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Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels

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Abstract

Superswelling acrylamide (AAm)/maleic acid (MA) hydrogels were prepared by free radical polymerization in aqueous solution of AAm with MA as comonomer with some multifunctional crosslinkers such as trimethylolpropane triacrylate and 1,4-butanediol dimethacrylate. AAm/MA hydrogels were used in experiments on swelling and adsorption of a water-soluble monovalent cationic dye such as Basic Blue 17 (Toluidin Blue). As a result of dynamic swelling tests, the influence of relative content of MA on the swelling properties of the hydrogel systems was examined. AAm/MA hydrogels were swollen in the range 1660–6050% in water, while AAm hydrogels swelled in the range 780–1360%. Equilibrium water content of AAm/MA hydrogels were calculated in the range 0.8873–0.9837. Water intake of hydrogels followed a non-Fickian type diffusion. The uptake of the cationic dye, BB-17 to AAm/MA hydrogels is studied by batch adsorption technique at 25 °C. In the experiments of the adsorption equilibrium, S-type adsorption in Giles's classification system was found. The binding ratio of hydrogel/dye systems was gradually increased with the increase of MA content in the AAm/MA hydrogels.
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1. Introduction

There has been increasing interest in the synthesis and various applications such as high water sorption of new hydrogels. Hydrogels are three-dimensional crosslinked polymeric structures which are able to swell in the aqueous environment. These materials are of great interest due to their promising applications such as sensors, separation membranes, adsorbents, and materials in medicine and pharmacy as drug delivery systems, in solving some ecological and biological problems as well as in modern technologies. Superswelling polymers can swell up to thousands of times their own weight in aqueous media. Swelling behaviour of superabsorbent polymers may be characterised by water sorption [1–3].

Many attempts have been made to develop new hydrogels through methods such as irradiation and chemically crosslinking. Hydrogels can be prepared by simultaneous copolymerization and crosslinking of one or more monofunctional and one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution. The latter involves two steps in which, in the first step, the linear polymer is synthesised in the absence of a crosslinking agent and in the second step, the synthesised polymer is crosslinked using either chemical reagents or irradiation [1–6].

In recent years, considerable researches have been done on the characterization and swelling behaviour of hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an

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initiator and a crosslinking agent [1–8]. Superswelling hydrogels exhibit a combination of unique physico-chemical properties, thus permitting their wide-ranging, and often exceptional, possibilities in practical applications (high and fine technologies, biotechnologies, ecology, medicine etc.). Gel properties may be programmed by the choice of the main polymer that forms the frame work and of either the comonomer content or irradiation doses [1–8].

Synthetic dyes represent a relatively large group of organic chemicals which are met in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only environment, but also on man. In order to minimise the possible damages to man and environment arising from the production and applications of cationic dyes, several researches were made around the world. The potential toxicity of some cationic dyes has been known for many decades. Some cationic dyes has not been used for founded to be carcinogenic [9]. The removal of color from textile waste waters is a major environmental problems because of the difficulty of treating such waters by conventional methods. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions [10,11].

The aim of this study is to investigate the swelling properties and adsorption characteristics of acrylamide (AAm) hydrogels with addition of an anionic monomer such as maleic acid (MA) and some multifunctional crosslinkers such as trimethylolpropane triacrylate (TMPTA) and 1,4-butanediol dimethacrylate (BDMA). Dynamic swelling studies are important for swelling characterization of hydrogel systems. These swelling properties will be effected that usable of its as biomaterial in medicine, pharmacy and veterinary. In this work, it has been aimed to study a convenient method for removing the water-soluble monovalent cationic dye from aqueous solutions by adsorption on novel polymeric adsorbent such as AAm/MA hydrogels. Water-soluble monovalent cationic dye, Basic Blue 17 (Toluidin Blue; BB-17) resembles the large molecular dye found in waste waters.

2. Experimental

2.1. Materials

AAm supplied by from Merck (Darmstad, Germany) and the anionic comonomer, MA supplied by from Merck (Darmstad, Germany). The initiator, ammonium persulfate (APS) and the activator N,N,N',N'-tetramethylethylenediamine (TEMED) supplied from Merck (Darmstad, Germany) and were used as the redox initiator pair. The multifunctional crosslinkers, TMPTA and BDMA were purchased from Aldrich Chemical Co. (Milwaukee, US). All chemicals were used as received. Gelation was made at room temperature and room atmosphere.

For adsorption studies, BB-17, (Toluidin Blue; Aldrich Chemical Co. Milwaukee, US) was used. All chemicals were used as received. Doubly distilled water were used in the copolymerizations and swelling studies. Chemical structure of used monomers, initiator, activator, crosslinkers and dye tabulated in Tables 1 and 2.
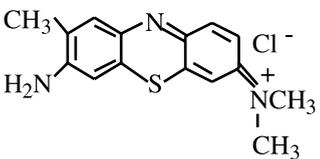
2.2. Copolymer preparation

For preparation of superswelling AAm/MA hydrogels, first, 1 g of AAm was dissolved in 1 ml distilled

Table 1
Used chemicals in the preparation of AAm/MA hydrogels

	Formula	Abbreviations
Acrylamide (propen amid)	$H_2C{=}CHCONH_2$	AAm
Maleic acid	$HOOCCH{=}CHCOOH$	MA
Ammonium persulfate	$(NH_4)_2S_2O_8$	APS
N,N,N',N'-tetramethyl-ethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TEMED
Trimethylol-propane triacrylate	$[H_2C{=}CHCO_2CH_2]_3CC_2H_5$	TMPTA
1,4-Butanediol dimethacrylate	$[H_2C{=}C(CH_3)CO_2CH_2CH_2]_2$	BDMA

Table 2
Some properties of BB-17 (Toluidin Blue)

Name	Chemical formula	Molar mass	Color index no.	λ_{max} (nm)
Toluidin Blue (BB-17)		305.83	52 040	626

water, and then 00, 20, 40, and 60 mg MA were added to the aqueous solutions of AAm. For investigation of the effect of crosslinkers on preparation of AAm/MA hydrogel systems, 0.25 ml of 1% concentration of BDMA, or 0.25 ml of 1% concentration of TMPTA was added to the aqueous solutions of AAm/MA. Then 0.2 ml of APS (5 g/100 ml water) was added this solution as initiator, and finally, 0.25 ml of TEMED (1 ml/100 ml water) was added onto solution.

These solutions mentioned above were placed in PVC straws (as the polymerization reactors) of 3 mm diameter. The polymerization was conducted for 24 h. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces of 3–4 mm length. These were dried in air and then under vacuum, and stored for swelling studies (Scheme 1).

2.3. Experiments of swelling and diffusion

The swelling behaviours of dried hydrogels were carried out by immersion in doubly distilled water at 25 ± 0.1 °C in a water bath. The water absorbed was determined by weighing the samples, after wiping, at various time intervals. Swollen gels weighed by an electronic balance (SARTORIUS, BP 210S, $d = 0.1$ mg).

2.4. Adsorption studies

The synthetic aqueous solutions of monovalent cationic dye, BB-17 (Table 2) were prepared in the concentration ranges of 2–20 mg l^{-1}. AAm/MA hydrogels containing 40 mg MA was selected for adsorption experiments. 0.1 g of dry gel were transferred into 50 ml of the synthetic aqueous solutions of the dye, and allowed the equilibrate for 4 days at 25 °C. The influences of MA content in the superswelling hydrogels was investigated for adsorption of dyes onto AAm/MA hydrogels. Su-

perswelling hydrogel samples weighing 0.1 g and prepared with 00, 20, 40 and 60 mg of MA were added 50 ml of concentration of 12 mg l^{-1} dye solutions and left for 4 days at 25 °C.

After adsorption, dye solution was separated by decantation from the superswelling 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. Schematic diagram of the hydrogel experiment is presented in Scheme 1.

3. Results and discussion

3.1. Preparation of crosslinked copolymers

In this study, AAm/MA hydrogels were prepared by free radical polymerization in aqueous solutions of AAm, MA and crosslinkers such as TMPTA and BDMA. The copolymerization of AAm with anionic comonomers such as itaconic acid [2], MA [12], crotonic acid [13] and succinic acid [14] have been studied by γ-radiation in previous studies. AAm/crotonic acid hydrogels crosslinked by TMPTA and BDMA have been studied, also [8].

In the polymerization, first step is a reaction between APS and TEMED in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an AAm and anionic comonomer such as MA or crosslinker 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
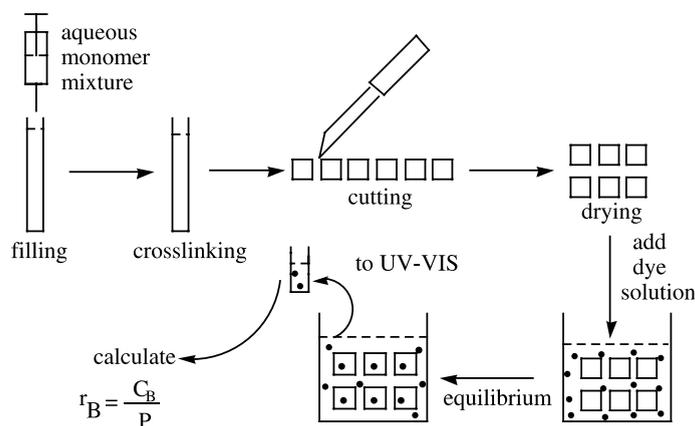
Scheme 1. Schematic diagram of the hydrogel experiment.

attached and activated in the same way. The polymer (AAm) or copolymer (AAm/MA) 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 forms a permanent link between them [6,15,16].

Polymerization and crosslinking process has been taken an hour in AAm/MA gelation. But, for all hydrogel systems, it has been waited for 24 h for good gelation. The crosslinked copolymers is colourless and some of them semi-transparent. They are soft and elastic, with a slippery or slimly surface. There is no difference an external appearance of crosslinked copolymeric samples about chancing of structure of crosslinker molecular structure.

3.2. Swelling measurements

A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the polymer and the solvent. The percentage swelling (or mass swelling) is the most important parameter about swelling studies. The percentage swelling ($\%S$) was calculated from the following equation [2,3]:

$$\%S = \frac{M_t - M_0}{M_0} \times 100 \tag{1}$$

where M_t is the mass of the swollen gel at time t, and M_0 is the mass of the dry gel at time 0.

The water intake of initially dry hydrogels was followed for a long time. Swelling isotherms of AAm/MA hydrogel systems by using two different crosslinkers are plotted and are shown in Figs. 1 and 2.

If Figs. 1 and 2 are investigated together, it can be seen that percentage swelling increases with time until a certain point, when it becomes constant. This value of percentage swelling may be named "equilibrium" (percentage) swelling. The values of equilibrium (percentage)
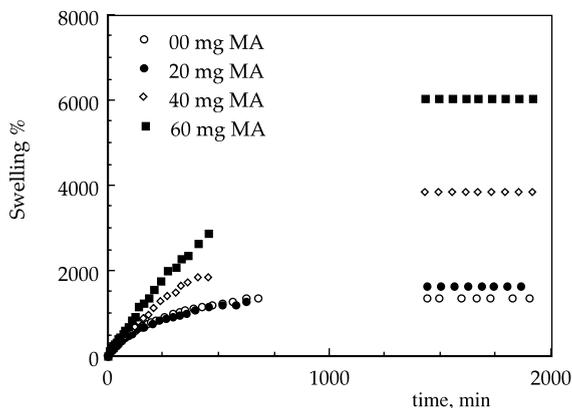

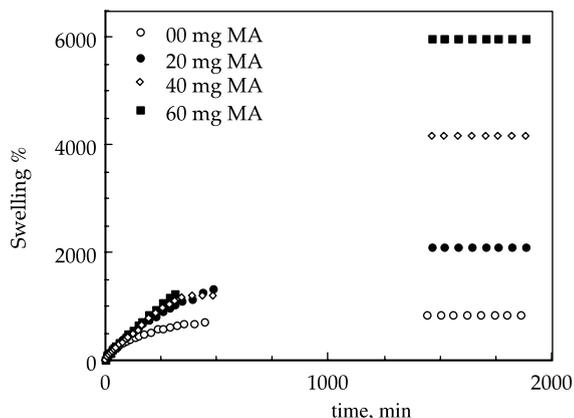Fig. 1. Swelling isotherms of AAm/MA hydrogels crosslinked by BDMA.

Fig. 2. Swelling isotherms of AAm/MA hydrogels crosslinked by TMPTA.

Table 3
The equilibrium (%) swelling of AAm/MA hydrogels

	MA (mg)			
	00	20	40	60
TMPTA	780	2100	4180	5980
BDMA	1360	1660	3860	6050

swelling of AAm/MA hydrogels are used for the calculation of some characterization parameters. The values of equilibrium swelling of AAm/MA hydrogels are given in Table 3.

Table 3 shows that the values of equilibrium swelling of AAm are among 780–1360%, but the values of equilibrium swelling of AAm/MA hydrogels vary between 1660–6050%. It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network [2,3]. The ionic charge content is important. MA contains many ionic units (–COOH). As it can be seen from Table 3, the swelling increase is due to an increase of the anionic units. The hydrophilic group numbers of AAm/MA copolymers are more than these of AAm, so, the swelling of AAm/MA copolymers is more than that of AAm copolymers. If the content of MA in AAm/MA copolymers increased, the equilibrium swelling of AAm/MA copolymers has increased.

The equilibrium degree of AAm hydrogels is 780 for crosslinked by TMPTA, and is 1360 for crosslinked by BDMA. This is an expected behaviour. The reason of this behaviour is molecular structure of crosslinkers. Firstly, BDMA is tetrafunctional crosslinkers and TMPTA is hexafunctional crosslinker. Because TMPTA is hexafunctional crosslinker, the less swelling values have been seen among other three crosslinkers. This chemical arrangement of TMPTA is caused that decreasing of swelling with the degree of crosslinking.

Swelling properties of hydrogels containing crosslinkers are changed by the structure of crosslinker, and generally, when crosslinkers are added to hydrogel systems, it is known that there would be a chancing in the swelling ratio of hydrogels, because the molecules of crosslinkers are placed between the chains of monomer and comonomers. Then, the hydrophilic group number is decreased, and swelling ratio is decreased, sometime [17,18]. But, there has not been seen important differences of equilibrium swelling of AAm/MA hydrogels crosslinked different crosslinkers. All values may be similar to same contents of MA. Here, The most effective condition is content of MA in the hydrogels.

3.3. Equilibrium water content

The water absorbed by AAm/MA is quantitatively represented by the equilibrium water content (EWC) [19,20], where

$$EWC = \frac{M_t - M_0}{M_t} \qquad (2)$$

Here M_t is the mass of the swollen gel at time t (equilibrium), and M_0 is the mass of the dry gel at time 0. EWC's of all AAm/MA hydrogel systems were calculated. The values of EWC of the hydrogels are tabulated in Table 4. All EWC values of the hydrogels (0.8873–0.9837) were greater than the percent water content values of the body about 0.60 (or 60%). Thus, the AAm/MA hydrogels were exhibit similarity of the fluid contents with those of living tissues. It can be said that AAm/MA hydrogel systems crosslinked by BDMA and TMPTA can be used as a new material as a biomaterial in medicine, pharmacy, veterinary and other applications such as water absorbency.

3.4. Determination of swelling power

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

The swelling mechanism of the samples was determinated using the following equation [21]:

$$F_{swp} = \frac{M_t - M_0}{M_0} = Kt^n \qquad (3)$$

In the above equation, M_t and M_0 are the mass of the swollen and dry sample at time t, respectively, t is the time, K is the swelling constant, and n is the swelling exponent [21,22].

For cylindrical shapes, $n = 0.45$–0.50 and corresponds to Fickian diffusion whereas $0.50 < n < 1.0$ indicates that diffusion is non-Fickian type. This equation is applied to the initial stages of swelling and plots of $\ln F_{swp}$ versus $\ln t$ yields straight lines up to almost 60% increase in the mass of hydrogel [21,22].

For the hydrogels, $\ln F_{swp}$ versus $\ln t$ plots were drawn using the kinetics of swelling and some representative results are shown in Fig. 3. The swelling exponents n were calculated from the slopes of the lines and are listed in Table 5. In Table 5, it is shown that the values of the
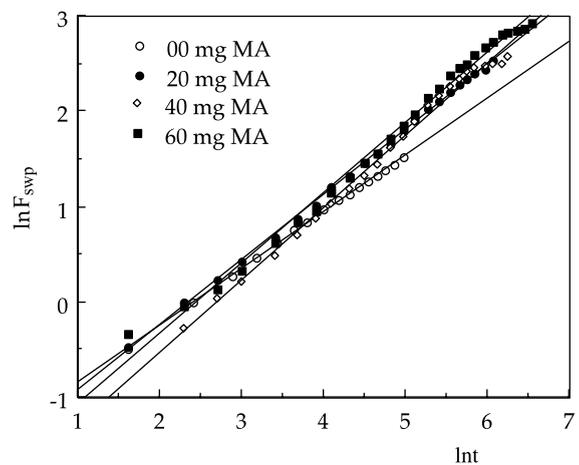

Fig. 3. Swelling kinetics curves of AAm/MA hydrogels crosslinked by TMPTA.

Table 4
EWC of AAm/MA hydrogels

	MA (mg)			
	00	20	40	60
TMPTA	0.8873	0.9457	0.9766	0.9835
BDMA	0.9316	0.9431	0.9747	0.9837

Table 5
Swelling exponents and swelling constants of AAm/MA hydrogels

	MA (mg)			
	40	20	40	60
Swelling exponents (n)				
TMPTA	0.594	0.683	0.761	0.733
BDMA	0.633	0.612	0.794	0.850
Swelling constants ($K \times 10^2$)				
TMPTA	23.10	19.90	12.72	16.80
BDMA	29.20	29.72	15.39	15.91

diffusional exponent range generally between 0.594 and 0.850. Average of swelling exponents is 0.7075. In the experiments, the number to determine type of diffusion (n) was found to be generally over 0.50. Hence the diffusion of water into AAm/MA hydrogel systems had a *non-Fickian* character [21,22]. In this diffusion, diffusion and relaxation are said to be isochronal effective [21,22].

3.5. Diffusion of water

The study of diffusion phenomena in hydrogels and water is of value in that it clarifies polymer behaviour. The complete swelling–time curves for hydrogels in water are used to calculated diffusion coefficient. Diffusion coefficients of hydrogels can be calculated by various methods. One of these methods is 'the short time approximation method'. The short time approximation is valid only for the first 60% of the swelling [23,24].

The diffusion coefficients of the cylindrical AAm/MA hydrogel are calculated from the following relation:

$$F = 4 \left[\frac{Dt}{\pi r^2} \right]^{1/2} - \pi \left[\frac{Dt}{\pi r^2} \right] - \frac{\pi}{3} \left[\frac{Dt}{\pi r^2} \right]^{3/2} + \cdots \quad (4)$$

where D in $cm^2\,s^{-1}$, t in s and r in cm is the radius of cylindrical polymer sample. A graphical comparations of related equations shows the semi-empirical Eq. (4) with $n = 0.5$ and $k = 4(D/\pi r^2)^{1/2}$.

For the hydrogels, F versus $t^{1/2}$ plots were plotted and diffusion curves of AAm/MA hydrogels crosslinked by TMPTA is shown in Fig. 4. The diffusion coefficients were calculated from the slope of the lines. The values of diffusion coefficient determined for the hydrogels are listed in Table 6.
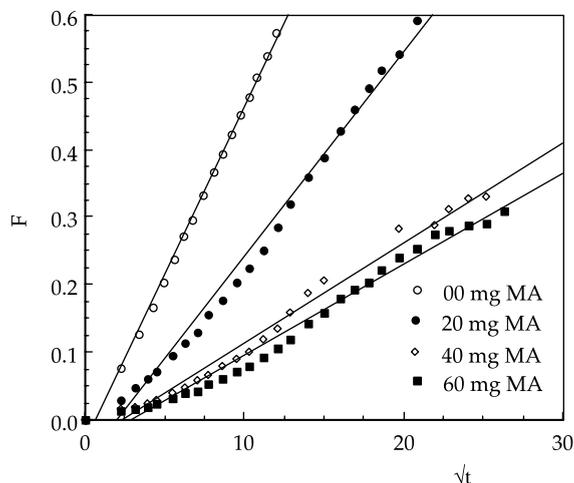

Fig. 4. Diffusion curves of AAm/MA hydrogels crosslinked by TMPTA.

Table 6
Diffusion coefficients (($D/cm^2\,s^{-1}$) $\times 10^6$) of AAm/MA hydrogels

	MA (mg)			
	00	20	40	60
TMPTA	94.44	60.76	15.17	25.05
BDMA	77.86	60.22	58.50	66.58

If Table 6 is examined, it is shown that the values of the diffusion coefficient of the hydrogels varied from 25.05×10^{-6} to 94.44×10^{-6} $cm^2\,s^{-1}$. Diffusion coefficients has not showed linear chancing to each others.

### 3.6. Adsorption of the monovalent cationic dyes

To observe adsorption of the dyes, AAm/MA hydrogels were placed in the aqueous solutions of monovalent cationic dye, BB-17, and the aqueous solutions of anionic dyes such as Orange II, Azocarmine B, Alizarin yellow G and Erytrosin B, and allowed to equilibrate for 4 days. At the end of this time, AAm/MA hydrogels in the aqueous solutions of BB-17 showed the dark colorations of the original solution. AAm hydrogel did not sorbed any dye from the solution, and AAm/MA hydrogel did not sorbed the anionic dyes. Since poly(acrylamide) is a non-ionic polymer, ionizable groups on the polymer were increased by the addition of MA to AAm monomer. Therefore these hydrogels have many carboxyl groups that can increase interaction between the cationic groups of monovalent cationic dyes and carboxyl groups of hydrogels. On the other hand, there will be anionic repulsion between anionic groups of anionic dyes and carboxyl group of MA in the hydrogels.

The other types of interaction between the superswelling hydrogel and the monovalent cationic dyes may be hydrophobic and hydrogen bond. Hydrophobic effects are specifically aqueous solutions interactions, which in the present case will involve the aromatic rings and the methyl and methine groups on the dyes molecules and the methine groups on the gel. Hydrogen bond will be expected to occur between amine group and nitrogen or sulfur atoms on the dye molecules and the amine and carbonyl groups on the monomer unit of crosslinked copolymer. But, electrostatic interactions between the dye molecules and the hydrogel is very dominant due to hydrophobic and hydrogen bonds (Scheme 2).

In a batch adsorption system at equilibrium, total solute concentration (C_I, $mol\,l^{-1}$) is [25,26]

$$C_I = C_B + C \quad (5)$$

where, C_B is the equilibrium concentration of the solute on the adsorbent in mol in 1 l solution (bound solute
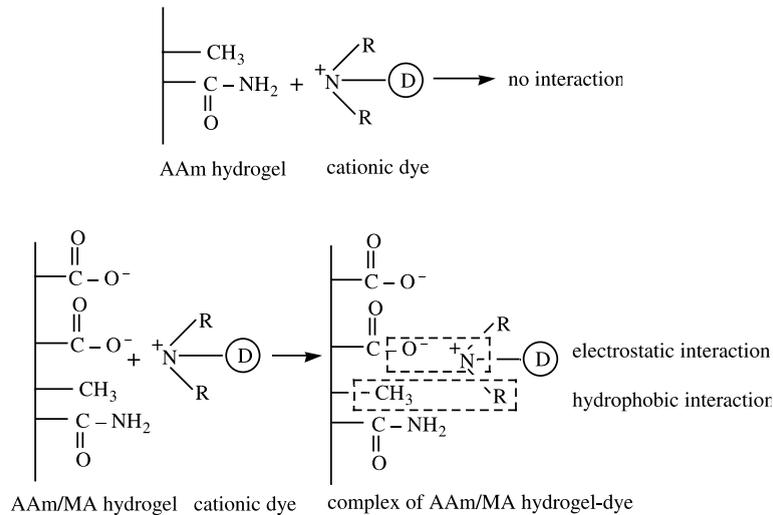
Scheme 2. Possible complexation process between AAm/MA hydrogel and dye molecule.

concentration) and C is the equilibrium concentrations of the solute in the solution in mol l^{-1} (free solute concentration). The value of the bound concentration may be obtained by difference by using Eq. (5). 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_B defined by

$$r_B = \frac{C_B}{P} \qquad (6)$$

Thus with C_B in mol l^{-1} and P in base mol (moles of monomer units) in l, r_B then represents the average number of molecules of solute bound each monomer unit at that free solute concentration.

Plots of the binding ratio (r_B) against the free concentrations of the dyes in the solutions (C, mg dye l^{-1}) are shown in Fig. 5.

Fig. 5 shows that adsorptions of the dye within AAm/MA hydrogels corresponds to type S adsorption isotherms in the Giles classification system for adsorption of a solute from its solution. In the S curves in the Giles classification system, initial direction of curvature shows that adsorption easier as concentration rises. In practice, the S curve usually appear when three conditions are fulfilled: the solute molecule (a) is monofunctional, (b) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (c) meets strong competition, for substrate sites, from molecules of the solvent or of another absorbed species [27].

The weakness of the adsorbent–adsorbate forces will cause the uptake at low concentrations to be small, but once a molecule has become adsorbed, the adsorbate–adsorbate forces will promote the adsorption of further
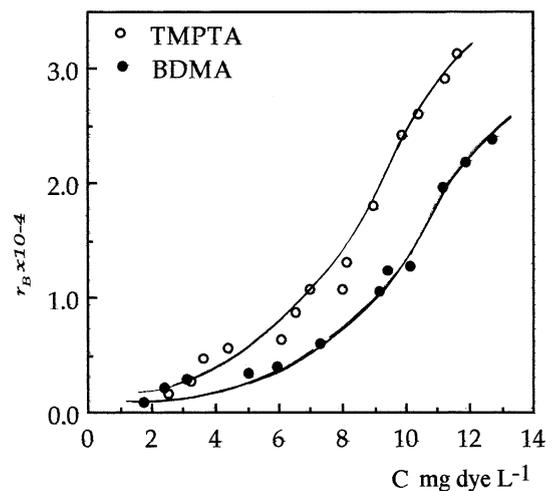

Fig. 5. Binding isotherms of AAm/MA hydrogel–dye systems.

molecules—a cooperative process—so that the isotherm will become convex to the concentration axis. Type S isotherms may originate through the adsorption of either non-polar molecules or polar molecules, always provided that the adsorbent–adsorbate force is relatively weak. A polar adsorbate of particular interest in this context is water, because the dispersion contribution to its overall interaction energy in unusually small compared with the polar contribution. Not surprisingly, water provided many examples of type S isotherm. Once, the hydrogel is covered with a layer of adsorbed water, however, the adsorbent–adsorbate interaction would be virtually reduce to the weak dispersion energy of water with dyes, so that a type S isotherm should results. In system that give rise to a type S isotherm,

Table 7
Binding ratios and % adsorptions of AAm/MA hydrogels

	MA (mg)		
	20	40	60
Binding ratios of BB-17			
TMPTA	0.867	0.994	1.02
BDMA	0.782	0.969	1.26
% Dye adsorption			
TMPTA	37.25	46.33	46.50
BDMA	36.00	44.58	56.25

however, the multilayer is being built up on some parts of the surface whilst the monolayer is still incomplete on other parts [27].

In later experiments, uptake of dye to AAm/MA hydrogels was measured effects of contents of MA. The binding ratio of the dye was calculated for uptake of dye within the hydrogel in 12 mg dye l^{-1} of aqueous solutions, and presented in Table 7. Table 7 presents that the binding ratio of the hydrogel/dye systems are increased. The binding ratio of dye/hydrogel systems gradually increased with the increase of content of MA in AAm/MA hydrogels. The percentage adsorptions of BB-17 onto AAm/MA hydrogels is changed among 36.0–56.0%. Increasing of carboxyl groups in the hydrogels with the increase of MA contents caused electrostatic interactions between the cationic groups of the dyes and the anionic groups of MA in the hydrogels.

4. Conclusion

In this study, AAm/MA hydrogels were prepared by free radical polymerization in solution. Some multifunctional crosslinker such as TMPTA and BDMA used at polymerization. Hydrogels were prepared in water, and swollen to equilibrium in water. Hydrogel systems swelled in the range 780–6050%. Equilibrium swelling data were used for determination of EWCs, some swelling parameters such as swelling exponent, swelling coefficients and diffusional behaviour of water of the hydrogel systems. The values of EWCs were calculated in the range 0.8873–0.9837. This result showed that AAm/MA hydrogels would be used as a new material (such as a biomaterial) on some biomedical applications, because EWCs was bigger than the percent water content value of the body about 0.60. The diffusion type of hydrogels was a non-Fickian diffusion character. It was seen that swelling of AAm/MA hydrogels increased with the increasing of content of MA.

The second part of this study has shown that AAm/MA hydrogels adsorb the monovalent cationic dye such as BB-17 while AAm hydrogels do not. Type *S* adsorption isotherms in Giles's classification system are found. The adsorptions of the dyes are increased with the content of MA in the hydrogels. The hydrogel systems has shown 36.0–56.0% adsorption of BB-17.

As a result, AAm/MA hydrogels can be used as a super water retainer for carrying of some substances in aquatic fields in pharmaceutical, agricultural, environmental and biomedical applications, or in the applications of immobilized biologically active molecules and AAm/MA hydrogels can be used as an adsorbent for the water pollutants such as cationic dyes, an important problems for the textile industry.

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