Novel composite sorbent AAm/MA hydrogels containing starch and kaolin for water sorption and dye uptake

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Abstract. A novel polymer/clay composite sorbent based on acrylamide/maleic acid, starch and clay such as kaolin was synthesized with free radical solution polymerization by using ammonium persulfate/*N,N,N',N'*-tetramethylethylenediamine as redox initiating pair in the presence of poly(ethylene glycol)diacrylate as a crosslinker. Surface morphology was characterized by the scanning electron microscopy technique. FT-IR analysis was used to identify the presence of different repeating units in the semi-interpenetrating polymer networks (semi-IPNs). Some swelling and diffusion characteristics were calculated for different semi-IPNs and hydrogels prepared under various formulations. The hydrogels were used in experiments on sorption of water-soluble cationic dye such as toluidine blue. Sorption of toluidine blue into the polymeric systems was studied by the batch sorption technique at 25 °C. Water uptake and dye sorption properties of the crosslinked polymeric systems were investigated as a function of chemical composition of the hydrogels.

Keywords. Acrylamide/maleic acid; composite hydrogel; swelling; dye adsorption; starch; kaolin.

1. Introduction

A lot of synthetic and naturally derived materials have been studied to form well-characterized hydrogels. Natural polymers such as polysaccharides have been studied by many workers (Lanthong *et al* 2006; Patrickios 2010; Hu *et al* 2012; Jing *et al* 2013; Mahdavinia and Asgari 2013). Because of their specific properties, they have been used in many fields of biomedical and biotechnological applications. Starch (St) is a raw material of scientific and industrial process areas. St is a natural, renewable, and biodegradable polymer produced by plants as a source of stored energy. It can be found in many plants. There are two kinds of St: native and modified. The modified St has been used in many industrial and scientific applications. Grafting of acrylamide, acrylonitrile, methacrylonitrile, alkyl methacrylates, vinyl ketones and acrylic acid onto St has been investigated (Lanthong *et al* 2006; Murthy *et al* 2006; Güçlü *et al* 2010; Le Corre *et al* 2010; Patrickios 2010). St grafted copolymers have been used as hydrogels, flocculants, and ion exchangers (Lanthong *et al* 2006; Murthy *et al* 2006; Güçlü *et al* 2010; Le Corre *et al* 2010; Patrickios 2010).

The polymer/clay hydrogel composite has received great attention because of its relatively low production cost and high adsorption capacity for some dyes and metal ions (Li and Wang 2005; Ekici *et al* 2006; Kaşgöz *et al* 2008; Kundakci *et al* 2008, 2009; Gu and Ye 2009; Güçlü *et al* 2010; Mahdavinia and Asgari 2013). To reduce costs and

improve the comprehensive water-absorbing properties of superabsorbent materials based on acrylic monomers, grafting acrylic monomers onto clay and fabricating a composite consisting of a polymer and clay is a priority (Li and Wang 2005; Ekici *et al* 2006; Kaşgöz *et al* 2008; Kundakci *et al* 2008, 2009; Gu and Ye 2009; Güçlü *et al* 2010; Mahdavinia and Asgari 2013). On the other hand, the development and characterization of nanostructured polymer/clay composites have received special attention because of the advantages in comparison to the traditional polymer composites. Minimal additions of nanoclay enhance mechanical, thermal, dimensional and barrier performance properties significantly because of the large contact area between polymer and clay on a nanoscale (Li and Wang 2005; Ekici *et al* 2006; Kaşgöz *et al* 2008; Kundakci *et al* 2008, 2009; Gu and Ye 2009; Güçlü *et al* 2010; Mahdavinia and Asgari 2013). In many previous studies, several kinds of superabsorbent composites based on attapulgite, sepiolite, montmorillonite, kaolin (K) and bentonite were prepared and these superabsorbent composites showed high water absorbency and water retention, good salt resistance, and low production costs in comparison with pure organic superabsorbent polymers under the same preparation condition (Li and Wang 2005; Ekici *et al* 2006; Kaşgöz *et al* 2008; Kundakci *et al* 2008, 2009; Gu and Ye 2009; Güçlü *et al* 2010; Mahdavinia and Asgari 2013).

Water uptake property of hydrogels or ‘hungry networks’ account for a great number of biomedical and technological applications. Highly swollen polymeric gel with the ability to absorb water in high amounts is again under investigation, because of its potential applications in bioengineering,

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biomedicine, and other related areas (Barakat and Sahiner 2008; Yu and Xiao 2008; Moraes *et al* 2009; Ozay *et al* 2009; Kumari *et al* 2010; Li 2010; Kabiri *et al* 2011; Karadağ and Üzümlü 2012). Studies have been reported on the use of hydrogels or hydrophilic characteristic crosslinked polymers or copolymers as adsorbents for the removal of heavy metals, for the recovery of dyes, for removal of toxic or radioactive elements from various effluents and for metal pre-concentration for environmental sample analysis from aqueous solutions (Barakat and Sahiner 2008; Yu and Xiao 2008; Moraes *et al* 2009; Ozay *et al* 2009; Kumari *et al* 2010; Li 2010; Kabiri *et al* 2011; Karadağ and Üzümlü 2012; Ortabay *et al* 2013).

In this study, it was of interest to increase the water and dye sorption capacity of AAm hydrogels with highly hydrophilic functional groups containing chemical reagents such as maleic acid (MA) with St and K via the free radical solution polymerization method. Several MA-based studies by free radical polymerization were reported (Saraydın *et al* 1995; Bajpai 2001; Karadağ *et al* 2002; Murali *et al* 2006; Murthy *et al* 2006). Because of good compatibility, versatility, and non-toxicity, diprotic acids such as maleic acid have been studied by many workers in the preparation of acrylamide-based copolymeric hydrogels (Murthy *et al* 2006).

Here, in this work we have investigated the incorporation of St and K and MA into AAm hydrogel during free radical solution polymerization synthesis. AAm is a highly hydrophilic monomer, MA is an anionic monomer, St is a natural polymer and K is clay. On the other hand, 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 polymer such as poly(ethylene glycol), polyacrylamide, poly(*N*-isopropyl acrylamide), poly(vinyl pyrrolidone), poly(vinyl alcohol) or poly(acrylic acid) (Barakat and Sahiner 2008; Ozay *et al* 2009; Patrickios 2010; Karadağ and Üzümlü 2012). Then, some swelling and some diffusional properties of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems were studied in water using dynamic swelling studies for swelling characterization. Water uptake and dye sorption properties of the hydrogel systems were investigated as a function of chemical composition of the hydrogels.

2. Experimental

Chemically crosslinked highly swollen acrylamide (AAm)/maleic acid (MA) hydrogels were prepared by free radical crosslinking copolymerization of AAm (Merck, Schuchardt, Germany) monomer with addition of an anionic co-monomer such as MA (Merck, Schuchardt, Germany) and a multifunctional crosslinker such as poly(ethylene glycol)diacrylate (PEGDA, $M_n = 700$) as a crosslinker, which were supplied from Aldrich, Steinheim, Germany. Starch (St) was purchased from Carlo Erba, Rodana, Italy, and kaolin (K) was purchased from Fluka, Steinheim, Germany.

To prepare highly swollen AAm hydrogel systems, acrylamide weighing 1.0 g/14.07 mmol was dissolved in 1.0 mL water. Then, 20 mg/0.1723 mmol of MA were added to aqueous other AAm solution (for AAm/MA hydrogels containing 20 mg MA). Then, 40 mg/0.3446 mmol, or 60 mg/0.5169 mmol, or 80 mg/0.6892 mmol of MA were added to other aqueous AAm solutions, respectively for containing different amount of MA. After these additions, for the synthesis, 0.25 mL/0.004 mmol of 1% concentration of PEGDA, 0.2 mL/0.044 mmol aqueous solutions of ammonium persulfate (APS) (5.0 g APS/0.022 mmol/100 mL water) (Merck, Darmstadt, Germany) and 0.25 mL/0.017 mmol 1% concentration of *N,N,N',N'*-tetramethylethylenediamine (TEMED) (Merck, Schuchardt, Germany) were added to these aqueous solutions. The solutions were placed in poly(vinyl chloride) (PVC) straws of 3 mm diameter and these mixture samples were kept in a hot air oven at 70 °C for 30 min. After gelation, fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm in length. They were dried in air and vacuum.

AAm/MA/St composite semi-IPNs were prepared using the same preparation method. But, 1.0 mL of 1.0% aqueous St solution was used instead of distilled water in the related preparation method. To prepare highly swollen AAm/MA/St (containing different contents of St) semi-IPNs, same method was used as mentioned above with the addition of 1.0 mL of 0.5% aqueous St solution, 1.0 mL of 1.5% aqueous St solution, or 1.0 mL of 2.0% aqueous St solution containing 1.0 g AAm and 60 mg MA.

For the preparation of AAm/MA/K and AAm/MA/St/K composite hydrogels, AAm/MA and AAm/MA/St hydrogels were placed in 1.0% kaolin (K)–water suspension systems, and they were mixed on the magnetic stirrer for 3 days.

For swelling studies, chemically crosslinked dried copolymeric hydrogels were accurately weighted and transferred into water. Water uptake with respect to time was obtained by periodically removing the samples from water; quickly blot drying, and reweighing. The measurements were taken at 25 ± 0.1 °C in a water bath.

Batch sorption studies were proceeding in all sorption experiments. Cationic dye, toluidine blue (TB) was used in sorption studies and some properties of TB are given in table 1. Solutions of TB concentration ranging from 3.00×10^{-5} to 6.00×10^{-5} M in distilled water were prepared. AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems were used in a known volume of dye solution until equilibrium was reached. For MA, St and K effects on the dye sorption, aqueous solutions of concentration of 5.00×10^{-5} M of TB were 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 an ambient temperature. The absorbances of these solutions were read at 626 nm for TB (Karadağ *et al* 2006, 2009). Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales.

Table 1. Some properties of Toluidine Blue.

Name	Chemical formula	Molar mass (g mol ⁻¹)	λ_{mak} (nm)	C.I. Nr.
Toluidine Blue, Basic Blue 17 (TB)		305.83	626	52040

Figure 1. The photographs of AAm/MA and AAm/MA/St hydrogel systems (as dry state or swollen state).

For structural characterization, FT-IR analysis was made. Spectra were taken on KBr discs using VARIAN FTS 800 FT-IR spectrophotometer.

The surface morphology of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems was visualized by a scanning electronic microscope PHILLIPS XL-30S FEG. For the characterization technique of the surface morphology of the samples, swollen samples were used.

3. Results and discussion

Highly swollen AAm/MA and AAm/MA/St hydrogel systems were prepared by free radical solution polymerization. The structure of copolymers is random. Then AAm/MA/K and AAm/MA/St/K hydrogel systems were prepared by loading of K. Dried AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems are glassy and very hard, but swollen gels are soft. The photographs of the crosslinked polymeric systems are presented as dry state or swollen state in figure 1. Swelling of the hydrogels was strong enough to retain their shape.

3.1 FT-IR analysis

FT-IR spectra of the hydrogel systems were evaluated and are presented in figure 2. In figure 2, more wide peak at

Figure 2. FT-IR spectra of the hydrogel systems containing of 60 mg MA. (1) AAm/MA; (2) AAm/MA/St; (3) AAm/MA/K and (4) AAm/MA/St/K.

3000–3500 cm⁻¹ than spectra of AAm/MA is seen. 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. It is thought that the peaks at 3600–3700 cm⁻¹ are O–H bands and absorption peaks between 3400 and 3600 cm⁻¹, which

is due to stretching bands of the OH groups of MA and K. Also, the peaks at 1110 cm^{-1} are Si–O bands and the peaks at $900\text{--}980\text{ cm}^{-1}$ are Al–O–H bands for K. There may be some peaks at 1400 for the bands of C–N for starch. The peaks observed between 1600 and 1700 cm^{-1} correspond to the C=O of the acrylate unit of MA. The peaks observed in this region also correspond to the C=O group of AAm. On the other hand, it is thought that the peaks at $1250\text{--}1300\text{ cm}^{-1}$ are C–N bands, and the peaks at $2800\text{--}2900\text{ cm}^{-1}$ and 1400 cm^{-1} show $-\text{CH}_2-$ groups on the polymeric chain. Broad peaks between 3200 and 3600 and a sharp peak at approximately $1600\text{--}1700\text{ cm}^{-1}$ in the IR spectra of IPN hydrogel can indicate the presence of the AAm and MA units along with S and K repeating units in the polymeric hydrogels (Xu *et al* 2005; Lanthong *et al* 2006; Pourjavadi *et al* 2008; Patel *et al* 2011).

3.2 Scanning electron microscopy (SEM) studies

SEM is the most used technique to investigate the shape, size, morphology, crosslink and porosity of hydrogels or other related materials. Six SEM micrographs of the crosslinked copolymeric samples are presented in figure 3 as representative. The micro-structural differentiations can be followed from figure 3. If figure 3 is examined, a lot number of porous and crosslinked structure can be seen.

3.3 Equilibrium swelling studies

The percentage swelling ($S\%$) of the hydrogels in distilled water was calculated from the following relation:

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

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

The water intake of initially dry hydrogels was followed for AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems containing 60 mg MA, and 1.0% K crosslinked by PEGDA in water, and swelling isotherms of AAm/MA/St hydrogels are shown in figure 4 as representative.

Figure 4 shows that swelling increases with time up to a certain level, then levels off. This value of swelling may be called as the equilibrium swelling percent ($S_{eq}\%$). $S_{eq}\%$ values of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems containing 60 mg MA, and 1.0% K are given in table 2. Table 2 shows that $S_{eq}\%$ of AAm hydrogels is 1050%, but $S_{eq}\%$ values of AAm/MA are 3200–5750% with the incorporation of MA groups into AAm hydrogels.

The values of $S_{eq}\%$ of AAm/MA/St semi-IPN hydrogels containing 1.0% St are 2815–5250% with the incorporation of St into AAm/MA hydrogels, while $S_{eq}\%$ value of AAm/St hydrogel is 1055%. On the other hand, $S_{eq}\%$ values

of AAm/MA/K hydrogels containing 1.0% of K are 5770–10650 with the incorporation of K groups into AAm/MA hydrogels, while $S_{eq}\%$ value of AAm/K hydrogels is 1175. $S_{eq}\%$ values of AAm/MA/St/K semi-IPN hydrogels containing 1.0% St and 1.0% K are 3400–8135 with the incorporation of St and K into AAm/MA hydrogels, while $S_{eq}\%$ value of AAm/St/K semi-IPN is 1170 (table 2). In table 2, $S_{eq}\%$ of the hydrogels increased with the MA content in the copolymers. $S_{eq}\%$ of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogels is higher than $S_{eq}\%$ of AAm hydrogels.

MA contains a lot of ionizable/anionic groups ($-\text{COOH}$). The increasing of the values of $S_{eq}\%$ is due to an increase in the ionizable/anionic units. The hydrophilic group numbers of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems are higher than those of AAm, and so the swelling values of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems are greater than that of AAm swelling values.

It was shown that there was a decrease in the equilibrium swelling percent ($S_{eq}\%$), of the semi-IPN systems when St was added to the hydrogel systems. Incorporation of St into the copolymer network leads to lower degrees of swelling. The reason of this is the polymeric structure of St. Here, it could be said that chains of St were placed in the crosslinked polymeric systems, instead of crosslinked AAm and MA groups. So, it was seen that there was a decrease in the value of the $S_{eq}\%$, because of the decrease in hydrophilic character at crosslinked polymeric systems. But there was an increase in the $S_{eq}\%$ of the hydrogel systems when K was added to the hydrogel systems. It was seen that there was an increase in the value of the $S_{eq}\%$, because of an increase in the hydrophilic character at crosslinked polymeric systems.

The water absorbed by AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems was quantitatively represented by equilibrium water content (EWC), and it can be calculated using the below equation (Saraydin *et al* 2004; Kundakcı *et al* 2008, 2009; Karadağ and Üzümlü 2012):

$$\text{EWC} = \frac{m_{eq} - m_0}{m_{eq}} \quad (2)$$

Here, m_{eq} is the mass of the swollen gel at time t (equilibrium), and m_0 the mass of the dry gel at time 0.

The values of EWC of all AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems were calculated. The values of EWC of the hydrogels are tabulated in table 2. They are changed between 0.9131 and 0.9908. It is seen that there is an increase in the values of EWC, if MA has been added to the hydrogel systems. Here, the main effect is the hydrophilic character of MA groups.

3.4 Diffusion

The following equation is used to determine the nature of diffusion of water into hydrogels (Peppas and Franson 1983;

Saraydın *et al* 2004; Kundakcı *et al* 2008, 2009; Karadağ and Üzümlü 2012):

$$F = \frac{M_t}{M_s} = kt^n. \quad (3)$$

Here, F is the fractional uptake at time t and, M_t and M_s the mass uptake of the solvent 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

Figure 3. SEM images of the hydrogel systems containing 60 mg MA.

transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. This is reflected by n between 0.5 and 1.0 (Peppas and Franson 1983; Saraydın *et al* 2004). The values of n and k were calculated from the slope and the intercept of the plot of $\ln F$ against $\ln t$, respectively.

For AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems, $\ln F$ vs $\ln t$ graphs are plotted and representative results are shown in figure 5. Diffusional exponents (n) and diffusion constant (k) are calculated and listed in table 3.

Table 3 shows that the number determining the type of diffusion (n) is over 0.50. Hence the diffusion of water into the hydrogel systems is generally found to have a non-Fickian character. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude.

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

(Dengre *et al* 2000; Çaykara *et al* 2006; Karadağ and Üzümlü 2012):

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

Here, D in $\text{cm}^2 \text{min}^{-1}$, r the radius of a cylindrical polymer sample, n the diffusional exponent and k a constant incorporating characteristic of the macromolecular network system and the penetrant. The values of diffusion coefficient determined for AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems are listed in table 3.

Table 3 shows that the values of the diffusion coefficient of the hydrogel systems vary from 0.45×10^{-4} to $10.22 \times 10^{-4} \text{cm}^2 \text{min}^{-1}$. It was seen that generally there was an increase in the values of the diffusion coefficient of the hydrogel systems by increasing of MA content. It can be said that there is no good relation between the values of the diffusion coefficient of the hydrogel systems.

3.5 Starch and kaolin effect on the swelling and diffusion

For investigation of the effect of mass/content of St and K on the swelling properties of AAm/MA/St and AAm/MA/St/K hydrogel systems containing 60 mg MA, 1.0% K and different contents of St such as 0.5%, 1.0%, 1.5% and 2.0%, the related swelling isotherms and swelling kinetics curves of hydrogel systems were constructed and representative swelling isotherms are shown in figure 6. Effect of St and K on some swelling and diffusion parameters at AAm/MA/St and AAm/MA/St/K hydrogel systems containing 60 mg MA, 1.0% K and different contents of St such as 0.5%, 1.0%, 1.5% and 2.0% is tabulated in table 4. For good characterization, changing of $S_{\text{eq}}\%$ values of the hydrogel systems by various contents of St is also shown in figure 6.

It was shown that there was a decrease in the equilibrium swelling percent ($S_{\text{eq}}\%$) of the semi-IPN systems when St was added to the hydrogel systems. Incorporation of St into the copolymer network leads to lower degrees of swelling. The reason of this is the polymeric structure of

Figure 4. Swelling isotherms of AAm/MA/St semi IPN hydrogels.

Table 2. Values of the equilibrium percentage swelling and equilibrium water contents of the hydrogels.

	AAm/MA	AAm/MA/St	AAm/MA/K	AAm/MA/St/K
MA/mg	Equilibrium swelling percent ($S_{\text{eq}}\%$)			
0	1050	1055	1175	1170
20	3200	2815	5770	3400
40	4345	3220	7495	4600
60	5145	4095	10090	6040
80	5750	5250	10650	8135
	Equilibrium water contents (EWC)			
0	0.9131	0.9135	0.9216	0.9212
20	0.9697	0.9657	0.9830	0.9714
40	0.9775	0.9699	0.9868	0.9787
60	0.9809	0.9762	0.9902	0.9837
80	0.9829	0.9813	0.9908	0.9879

St. Here, it could be said that chains of St were placed in the crosslinked polymeric systems, instead of crosslinked AAm and MA molecules. So, it was seen that there was a decrease in the value of the $S_{eq}\%$, because of the decrease in the hydrophilic character at crosslinked polymeric systems. But there was generally an increase in the $S_{eq}\%$ of the hydrogel systems when K was added to the hydrogel systems. It was seen that there was an increase in the value of the $S_{eq}\%$, because the increase in the hydrophilic character at crosslinked polymeric systems.

3.6 Equilibrium sorption studies

To observe the sorption of toluidine blue (TB) onto AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems containing 60 mg MA, and 1.0% K, the hydrogel systems were placed in aqueous solutions of TB and allowed to equilibrate for four days at 25 °C. At the

Figure 5. Swelling kinetic curves of AAm/MA hydrogels.

end of this period, AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems in the TB solutions showed the dark coloration. But AAm hydrogel did not sorb any dye from the solution.

In the sorption system at equilibrium, the total solute (dye) concentration, C_0 , is calculated using the following equation (Molyneux 1984; Molyneux and Vekavakayanondha 1986):

$$C_0 = C_b + C. \quad (5)$$

Here, C_b is the equilibrium concentration of the solute (dye) on the sorbent per liter solution (bound solute concentration) and C the equilibrium concentration of the solute in the solution (free solute concentration). The value of the bound concentration may be obtained using (5).

For equilibrium sorption studies, dye removal capacity (q) (mass amount as 'mol' of sorption per unit mass (as gram)) of the adsorbent, adsorption percentage (Ads%), and partition coefficient (K_d) can be investigated.

The dye removal capacity (q) of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems containing 60 mg MA, and 1.0% K was evaluated using the following equation:

$$q = \frac{(C_b)v}{m}, \quad (6)$$

where q is the dye removal capacity of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems (mol g^{-1}), v the volume of the aqueous phase (L) and m the mass of dry hydrogels. C_b has been defined earlier.

Adsorption percentage (Ads%) of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems was calculated using following equation:

$$\text{Ads}\% = \frac{C_0 - C}{C_0} \times 100. \quad (7)$$

C_0 and C have been defined earlier.

Table 3. Some diffusion parameters of hydrogel systems.

	AAm/MA	AAm/MA/St	AAm/MA/K	AAm/MA/St/K
MA/mg	Diffusion exponent (n)			
0	0.61	0.54	0.67	0.63
20	0.70	0.70	0.81	0.71
40	0.77	0.73	0.91	0.78
60	0.81	0.76	0.92	0.76
80	0.86	0.81	0.99	0.81
	Diffusion constant ($k \times 10^3$)			
0	29.85	37.61	19.37	25.59
20	8.65	7.76	4.87	8.68
40	5.16	7.08	3.21	5.33
60	3.62	5.20	3.42	5.24
80	2.98	3.38	2.40	3.23
	Diffusion coefficient ($D \times 10^4$) ($\text{cm}^2 \text{min}^{-1}$)			
0	1.24	0.45	1.63	1.23
20	1.80	1.25	3.23	2.19
40	2.39	1.64	5.50	2.76
60	2.73	2.16	8.18	2.61
80	3.94	2.16	10.22	2.72

Figure 6. Swelling isotherms of AAm/MA/St hydrogels with various contents of St.

Firstly, uptake of dye measured effects of contents of MA. The dye removal capacity, that is, the amount of dyes sorbed onto unit dry mass of the gel was calculated for uptake of dye within the hydrogel in 5.00×10^{-5} M of TB in L of aqueous solutions and presented in table 5. Also, Ads% of the hydrogel systems has been calculated and presented in table 5, too.

Table 5 presents the dye removal capacity of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems (3.14×10^{-6} – 41.89×10^{-6} mol g⁻¹) and their adsorption percentage (24.36–94.00%) is increased by increasing the content of MA. If the dye removal capacity and adsorption percentage of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems are

Table 4. Some swelling and diffusion parameters of AAm/MA/St and AAm/MA/K hydrogels having of 60 mg MA with different St and 1.0% K contents.

Content of St	0.5%	1.0%	1.5%	2.0%
<i>Equilibrium swelling percent ($S_{eq}\%$)</i>				
Kaolin	4960	4095	3395	2965
	7735	6040	4895	1715
<i>Equilibrium water contents (EWC)</i>				
Kaolin	0.9798	0.9762	0.9714	0.9674
	0.9872	0.9837	0.9800	0.9449
<i>Diffusion exponent (n)</i>				
Kaolin	0.79	0.76	0.71	0.71
	0.78	0.76	0.70	0.61
<i>Diffusion constant ($k \times 10^3$)</i>				
Kaolin	3.94	5.20	6.29	6.65
	4.30	5.24	6.64	13.13
<i>Diffusion coefficient ($D \times 10^4$) (cm² min⁻¹)</i>				
Kaolin	2.83	2.16	1.35	0.92
	3.53	2.61	1.49	0.79

Table 5. Some adsorption parameters of the hydrogel systems in aqueous solutions of TB.

	AAm/MA	AAm/MA/St	AAm/MA/K	AAm/MA/St/K
<i>Adsorption percentage (Ads%)</i>				
MA/mg				
20	24.36	24.65	70.90	81.51
40	30.10	31.33	78.31	85.57
60	27.27	25.16	90.80	88.84
80	34.45	42.08	89.13	94.00
<i>Dye removal capacity ($q \times 10^6$) (mol g⁻¹)</i>				
20	10.20	7.03	3.14	30.97
40	9.85	8.56	4.23	29.75
60	11.65	7.93	7.80	33.15
80	13.05	12.43	7.10	41.89
<i>Partition coefficient (K_d)</i>				
20	0.32	0.33	2.44	4.41
40	0.43	0.46	3.61	5.93
60	0.37	0.34	9.87	7.96
80	0.53	0.73	8.20	15.65

Figure 7. Equilibrium sorption isotherms of AAm/MA/St hydrogels in aqueous solutions of TB.

Figure 8. Equilibrium sorption isotherms of AAm/MA/St/K hydrogels in aqueous solutions of TB.

Table 6. Some adsorption parameters of AAm/MA/St and AAm/MA/K hydrogels having of 60 mg MA with different St and 1.0% K contents in aqueous solutions of TB.

Content of St	0.5%	1.0%	1.5%	2.0%
<i>Adsorption percentage (Ads%)</i>				
Kaolin	30.82	25.16	38.96	36.34
	86.08	88.84	84.19	81.65
<i>Dye removal capacity ($q \times 10^6$) (mol g⁻¹)</i>				
Kaolin	7.96	7.93	9.76	9.05
	24.40	33.15	25.21	22.51
<i>Partition coefficient (K_d)</i>				
Kaolin	0.45	0.34	0.64	0.57
	6.18	7.96	5.33	4.45

examined, it was seen that it was seen that there was not good relationship with the addition of St and K.

Partitioning of dissolved constituents between an aqueous phase and adsorbents in water 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 (Şahiner *et al* 1998; Schwarte and Peppas 1998)

$$K_d = \frac{C_b}{C}. \quad (8)$$

Here, K_d is the empirical partition coefficient at equilibrium. C_b and C have been defined earlier. Partition coefficients of TB between dye solution and AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems containing 60 mg MA and 1.0% K were calculated, and are shown in table 5. K_d values of the hydrogel systems range from 0.32 to 15.65 as shown in table 5. Here, some of K_d values of the hydrogels are higher than 1.0. So, it can be said that synthesized AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems could be used as a potential water adsorbent (Şahiner *et al* 1998; Schwarte and Peppas 1998).

Equilibrium adsorption isotherms of AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems containing 60 mg MA and 1.0% K were plotted, and equilibrium adsorption isotherms of AAm/MA/St and AAm/MA/St/K hydrogels are presented in figures 7 and 8.

In figures 7 and 8, the dye removal capacity (mol amount of sorption TB per unit mass) of the hydrogel systems is increased with the increasing concentration TB sorbed onto unit dry mass of the gel. The reason of this is the hydrophilic effect and dye sorption capability of co-monomer.

There can be many reasons for non-covalent interactions in the binding of TB by AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems. The main interactions between the hydrogel and the monovalent cationic dye 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 repeating units of crosslinked polymer. Hydrophobic effects are especially aqueous solutions interactions, which in the present case will involve those aromatic rings 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.

3.7 Starch and kaolin effects on the sorption of TB

For investigation of starch (St) and kaolin (K) effects on dye sorption, some adsorption parameters such as dye removal capacity, adsorption percentage and partition coefficient of AAm/MA/St and AAm/MA/St/K hydrogel systems containing 60 mg MA, 1.0% K and different contents of St such as 0.5%, 1.0%, 1.5% and 2.0% contents in aqueous solutions of TB were calculated and are tabulated in table 6.

It was shown that the values of the dye removal capacity of AAm/MA/St and AAm/MA/K hydrogels were between 7.93×10^{-6} and 33.15×10^{-6} mol g⁻¹. Also, incorporation of St and K into the copolymer network leads to different values of adsorption percentage (25.16–38.96% for St addition and 81.65–88.84% for K addition) and partition coefficient (0.34–0.64 for St addition and 4.45–7.96 for K addition) of AAm/MA/S and AAm/MA/S/K hydrogel systems. But, it was said that if K chains were placed in the crosslinked polymeric systems, it was seen that it decreased the sorption parameters. Here, some of K_d values of the hydrogels are higher than 1.0. So, again, it can be said that synthesized AAm/MA/St/K hydrogel systems could be used as potential water adsorbent for removal of the dye molecules or other big molecular structures similar to dye molecules.

4. Conclusions

Incorporation of hydrophilic group containing chemicals such as maleic acid and the polymers such as starch and a clay such as kaolin in AAm hydrogels can be obtained successively by the free radical solution polymerization method. Multifunctional crosslinkers such as PEGDA were used in the polymerization process. AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems have showed high water absorbency. Some swelling and diffusion properties were discussed for different semi-IPNs and hydrogels prepared under various formulations. To determine the sorption characteristics of a cationic dye such as 'Toluidine blue' into the hydrogel systems, some sorption parameters have been calculated. For equilibrium sorption studies, dye removal capacity, adsorption percentage and partition coefficient of the hydrogel systems have been investigated. Consequently, AAm/MA, AAm/MA/St, AAm/MA/K and AAm/MA/St/K hydrogel systems developed in this study may serve as a potential device for water and dye sorbent. The use of these types of materials in agriculture, environment, separation and purification makes hydrogels more popular.

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