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Uptake of Basic Blue 17 from aqueous solutions by using chemically crosslinked polyelectrolyte AAm/AASS hydrogels

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Abstract In this study, the removal of a cationic thiazin dye such as Basic Blue 17 (Toluidin Blue, BB 17) by chemically crosslinked acrylamide (AAm)/acrylic acid sodium salt (AASS) hydrogels was investigated. Super water retainer AAm/AASS hydrogels with various compositions were prepared from ternary mixtures of AAm, AASS and water by free radical polymerization in aqueous solution using multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA), N,N' methylenebisacrylamide (NMBA), 1,4 butanediol dimethacrylate (BDMA) and trimethylolpropane triacrylate (TMPTA). Adsorption of Basic Blue 17 from aqueous solutions was studied by batch sorption technique at 25°C. The effect of Basic Blue 17 concentration and mass of adsorbent on the dye adsorption were examined.

In the experiments of the sorption, *C type* and *L type sorption* in the Giles classification system was found. Some binding parameters such as initial binding constant (K_i), equilibrium constant (K), monolayer coverage (*n*), site-size (*u*), and maximum fractional occupancy ($\hat{O}$) for AAm/AASS hydrogel-dye binding system were calculated by using Klotz linearization method. Finally, the amount of sorbed Basic Blue 17 per gram of dry hydrogel (q) was calculated to be 1.96–21.35 μmol dye per gram for AAm/AASS hydrogels. Adsorption of Basic Blue 17 was changed range 39.17–96.63%. AAm/AASS hydrogels crosslinked by TMPTA, EGDMA, BDMA or NMBA can be used a sorbent in biotechnology, environment, sorption, separation, purification, immobilization and enrichment of some species.

1 Introduction

Hydrogels are three-dimensional networks of hydrophilic polymer chains with properties between liquids and solids. Hydrogels are chemically or physically crosslinked polymers that can absorb large amounts of water without dissolving and without loosing their shapes. They are a unique class of polymeric materials that imbibe enormous amount of water when left in a water reservoir for long times. They are crosslinked macromolecules with segments of hydrophilic groups (Omidian et al., 2005; Fernandez et al., 2005; Devine et al., 2005).

Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, food industry and water purification and separation process. Due to 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, environmental applications. Although many naturally occurring polymers may be used to produce this type of materials, the structural

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versatility available in synthetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility (Gombotz and Hoffman, 1986; Peppas and Mikos, 1986; Şahiner et al., 1998; Güven et al., 1999; Kioussis et al., 2000; Byrne et al., 2002; Gupta et al., 2002; El-Hag Ali et al., 2003; Crini, 2005).

In recent years polymeric gels (hydrogels) are the objects of intensive studies. Hydrogels have special properties due to their intermediate state between a liquid and a solid. The ability to absorb and to store much water and water solutions make hydrogels unique materials for a variety of applications. Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, food industry and water purification and separation process (Karadağ et al., 1996; Saraydın et al., 1996; Karadağ et al., 2002a; Karadağ and Saraydın 2002b; Karadağ and Saraydın 2002c; Ekici et al., 2003; Şolpan et al., 2003). Polyacrylamide based hydrogels find many applications such as purification of wastewater and metal extraction (Karadağ et al., 1995; Saraydın et al., 1995; Güven et al., 1999; Yao and Zhou, 1999; Durmaz and Okay, 2002; Şolpan et al., 2003; Saraydın et al., 2004).

Many methods have been proposed for the removal of heavy metals, the removal of the herbicides, the treatment of slaughter wastewaters, septic tank effluents and dairy wastes (Ho and McKay, 1998). Chemical precipitation, membrane extraction, coagulation, complexing, solvent extraction, ion change, and adsorption are some of the commonly used process, but each has its own merits and demerits in its applications. Adsorption is the most popular method for wastewater treatment due to its easy and inexpensive operation. Adsorption or ion exchange using different polymeric materials and synthetic resins is the method of choice in much wastewater treatment process 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 heavy metals, for the recovery of dyes, for removal of toxic or radioactive elements from various effluents and for metal preconcentration for environmental sample analysis from aqueous solutions (Rifi et al., 1995; Li et al., 2002; Manju et al., 2002; Ekici et al., 2003; Wang et al., 2005).

Dyes in water affect the nature of the water, inhibiting sunlight penetration into the stream and reducing the photosynthetic reactions. On the other hand, some dyes are carcinogenic and toxic (Zollinger, 1991; Wang et al., 2005). Effective removal of dyes, in connection with wastewater treatment strategy, still remains a major topic of present research. The use of polymer hydrogels for the removal of dyes from wastewater has been continued to attract considerable attention in recent years. This paper deals with experimental investigations of the sorption behavior of AAm/AASS hydrogels for Basic Blue 17 removal from aqueous solutions.

2 Materials and methods

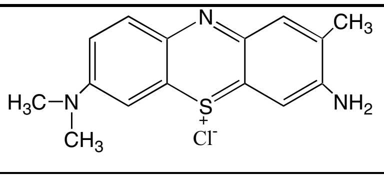
2.1 Experimental materials

The sources of water, the monomers, acrylamide (AAm) and acrylic acid sodium salt (AASS) were given before (Karadağ and Saraydın 2002b). Cationic dye, Basic Blue 17 was obtained from Aldrich (Darmstadt, Germany). Some properties of Basic Blue 17 were given in Table 1.

2.2 Preparation of AAm/AASS hydrogels

Chemically crosslinked AAm/AASS hydrogels were prepared by free radical crosslinking copolymerization

Table 1 Some properties of Basic Blue 17

Name	Chemical Formula	Molar Mass ($g\,mol^{-1}$)	λ_{mak}(nm)	C.I. Nr.
Toluidin Blue, Basic Blue 17 (BB-17)		305.83	626	52040

of AAm monomer with addition of an anionic comonomer such as AASS and some multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA), *N,N′* methylenebisacrylamide (NMBA), 1,4 butanediol dimethacrylate (BDMA) and trimethylolpropane triacrylate (TMPTA). The modes of purification and specifications of the sources of water, the monomers, crosslinkers, initiator; ammonium persulphate (APS) and activator; *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TEMED) were given in our related study (Karadağ and Saraydın, 2002b).

2.3 Sorption studies

Solutions of the dye, Basic Blue 17, containing 6.54–52.32 μmol L^{-1} Basic Blue 17 in distilled water was prepared. AAm/AASS hydrogels containing 40 mg AASS was used in a known volume of dye solution until equilibrium was reached. 0.1 g of AAm/AASS hydrogels were transferred into 50 mL of the aqueous Basic Blue 17 solution and allowed to equilibrate for four days at 25°C in a water bath. For AASS effect on the dye sorption, dye solution of concentration of 30.0 μmol L^{-1} 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 626 nm. Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales. The amounts of dye sorbed were determined from the initial and final concentrations of the solutions, calculated from the measured absorbances.

The adsorption percentage (*Ads. %*) was calculated as;

$$Ads.\% = \frac{C_o - C}{C_o} \times 100 \tag{1}$$

Where C_o and C are the concentrations of Basic Blue 17 in the initial solution and the aqueous phase after treatment for a certain period time, respectively (μmol L^{-1}).

The amount (μmol) of sorption per unit mass of the AAm/AASS hydrogels, (q) were evaluated by using the following equation (Ekici et al., 2003):

$$q = \frac{(C_o - C)v}{m} \tag{2}$$

Where q is the amount (μmol) of Basic Blue 17 sorbed onto unit dry mass of the AAm/AASS hydrogels (μmol g^{-1}), and v, is the volume of the aqueous phase (L) and m is the amount of dry AAm/AASS hydrogels (g).

3 Results and Discussion

3.1 Preparation

AAm/AASS hydrogels were prepared by free radical crosslinking copolymerization of acrylamide monomer with addition of sodium acrylate and some multifunctional crosslinkers such as ethylene glycol dimethacrylate (EGDMA), *N*,*N′* methylenebisacrylamide (NMBA), 1,4 butanediol dimethacrylate (BDMA) and trimethylolpropane triacrylate (TMPTA). (Tanaka, 1981; Hennink and van Nostrum, 2002; Karadağ et al., 2002a; Karadağ and Saraydın, 2002b; Karadağ and Saraydın 2002c). Possible copolymerization mechanism is presented in Figure 1. Some information and experimental details of used water, the monomers, acrylamide and sodium acrylate, the crosslinkers; EGDMA, NMBA, BDMA and TMPTA, initiator, ammonium persulphate (APS) and activator; *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TEMED) were given in our previous study (Karadağ and Saraydın, 2002b).

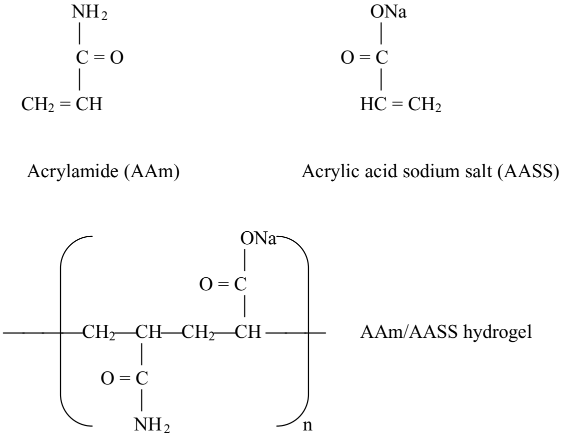


Fig. 1 The molecular formula of acrylamide (AAm), acrylic acid sodium salt (AASS) and possible crosslinked acrylamide/acrylic acid sodium salt copolymer (AAm/AASS hydrogel)

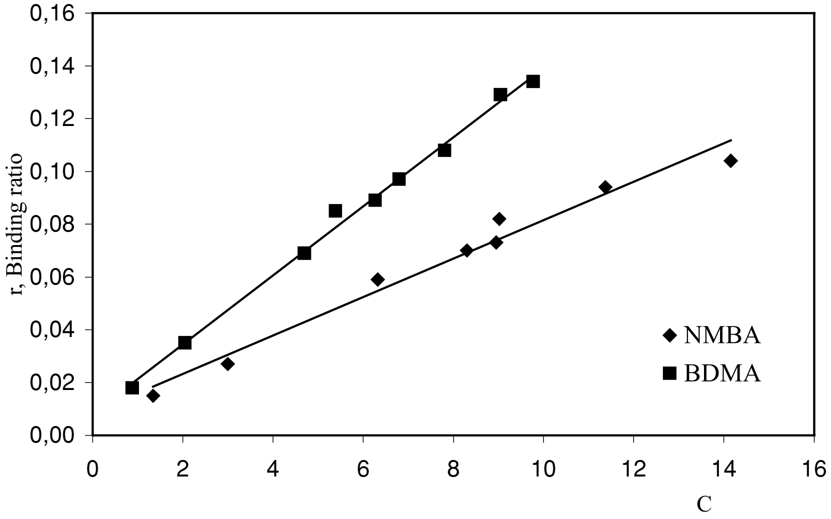


Fig. 2 Binding isotherm of AAm/AASS hydrogel crosslinked by NMBA and BDMA for Basic Blue 17 binding system

3.2 Binding characterization

To observe the sorption of Basic Blue 17, AAm/AASS hydrogels were placed in aqueous solutions of Basic Blue 17 and allowed to equilibrate for four days at 25°C. At the end of this period AAm/AASS hydrogels in the Basic Blue 17 solutions showed the dark blue (the color of Basic Blue 17 salt) coloration. But acrylamide hydrogel did not sorb any dye molecules from dye solutions.

In the sorption system at equilibrium, the total solute (dye) concentration; C_o is following equation:

$$C_o = C_b + C \tag{3}$$

Where C_b is the equilibrium concentration of the solute (dye) on the sorbent per liter solution (bound solute concentration) and C is the equilibrium concentration of the solute in the solution (free solute concentration). The value of the bound concentration may be obtained by using Eq. 3. For a fixed free solute concentration, C_b is proportional to the polymer concentration on the binding system; the amount bound can therefore be conveniently expressed as the binding ratio r, defined by

$$r = C_b/P \tag{4}$$

Thus, with in and P is base mol (moles of monomer units) per liter solute represents the average number of molecules of solute bound each monomer unit at that free solute concentration (Molyneux, 1984, Molyneux and Vekavakayanondha, 1986). To determine the sorption kinetics of Basic Blue 17 into AAm/AASS hydrogels, some plots of the binding ratio (r) against the free concentration of dyes are shown in Figure 2 and Figure 3. Fig. 2 and Fig. 3 show that sorption of Basic Blue 17 with in AAm/AASS hydrogels corresponds to *C type* sorption isotherms for crosslinked by NMBA and BDMA, and to *L type* sorption isotherms for crosslinked by EGDMA and TMPTA in the Giles classification system for sorption of the dye from its solution (Giles et al., 1974a; Giles et al., 1974b).

The binding data was interpreted on the basis of the uniform site-binding ($u.s.b.$) model, which in statistical-thermodynamic terms corresponds to a formation of an ideal localized one-dimensional monolayer of solute on the polymer chains (Molyneux, 1984; Molyneux and Vekavakayanondha, 1986). This leads to the hyperbolic (Langmuir) form of the binding isotherm, which applies to many polymer/solute (dye molecule) binding system.

$$r = \frac{nKC}{1 + KC} \tag{5}$$

Where K is the binding constant, i.e. the equilibrium constant for the attachment of a dye molecule onto a site by a specific combination of non-covalent forces. Here n is the site density (the limiting value of r for monolayer coverage) which is therefore of density of the sites along the polymer chain. To reciprocal of n is the site-size, u, which may be taken to represent either average number of monomer units occupied by the bound solute molecule, more generally the average spacing of solute molecules when the chain is saturated. The initial binding constant, K_i is the initial slope of

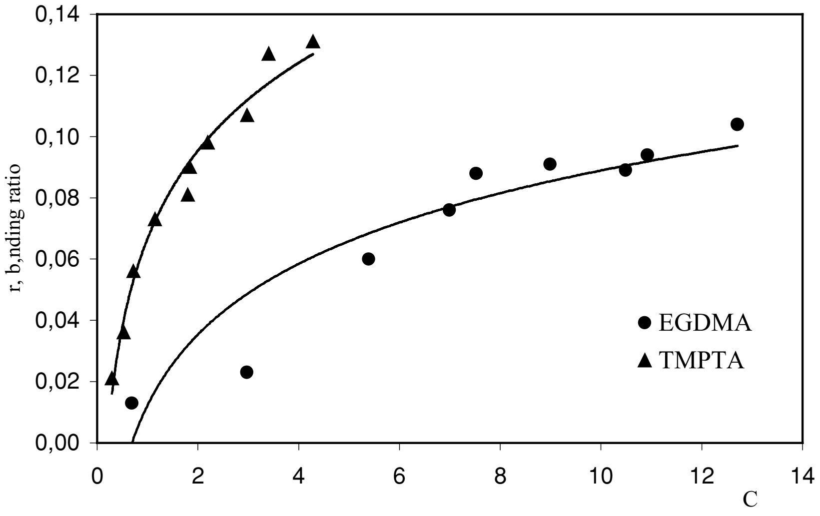


Fig. 3 Binding isotherm of AAm/AASS hydrogel crosslinked by EGDMA and TMPTA for Basic Blue 17 binding system

the binding isotherm, and therefore the average binding strength of a solute molecule by a single monomer unit on an occupied chain. K_i is equal to the product Kn.

To get the best values for the binding parameters from the experimental data, the linearization methods of Eq. 5 have been developed by some researches as Klotz, Scatchard and Langmuir (Molyneux, 1984; Molyneux and Vekavakayanondha, 1986).

3.3 Klotz linearization method

If the isotherm (Eq. 5) is multiplied out and then divided throughout by $C\,K\,n\,r$, this gives;

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nK}\frac{1}{C} \tag{6}$$

Thus if this isotherm holds than a plot of $1/r$ vs. $1/C$ will be straight line of slope $1/Kn$, ordinate intercept $1/n$. This is very simple method of plotting, with the scatter in the r and C values reflected in the scatter in the ordinate and abscissa values, respectively. Its limitations are that the intercepts may be small and hence difficult to read off.

The Klotz plots of AAm/AASS hydrogel – Basic Blue 17 binding systems are shown in Figure 4–7, respectively, and the binding parameters for AAm/AASS hydrogel-Basic Blue 17 binding systems are calculated from the intercept and slopes of the binding isotherm method.

The binding parameters K_i, K, n and u are listed in Table 2 for AAm/AASS hydrogel – Basic Blue 17 binding systems. In Table 2, the final column contains

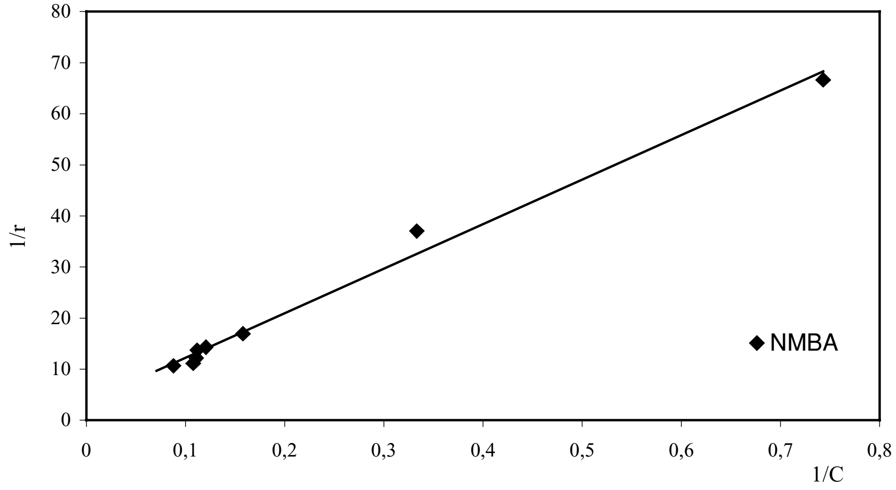


Fig. 4 Klotz plot of AAm/AASS hydrogel crosslinked by NMBA for dye binding system

Fig. 5 Klotz plot of AAm/AASS hydrogel crosslinked by EGDMA for dye binding system

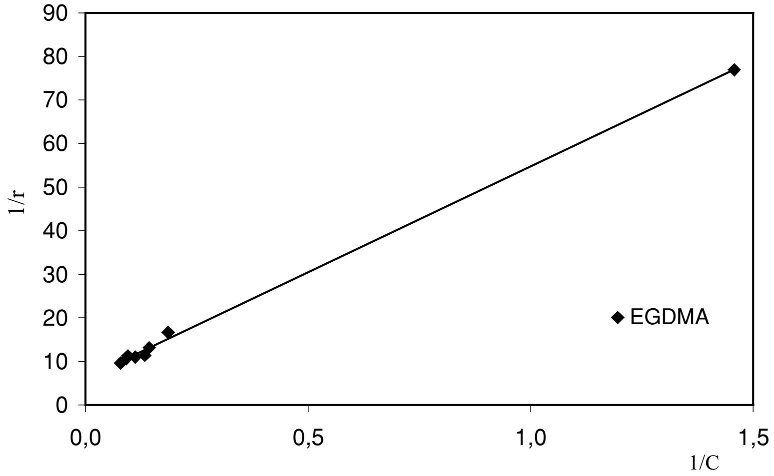


Fig. 6 Klotz plot of AAm/AASS hydrogel crosslinked by BDMA for dye binding system

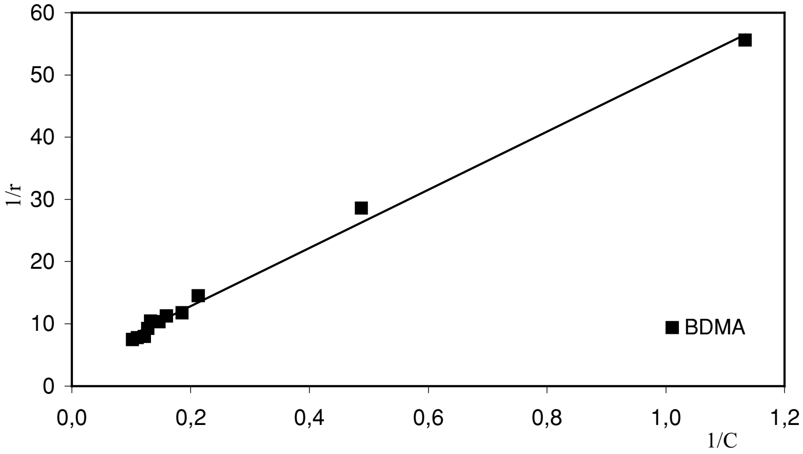


Fig. 7 Klotz plot of AAm/AASS hydrogel crosslinked by TMPTA for dye binding system

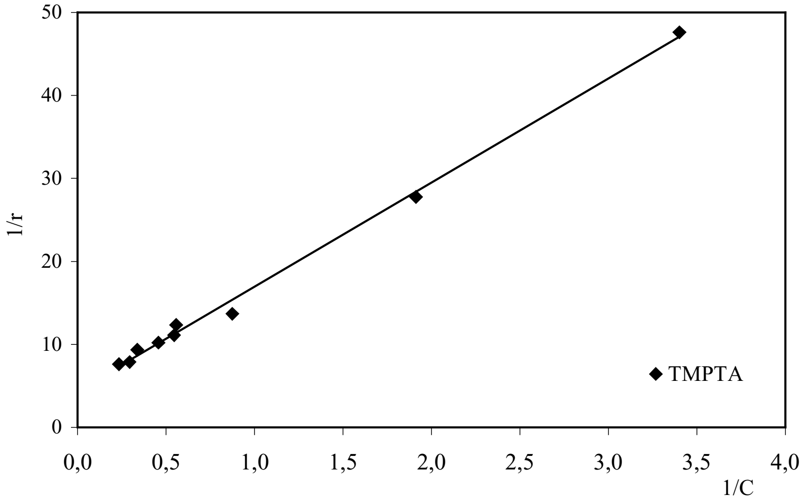


Table 2 Some binding parameters of AAm/AASS hydrogel-dye binding system

	K_i (L μmol^{-1})	K (L μmol^{-1})	n	θ	u
EGDMA	0.0202	0.1256	0.1614	0.7335	6.1931
NMBA	0.0113	0.0375	0.3013	0.4307	3.3186
BDMA	0.0211	0.0711	0.2969	0.4529	3.3672
TMPTA	0.0744	0.3139	0.2467	0.5715	4.0523

Table 3 Changing of the amount of sorbed Basic Blue 17 onto unit dry AAm/AASS hydrogel with AASS content

	AASS, mg							
	10	20	30	40	50	60	70	80
BDMA								
q (μmol g^{-1})	11.25	14.88	15.89	15.30	16.48	16.58	16.28	16.74
EGDMA								
q (μmol g^{-1})	12.85	15.50	15.50	14.55	16.02	15.11	15.50	15.66
NMBA								
q (μmol g^{-1})	7.55	9.35	13.44	15.07	13.96	15.24	16.55	16.12
TMPTA								
q (μmol g^{-1})	15.47	16.61	18.54	17.89	18.38	18.47	18.05	18.51

the derived values of the $\hat{O}$, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy $\hat{O}$:

$$\hat{O} = r/n \tag{7}$$

Using the value of r at the maximum experimental free dye concentration and with the site-density obtained for the ($u.s.b$) model (Molyneux, 1984, Molyneux and Vekavakayanondha, 1986).

3.4 Equilibrium adsorption studies

The adsorption percentage (*Ads. %*) and the amount (μmol) of sorption Basic Blue 17 per unit mass of the AAm/AASS hydrogels were evaluated by using Equation 1 and Equation 2. The amount of Basic Blue 17 sorbed onto unit dry mass of the gel was calculated for uptake of dye within the hydrogel in 30.0 μmol Basic Blue 17 in L of aqueous solutions, and presented in Table 3. Table 3 presents that the amount of Basic Blue 17 sorbed onto unit dry mass of the AAm/AASS hydrogels (7.55–18.54 μmol g^{-1}). The values of sorption % of dye concentration of 30.0 μmol L^{-1}onto AAm/AASS hydrogels crosslinked by four different crosslinkers have been present in Fig. 8 and 9. The amount of Basic Blue 17 sorbed onto unit dry mass of the AAm/AASS hydrogels gradually increased with the increase of content of AASS in the hydrogels. The

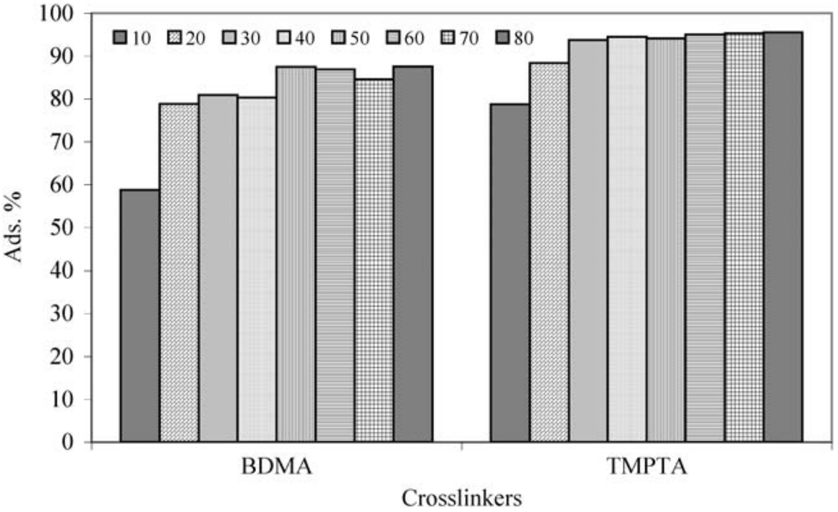


Fig. 8 The values of sorption % of dye concentration of 30.0 μmol L^{-1}onto AAm/AASS hydrogels crosslinked by BDMA and TMPTA

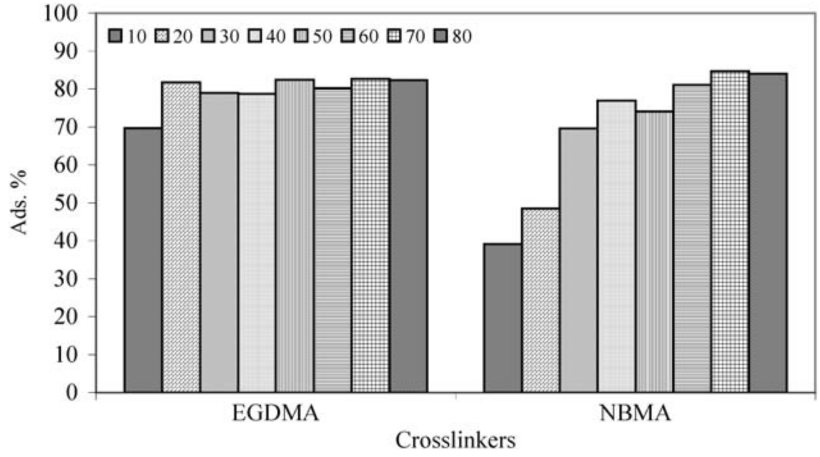


Fig. 9 The values of sorption % of dye concentration of 30.0 μmol L^{-1}onto AAm/AASS hydrogels crosslinked by EGDMA and NMBA

percentage sorptions of Basic Blue 17 onto AAm/AASS hydrogels are changed among 39.17–95.58%.

The amount of Basic Blue 17 sorbed onto unit dry mass of the AAm/AASS hydrogels (containing 40 mg AASS) was calculated for uptake of dye within the hydrogel in 6.54–52.32 μmol Basic Blue 17 in L of aqueous solutions, and presented in Table 4. The values of sorption % of various dye concentration of AAm/AASS hydrogels (containing 40 mg AASS) crosslinked by four different crosslinkers have been present in Fig. 10 and 11. Then, equilibrium Basic Blue 17 adsorption isotherm of AAm/AASS hydrogels (containing 40 mg AASS) was presented in Fig. 12. For this, the amount of sorption dye per unit mass of the AAm/AASS hydrogels (q) was plotted to the dye concentration. To Fig. 12, the amount of sorption dye per unit mass of the AAm/AASS hydrogels are increased with the increasing concentration of dye. The amount of sorption dye per unit mass of the AAm/AASS hydrogels are increased with the increasing concentration of dye.

At the end of sorption studies, it can be said that the best sorption results was followed with the TMPTA crosslinked AAm/AASS hydrogel systems.

There can be some reasons for non-covalent interactions in the binding of Basic Blue 17 by AAm/AASS hydrogels. These interaction types are represented as possible as simply interactions in Fig. 13. The main interactions between the hydrogel and dye may be hydrogen bonding. Specially, hydrogen bonding will be expected to occur between dye molecules and oxygen and nitrogen atoms as the amine and carbonyl groups on the repeating monomeric unit of crosslinked polymer. With the incorporation AASS groups into crosslinked

Table 4 Effect of concentration of Basic Blue 17 on the amount sorbed on dry AAm/AASS hydrogel (containing 40 mg AASS) with different crosslinkers

C, μmol L^{-1}	BDMA q, μmol g^{-1}	EGDMA q, μmol g^{-1}	NMBA q, μmol g^{-1}	TMPTA q, μmol g^{-1}
52.32	20.31	17.92	19.65	21.35
49.05	19.52	15.79	15.69	19.75
45.78	19.03	14.26	16.84	20.34
42.51	16.32	13.54	14.22	19.26
39.24	15.01	13.83	13.64	16.19
35.97	14.94	13.37	12.49	14.88
32.70	13.54	11.51	11.05	13.70
29.43	12.82	8.99	10.14	12.29
26.16	10.43	9.12	8.99	11.08
19.62	6.90	5.04	5.72	8.53
13.08	5.33	3.50	4.12	5.43
6.54	2.71	1.96	2.26	3.14

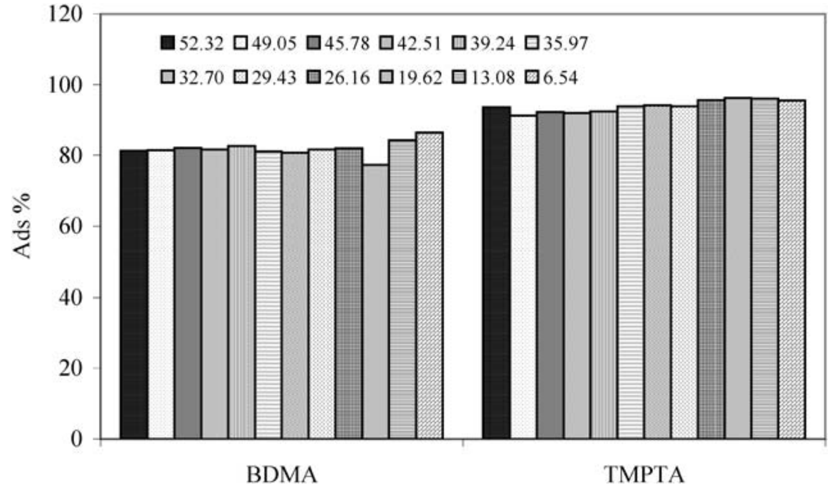


Fig. 10 The values of sorption % of AAm/AASS hydrogels crosslinked by BDMA and TMPTA (containing 40 mg AASS)

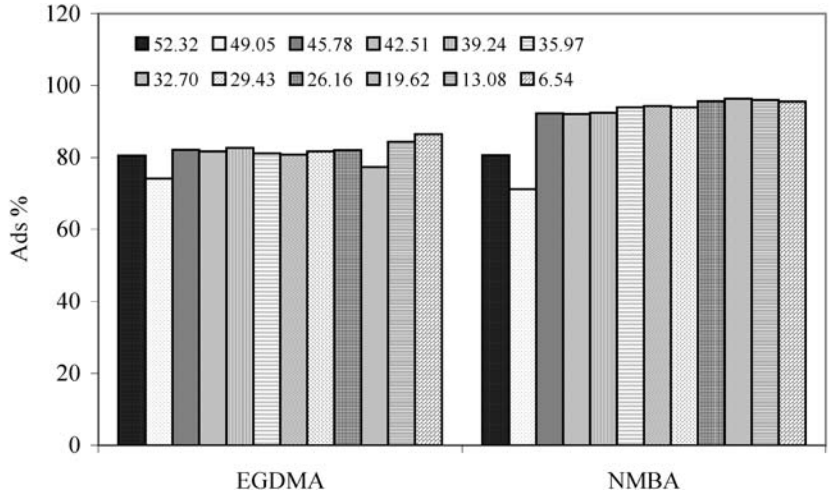


Fig. 11 The values of sorption % of AAm/AASS hydrogels crosslinked by EGDMA and NMBA (containing 40 mg AASS)

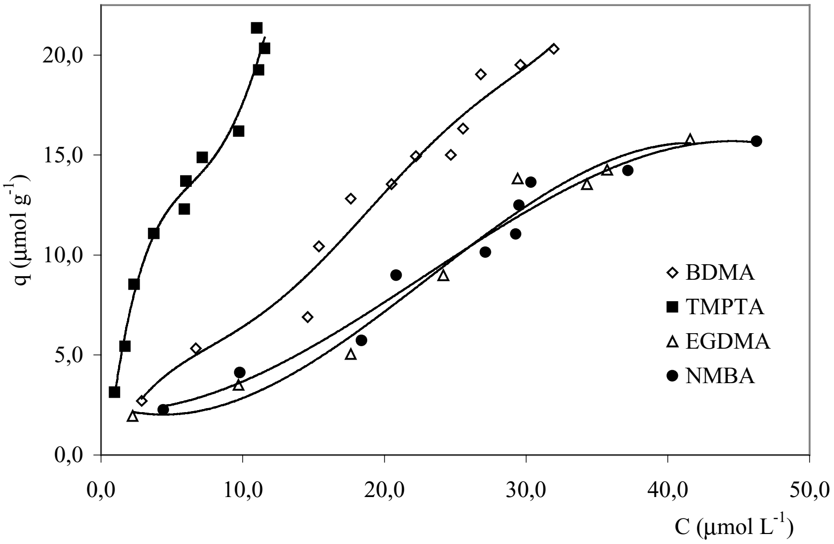


Fig. 12 Equilibrium Basic Blue 17 adsorption isotherm of AAm/AASS hydrogels

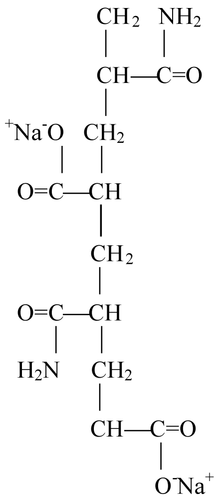
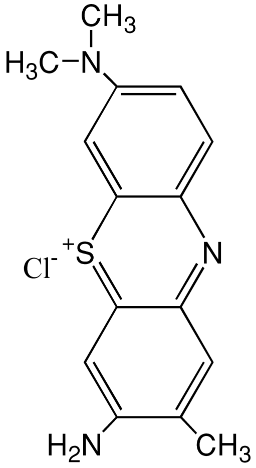
Copolymer Chain	Toluidin Blue	Interaction type	Copolymer	Dye
		Hydrogen bonding	N and O atom C=O, methine, methyl	H atom Amine
		Hydrophobic	Hydrogen atom	Benzene ring
		Dipole-dipole	Amide group	Benzene ring
		Dipole-induced dipole	Amide group	Polarisable aromatic group

Fig. 13 Possible interactions between AAm/AASS hydrogel and Basic Blue 17

copolymeric structure, hydrophilicity of AAm/AASS copolymers becomes greater than that of crosslinked acrylamide, so, the swelling of AAm/AASS hydrogels is greater than the swelling of crosslinked acrylamide hydrogels in water or aqueous media.

The results of swelling studies are parallel behavior to the results of sorption studies. The ionic charge content in the polymeric structure is important. AASS contains many ionic units (–COONa). The swelling degrees of the hydrogels increase due to increase of the hydrophilic units on hydrogel structure (Fig. 1) (Karadağ and Saraydın 2002b). Therefore AAm/AASS hydrogels have many ionic groups that can increase interaction between the cationic dye and anionic groups of hydrogels. So, it can be seen that swelling or sorption capability of AAm/AASS hydrogels are increased with increasing AASS content in copolymeric structure. The most important effect is hydrophilicity of copolymeric gels. Hydrophilicity of AAm/AASS copolymers becomes greater than that of crosslinked acrylamide, when addition of AASS to the copolymeric structure.

4 Conclusion

AAm/AASS hydrogels have been investigated for removal of Basic Blue 17 from aqueous solution. The present work has given the quantitative information on the binding characteristic of a cationic dye such as Basic Blue 17 with AAm/AASS hydrogels. AAm/AASS hydrogels have sorbed Basic Blue 17 molecules, while crosslinked acrylamide hydrogels do not. *C* and *L type* sorption isotherms in Giles classification system were found. For good characterization of the binding isotherms, Klotz linearization method was used. Some binding parameters were found. This linearization method, (Klotz) can be used in the hyperbolic binding system for dye-polymer binding process.

The sorptions of cationic dye such as Basic Blue 17 are increased with the content of AASS in the hydrogels. The moles of sorbed dye molecules per gram of dry hydrogel (q) were calculated as 1.96–21.35 μmol dye per gram for AAm/AASS hydrogels. The percentage sorptions of Basic Blue 17 onto AAm/AASS hydrogels are changed among 39.17–96.33%. At the end of sorption studies, it can be said that the best adsorbent for Basic Blue 17 or related organic structure is the TMPTA crosslinked AAm/AASS hydrogel systems (91.27–96.33% sorption).

At the end of this study, it is seen that chemically crosslinked AAm/AASS hydrogels may be used a sorbent for removal of dyes. 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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