

Kinetics of Adsorption of Methylene Blue and Rhodamine 6G on Acrylic Acid-Based Superabsorbents

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ABSTRACT: Superabsorbent polymers (SAPs) of acrylic acid, sodium acrylate, and acrylamide (AM), crosslinked with ethylene glycol dimethacrylate, were synthesized by inverse suspension polymerization. The equilibrium swelling capacities of the SAPs were determined and these decreased with increasing AM content. The adsorption of the two cationic dyes, methylene blue and rhodamine 6G, on the dry as well as equilibrium swollen SAPs was investigated. The amount of the dye adsorbed at equilibrium per unit weight of the SAPs and the rate constants of adsorption were determined. The amount of the dye adsorbed at equilibrium by the SAPs decreased with increasing mol % of AM in the SAPs. The amount of the

dye adsorbed at equilibrium was almost equal for the dry and equilibrium swollen SAPs. However, the equilibrium swollen SAPs adsorbed dyes at a higher rate than the dry SAPs. The higher rate of adsorption was attributed to the availability of all the anionic groups present in the fully elongated conformation of the SAPs in the equilibrium swollen state. The effect of initial dye concentration on the adsorption was also investigated and the adsorption was described by Langmuir adsorption isotherms. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: acrylic acid; hydrogels; superabsorbents; adsorption; cationic dyes

INTRODUCTION

The superabsorbent polymers (SAPs) are crosslinked three-dimensional networks of hydrophilic polymers, which can absorb and retain more than 100 times of liquid of their own weight.¹ The superabsorbent characteristics of the SAPs arise due to the presence of the ionic groups in the three-dimensional networks. The presence of even a small amount of these ionic groups causes a high osmotic pressure difference between the network and the surrounding medium.² The inflow of water to balance the osmotic pressure difference results in the swelling of the SAPs. Due to the high water absorption and retention properties, SAPs are widely used in the personal hygiene products, such as baby diapers, sanitary napkins, and adult incontinence products.³ The SAPs also find biomedical applications such as drug-delivery contact lenses,⁴ controlled drug release devices,^{5,6} scaffolds for tissue engineering,⁶ and wound-healing dressings.⁷ They are also used to improve the water retention of soil and for the water purification and separation processes.

In the field of water purification, the SAPs are used for the removal of dyes and metal ions. The SAPs contain ionic repeat units that adsorb oppositely charged materials such as cationic or anionic dyes and metal ions from aqueous solutions. The removal of anionic dyes has been carried out by cationic hydrogels of poly(*N,N*-diethylamino ethyl methacrylate) crosslinked with ethylene glycol dimethacrylate,⁸ epichlorohydrin crosslinked hydroxyl propyl cellulose hydrogel,⁹ and poly(vinyl alcohol) and carboxymethyl cellulose copolymer hydrogels synthesized by electron beam irradiation.¹⁰ Recently, hydrogel nanocomposites of acrylamide (AM), itaconic acid and montmorillonite,¹¹ poly(2-(*N,N*-dimethylamino) ethyl methacrylate-*co*-2-acrylamido-2-methylpropane sulfonic acid-*co*-2-hydroxyethyl methacrylate) terpolymer/montmorillonite nanocomposite hydrogels,¹² and starch-graft-acrylic acid/montmorillonite superabsorbent nanocomposite hydrogels¹³ have been employed for the removal of cationic dyes, anionic dyes and metal ions, respectively. Chitosan-*g*-poly(acrylic acid)/attapulgite composites,¹⁴ chitosan-*g*-poly(acrylic acid)/biotite composites,¹⁵ chitosan-*g*-poly(acrylic acid)/halloysite composites,¹⁶ chitosan-*g*-poly(acrylic acid)/vermiculite hydrogels nanocomposites,¹⁷ carboxymethyl cellulose-*g*-poly(acrylic acid)/attapulgite hydrogel composites,¹⁸ and pH-responsive bisaromatic hydrogelator derived from isophthalic acid¹⁹ have been used for the adsorption of a cationic dye methylene blue (MB). Gamma

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irradiation synthesized Na-alginate/AM hydrogels,²⁰ chitosan hydrogel/SiO₂, and chitin hydrogel/SiO₂ hybrid materials,²¹ polyvinyl alcohol and activated carbon-based hydrogels and composites,²² semi-interpenetrating network hydrogels composed of polyethylene glycol and random copolymer of AM/sodium methacrylate,²³ macroporous hydrophobically modified poly(acrylic acid-acrylamide) hydrogel²⁴ and poly(acrylic acid-co-acrylamide)/attapulgitite composites²⁵ have been employed for the adsorption of various cationic dyes.

Although there are several studies on the adsorption of dyes and metal ions by dry hydrogels, none of these studies report the adsorption by hydrogels swollen to equilibrium. The understanding of the adsorption characteristics of the equilibrium swollen SAPs is important, as the SAPs from the domestic waste in contact with textile effluents may be either in dry or in equilibrium swollen state. In our previous study,²⁶ the adsorption of four cationic dyes Acriflavine, Auramine-O, Azure-I, and Pyronin-Y on dry ethylene glycol dimethacrylate (EGDMA) cross-linked poly(acrylic acid-co-sodium acrylate-co-acrylamide) superabsorbents was investigated. In this study, we investigate the adsorption of different dyes (MB and rhodamine 6G) on both the dry and swollen polymer. This study also investigates the adsorption isotherm and detailed adsorption kinetics. The effluents from textile industries normally contain mixtures of dyes. Thus, in this investigation, adsorption of dyes from their mixtures and adsorption of one dye over the SAP that has already adsorbed another dye has also been investigated.

In this study, acrylic acid (AA), sodium acrylate (SA), and acrylamide-based superabsorbents were synthesized by inverse suspension polymerization. The AM content was varied from 20–80 mol % and the crosslinking was imparted by ethylene glycol dimethacrylate. The synthesized SAPs were used to carry out the adsorption of two cationic dyes namely MB and rhodamine 6G in batch experiments. The dry as well as equilibrium swollen SAPs were used to carry out the adsorption. The adsorption of dyes was found to follow the first-order kinetics; the equilibrium swelling capacity and the rate constant of the adsorption were determined. The effect of initial dye concentration on the adsorption was also investigated. The experimental data for adsorption of the dyes fitted well with Langmuir adsorption isotherms. The effect of adsorption of one dye over the adsorption of the other dye and the simultaneous adsorption of the two dyes from their mixtures were also studied. To the best of our knowledge, this is the first study investigating the effect of the equilibrium swollen state of the SAPs on the adsorption of the dyes. This is also the first study that investigates the simultaneous adsorption of a dye mixture.

EXPERIMENTAL

Materials

Monomers, AA and AM, were purchased from Merck Limited (India) and S.D. Fine-Chem (India), respectively. EGDMA (98% pure), used as crosslinker, was obtained from Aldrich Chemicals (USA). The dyes, MB (minimum assay 96%), rhodamine 6G (R6G) (minimum assay 95%), and surfactant (Span-80) were obtained from Rolex Chemicals (India). Sodium hydroxide (NaOH) (assay 97%) and potassium persulfate (KPS) (assay 98%) were obtained from S. D. Fine-Chem (India). Methanol (HPLC grade) was purchased from Merck Limited (India). Milli-Q deionized (DI) water was used for all the experiments.

Synthesis of the SAPs

The SAPs with varying AA and AM contents were synthesized by inverse suspension polymerization. The polymerization was carried out in a four-necked round bottom flask having a reflux condenser, an inlet for N₂ and a temperature sensor. The fourth inlet was used to add the reactants. The reactants were mixed using a magnetic stirrer during the polymerization. The flask was maintained at the desired temperature using a temperature controller.

The dispersed phase contained of the monomers, namely AA, SA, AM, and the initiator KPS. The volume of the dispersed phase was maintained as 30 mL (1/3 of the continuous phase) for all the polymerizations. The required amount of AM was dissolved in 10 mL of DI water. The required volume of AA was taken in a beaker and neutralized by NaOH solution. NaOH required to neutralize the AA to a partial neutralization degree of 75% was dissolved in $(20 - V_{AA})$ mL of DI water. NaOH solution was added dropwise to AA under constant stirring and partially neutralized AA/SA was obtained. AA/SA mixture was added to the AM solution under stirring. Finally, initiator KPS (0.5 mol % of total monomers) was added to the monomer mixture and dissolved under nitrogen bubbling for 15 min.

For the preparation of continuous phase, 90 mL of toluene was taken in a four-necked round bottom flask. A water-in-oil surfactant Span-80 (0.33 vol % of toluene) was added to the flask and heated to 50°C under N₂ bubbling and stirring. The crosslinking agent, EGDMA of 0.5 mol % of the total monomers, was added to the flask and dissolved by raising the temperature to 80°C.

The dispersed phase was added dropwise to the continuous phase and polymerization was carried out at 80°C for 2 h under nitrogen bubbling. After the polymerization, the polymer was taken out of the flask and added to excess of methanol to remove unreacted monomers and water. The polymer was

TABLE I
Characteristics of the Cationic Dyes Used for the Adsorption Studies

Dye	Chemical formula	MW	λ_{\max} (nm)	CAS number	CI number	Molecular size (\AA^3)
Rhodamine 6G (R6G)	$\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$	479.01	525	989-38-8	45160	$13.07 \geq 12.17 \geq 5.66$
Methylene Blue (MB)	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$	373.86	664	7220-79-3	52015	$11.14 \geq 6.64 \geq 8.07$

further dried in a hot-air oven maintained at 80°C for 72 h. Poly(acrylic acid-co-sodium acrylate-co-acrylamide) superabsorbents with 20, 40, 60, and 80 mol % AM content were termed as AA/SA/AM-1, AA/SA/AM-2, AA/SA/AM-3, and AA/SA/AM-4, respectively. AA/SA ratio was maintained at 25/75 mol % for all the copolymeric SAPs.

Fourier transform infrared spectroscopy

Fourier transform infrared spectra of the synthesized polymers were collected on a Perkin Elmer Spectrum RX-I spectrometer. The spectra were recorded in transmission mode at a resolution of 4 cm^{-1} in the range of 4000–500 cm^{-1} .

Determination of the equilibrium swelling capacity of superabsorbents

The swelling capacity of the SAPs was determined by gravimetry. A known weight of the dry polymer was kept in a plastic basket and immersed in beakers containing 500 mL of DI water. The baskets were taken out at different times and excess water was removed by wiping with tissue papers. The weight of the swollen samples was measured and then they were returned to the respective beakers. The SAP achieves its equilibrium swelling capacity when it does not absorb water further. The equilibrium swelling capacity, S_{eq} (g of water/g of SAP), is defined as,

$$S_{\text{eq}} = \frac{W_{\text{eq}} - W_d}{W_d} \quad (1)$$

where W_d and W_{eq} are the weights of the SAP in its dry and equilibrium swollen states, respectively.

Adsorption of dyes on the SAPs

The adsorption of the two cationic dyes namely MB and rhodamine 6G (R6G) on the SAPs was investigated. The chemical formula, molecular weight, λ_{\max} , CAS number, color index number, and molecular sizes for these dyes are listed in Table I. The adsorption of the dyes was carried out in batch experiments in which 400 mL of the dye solution of required concentration was taken in a beaker and the pre-weighed amount of the SAP was added to it. During the experiments, the beakers were kept cov-

ered with aluminum foil and approximately 0.5 mL of the dye solution was taken out at various times. The samples were filtered and analyzed on a Shimadzu UV-1700 PharmaSpec UV-Vis spectrophotometer equipped with UVProbe 2.31 software. The samples were scanned in the wavelength range of 400–800 nm in the absorbance mode. The absorbance values at the λ_{\max} (the wavelength corresponding to the maximum absorbance) were converted to the concentration using the predetermined calibration curves for each dye. The amount of dye adsorbed per unit mass of the SAP (q), % removal efficiency (RE) of the hydrogel, and the partition coefficient (PC) are calculated using the following relations:

$$q = \frac{(C_0 - C)V}{W} = \text{amount of dye adsorbed per unit weight of the SAP at time } t \text{ (mg/g),}$$

$$q_{\text{eq}} = \frac{(C_0 - C_e)V}{W} = \text{amount of dye adsorbed per unit weight of the SAP at equilibrium (mg/g),}$$

$$\text{RE (\%)} = \left(\frac{C_0 - C}{C_0} \right) \times 100 = \text{removal efficiency,}$$

$$\text{PC} = \frac{C_0 - C}{C} = \text{partition coefficient,}$$

where C_0 and C are the initial dye concentration and dye concentration at time t , respectively (in mg/L). C_{eq} is the equilibrium dye concentration (mg/L), V is the volume of dye solution (L), and W is the weight of the dry SAP (g). The amount of dye adsorbed per unit mass of the SAP (q), RE, and PC indicate the efficacy of an adsorbent for the removal of dissolved materials from the solution.

The adsorption of MB and R6G by the SAPs was studied by carrying out the following experiments. The effect of the AM content on the adsorption was investigated for the adsorption of R6G on AA/SA/AM superabsorbents of 20, 40, 60, and 80 mol % AM content. The adsorption of dyes has been carried out by the SAP in its dry as well as equilibrium swollen state. To carry out the adsorption on the swollen SAP, the dry SAP was swollen to its equilibrium swelling capacity. Once the SAP achieved its equilibrium swelling capacity, the excess water was drained out and the swollen gel was used for the adsorption of dyes. The adsorption of MB and R6G on AA/SA/AM-1 was carried out from the individual dye solution as well as the mixtures of the two

dyes. The effect of the initial concentration of MB and R6G has been investigated for both dry as well as equilibrium swollen SAP. To test the efficiency of the SAP and possibility of desorption of the already adsorbed dye, the SAP used for the adsorption of first dye was transferred to the second dye solution and the adsorption of the second dye was investigated. All the experiments mentioned above were repeated at least three times.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy

In the FTIR spectra, given elsewhere,²⁷ of AA/SA/AM superabsorbents the characteristic peak of C=O of AM was observed at 1667 cm^{-1} and N—H stretching of AM group was observed at 3436.5 cm^{-1} . The peak at 1721 cm^{-1} corresponds to C=O of acrylate and the peak at 1561 cm^{-1} indicates the presence of $\text{COO}^{-}\text{Na}^{+}$ groups.

Equilibrium swelling capacities of the SAPs

The equilibrium swelling capacities, S_{eq} , of the various SAPs, calculated using eq. (1), decreased with increasing content of AM in the SAPs. The S_{eq} of AA/SA/AM-1, AA/SA/AM-2, AA/SA/AM-3, and AA/SA/AM-4 were found to be 622, 496, 285, and 215 g of water/g of SAP, respectively. The percentages of water in AA/SA/AM-1, AA/SA/AM-2, AA/SA/AM-3, and AA/SA/AM-4 superabsorbents were 99.84, 99.80, 99.65, and 99.54%, respectively. The detailed description of the kinetics of swelling of these SAPs is given elsewhere.²⁷

Adsorption of dyes

After the dry SAP is added to the dye solution, the swelling of the SAP and the adsorption of the dye from aqueous solution take place simultaneously. The adsorption of dyes onto the SAPs occurs due to the electrostatic attraction between the negatively charged repeat units of the SAPs and positively charged dye molecules. The adsorption occurs at a faster rate in the beginning and the amount of the dye adsorbed per unit weight of the SAP (q) saturates after a certain period of time. By this time, the SAP has adsorbed the maximum possible amount of dye, q_{eq} , from the aqueous solution and further decoloration of the dye solution does not take place. The amount of the dye adsorbed by the SAP and the rate of adsorption depends on the content of AM in the SAP, amount of the SAP employed for the adsorption, type of the dye, and the initial concentration of the dye.

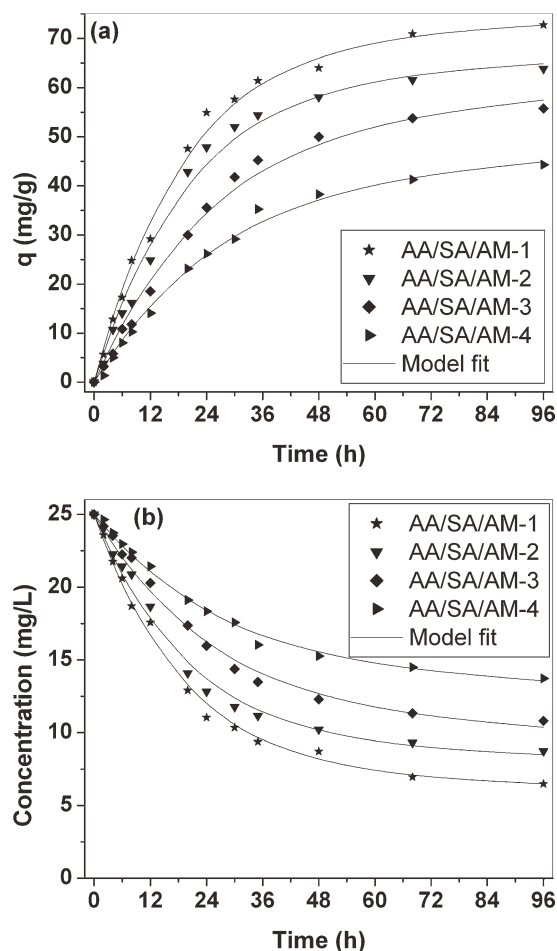


Figure 1 Variation in the (a) amount and (b) concentration of R6G adsorbed with time for the SAPs with varying AM content.

First-order kinetics of the adsorption of the dyes

A first-order model was found to describe the kinetics of the adsorption of dyes on the SAPs.

$$\frac{dq}{dt} = k_a(q_{\text{eq}} - q) \quad (2)$$

where k_a is the rate constant for the adsorption (h^{-1}). At time $t = 0$, $C = C_0$, $q = 0$, thus

$$q = q_{\text{eq}}[1 - \exp(-k_a t)] \quad (3)$$

The experimental data for the adsorption of MB and R6G was fitted by using eq. (3).

Effect of AM content in the SAPs for the adsorption of R6G

Figure 1(a) shows the increase in the amount of the dye adsorbed per unit weight of SAP with time for the adsorption of R6G on the SAPs with 20–80 mol % AM content. The decreasing concentration of the

TABLE II
The Effect of AM Content in the SAPs on the Adsorption of R6G from 25 mg/L Solution

SAP	AA (mol %)	SA (mol %)	AM (mol %)	q_{eq} (mg/g)	k_a (h^{-1})	RE (%)	PC
AA/SA/AM-1	20	60	20	73	0.050	74.7	2.9
AA/SA/AM-2	15	45	40	65	0.047	69.3	2.3
AA/SA/AM-3	10	30	60	59	0.036	62.8	1.7
AA/SA/AM-4	5	15	80	47	0.034	47.1	0.9

dye in aqueous solution with time is plotted in Figure 1(b). The dye adsorption followed first-order kinetics, given by eq. (3). The amount of the dye adsorbed at equilibrium (q_{eq}) and rate constant of adsorption (k_a) are listed in Table II. It is evident from Figure 1(a) and Table II that the amount of dye adsorbed per unit weight of the SAP (q_{eq}) decreases with increasing mol % of AM in the SAPs. The SAPs based on AA/SA/AM have both ionic and non-ionic repeat units. The ionic repeat units are due to the anionic AA/SA, while AM is responsible for the non-ionic repeat units in the SAPs. The cationic dyes are adsorbed on the SAPs due to the electrostatic attraction forces between the cationic dye molecules and the anionic groups in the SAPs. The non-ionic content of the polymer increases with the increase in the mol % of AM and decreases the number of anionic repeat units. The decreased number of anionic repeat units results in decline in the amount of the dye adsorbed at equilibrium.

These results are in agreement with the studies of AM and SA hydrogels crosslinked with glutaraldehyde and divinylbenzene,²⁸ AM/maleic acid-based superabsorbents crosslinked with TMPTA and BDMA,²⁹ γ radiation synthesized acrylic/maleic acid hydrogels,³⁰ AM-AA hydrogels synthesized by ⁶⁰Co- γ radiation³¹ and radiation synthesized copolymeric hydrogels of acrylamide, N-vinyl-2-pyrrolidone, itaconic acid, and maleic acid,³² where the amount of dye adsorbed per unit weight of the dry hydrogel increased with increase in the anionic monomer content of the hydrogels at equilibrium. The removal efficiency of the SAP and the PC also decrease with increasing AM content in the SAP (Table II). As AA/SA/AM-1 (20 mol % AM content) showed the maximum adsorption capacity, further adsorption studies were carried out using this polymer.

Effect of the dry and equilibrium swollen SAPs on the adsorption of dyes

The SAPs discarded from personal hygiene products, coming into contact with textile waste may be in both the dry and equilibrium swollen state. Thus, the investigation of the effect of the dry and equilibrium swollen states of the SAP on the adsorption of

dyes becomes important. Dry and equilibrium swollen AA/SA/AM-1 was used to adsorb MG and R6G from 25 mg/L aqueous solutions. Figure 2(a,b) show the variation in the amount of dye adsorbed per unit weight of the SAP with time for the adsorption of MB and R6G, respectively. The inset of these figures depicts the reduction in the concentration of the dye with time. Both the dry and swollen SAPs follow the first-order kinetics for the adsorption of the dye given by eq. (3). The amount of the dye adsorbed at equilibrium (q_{eq}) and rate constant of adsorption are

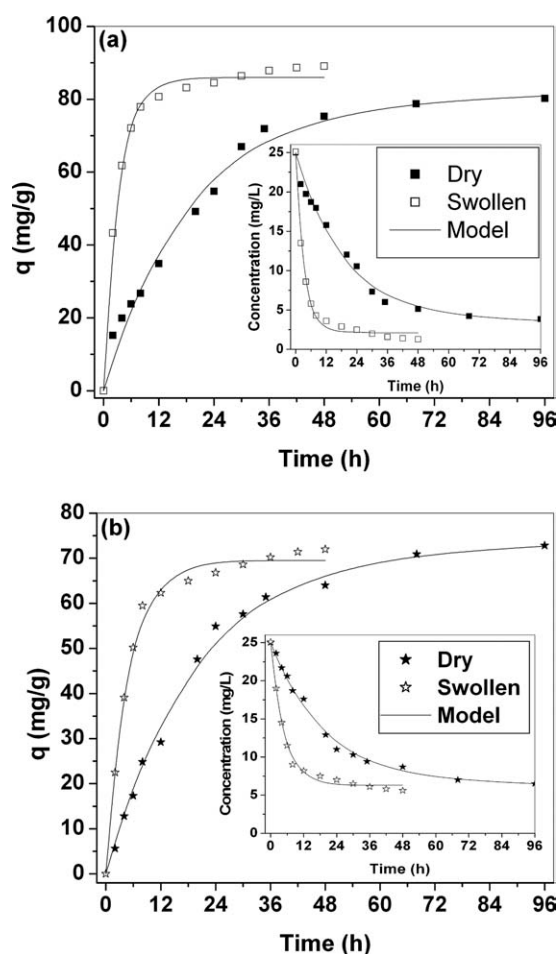


Figure 2 Variation in the amount of (a) MB and (b) R6G adsorbed by the dry and equilibrium swollen AA/SA/AM-1 with time. The inset figures show the concentration vs. time profiles.

TABLE III
Kinetic Parameters for the Adsorption of MB and R6G on Dry and Equilibrium Swollen AA/SA/AM-1 from 25 mg/L Dye Solutions

Dye	AA/SA/AM-1	q_{eq} (mg/g)	k_a (h^{-1})
MB	Dry	81	0.052
MB	Swollen	86	0.318
R6G	Dry	73	0.050
R6G	Swollen	69	0.209

listed in Table III. It is evident from the Figure 2(a,b) and Table III that the amount of dye adsorbed per unit weight of the SAP is almost the same for the dry and equilibrium swollen SAP at equilibrium, but the equilibrium swollen SAP adsorbs dyes at a much faster rate than the dry SAP. The adsorption of the dye occurs due to the electrostatic attraction between anionic repeat units of the SAP and the cationic dye molecules. When the adsorption of the dyes is carried out using dry SAPs the adsorption of the dye and the swelling of the SAP take place simultaneously. Not all the anionic repeat units are available at the beginning, hence initially the dye is adsorbed by the anionic groups at the surface of the SAP. As the SAP swells, more anionic groups become available and the dye is adsorbed till all the anionic sites are covered. During the adsorption of dyes onto the equilibrium swollen SAPs, already absorbed water molecules are replaced by the dye molecules. In the case of equilibrium swollen SAP, the chains are in fully elongated conformations² and, hence all the anionic repeat units are accessible from the beginning for the adsorption of cationic dye molecules. Thus, the dye is adsorbed at much faster rate by the equilibrium swollen SAPs. As the number of anionic repeat units per unit weight of the SAP is almost the same in both dry and equilibrium swollen SAP the amount of dye adsorbed per unit weight of the SAP is also almost equal.

Effect of initial dye concentration

The effect of the initial dye concentration was investigated for the adsorption of MB and R6G on both dry as well as the equilibrium swollen SAPs. Figure 3(a,b) show the variation of amount adsorbed and the concentration with time, respectively, for the adsorption of R6G on dry AA/SA/AM-1. The amount of the dye adsorbed per unit weight of the SAP (q) increased with increasing initial dye concentration and became almost constant beyond an initial dye concentration of 500 mg/L. It can be seen from Figure 3(b) that almost all the dye is adsorbed when the initial dye concentration is up to 100 mg/L. Similar q vs. time and concentration vs. time profiles were obtained for the adsorption of R6G on the equilib-

rium swollen AA/SA/AM-1. When the initial dye concentration is low, the concentration of the anionic groups in the SAP is more than the concentration of the cationic dye molecules, and therefore, the SAP adsorbs almost all the dye from the aqueous solution. Beyond a certain initial dye concentration, the concentration of the dye molecules exceeds the concentration of the anionic groups in the SAP, hence not all the dye can be adsorbed and the SAP becomes saturated after adsorbing a certain amount of the dye.

The plots for the adsorption of MB on dry AA/SA/AM-1 are shown in Figure 4(a,b), respectively. The amount of dye adsorbed by the SAP increased with the initial dye concentration and became constant beyond 250 mg/L. Similar results were obtained for the adsorption of MB on the equilibrium swollen AA/SA/AM-1.

Adsorption isotherms

An adsorption isotherm describes the relationship between the amount of the adsorbate adsorbed at equilibrium by adsorbent and the equilibrium concentration of adsorbate in the solution.

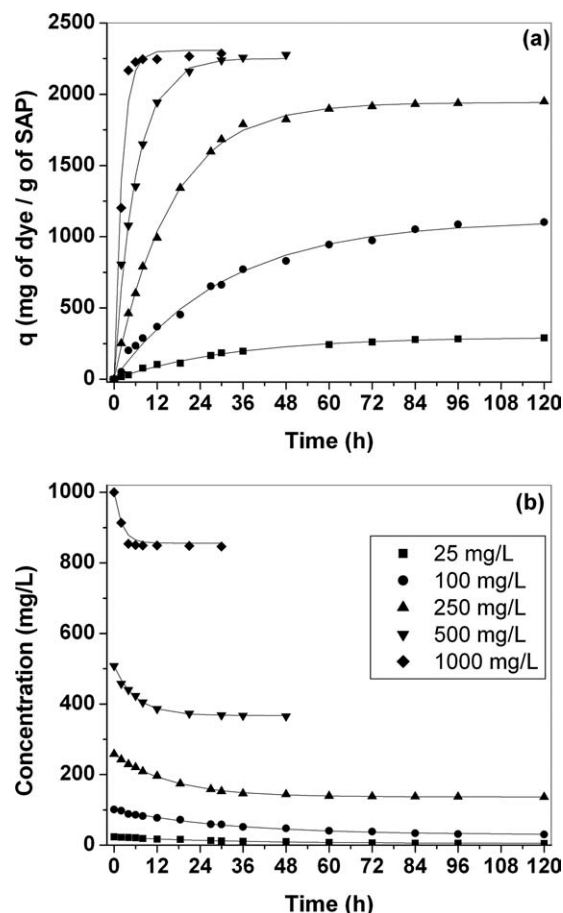


Figure 3 Variation in the (a) amount and (b) concentration of R6G adsorbed on dry AA/SA/AM-1 with time for various initial concentrations of R6G.

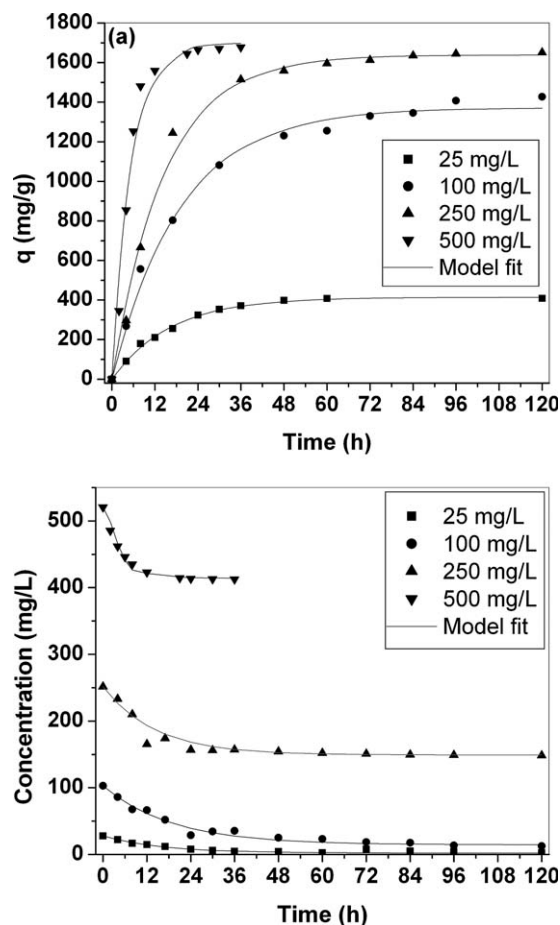


Figure 4 Variation in the (a) amount and (b) concentration of MB adsorbed on dry AA/SA/AM-1 with time for various initial concentrations of MB.

The Langmuir isotherm^{32,33} assumes monolayer adsorption of the adsorbent over the adsorbate and is given by

$$q_{eq} = \frac{q_m k_l C_{eq}}{1 + k_l C_{eq}} \quad (4)$$

The linear form of Langmuir adsorption isotherm is

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_m} + \frac{1}{q_m k_l} \quad (5)$$

where C_{eq} is the equilibrium adsorbate concentration in mg/L, q_{eq} is the amount of the adsorbate adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_m is the maximum amount of the adsorbate adsorbed per unit weight of the adsorbent (mg/g) and k_l is the Langmuir adsorption constant (L/mg).

Freundlich isotherm is an empirical relation between the equilibrium dye uptake and equilibrium dye concentration and was proposed to account for the surface heterogeneity and is given as^{32,33}

$$q_{eq} = k_f C_{eq}^{1/n} \quad (6)$$

The parameter n in the equation signifies the heterogeneity. The isotherm underpredicted the uptake at intermediate equilibrium concentrations and overpredicted the uptake at high equilibrium concentrations.

A composite isotherm, such as the Langmuir-Freundlich isotherm^{32,33} is often used to describe adsorption, whose expression is given by

$$q_{eq} = \frac{q_m k_{lf} C_{eq}^{n_{lf}}}{1 + k_{lf} C_{eq}^{n_{lf}}} \quad (7)$$

The isotherm has three parameters and it reduces to Langmuir isotherm for $n_{lf} = 1$ and to Freundlich isotherm at low concentrations. Fitting of the data using this isotherm gave n_{lf} of 1.02 indicating that the two parameter Langmuir isotherm is satisfactory for fitting the experimental data. Thus the Langmuir isotherm describes the adsorption process fairly well and was used to model the experimental data.

Figures 5 and 6 show the variation of the amount of dye adsorbed at equilibrium with equilibrium concentration for the adsorption of R6G and MB on dry and equilibrium swollen AA/SA/AM-1. The insets in these figures show the linearized Langmuir

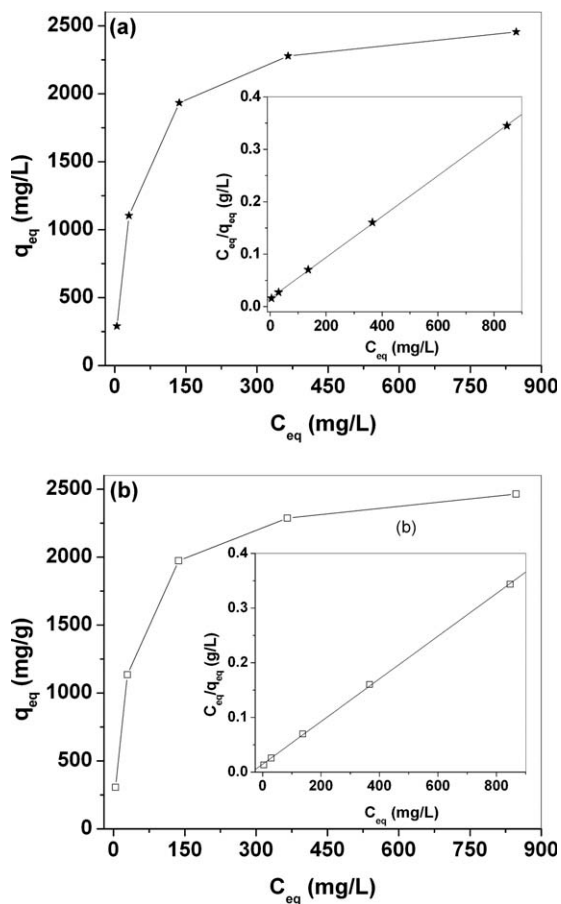


Figure 5 Variation of the amount of R6G adsorbed at equilibrium (q_{eq}) with equilibrium concentration (C_{eq}) on (a) dry and (b) equilibrium swollen AA/SA/AM-1. The inset figures show the Langmuir adsorption isotherms.

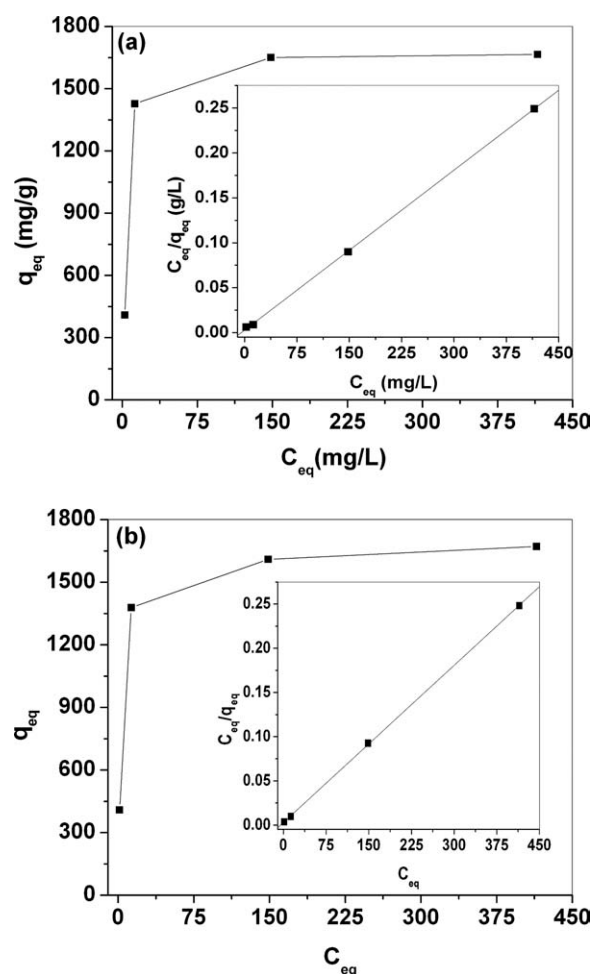


Figure 6 Variation of the amount of MB adsorbed at equilibrium (q_{eq}) with equilibrium concentration (C_{eq}) on (a) dry and (b) equilibrium swollen AA/SA/AM-1. The inset figures show the Langmuir adsorption isotherms.

adsorption isotherms for the corresponding adsorption curves. The parameters determined from the linear form of Langmuir adsorption isotherm [eq. (5)] are listed in Table IV. The Langmuir isotherm is able to correlate the experimental data well indicating that the adsorption is due to monolayer coverage. From the maximum adsorption capacity q_m obtained from the Langmuir adsorption isotherms, it can be observed that both the dry and equilibrium swollen SAPs adsorb similar amounts of the dye. The AA/SA/AM superabsorbents showed better

TABLE IV
Parameters Obtained from Langmuir Isotherms for the Adsorption of MB and R6G on Both Dry and Swollen SAP

SAP	Dye	q_m (g/L)	k_l (L/mg)
Dry AA/SA/AM-1	R6G	2570	0.024
Swollen AA/SA/AM-1	R6G	2564	0.027
Dry AA/SA/AM-1	MB	1686	0.223
Swollen AA/SA/AM-1	MB	1686	0.217

adsorption capacity for MB (1686.3 mg/g) as compared to that exhibited by poly(*N,N*-dimethylacrylamide-*co*-sodium acrylate)³⁴ and other hydrogels reported in the literature.

Adsorption cycles

To investigate how the adsorption of one dye affects the adsorption of the other dye, SAPs used for the adsorption of R6G (or MB) were transferred to the aqueous solution of MB (or R6G). The adsorption of the first dye was done on the equilibrium swollen AA/SA/AM-1. The concentration of the first and second dye was 25 mg/L. The variation of amount adsorbed and concentration with time profiles are shown in Figure 7(a,b), respectively, for the adsorption of R6G on equilibrium swollen AA/SA/AM-1 and then for the adsorption of MB on R6G-adsorbed AA/SA/AM-1 (swollen to equilibrium). Experiments were also carried out for the adsorption of MB on equilibrium swollen AA/SA/AM-1 and then for the adsorption of R6G on MB-adsorbed AA/SA/AM-1 (swollen to equilibrium). The variation of the

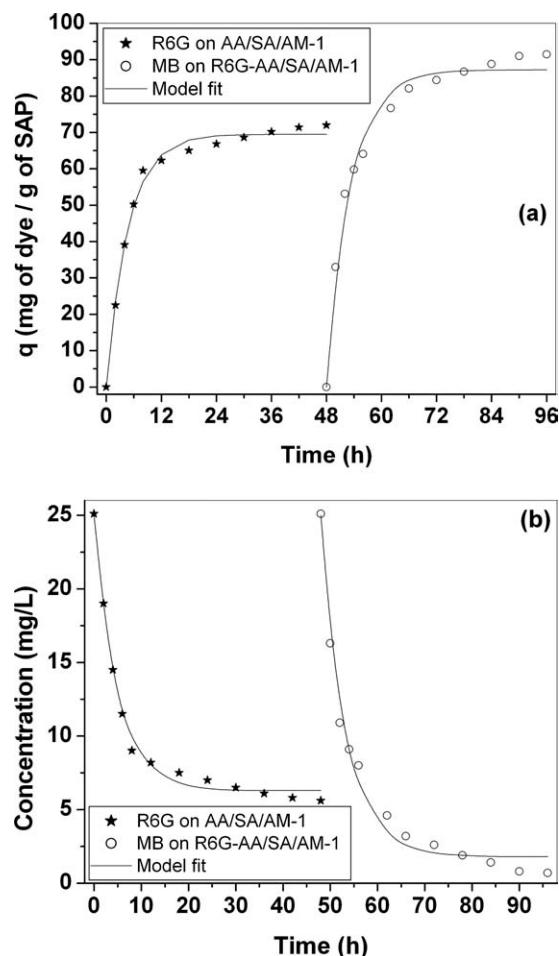


Figure 7 Variation in the (a) amount and (b) concentration of R6G and MB adsorbed on the equilibrium swollen AA/SA/AM-1 with time.

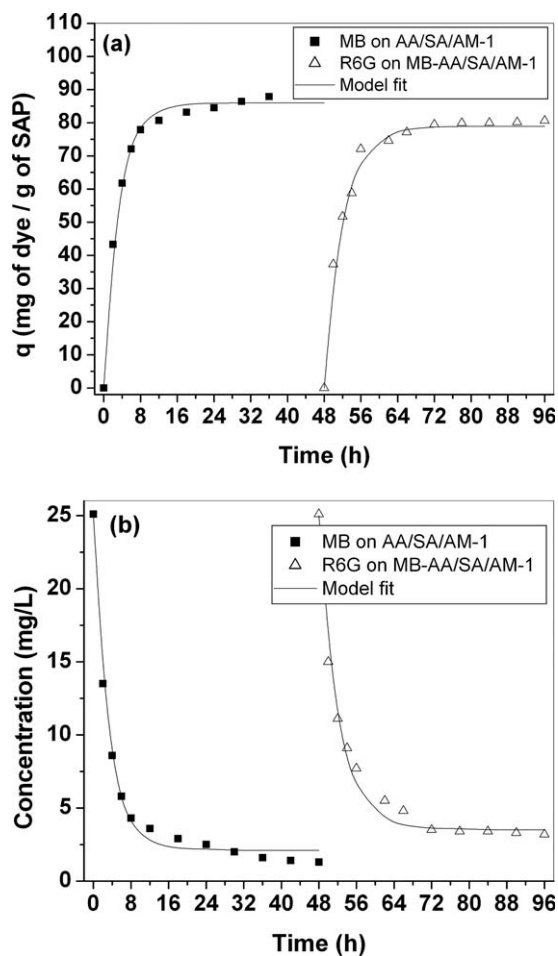


Figure 8 Variation in the (a) amount and (b) concentration of MB and R6G adsorbed on the equilibrium swollen AA/SA/AM-1 with time.

amount adsorbed and concentration with time plots are shown in Figure 8(a,b), respectively. The equilibrium amount and the rate constant values determined from the first-order model [eq. (3)] fits are listed in Table V. In both the cases, the rate constants for the adsorption of the second dye are lower than that for the first dye. From the Figure 7(a) and Table V, it can be inferred that the adsorption of R6G on AA/SA/AM-1 (swollen to equilibrium) does not affect the adsorption of MB on R6G-adsorbed AA/SA/AM-1 (swollen to equilibrium). The amount of MB adsorbed on R6G-adsorbed AA/SA/AM-1

TABLE V
Kinetic Parameters for the Adsorption of First and Second Dye on Equilibrium Swollen AA/SA/AM-1 from 25 mg/L Solutions

Dye	Adsorbent	q_{eq} (mg/g)	k_a (h^{-1})
R6G	AA/SA/AM-1	69	0.209
MB	R6G-AA/SA/AM-1	87	0.198
MB	AA/SA/AM-1	86	0.318
R6G	MB-AA/SA/AM-1	79	0.253

(swollen to equilibrium), 87 mg/g, is almost equal to that adsorbed by AA/SA/AM-1 (swollen to equilibrium), 86 mg/g. But the amount of R6G adsorbed on MB-adsorbed AA/SA/AM-1 (swollen to equilibrium) is found to be more than that adsorbed on AA/SA/AM-1 (swollen to equilibrium) [see Fig. 8(a) and Table V], indicating that the adsorption of the MB on the SAP increases the adsorption of R6G.

Adsorption of dyes from the mixture

Often the waste water from the textile industries contains more than one pollutant. Thus, to investigate the adsorption of multiple pollutants from the aqueous solutions, the adsorption of MB and R6G from their mixture was also carried out. The concentration of the two dyes, in mg/L, was maintained the same in the mixtures. The mixtures contained 12.5 and 25.0 mg/L of the each dye and the adsorption was carried out on equilibrium swollen AA/SA/AM-1. The variation in the amount of the two

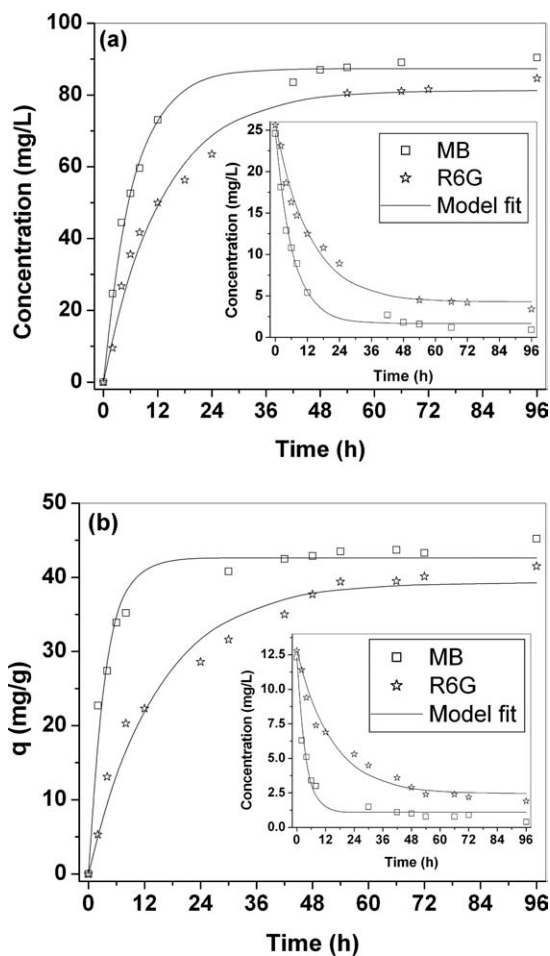


Figure 9 Variation in the amount of R6G and MB adsorbed on the equilibrium swollen AA/SA/AM-1 with time from a mixture of (a) 25.0 mg/L and (b) 12.5 mg/L of each dye. The inset figures show the time variation of concentration.

TABLE VI
Kinetic Parameters for the Adsorption of MB and R6G from Mixtures

MB-R6G mixture	Dye	q_{eq} (mg/g)	k_a (h^{-1})
12.5 mg/L each	R6G	42	0.053
	MB	43	0.277
25.0 mg/L each	R6G	81	0.079
	MB	87	0.157

dyes adsorbed from the mixtures of concentration 25.0 and 12.5 mg/L are shown in Figure 9(a,b), respectively. The adsorption of the two dyes from the mixtures occurs in a similar manner as that from the individual solution of each dye. The amounts of the two dyes adsorbed from the mixtures are listed in Table VI. The SAP adsorbs slightly more amount of MB than R6G from both the mixtures. The rate constant for the adsorption is higher for MB than that of R6G. The rate constants of adsorption of each dye from the mixture are lower than that of the adsorption from the individual dye solution. The equilibrium swollen AA/SA/AM-1 adsorbs almost the same amount of MB (87 mg/g, Table VI) from 25.0 mg/L mixture as that adsorbed from 25.0 mg/L MB solution (86 mg/g, Table III). But, the amount of R6G (81 mg/g, Table VI) from 25.0 mg/L mixture was found to be higher than that adsorbed from 25.0 mg/L R6G solution (69 mg/g, Table III). Thus, the adsorption of MB seems to be enhancing the adsorption of R6G from the mixture.

CONCLUSIONS

The equilibrium swelling capacity of AA, SA, and acrylate-based superabsorbents crosslinked with EGDMA decreased with an increase in the AM content. Adsorption of the cationic dyes MB and R6G on the SAPs was carried out and was found to follow the first-order kinetics. The amount of dye adsorbed per unit weight of the SAP decreased with increasing mol % of AM in the superabsorbents. Although the amount of dye adsorbed at equilibrium by the dry and equilibrium swollen SAPs were the equal, the equilibrium swollen SAP adsorbed the dyes at higher rate than the dry SAP. The higher rate of adsorption by equilibrium swollen SAP results from the availability of all the anionic repeat units from the beginning for the adsorption of dyes. The amount of dye adsorbed by the SAPs increased with increasing initial dye concentration up to a certain concentration and became almost constant beyond this concentration. The adsorption of MB and R6G on both the dry as well as equilibrium swollen SAPs followed the Langmuir isotherms. The effect of the adsorption of one dye over the adsorption of the other dye was investigated. The dye adsorption was also carried out

from the mixtures of the two dyes. The adsorption of MB was unaffected by the presence of R6G in the mixture but the adsorption of R6G was enhanced by the presence of MB in the mixture.

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