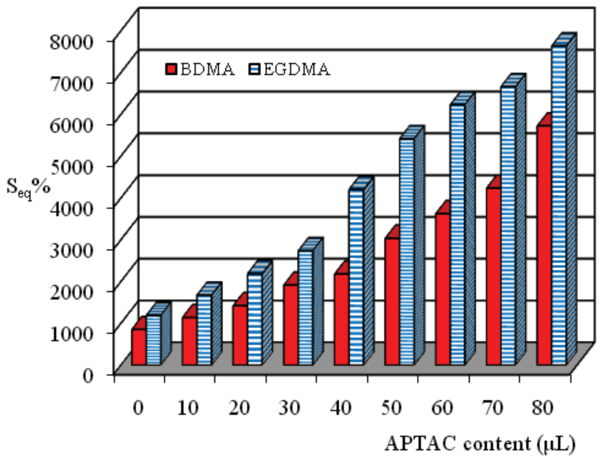


Fig. 10. Changing of S_{eq}% values of the hydrogel systems by various contents of APTAC.

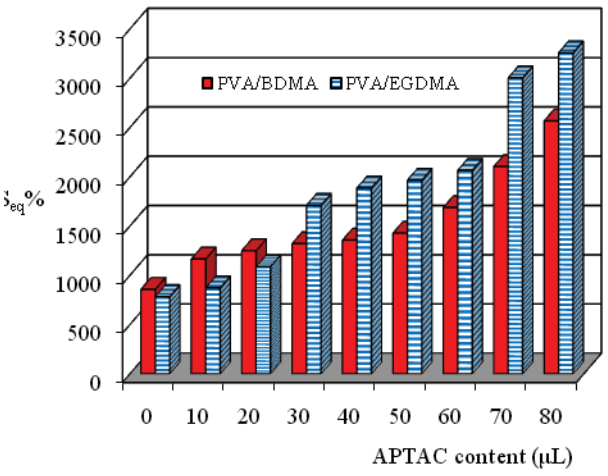


Fig. 11. Changing of S_{eq}% values of the semi-IPN systems by various contents of APTAC.

This arrangement could be related to molecular structure and amount of used crosslinkers. The different but very close mole numbers (0.0226 mmol of BDMA or 0.0265 mmol of EGDMA) of crosslinkers were used for the synthesis. For this reason, we agreed that different equilibrium swelling percent values could be resulted from number of hydrophobic groups. EGDMA has higher equilibrium swelling percent values because BDMA has two more hydrophobic $–CH_2$ groups than EGDMA.

3.5. Diffusion

Due to the importance of crosslinked swellable hydrogel in many fields such as biomedical and pharmaceutical, diffusion of water into or out of the hydrogels is important, and the equation below is used for the calculation of the diffusion parameters.

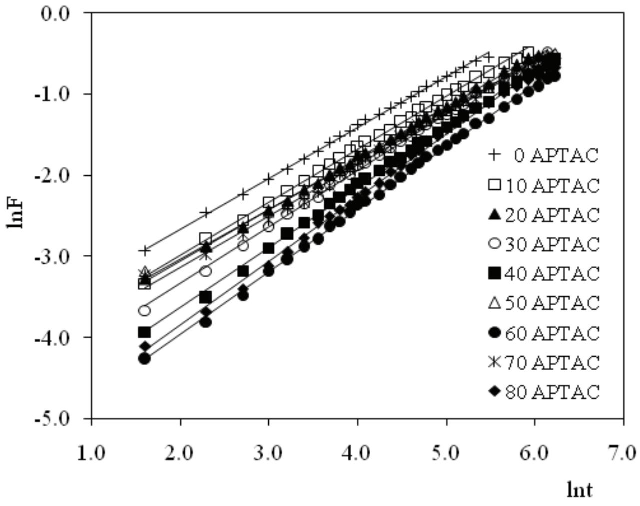


Fig. 12. Plots of lnF vs. lnt for AAm/APTAC hydrogels crosslinked by EGDMA.

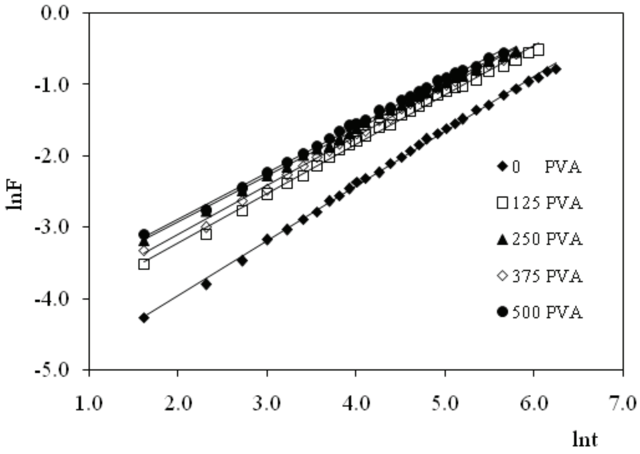


Fig. 13. Plots of lnF vs. lnt for AAm/APTAC/PVA semi-IPNs crosslinked by EGDMA.

$$F = \frac{M_t}{M_s} = kt^n \tag{2}$$

Here, F is the fractional uptake at time t. M_t and M_s are the mass uptake of the solvent at time t and the equilibrium, respectively, and k is a constant incorporating the characteristic of the macromolecular network and the diffusing species. The n is the diffusion exponent that elucidates the transport mechanism. Eq. (2) is applied only to the initial 60% of the normalized solvent absorption of the swelling curve. To determine the diffusion coefficient, the plot of lnF vs. lnt is constructed and shown in Figs. 12 and 13. The two limit values for n are 0.5 and 1, which correspond to Fickian (Case I) and non-Fickian (Case II) type of diffusions,

Table 4
Some diffusion parameters of of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs

APTAC/μL	0	10	20	30	40	50	60	70	80
	Diffusion exponent (n)								
BDMA	0.5279	0.5904	0.6180	0.6216	0.6023	0.6144	0.5903	0.6745	0.7482
PVA/BDMA	0.6071	0.6093	0.6296	0.6001	0.6359	0.5643	0.6100	0.6164	0.6266
EGDMA	0.6249	0.6528	0.6340	0.6945	0.7334	0.6084	0.7692	0.6336	0.7815
PVA/EGDMA	0.5951	0.5981	0.6128	0.6571	0.6601	0.5975	0.6465	0.6632	0.6424
	Diffusion constant ($k \times 10^2$)								
BDMA	4.26	2.52	1.96	1.67	1.62	1.60	1.91	1.02	0.64
PVA/BDMA	2.44	1.92	1.87	2.09	1.85	2.60	1.89	1.61	1.37
EGDMA	1.99	1.36	1.31	0.89	0.61	1.42	0.41	1.22	0.45
PVA/EGDMA	2.67	2.44	2.11	1.34	1.25	1.84	1.47	1.01	1.29
	Diffusion coefficient ($D \times 10^6$)								
BDMA	82	125	134	143	105	161	170	212	302
PVA/BDMA	135	94	167	136	185	130	177	155	167
EGDMA	132	91	62	162	182	127	185	158	385
PVA/EGDMA	102	90	90	144	151	93	152	180	210

respectively. From the slope of the plots, it was found that the value of diffusional exponents n is between 0.5 and 1, indicating that the water diffusion into AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs is non-Fickian anomalous character implying that the relaxation rate to polymer chains is slow. The relaxation and diffusion time are of the same order of magnitude. As solvent diffuses into the hydrogel, rearrangement of chains does not occur immediately. Table 4 shows the diffusional parameters [3, 22, 39].

The study of diffusion phenomena of water 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 [40, 41]:

$$D = \pi\, r_o^2 \left(\frac{k}{4}\right)^{1/n} \tag{3}$$

Here, D is in cm^2 min^{-1}, r_o is the radius of a cylindrical polymer sample, n and k are defined earlier. The values of diffusion coefficient determined for AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs are listed in Table 4. Table 4 shows that the values of the diffusion coefficient of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs vary from 62×10^{-6} cm^2 min^{-1} to 385×10^{-6} cm^2 min^{-1}. It was seen that an increasing of the values of the diffusion coefficient of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs by increasing of APTAC content. Hydrophilicity of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs becomes greater than that of AAm; therefore, the diffusion of water of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs is greater than the diffusion of water of AAm hydrogels.

3.6. PVA effect on the swelling and diffusion

To investigate the PVA effect on the swelling properties of AAm/APTAC/PVA semi-IPNs, swelling isotherms and lnF vs. lnt graphs are plotted and representative results are shown in Fig. 13. Effect of PVA content on some swelling and diffusion parameters of AAm/APTAC/PVA semi-IPN systems containing 60 μL APTAC are tabulated in Table 5.

It was shown that a decreasing of the equilibrium percentage swelling ratio (S_{eq}%) of AAm/APTAC/PVA semi-IPN systems when PVA has been added to the hydrogel systems. Incorporation of PVA into the copolymer network leads to lower degrees of swelling. Here, it can be said that PVA chains was placed in the crosslinked polymeric systems, instead of crosslinked AAm and APTAC molecules; it was seen that decreasing of the value of S_{eq}% is because of decreasing of hydrophilic character at crosslinked polymeric systems. In addition of this phenomenon, the PVA chains are located in the free space of crosslinked polymer networks; water diffusion is prevented by the PVA chains. This has also caused the decreasing of the equilibrium percentage swelling and related parameters.

3.7. Equilibrium sorption studies

To observe the sorption of an anionic dye such as calconcarboxylic acid (CCA), AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs were placed in aqueous solutions of CCA and allowed to equilibrate for 4 d at 25°C. At the end of this period, AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs in the CCA solutions showed the dark coloration, but AAm hydrogel did not show any coloration.

For equilibrium sorption studies, the dye removal capacity (q) (mass amount as "mol" of sorption per unit mass

Table 5
Some swelling kinetics and diffusion parameters of AAm/APTAC/PVA semi-IPNs having of 60 μL APTAC crosslinked by BDMA or EGDMA

20% of aq. PVA solution (μL)	0	125	250	375	500
APTAC/60 μL	Equilibrium percentage swelling ratio (Seq%)				
BDMA	3,622	1,704	1,687	1,585	1,450
EGDMA	6,229	2,103	2,064	1,883	1,598
	Diffusion exponent (*n*)				
BDMA	0.6389	0.6595	0.6100	0.6326	0.7135
EGDMA	0.7692	0.6909	0.6465	0.6897	0.6506
	Diffusion constant (k × 102)				
BDMA	1.40	1.65	1.89	1.76	1.25
EGDMA	0.41	1.00	1.47	1.13	1.52
	Diffusion coefficient (D × 106)				
BDMA	127	182	177	160	268
EGDMA	185	89	152	153	130

(as gram)) of the adsorbent, adsorption percentage (Ads%), and partition coefficient (K_d) were investigated. The dye removal capacity (q) of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs were evaluated by using the following equation:

$$q = \frac{(C_o - C)v}{m} \tag{4}$$

where q is the dye removal capacity of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs (mol g^{-1}), C_o and C are the concentrations of CCA 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), m is the mass of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs in gram [2, 42–44].

Ads% of AAm/APTAC hydrogel and AAm/APTAC/PVA semi-IPNs were calculated by using the following equation:

$$\text{Ads\%} = \frac{C_o - C}{C_o} \times 100 \tag{5}$$

C_o and C were defined earlier.

First, it was examined that the effect of content of APTAC monomers for uptake of the dye. The q, the amount of dye sorbed onto unit dry mass of the gel, was calculated for uptake of dye within the hydrogel in 2.00×10^{-3} M of CCA aqueous solutions and results are presented in Table 6. Table 6 presents q of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs, (1.02×10^{-4} to 4.80×10^{-4} mol g^{-1}), and Ads% of these hydrogel systems (13%–73%) is increased with increasing of content of APTAC. It can be easily explained by increasing ionic charge of the hydrogels and semi-IPNs with the addition of APTAC into the copolymeric systems. Electrostatic attraction between the polymer chains and the anionic dye molecules caused the rising of the adsorption parameters [2, 44].

Different CCA solutions were used to investigate the effect of solution concentration on to sorption. The concentration range of CCA solutions are between 0.4×10^{-3} and 4.2×10^{-3}. Equilibrium adsorption isotherms of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs were plotted and the representative isotherms of are presented in Fig. 14 (for BDMA) and Fig. 15 (for EGDMA). In Figs. 14 and 15, the q values of the hydrogel systems are increased with increasing concentration of CCA that sorbed unit dry mass of the gel. The reason of this is the hydrophilic effect and dye sorption capability of comonomer. A representative digital photo image is given in Fig. 16 to show the colors of hydrogels and solutions after sorption process.

Partitioning of dissolved constituents between an aqueous phase and adsorbents in waters and sediments has commonly been described by an empirical partition coefficient (K_d) that simply relates the total concentration of a dissolved species to the total concentration of the adsorbed species.

$$K_d = \frac{C_o - C}{C} \tag{6}$$

Here, K_d is empirical partition coefficient at equilibrium. C_o and C were defined earlier. Partition coefficients of CCA between dye solution and hydrogels were calculated, and are shown in Table 6. In Table 6, K_d values of AAm/APTAC hydrogels are 0.15–2.18, but K_d values of AAm/APTAC/PVA semi-IPNs are 0.20–2.68 with the incorporation of PVA groups into the hydrogels. The K_d values of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs which have high APTAC contents are higher than 1.0. Therefore, it can be said that synthesized crosslinked polymeric systems with high content of APTAC could be used as potential water adsorbent for the removal of the dye molecules or other big molecular structures similar to dye molecules [44, 45].

The ionic charge content of the polymeric structures is very important to remove some toxic species from aqueous solutions via adsorption. APTAC comonomer has ionizable unit

Table 6
Some adsorption parameters of of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs in aqueous solutions of CCA

APTAC/μL	10	20	30	40	50	60	70	80
	Dye removal capacity (q × 10^4)							
BDMA	1.06	1.08	2.16	2.54	2.77	3.83	3.95	3.96
PVA/BDMA	1.26	1.45	2.14	2.50	3.59	3.64	4.16	4.80
EGDMA	1.07	1.02	1.57	2.26	3.18	3.19	4.01	4.63
PVA/EGDMA	1.35	1.77	2.29	2.56	3.22	3.70	3.93	4.29
	Adsorption percentage (Ads%)							
BDMA	13	14	26	28	35	48	49	51
PVA/BDMA	17	18	33	40	54	55	62	71
EGDMA	14	15	24	34	41	52	62	69
PVA/EGDMA	23	30	34	40	51	63	69	73
	Partition coefficient (K_d)							
BDMA	0.15	0.16	0.36	0.40	0.54	0.93	0.94	1.04
PVA/BDMA	0.20	0.22	0.48	0.66	1.18	1.21	1.60	2.42
EGDMA	0.16	0.18	0.31	0.50	0.70	1.07	1.60	2.18
PVA/EGDMA	0.30	0.44	0.51	0.67	1.03	1.74	2.18	2.68

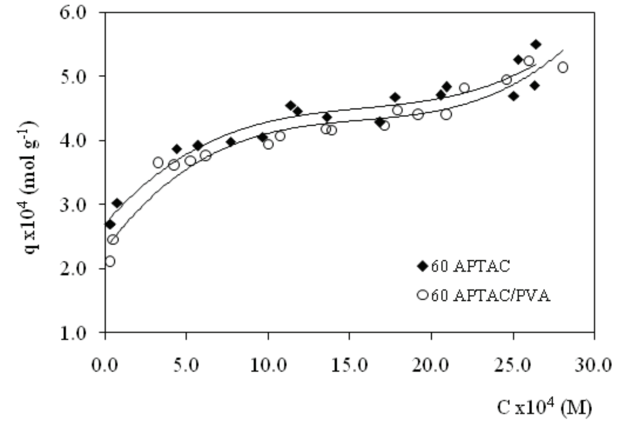


Fig. 14. Equilibrium sorption isotherms of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs crosslinked by BDMA in aqueous solutions of CCA.

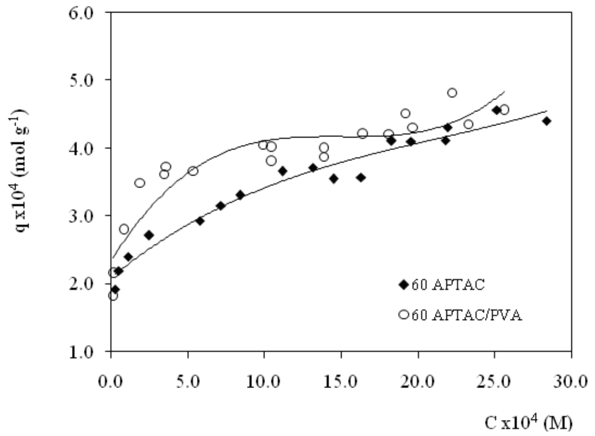


Fig. 15. Equilibrium sorption isotherms of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs crosslinked by EGDMA in aqueous solutions of CCA.

($–N(CH_3)_3Cl$) in aqueous medium. Because of the hydrophilic functional groups and ionizable units of APTAC, swelling percentage and the sorption capacity of the hydrogels and semi-IPNs increase due to increasing of the APTAC content in the copolymeric structure. AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs have many ionic groups that can increase the interaction between the anionic dye molecules and cationic groups of hydrogels. When Table 6 is compared with Table 3, it can be easily seen that the results of sorption studies are parallel character to the results of swelling studies.

3.8. PVA effect on the sorption of CCA

For investigation of the effect of mass/content of PVA on the sorption properties of AAm/APTAC/PVA semi-IPNs, some sorption parameters such as dye removal capacity, adsorption percentage and partition coefficient of AAm/APTAC/PVA semi-IPNs containing 60 μL APTAC are tabulated in Table 7.

It can be seen that there is no significant decreasing or increasing of removal capacity and adsorption percentage of AAm/APTAC/PVA semi-IPNs crosslinked with BDMA when PVA has been added to the hydrogel systems. Moreover, adsorption parameters of AAm/APTAC/PVA semi-IPNs crosslinked with EGDMA are increased due to increasing of PVA content. All K_d values of AAm/APTAC/PVA semi-IPNs (except 0 PVA crosslinked with BDMA) are higher than 1.0. Therefore, it can be said that synthesized crosslinked AAm/APTAC/PVA semi-IPNs could be used as potential water adsorbent for the removal some toxic species from aqueous solutions [44, 45].

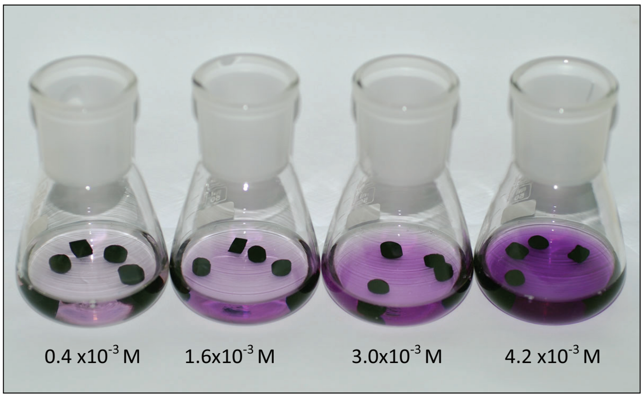


Fig. 16. The digital photo image of AAm/APTAC/PVA semi-IPNs crosslinked by BDMA in various concentrations of aqueous CCA solutions.

Table 7
Some adsorption parameters of AAm/APTAC/PVA semi-IPNs having of 60 μL APTAC crosslinked by BDMA or EGDMA in aqueous solutions of CCA

20% of aq. PVA solution (μL)	0	125	250	375	500
APTAC/60 μL	Dye removal capacity (q × 10^4)				
BDMA	3.83	3.69	3.64	3.53	3.53
EGDMA	3.19	3.60	3.70	3.74	3.79
	Adsorption percentage (Ads%)				
BDMA	48	57	55	54	50
EGDMA	52	60	63	60	61
	Partition coefficient (K_d)				
BDMA	0.93	1.35	1.21	1.16	1.00
EGDMA	1.07	1.50	1.74	1.49	1.57

4. Conclusion

Incorporation of hydrophilic group containing chemicals such as APTAC and a polymer such as PVA in AAm hydrogels can be obtained successively by free radical solution polymerization method. Multifunctional crosslinkers such as BDMA and EGDMA used at the polymerization process. AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs showed high water absorbency. The equilibrium percentage swelling ranges are 782%–7,633% for AAm/APTAC hydrogels and 871–3,257% for AAm/APTAC/PVA semi-IPNs. It was seen that swelling of AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs increased with the increasing of content of APTAC. However, it was seen that S_{eq}% values were decreased from 6,229% to 1,450% when the adding of PVA.

Sorption parameters were also investigated to determine the sorption kinetics of CCA into AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs.

Consequently, AAm/APTAC hydrogels and AAm/APTAC/PVA semi-IPNs developed in this study may serve as a potential device for water and dye sorbent. The utilization of these types of materials, in pharmaceuticals, agriculture, biotechnology, environment, separation, purification and immobilization makes hydrogels more popular.

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