

Adsorption of Anionic Dyes on a Reversibly Swelling Cationic Superabsorbent Polymer

Neelesh Bharti Shukla, Giridhar Madras

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

Correspondence to: G. Madras (E-mail: giridhar@chemeng.iisc.ernet.in)

ABSTRACT: A cationic monomer [2-(methacryloyloxy)ethyl]trimethylammonium chloride was polymerized using *N,N'*-methylenebisacrylamide as the crosslinker to obtain a cationic superabsorbent polymer (SAP). This SAP was characterized by Fourier transform-infrared spectroscopy, and the equilibrium swelling capacity was determined by swelling in water. The SAP was subjected to cyclic swelling/deswelling in water and NaCl solution. The conductivity of the swelling medium was monitored during the swelling/deswelling and was related to the swelling/deswelling characteristics of the SAP. The adsorption of five anionic dyes of different classes on the SAP was carried out and was found to follow the first-order kinetics. The Langmuir adsorption isotherms were found to fit the equilibrium adsorption data. The dye adsorption capacity of the SAP synthesized in this study was higher than that obtained for other hydrogels reported in the literature. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: superabsorbent; hydrogels; swelling; deswelling; adsorption

Received 18 January 2012; accepted 20 April 2012; published online

DOI: 10.1002/app.37929

INTRODUCTION

The three-dimensional networks of polymers that are able to absorb and retain more than 100 times of liquid of their own weight are called superabsorbent polymers (SAPs).¹ The SAPs contain ionic groups in the three-dimensional networks, which results in the superabsorbent characteristics, and allows them to adsorb oppositely charged materials from the swelling medium. The presence of ionic groups results in a very high osmotic pressure difference between the network and surrounding medium.² The osmotic pressure is balanced by the inflow of large amount of water resulting in the high degree of swelling of the SAPs. The superabsorbent nature of these SAPs makes them an obvious material of choice for personal hygiene products, such as diapers and sanitary napkins.³ They are also used as contact lenses,⁴ controlled drug release devices,^{5,6} tissue engineering scaffolds,⁶ and wound-healing dressing⁷ in the field of biomedical engineering.

Although most of the commercially used SAPs are anionic based on acrylic acid monomer,⁸ cationic SAPs may be useful in the field of water purification for the removal of anionic impurities. Cationic hydrogels of poly(*N,N*-diethylamino ethyl methacrylate) (PDEAEMA) crosslinked with ethylene glycol dimethacrylate,⁹ epichlorohydrin crosslinked hydroxyl propyl cellulose

hydrogel,¹⁰ and poly(vinyl alcohol) and carboxymethyl cellulose copolymer hydrogels synthesized by electron beam irradiation¹¹ have been used for the adsorption of anionic dyes. The copolymer of acrylamide and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) was used for the removal of toluidine blue.¹² METAC has been grafted onto sawdust and used for the removal of anionic dyes.¹³ A cationic magnetic hydrogel based on (3-acrylamidopropyl)trimethylammonium chloride has been used for the removal of natural organic matter.¹⁴ Cationic hydrogels have also been used for the removal of Cr(VI) from ground water and soil.¹⁵ Selective adsorption of Hg(II) has also been carried out by METAC based water-insoluble resin.¹⁶

Compared to the significant literature available on the synthesis of anionic superabsorbents, there are relatively few studies on cationic superabsorbents. In this study, a cationic SAP of METAC was synthesized by solution polymerization using *N,N'*-methylenebisacrylamide (MBA) as crosslinker. The superabsorbent was subjected to cyclic swelling/deswelling in deionized (DI) water and NaCl solution. The SAP was found to follow first-order kinetics during the swelling/deswelling cycles. The equilibrium swelling capacities, limiting swelling capacities, and the rate constant of swelling/deswelling were determined. To the best of our knowledge, this is the first study where the conductivity of the medium was monitored during the

© 2012 Wiley Periodicals, Inc.

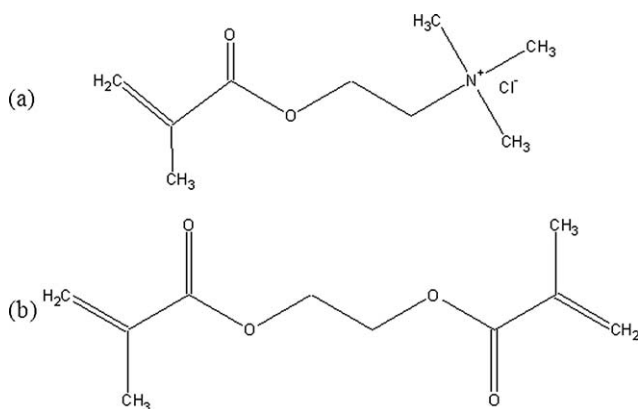


Figure 1. (a) [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride; (b) *N,N'*-methylenebisacrylamide.

swelling/deswelling cycles and related to the swelling/deswelling characteristics of the cationic SAP. The SAP was also used to adsorb five anionic dyes belonging to different classes. The adsorption of the dyes followed first-order kinetics and the equilibrium data was fitted satisfactorily with Langmuir adsorption isotherm. The SAP synthesized in this study exhibited higher adsorption capacities compared to other materials reported in the literature.

EXPERIMENTAL

Materials

Monomer METAC was purchased from Sigma-Aldrich (St. Louis, MO). Initiator ammonium persulfate (APS) and crosslinking agent MBA were procured from S.D. Fine-Chem (Mumbai, India). Accelerator *N,N,N',N'*-tetramethylethylenediamine (TEMED) was obtained from Fluka. Dyes, congo red (CR), and orange G (OG) were purchased from S.D. Fine-Chem (Mumbai, India). Alizarin cyanine green (ACG), fluorescein sodium (FL), and indigo carmine (IC) were procured from Rolex Industries Limited, Mumbai. Milli-Q deionized (DI) water was used for all the experiments.

Synthesis of the Cationic SAP

Poly[2-(methacryloyloxy)ethyl]trimethylammonium chloride (PMETAC) SAP crosslinked with MBA was synthesized by solution polymerization in aqueous medium using a redox initiator system APS/TEMED. Figure 1 shows the chemical structures of the monomer and crosslinker. 5.66 mL of METAC (80 wt % solution in water) was taken in 25 mL beaker and 3.41 mL MBA solution (5 wt % solution) was added to it under continuous stirring. 0.0275 g of APS (initiator) was added to the monomer-crosslinker mixture and allowed to dissolve completely. 2.8 mL of TEMED accelerator (5 wt % solution) was added to it. This reaction mixture was allowed to polymerize at room temperature for 24 h. The obtained polymer was swollen in excess DI water and water was changed four times to remove the residual monomer and water soluble polymer. The swollen polymer was dried in a hot air oven at 80°C until constant weight of dry polymer was obtained.

Fourier Transform-Infrared Spectroscopy

Fourier transform-infrared (FTIR) spectroscopy study was carried out on a Perkin Elmer FT-IR Spectrum RX-I spectrometer. The dry polymer was ground into fine powder and was mixed with KBr to form thin disks (10 mm diameter). The FT-IR spectrum of the polymer was recorded in transmission mode in the range of 400–4400 cm⁻¹ at a resolution of 4 cm⁻¹.

Determination of Equilibrium Capacity of the SAP

0.10 (±0.0050) g of the dry SAP was taken in a basket made of nylon mesh and immersed in 500 mL of DI water. The baskets were taken out at different times and the excess water was allowed to drain. The baskets were weighed and then returned to the beakers. The swelling capacity (*S*), g of water/g of SAP, was determined by following equation:

$$S = \frac{W_s - W_d}{W_d}$$

where *W_d* and *W_s* are the weights of the dry and swollen SAP, respectively. The SAP achieved its equilibrium swelling capacity (*S_{eq}*) when no more water was absorbed.

Reversible Swelling/Deswelling Characteristics

Swelling Cycle 1. For the first swelling cycle, 0.10 (±0.0050) g of the SAPs were taken in nylon baskets and immersed in 500 mL of DI water. The baskets were taken out at various times and wiped with tissue papers to remove the excess water. The baskets were weighed to determine swelling capacity before being returned to the beakers. This was done until the SAPs achieved their equilibrium swelling capacity *S_{eq}* and did not absorb water anymore.

Deswelling Cycle 1. The SAPs swollen to equilibrium in the first swelling cycle were transferred to 400 mL of 0.1 M NaCl solution. The samples were periodically removed and weighed until they achieved the limiting swelling capacity, *S_{lim}*.

Swelling Cycle 2 and Deswelling Cycle 2. After the completion of the first deswelling cycle, the SAPs were transferred to DI water for swelling to equilibrium and subsequently to 0.1 M NaCl for deswelling to the limiting swelling capacity.

Swelling Cycle 3 and Deswelling Cycle 3. At the end of the second deswelling cycle, the SAP was subjected to third swelling and deswelling cycles, as described previously.

Adsorption of Dyes

The adsorption of five anionic dyes of different classes, namely ACG, CR, FL, IC, and OG, on the cationic SAP was investigated in batch experiments. Table I shows the class, chemical formula, color index number, λ_{max} , molecular weight, and molecular sizes of the dyes. To carry out the adsorption experiments 0.10 (±0.0050) g of dry polymer was added to 400 mL of dye solution. The beakers containing polymer and dye solutions were covered with aluminum foil and stored in dark. At various times, about 0.5 mL of dye solution was taken out and analyzed to determine the dye concentration. The sample analysis was done on a Shimadzu UV-1700 PharmaSpec UV-Vis spectrometer and the spectra were recorded using UVProbe 2.31 software. The samples were analyzed in absorbance mode in the

Table I. Characteristics of Dyes

Dye	Class	Chemical formula	C. I. No.	λ_{\max} (nm)	MW (g/mol)	Molecular size (\AA^3)
Fluorescein sodium (FL)	Xanthene, Fluorene, Fluorone	$\text{C}_{20}\text{H}_{10}\text{Na}_2\text{O}_5$	45350	490	376.28	$8.71 \times 9.20 \times 5.39$
Orange G (OG)	Monoazo	$\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$	16230	480	452.38	$13.08 \times 7.53 \times 4.98$
Indigo carmine (IC)	Indigo	$\text{C}_{16}\text{H}_8\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$	73015	610	466.36	$15.66 \times 5.52 \times 4.08$
Alizarin cyanine green (ACG)	Anthraquinonic	$\text{C}_{28}\text{H}_{20}\text{N}_2\text{Na}_2\text{O}_8\text{S}_2$	61570	640	622.59	$12.06 \times 12.82 \times 4.42$
Congo red (CR)	Diazo	$\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$	22120	495	696.67	$26.56 \times 7.19 \times 4.37$

wavelength range of 400–800 nm. Predetermined calibration curves were used to convert the absorbance values at the wavelength corresponding to the maximum absorption (λ_{\max}) to the concentration of dye. The adsorption of dyes over the polymer was quantified using following relations,

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

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

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

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

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

RESULTS AND DISCUSSION

Fourier Transform-Infrared Spectroscopy

Figure 2 shows the FTIR spectrum of PMETAC. The characteristic peak at 1727.2 cm^{-1} is attributed to the stretching vibrations of the carbonyl group. The peak at 1482 and 955 cm^{-1} are assigned to the bending and stretching vibrations of quaternary ammonium group, respectively. Thus, the formation of PMETAC was confirmed.

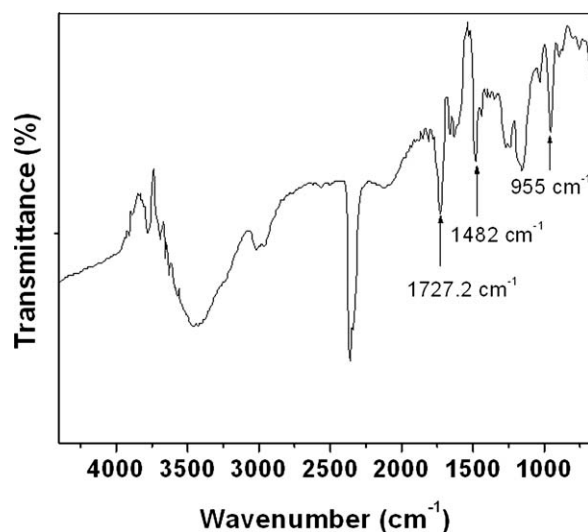
Equilibrium Swelling Capacity of the SAP

The crosslinked PMETAC contains positively charged quaternary ammonium groups (fixed charges) and negatively charged chloride ions (mobile ions) in its repeat units. The electrostatic repulsion force between the fixed charges expands the polymer network and imparts the superabsorbent nature to the polymer.¹⁷ The concentration difference of the mobile ions, inside the polymer network and outside in swelling medium, causes an osmotic pressure difference. Large amount of water flows into the polymer network to balance the osmotic pressure and gives the charged crosslinked network its superabsorbent charac-

teristics. The polymer swells until the swelling force is overcome by the elastic repulsive force. The swelling capacity at this stage is known as the equilibrium swelling capacity of the SAP. Figure 3 shows the variation in the swelling capacity of the polymer with time. The swelling of the SAP followed first-order kinetics. Similar first-order swelling kinetics has been exhibited by hydrogels of acrylamide with anionic monomers,¹⁸ carboxymethyl cellulose-g-poly(acrylamide-co-2-acrylamido-2-methylpropan sulfonic acid),¹⁹ and anionic and cationic starch-based superabsorbents.²⁰ It is evident from the Figure 3 that the PMETAC superabsorbent exhibited an equilibrium swelling capacity (S_{eq}) of 141.8 g of water/g of SAP. The equilibrium swelling capacity of the cationic SAP in this study was almost equal to the ethylene glycol dimethacrylate crosslinked [*N*-vinyl pyrrolidone/2-(methacryloyloxyethyl)trimethylammonium chloride] based hydrogels (78–155 g/g, depending on the composition and the crosslinker concentration),²¹ and much higher than that of the radiation synthesized MALETMC-based copolymeric hydrogels (10 g/g).²²

Swelling/Deswelling Kinetics of the SAP

The swelling/deswelling cycles 1, 2, and 3 of the SAP are shown in Figure 4(a-c), respectively. The SAP in this study followed first-order swelling/deswelling kinetics during the three swelling/deswelling cycles. Similar swelling/deswelling behavior was observed for poly(acrylic acid-co-acrylamide-co-sodium acrylate)

**Figure 2.** FTIR spectrum of PMALETMAC.

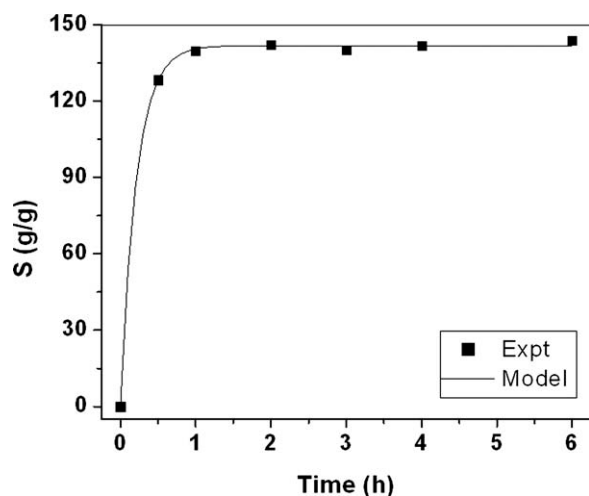


Figure 3. Variation in the swelling capacity of the SAP with time.

SAPs.¹⁷ We directly use the equations describing swelling/deswelling kinetics, derived in the previous work.¹⁷ Swelling cycle 1 is described by,

$$S = S_{eq}[1 - \exp(-k_s t)] \quad (1)$$

and swelling cycle 2 and 3 are described by

$$S = S_{eq} - (S_{eq} - S_0) \exp(-k_s t) \quad (2)$$

The deswelling cycles 1, 2, and 3 are given by

$$S = S_{lim} + (S_0 - S_{lim}) \exp(-k_d t) \quad (3)$$

where k_s and k_d are the swelling and deswelling rate constants, respectively. S_0 , S_{eq} , and S_{lim} are the initial, equilibrium, and limiting swelling capacities of the SAPs, respectively.

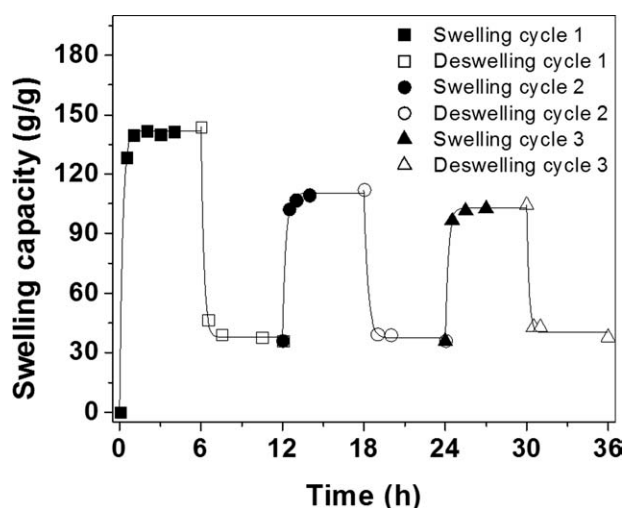


Figure 4. Variation in the swelling capacity of the SAP during three cycles.

The eqs. (1)–(3) satisfactorily describe the swelling and deswelling kinetics of the SAPs over multiple cycles.

In Figures 4(a–c), the experimental data has been fitted by the first-order eqs. (1)–(3) and the kinetic parameters are given in Table II. The experimental data was fitted using the nonlinear curve fit option of origin software and R^2 was more than 0.998 for all the fittings. It can be observed from Table II that the equilibrium swelling capacities achieved by the SAPs in swelling cycle 2 and 3 are almost equal, but are lower than that in the swelling cycle 1. During the deswelling cycle1, NaCl diffuses into the swollen SAP. This NaCl is released into the swelling medium during the swelling cycle 2 and 3. Therefore, the swelling medium effectively turns into NaCl solution. Thus, the osmotic pressure difference between the SAP and the medium is decreased and the SAP swells to a lower extent. This diffusion of NaCl was verified by monitoring the conductivity of the swelling/deswelling medium by a conductivity meter (Eutech 11+, Eutech Instruments). The amount of the NaCl released in the swelling medium during swelling cycles 2 and 3 was found to be almost the same, as confirmed by the conductivity measurements. Hence, the SAPs achieve almost the same equilibrium swelling capacity during the swelling cycle 2 and 3 (Table II). Similar swelling/deswelling behavior has been observed for poly(acrylic acid-co-acrylamide-co-sodium acrylate) SAPs.¹⁷ The limiting swelling capacities of the SAPs are almost equal in all the deswelling cycles (Table II).

Adsorption of Dyes

When the cationic SAP is added to an anionic dye solution, the swelling of the SAP and the adsorption of the dye occur simultaneously. The adsorption of the dye onto the SAP occurs due to the electrostatic attraction between the cationic groups of the SAP and the anionic groups of the dye. The SAP adsorbs dye and becomes colored and the dye solution turns clearer due to the removal of the dye. The amount of the dye adsorbed by the SAP increases at a faster rate in the beginning and levels off after a certain period of time. The SAP adsorbs the maximum possible amount of the dye and the further decoloration of the dye solution does not take place. The adsorption of five anionic dyes ACG, CR, FL, IC, and OG on the cationic superabsorbent

Table II. Various Parameters for Swelling/Deswelling Cycles

	Equilibrium swelling capacity (g/g)	Swelling rate constant (h^{-1})	R^2
Swelling cycle 1	141.8	4.69	1.000
Swelling cycle 2	110.0	4.41	0.998
Swelling cycle 3	102.9	4.73	0.999
	Limiting swelling capacity (g/g)	Deswelling rate constant (h^{-1})	R^2
Deswelling cycle 1	37.8	4.92	0.999
Deswelling cycle 2	37.4	3.52	0.999
Deswelling cycle 3	40.2	6.23	0.999

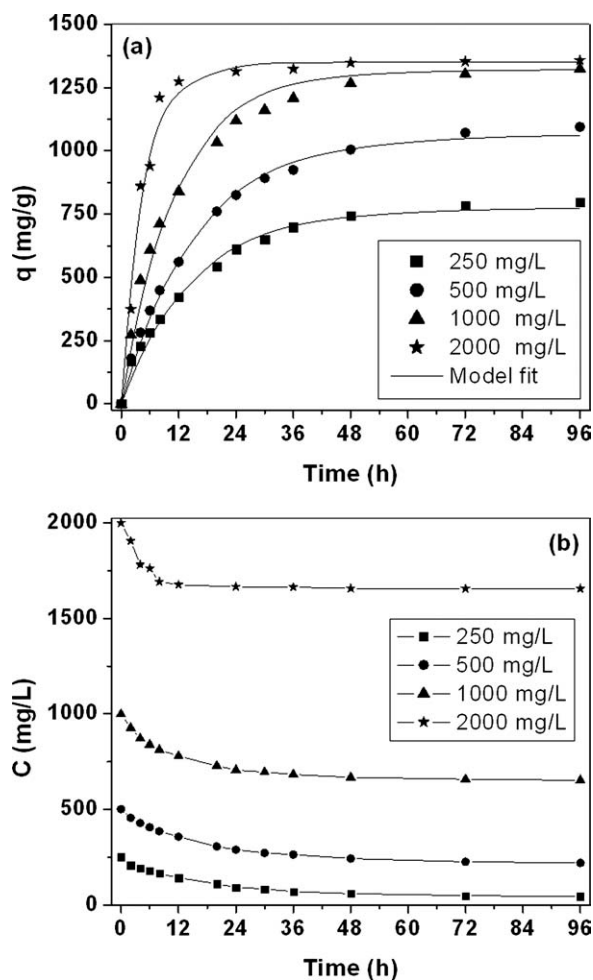


Figure 5. Variation in the (a) amount and (b) concentration of FL adsorbed on PMALETMAC for different initial concentrations of FL.

PMETAC was carried out. Various initial concentrations of the dyes were also used.

First-Order Model for the Adsorption of Dyes. A first-order model was found to fit the experimental data satisfactorily.

$$\frac{dq}{dt} = k_a(q_{eq} - q) \tag{4}$$

Where q and q_{eq} are the amounts of the dye adsorbed per unit weight of the SAP (mg/g) at any time t and at equilibrium, respectively. k_a denotes the rate constant for the adsorption (h^{-1}). At time $t = 0$, $C = C_0$, $q = 0$, thus we get,

$$q = q_{eq}[1 - \exp(-k_a t)] \tag{5}$$

Table III. Kinetic Parameters for the Adsorption of FL

C_0 (mg/L)	q_{eq} (mg/g)	k_a (h^{-1})	RE (%)	PC
250	774	0.07	82.3	4.6
500	1063	0.06	56.1	1.3
1000	1320	0.09	34.7	0.5
2000	1350	0.22	17.2	0.2

The experimentally obtained amount of the dye adsorbed with time for all the dyes was fitted using eq. (5).

The Effect to Initial Dye Concentration. The same amount of the SAP was brought into contact with dye solutions of different initial concentrations, to investigate the effect of the initial concentration of the dye (C_0) on the adsorption. Figure 5(a) shows the increase in amount of the FL adsorbed per unit weight of SAP (q), and Figure 5(b) shows the reduction in the dye concentration (C) with adsorption time for various initial dye concentrations. The adsorption of FL followed first-order kinetics given by eq. (5) and the rate parameters obtained are listed in Table III. At equilibrium, the amount of the dye adsorbed per unit weight of the SAP (q_{eq}) increased with an increase in the initial dye concentration and became almost constant beyond an initial dye concentration of 1000 mg/L (Figure 5(a), Table III). When the initial dye concentration is low, the concentration of the cationic groups in the SAP is more than the concentration of the anionic 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 cationic groups in the SAP. Therefore, the dye cannot be

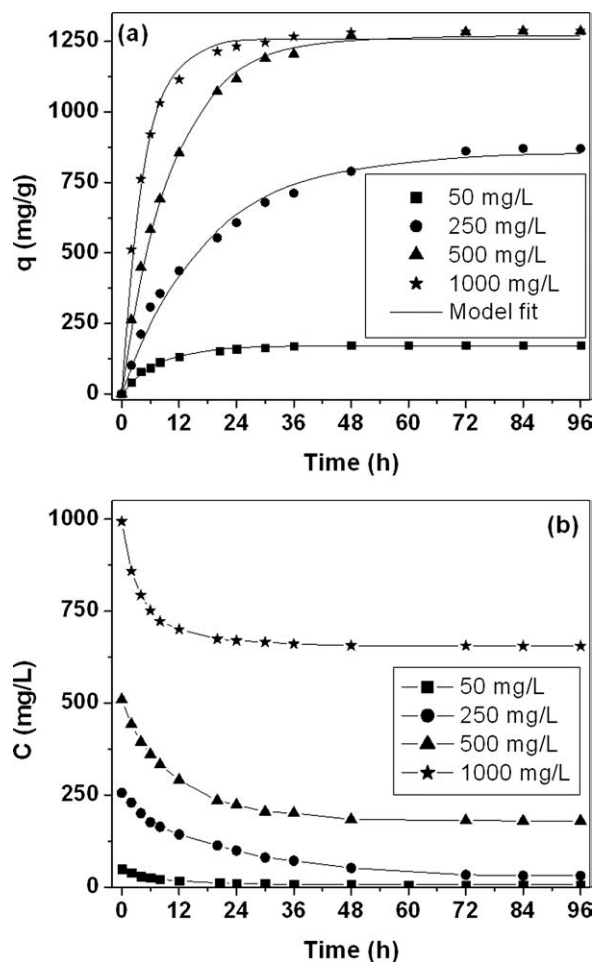


Figure 6. Variation in the (a) amount and (b) concentration of IC adsorbed on PMALETMAC for different initial concentrations of IC.

Table IV. Kinetic Parameters for the Adsorption of IC

C_0 (mg/L)	q_{eq} (mg/g)	k_a (h^{-1})	RE (%)	PC
50	171	0.13	87.8	7.2
250	866	0.06	86.7	6.5
500	1269	0.10	63.8	1.8
1000	1259	0.22	34.5	0.5

completely adsorbed and the SAP becomes saturated after adsorbing a certain amount of the dye.

The adsorption of ACG, CR, IC, and OG also followed the first-order kinetics. Similar first-order adsorption kinetics has been observed for the adsorption of cationic dyes on acrylic acid/acrylamide based SAPs.⁸ The plots of amount of dye adsorbed and dye concentration with time for the adsorption of IC on the SAP are shown in Figure 6(a) and (b), respectively. As can be noticed from the Figure 6(a) and Table IV, the amount of dye adsorbed by the SAP increased with the initial dye concentration and became constant beyond 500 mg/L. Radiation-induced cationic PDEAEMA hydrogel crosslinked by ethylene glycol dimethacrylate⁹ has been used for the removal of IC. The maximum amount of IC adsorbed by the hydrogel was found to be 96.7 mg/g. Thus, the amount of IC adsorbed by PMETAC (1341 mg/g) in this study is much higher than that by the PDEAEMA. The maximum amount of the CR adsorbed by PMETAC was 1043 mg/g, which was much higher than that adsorbed by chitosan hydrogel beads impregnated with cetyl trimethyl ammonium bromide²³ (385.9 mg/g). Graft polymerized METAC onto saw dust has been used for the removal of OG.¹³ The PMETAC also adsorbed higher amount of OG (1490 mg/g), as compared to that adsorbed by the modified saw dust¹³ (430 mg/g). Thus, the cationic SAP used in this study is able to adsorb much larger amounts of dyes when compared to the other adsorbents reported in literature.

The RE and the PCs of FL and IC are listed in Tables III and IV, respectively. The RE of the SAP, described as the percentage of the dye adsorbed by the SAP, decreases with increasing initial dye concentration. The PC, the ratio of the dye in the SAP to that in the dye solution, also decreases with increasing initial dye concentration. The RE and PC denote the efficacy of the adsorbate in removing adsorbent. The decreasing RE and PC with increasing initial dye concentration suggest that fraction of the dye adsorbed by the SAP decreases with increasing C_0 . Similar results were obtained for the other anionic dyes used in this study.

Adsorption Isotherm. Various adsorption isotherms were tried and the experimental data was found to fit satisfactorily with the Langmuir adsorption isotherm. The Langmuir adsorption isotherm²⁴ assumes the monolayer adsorption of the adsorbent onto the adsorbate and is given by

$$q_{eq} = \frac{q_m k_l C_{eq}}{1 + k_l C_{eq}} \quad (6)$$

The linear form of the Langmuir adsorption isotherm is

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_m} + \frac{1}{q_m k_l} \quad (7)$$

where C_{eq} is the equilibrium adsorbate concentration (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).

The variation in the amount of dye adsorbed at equilibrium (q_{eq}) with the equilibrium dye concentration for FL and IC are plotted in Figure 7(a) and (b), respectively. The inset figures show the linear plots of C_{eq}/q_{eq} versus C_{eq} . Similar plots were obtained for ACG, CR, and OG. The parameters obtained from the linear form of the Langmuir adsorption isotherm [eq. (6)] are listed in Table V.

Comparison of Adsorption of Various Dyes. Figure 8 shows the variation in the concentrations of ACG, CR, IC, FL, and OG ($C_0 = 1000$ mg/L) with adsorption time. The cationic SAP

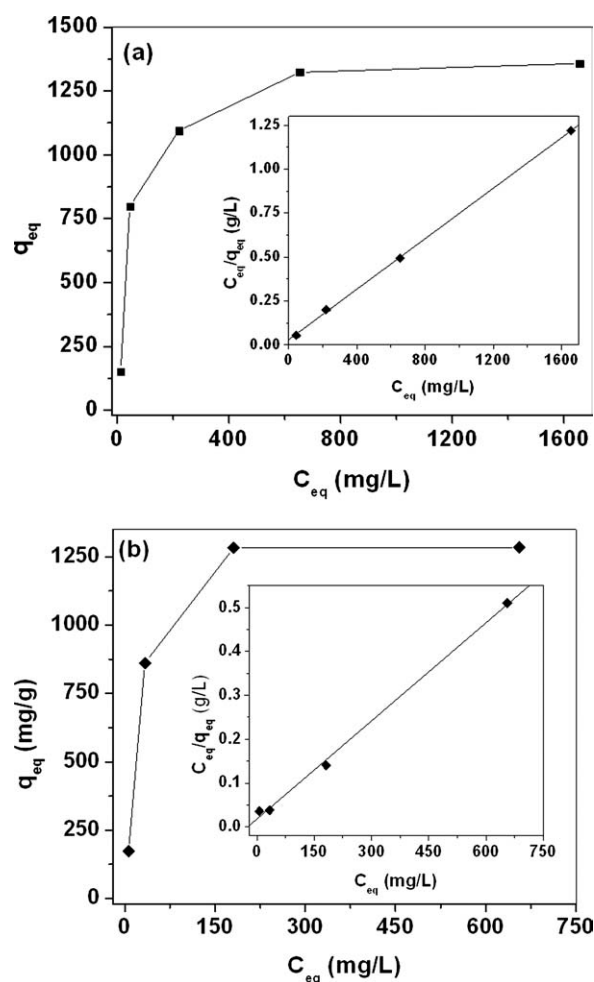


Figure 7. The amount of dye adsorbed at equilibrium versus the equilibrium dye concentration for (a) FL, (b) IC. The inset figures show the Langmuir adsorption isotherms.

Table V. Parameters Obtained from Langmuir Adsorption Isotherms

Dye	MW (g/mol)	k_l	q_m (mg/g)	q_m (mmol/g)	R^2
FL	376.28	0.023	1394	3.71	0.998
OG	452.38	0.128	1490	3.29	0.998
IC	466.36	0.041	1341	2.88	0.997
ACG	622.59	0.043	1011	1.63	0.999
CR	696.67	0.091	1043	1.50	0.999

is able to adsorb all the anionic dyes belonging to different classes. The adsorption of the dyes onto the superabsorbent occurs due to the electrostatic attraction between the anionic groups of the dye and the cationic quaternary ammonium group of the SAP. Thus, the type of the anionic groups, the number of anionic groups, and their placement in dye molecule will have a significant effect on the adsorption of the dyes than the class of the dye. Although the dyes belong to different classes, ACG, CR, IC, and OG contain two SO_3^- groups per dye molecule and FL contains one COO^- and O^- group per dye molecule. Thus, all the dyes are divalent, that is, they contain a -2 charge.

The adsorption of various anionic dyes can be compared based on the parameters obtained from the Langmuir adsorption isotherms. Table V lists the maximum amount of the dye adsorbed per unit weight of the SAP, q_m (in mg/g and mmol/g) for all the dyes, obtained from the Langmuir adsorption isotherms. The maximum amount of the dye adsorbed by the SAP (q_m in mmol/g) follows the following order: FL > OG > IC > ACG > CR. Thus, the q_m (in mmol/g) decreases with increasing MW of the dye (Table V). Further, the time taken to reach q_{eq} also increased with increasing MW and was found to be 24, 30, 36, 72, and 96 h for FL, OG, IC, ACG, and CR, respectively. As the MW (and the size, Table I) of the dye molecule increases, it becomes more difficult for larger dye molecule to access the inner cationic sites of the superabsorbent. Thus, not all the sites

are accessible and the maximum amount of the dye that can be adsorbed decreases.

CONCLUSIONS

A cationic superabsorbent poly([2-(methacryloxy)ethyl]trimethyl ammonium chloride) (PMETAC) crosslinked with MBA was synthesized by solution polymerization and characterized by FTIR. The SAP was found to have an equilibrium swelling capacity of 141.8 g of water/g of the SAP. The SAP exhibited the reversible swelling/deswelling behavior when the medium was changed between DI water and NaCl solution. The equilibrium swelling capacity achieved by the SAP in the swelling cycle 2 and 3 was found to be lower than that in swelling cycle 1 due to the diffusion of NaCl into the SAP during the deswelling cycles. This NaCl was released in the swelling medium during swelling cycle 2 and 3. The adsorption of anionic dyes of different classes followed first-order kinetics, and the equilibrium was satisfactorily described by Langmuir adsorption isotherms. The maximum amount of the dyes adsorbed by the SAP (in mmol/g) decreased with increasing MW of the dye.

ACKNOWLEDGMENTS

The authors thank the department of science and technology for financial support.

REFERENCES

1. Güven, O.; Şen, M.; Karadağ, E.; Saraydın, D. *Radiat. Phys. Chem.* **1999**, *56*, 381.
2. Kajjari, P. B.; Manjeshwar, L. S.; Aminabhavi, T. M. *Ind. Eng. Chem. Res.* **2011**, *50*, 13280.
3. Gürdağ, G.; Kurtuluş, B. *Ind. Eng. Chem. Res.* **2010**, *49*, 12675.
4. Sato, T.; Uchida, R.; Tanigawa, H.; Uno, K.; Murakami, A. *J. Appl. Polym. Sci.* **2005**, *98*, 731.
5. Mullarney, M. P.; Seery, T. A. P.; Weiss, R. A. *Polymer* **2006**, *47*, 3845.
6. Dash, M.; Chiellini, F.; Ottenbrite, R. M.; Chiellini, E. *Prog. Polym. Sci.* **2011**, *36*, 981.
7. Kajjari, P. B.; Manjeshwar, L. S.; Aminabhavi, T. M. *Ind. Eng. Chem. Res.* **2011**, *50*, 7833.
8. Shukla, N. B.; Madras, G. *J. Appl. Polym. Sci.* **2012**, *124*, 3892.
9. Sari, M. M. *Water Sci. Technol.* **2010**, *61*, 2097.

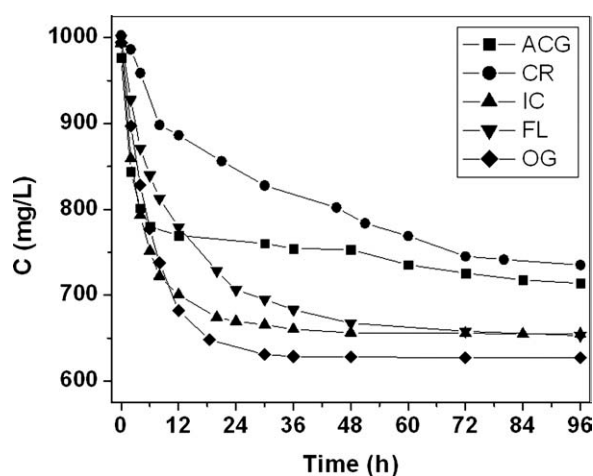


Figure 8. Variation in the concentration of anionic dyes during the adsorption on PMALETMAC.

10. Yan, L.; Shuai, Q.; Gong, X.; Gu, Q.; Yu, H. *Clean Soil, Air, Water* **2009**, *37*, 392.
11. Taleb, M. F. A.; El-Mohdy, H. L. A.; El-Rehim, H. A. A. *J. Hazard. Mater.* **2009**, *168*, 68.
12. Shen, J.; Ren, L.; Zhuang, Y. Y. *J. Hazard. Mater.* **2006**, *136*, 809.
13. Marchetti, V.; Ge Arardin, P.; Loubinoux, B. *Holz als Roh- und Werkstoff* **2000**, *58*, 53.
14. Rao, P.; Lo, I. M. C.; Yin, K.; Tang, S. C. N. *J. Environ. Manag.* **2011**, *92*, 1690.
15. Tang, S. C.; Yin, K.; Lo, I. M. *J. Contam. Hydrol.* **2011**, *125*, 39.
16. Rivas, B. L.; Maturana, H. A.; Villegas, S. *Polym. Bull.* **1997**, *39*, 445.
17. Shukla, N. B.; Madras, G. *Ind. Eng. Chem. Res.* **2011**, *50*, 10918.
18. Yao, K.-J.; Zhou, W.-J. *J. Appl. Polym. Sci.* **1994**, *53*, 1533.
19. Pourjavadi, A.; Ghasemzadeh, H.; Mojahedi, F. *J. Appl. Polym. Sci.* **2009**, *113*, 3442.
20. Castel, D.; Ricard, A.; Audebert, R. *J. Appl. Polym. Sci.* **1990**, *39*, 11.
21. Dadhaniya, P. V.; Patel, M. P.; Patel, R. G. *Polym. Bull.* **2006**, *58*, 359.
22. Mun, G. A.; Nurkeeva, Z. S.; Khutoryanskiy, V. V.; Serga-ziyev, A. D.; Rosiak, J. M. *Radiat. Phys. Chem.* **2002**, *65*, 67.
23. Chatterjee, S.; Lee, D. S.; Lee, M. W.; Woo, S. H. *Bioresour. Technol.* **2009**, *100*, 2803.
24. Chen, C. Y.; Wang, P.; Zhuang, Y. Y. *J. Environ. Sci.* **2005**, *17*, 1018.