

Synthetic Polymeric Absorbent for Dye Based on Chemically Crosslinked Acrylamide/Mesaconic Acid Hydrogels

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ABSTRACT: Adsorption properties of copolymers of acrylamide and mesaconic acid (CAME) in aqueous Basic Blue 12 (Nile blue chloride) solution have been investigated. Chemically crosslinked CAME hydrogels with various compositions were prepared from ternary mixtures of acrylamide (A), mesaconic (ME) acid, and water by free radical polymerization in aqueous solution, using a multifunctional crosslinker such as ethylene glycol dimethacrylate (EGDMA). Dynamic swelling tests in water was applied to the hydrogels. Weight swelling ratio (S) values have been calculated. Sorption of Basic Blue 12 (BB 12) onto CAME hydrogels was studied by batch sorption technique at 25°C. In the experiments of the sorption, 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 (O) for CAME hydrogels-BB 12 binding system were calculated by using Klotz, Scatchard, and Langmuir linearization methods. Finally, the amount of sorbed BB 12 per gram of dry hydrogel (q) was calculated to be 2.28×10^{-6} – 7.91×10^{-6} mol BB 12 per gram for hydrogels. Sorption % was changed range 16.09–58.86%. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 405–413, 2006

Key words: adsorption; crosslinking; dyes/pigments; hydrogel; swelling

INTRODUCTION

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. Hydrogels may be conveniently described as hydrophilic polymers that are swollen by, but do not dissolve in water. They are three-dimensional crosslinked polymeric structures that are able to swell in the aqueous environment. Crosslinked polymers capable of imbibing large volumes of water have found widespread applications in bioengineering, biomedicine, food industry, and water purification and separation process. Because of characteristic properties such as swell ability in water, hydrophilicity, biocompatibility, and lack of toxicity, hydrogels have been utilized in a wide range of biological, medical, pharmaceutical, environmental applications. Although many naturally occurring polymers may be used to produce this type of materials, the structural versatility available in syn-

thetic hydrogels has given them distinctive properties, which in turn have enhanced their practical utility.^{1–8}

Effective removal of dyes, in connection with wastewater treatment strategy, still remains a major topic of present research. Many methods have been proposed for the removal of dyes, heavy metals, and other hazardous materials. 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 or ion exchange using different polymeric materials and synthetic resins is the method of choice in many 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 dyes, for the recovery of metals, for removal of toxic or radioactive elements from various effluents, and for metal preconcentration for environmental sample analysis from aqueous solutions.^{9–14}

Recently, it was determined that crosslinked polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl, and sulfonic acid groups could be used as complexing agents for removal of dyes from aqueous solutions.^{6,13,15} Polyacrylamide based hydrogels find many applications such as purification of wastewater and metal extraction.^{7,13,15}

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TABLE I
Monomers and Crosslinkers Used in the Preparation of Hydrogel Systems

	Formula	
Acrylamide (Propene amide)	$H_2O=CHCONH_2$	A
Mesaconic acid (Methyl fumaric acid)	$HO_2CCH=C(CH_3)CO_2H$	ME
Ammonium persulphate	$(NH_4)_2S_2O_8$	APS
<i>N,N,N',N'</i> -Tetramethylethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TEMED
Ethylene glycol dimethacrylate	$[H_2C=C(CH_3)CO_2CH_2]_2$	EGDMA

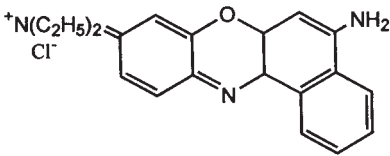
The use of polymer hydrogels for the removal of dyes from wastewater has continued to attract considerable attention in recent years. CAME hydrogels were prepared by free radical crosslinking copolymerization. The aim of this study is to investigate the sorption properties of CAME hydrogels with addition of an anionic monomer such as mesaconic acid.

EXPERIMENTAL

Materials and methods

CAME hydrogels were prepared by free radical crosslinking copolymerization of acrylamide monomer (Merck, Darmstad, Germany) with addition of an anionic comonomer such as mesaconic acid (ME) (Aldrich Chemical Co., Milwaukee, WI) and a multifunctional crosslinker such as ethylene glycol dimethacrylate (EGDMA) (Merck). The initiator, ammonium persulphate (APS) and the activator *N,N,N',N'*-tetramethylethylenediamine (TEMED) were also supplied by Merck and used as the redox initiator pair. All chemicals were used as received. Cationic dye, Basic Blue 12 (BB 12), (Nile blue chloride) was obtained from Merck (Darmstadt, Germany). Some properties of monomers and dye are listed in Table I and Table II. At the same time, the sources of water, the monomers, acrylamide (A) and mesaconic acid (ME) were given before too¹⁶

TABLE II
Some Properties of BB 12

Name	Basic Blue 12, BB 12 (Nile blue chloride)
Chemical Formula	
λ_{max} (nm)	600
Color Index No	51180

Preparation of CAME hydrogels

Crosslinked CAME hydrogels were prepared by free radical crosslinking copolymerization of acrylamide (A) monomer with addition of an anionic comonomer such as ME and a multifunctional crosslinker such as EGDMA. The modes of purification and specifications of the sources of water, the monomers A and ME, crosslinker; EGDMA, initiator; ammonium persulfate (APS), and activator; *N,N,N',N'*-tetramethylethylenediamine (TEMED) were given in our related study.¹⁶ To prepare super absorbent CAME hydrogel systems, acrylamide (A) weighing 1 g was dissolved in 1 mL aqueous solutions containing 0, 20, 40, 60, and 80 mg mesaconic acid (ME). For the synthesis, 0.25 mL of 1% concentration crosslinker solution was added to this aqueous solution. Then, 0.20 mL of APS (5 g/100 mL water) and 0.25 mL of TEMED (1 mL/100 mL water) were added to the solution.

The solutions were placed in PVC straws of 3 mm diameter. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm in length. They were washed and thoroughly rinsed with distilled water, blot dried with filter paper, dried in air and vacuum, and stored for swelling studies.

Swelling measurements in water

Equilibrium swelling experiments were used to investigate the swelling properties of the materials prepared using the various preparation methods. Dry gels were weighed and then immersed in distilled water at $(25 \pm 0.1)^\circ C$. Swollen gels were removed from water at predetermined times, blotted dry, and weighed in air. From these measurements, the values of the weight swelling ratio were determined. The weight swelling ratio, *S* is defined as

$$S = \frac{W}{W_0} \quad (1)$$

where *W* is the weight of a swollen sample and *W*₀ is the initial dry weight.^{17,18}

Sorption studies

Solutions of the dye, BB 12, containing 0.3×10^{-5} – 5.0×10^{-5} mol L⁻¹ BB-12 in distilled water were prepared. CAME hydrogels containing 60 mg ME was used in a known volume of dye solution until equilibrium was reached. For ME effect on the dye sorption, dye solution of concentration of 3.0×10^{-5} mol 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 600 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 amount (mol) of sorption per unit mass of the CAME hydrogels were evaluated by using the following equation:

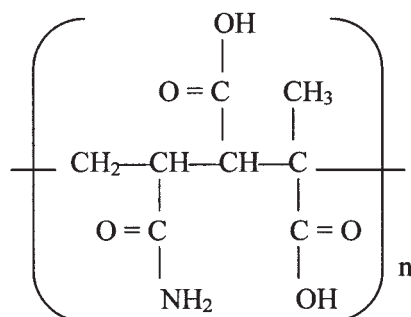
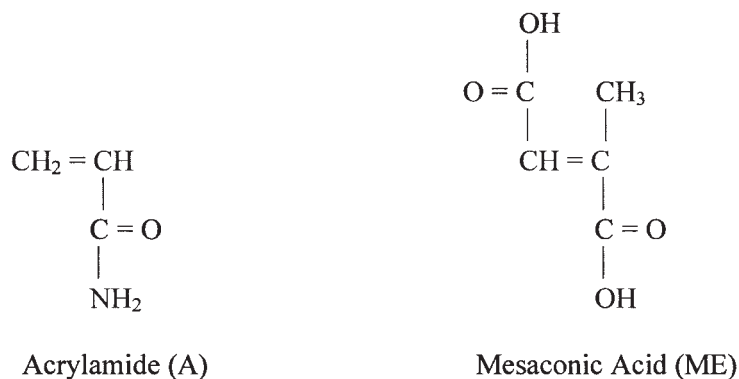
$$q = \frac{(C_0 - C)v}{m} \quad (2)$$

where q is the amount (mol) of dyes sorbed onto unit dry mass of the CAME hydrogels (mol g⁻¹), C_0 and C are the concentration of the dye in the initial solution and the aqueous phase after treatment for a certain period of time, respectively, (mol L⁻¹), v is the volume of the aqueous phase (L), and m is the amount of dry CAME hydrogels (g).

RESULTS AND DISCUSSION

Preparation

CAME hydrogels were prepared by free radical crosslinking copolymerization of acrylamide (A) monomer with addition of ME (Scheme 1) and a multifunctional crosslinker such as EGDMA.^{19–23} Some information and experimental details of used water, the monomers; acrylamide (A) and ME, the crosslinker; EGDMA, initiator; ammonium persulfate (APS), and activator; *N,N,N',N'*-tetramethylethylenediamine (TEMED) were given in our previous study.¹⁶ At polymerization, the first step is a reaction



Crosslinked Acrylamide / Mesaconic Acid Copolymer (CAME hydrogel)

Scheme 1

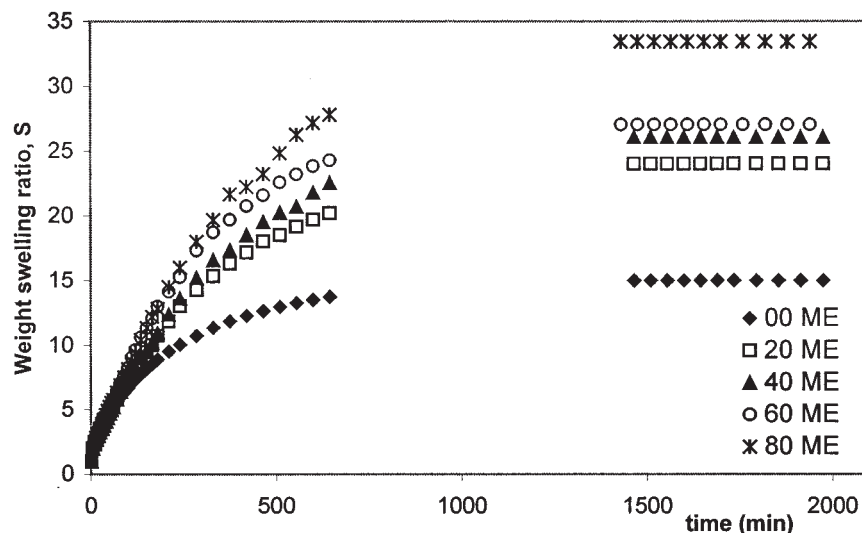


Figure 1 Swelling isotherms of CAME hydrogels.

between APS and TEMED, in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an acrylamide and anionic comonomer such as crosslinker or ME molecules; in the process, the unpaired electron is transferred to the monomeric units, so that they in turn become reactive. Another monomer or comonomers can therefore be attached and activated in the same way. The polymer, crosslinked acrylamide (CA) or copolymeric hydrogel (CAME hydrogels), can continue growing indefinitely, with the active center being continually shifted to the free end of the chain. Crosslinker molecules can be incorporated into chains simultaneously and form a permanent link between them. Our many other works were reported about the preparation and swelling properties of chemically crosslinked copolymers containing acrylamide and some other hydrophilic comonomers such as maleic acid,¹⁵ crotonic acid,²⁰ and sodium acrylate.²¹

Swelling

A fundamental relationship exists between the swelling of a polymer in a solvent and the nature of the polymer and the solvent. The water intake of initially dry hydrogels was followed for a period of time, gravimetrically. Swelling isotherms of the hydrogels were constructed and representative swelling curve is shown in Figure 1.

Figure 1 show that weight swelling ratio increases with time up to certain level, then levels off. This value of swelling ratio may be called the equilibrium weight swelling ratio (S_{eq}). S_{eq} values of CAME are given Table III.

Table III shows that S_{eq} values of CA hydrogels is 15.00, but S_{eq} of CAME hydrogels are 24.01–33.43 with the incorporation ME groups into crosslinked copolymeric structure. Hydrophilicity of CAME copolymers becomes greater than that of CA, so, the swelling of CAME hydrogels is greater than the swelling of CA hydrogels.

Sorption and binding

To observe the sorption of BB 12, CAME hydrogels were placed in aqueous solutions of BB 12 and allowed to equilibrate for 4 days at 25°C. At the end of this period, CAME hydrogels in the BB 12 solutions showed the dark coloration. But acrylamide hydrogel did not sorb any dye from solution.

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

$$C_t = C_b + C \quad (3)$$

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

TABLE III
The Values of the Equilibrium Weight Swelling Ratio (S_{eq}) of CAME hydrogels

ME (mg)	00	20	40	60	80
	15.00	24.01	26.10	27.03	33.43

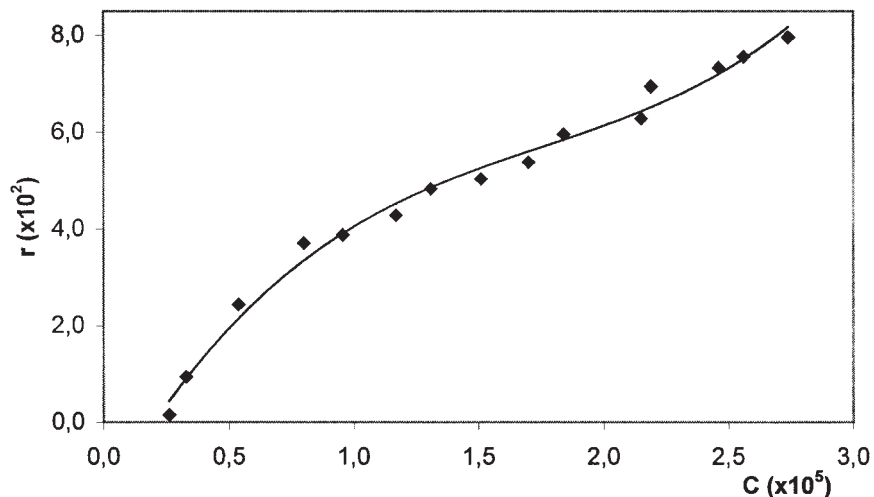


Figure 2 Binding isotherm of CAME hydrogel-BB 12 binding system.

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 n 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.^{24,25} To determine the sorption kinetics of BB 12 into CAME hydrogels, a plot of the binding ratio (r) against the free concentration of BB 12 is shown in Figure 2. Figure 2 shows that sorption of the dye with in CAME hydrogels

corresponds to *L type* sorption isotherms in the Giles classification system for sorption of the dye from its solution.²⁶ In this type adsorption isotherm, the initial curvature shows that it becomes increasingly difficult for a bombarding dye molecule to find a vacant site available as more and more sites on the crosslinked CAME hydrogels are filled. This implies that either the adsorbed dye molecule is not oriented vertically or there is no strong competition from the solvent, water.

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

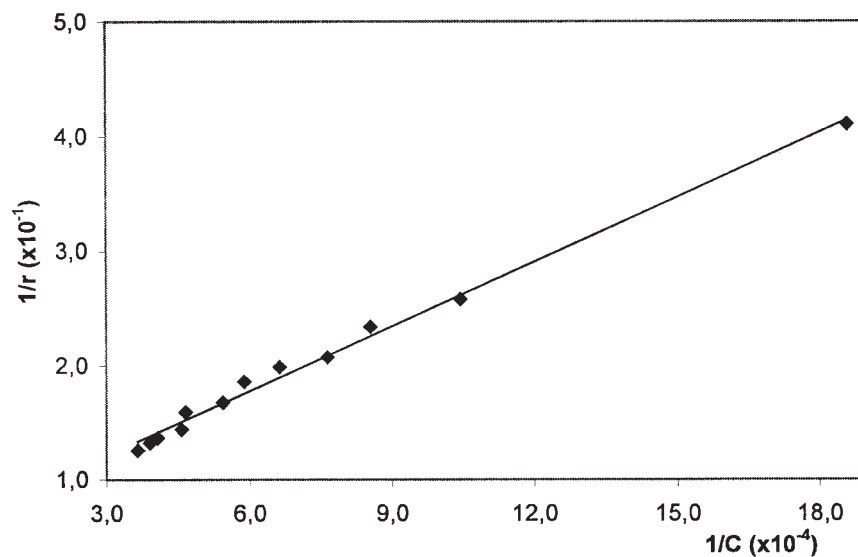


Figure 3 Klotz plot of CAME hydrogel-BB 12 binding system.

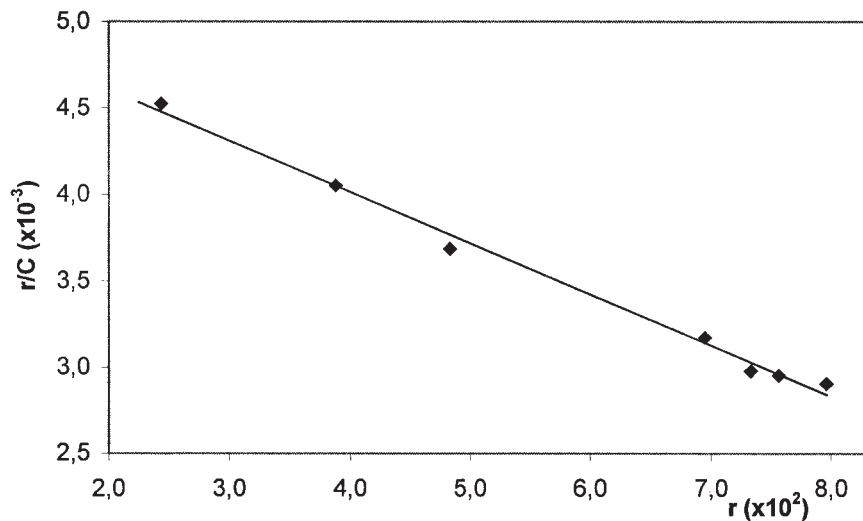


Figure 4 Scatchard plot of CAME hydrogel-BB 12 binding system.

solute on the polymer chains.^{24,25} This leads to the hyperbolic (Langmuir) form of the binding isotherm, which applies to many polymer/solute (dye molecules) binding system.

$$r = \frac{nKC}{1 + KC} \quad (5)$$

where K is the binding constant, *i.e.*, the equilibrium constant for the attachment of a molecule of dye onto a site by a specific combination of noncovalent 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 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 $K n$.

To get the best values for the binding parameters from the experimental data, the linearization methods of eq. (5) have been developed by some researchers as Klotz, Scatchard, and Langmuir.^{24,25}

Klotz method

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

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nk} \frac{1}{C} \quad (6)$$

Thus, if this isotherm holds than a plot of $1/r$ versus $1/C$ will be straight line of slope $1/Kn$, ordinate intercept $1/n$. This is very a 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.

Scatchard method

Multiplying eq. (5) by $K n r$ and rearranging gives;

$$\frac{r}{C} = Kn - Kr \quad (7)$$

so that in this case, a plot of r/C versus r should be a straight line of slope $-K$, ordinate intercept $K n$.

Langmuir method

Multiplying the Klotz form of eq. (5) by C gives;

$$\frac{C}{r} = \frac{1}{nK} + \frac{C}{n} \quad (8)$$

so that here a plot of C/r versus C should be a straight line of slope $1/n$, ordinate intercept $1/nK$.

The Klotz, Scatchard, and Langmuir plots of CAME hydrogel-BB 12 binding systems are shown in Figures 3–5, respectively, and the binding parameters for CAME hydrogel-BB 12 binding systems are calculated from the intercept and slopes of the binding isotherm methods.

The binding parameters K_i , K , n , and u are listed in Table IV for CAME hydrogel-BB 12 binding systems. In Table IV, the final column contains the derived

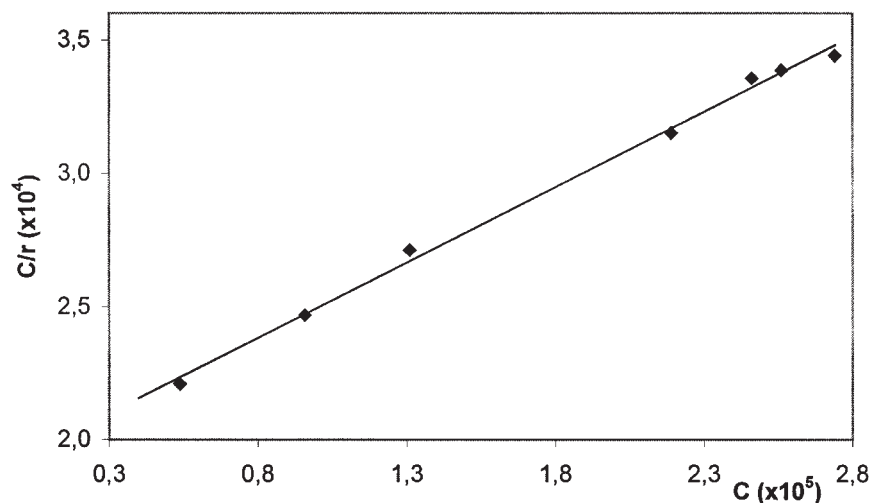


Figure 5 Langmuir plot of CAME hydrogel-BB 12 binding system.

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

$$\hat{O} = r/n \quad (9)$$

Using the value of r at the maximum experimental free dye concentration and with the site-density obtained for the (*u.s.b*) model.

The calculated parameters determined by using Klotz, Scatchard, and Langmuir linearization methods are nearly equal to each other. Then, linearization methods (Klotz, Scatchard, and Langmuir) can be used in the hyperbolic binding system for dye-polymers binding process.

In later experiments uptake of dye to was measured effects of contents of ME. The amount of dyes sorbed onto unit dry mass of the gel was calculated for uptake of dye within the hydrogel in 3.0×10^{-5} mol dye in L of aqueous solutions, and presented in Table V. Table V shows that the amount of dyes sorbed onto unit dry mass of the CAME hydrogels (2.28×10^{-6} – 7.91×10^{-6} mol g^{-1}), q are increased. The amount of dyes sorbed onto unit dry mass of the CAME hydrogels gradually increased with the increase of content of ME in CAME hydrogels. The

percentage sorptions of BB 12 onto CAME hydrogels is changed among 16.09–58.86%.

The ionic charge content in the polymeric structure is important. ME contains many ionic units (–COOH). The swelling degree of the hydrogels increase because of increase of the hydrophilic units on hydrogel structure (Table I and Scheme 1). Therefore, CAME hydrogels have many ionic groups that can increase interaction between the cationic dye molecules and anionic groups of hydrogels.

There can be many reasons for noncovalent interactions in the binding of BB 12 by CAME hydrogels. These interaction types are represented as possible interactions in Figure 6. The main interactions between the hydrogel and the monovalent cationic dyes may be hydrophobic and hydrogen bonding. Specially, hydrogen bonding will be expected to occur between amine groups and nitrogen atoms on the dye molecules and the amine and carbonyl groups on the monomer unit of crosslinked polymer. Hydrophobic effects are specially aqueous solutions interactions which in the present case will involve the 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.

The results of swelling studies are parallel character to the results of sorption studies. Both of them,

TABLE IV
Some Binding Parameters of CAME Hydrogel-BB 12 Binding System

	$K_i (\times 10^{-3}/L \text{ mol}^{-1})$	$K_i (\times 10^{-3}/L \text{ mol}^{-1})$	n	u	\hat{O}
Klotz	5.32	3.45	0.1541	6.49	0.5165
Scatchard	5.20	2.96	0.1757	5.69	0.4530
Langmuir	5.18	2.93	0.1768	5.66	0.4502

TABLE V
The Amount of Dyes Sorbed onto Unit Dry Mass and % Sorptions of CAME Hydrogel-BB 12 Binding System

ME (mg)	20	40	60	80
$q/\times 10^6$	2.28	4.61	6.26	7.91
% sorption	16.09	33.40	49.67	58.86

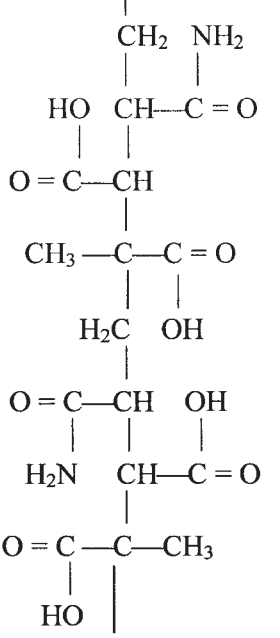
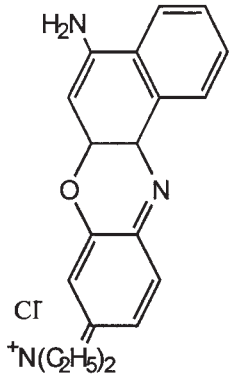
copolymer chain	Nile blue	Interaction type	Copolymer	Dye
		Hydrogen bonding	N and O atom C=O, methine, methyl	H atom Amine
		Hydrophobic	Hydrogen atom	Benzene ring
		Dipole-dipole	Amide group	Benzene ring
		Dipole-induced dipole	Amide group	Polarisable aromatic group

Figure 6 Schematic representation of noncovalent interactions in the binding of BB 12 by CAME hydrogels.

it can be seen that swelling or sorption capability of CAME hydrogels are increased with increasing ME content in copolymeric structure. The most important effect is hydrophilicity of copolymeric gels. Hydrophilicity of CAME copolymers becomes greater than that of CA, on addition of ME to the copolymeric structure.

CONCLUSIONS

The present work has given the quantitative information on the binding characteristic of BB 12 with CAME hydrogels. CAME hydrogels have sorbed the monovalent cationic dye such as Basic Blue 12, while CA hydrogels do not. *L type* sorption isotherm in Giles classification system are found. For good characterization of the binding isotherms, Klotz, Scatchard, and Langmuir linearization methods were used. Some binding parameters were found. The sorptions of the dyes are increased with the content of ME in the hydrogels. The moles of sorbed BB 12 per gram of dry hydrogel (q) was calculated. The percentage sorptions of BB 12 onto CAME hydrogels is changed among 16.09–58.86%.

At the end of this study, it is seen that chemically crosslinked CAME hydrogels may be used as a sorbent for removal of some agents and dye molecules. The utilization of these types of hydrogels in biomedicine, controlled drug delivery, pharmaceuti-

cals, agriculture, biotechnology, environment, sorption, separation, purification, immobilization, and enrichment of some species makes hydrogel more popular.

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