

Poly(Acrylamide/Laponite) Nanocomposite Hydrogels: Swelling and Cationic Dye Adsorption Properties

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ABSTRACT: Super adsorbent polyacrylamide (PAAm)/nanoclay (laponite, Lap) hydrogels were prepared by *in situ* free radical polymerization of AAm in an aqueous solution with clay as a crosslinker. The swelling properties and water-soluble cationic dye adsorption behaviors of the PAAm/laponite (PAAm/Lap) nanocomposite (NC) hydrogels were investigated. The parameters of swelling and diffusion of water in dye solutions were evaluated for the PAAm/Lap NC hydrogels. The adsorption behavior of the monovalent cationic dyes such as Basic Blue 12 (BB 12), Basic Blue 9 (BB 9), and Basic Violet 1 (BV 1), were studied on the NC hydrogels. The effects of the clay content of the hydrogel on its cationic dye uptake behavior were studied. The adsorption studies indicated that the rates of dye uptake by the NC hydrogels increased in the follow-

ing order: BB 9 > BB 12 > BV 1. This order is similar to the swelling results of the PAAm/Lap NC hydrogel in the dye solutions. The equilibrium uptakes of the different dyes by the PAAm/Lap NC hydrogel were nearly the same. In the dye absorption studies, S-type adsorption in the Giles classification system was found for the BB 12 and BV 1 dyes, whereas L-type was observed for the BB 9 dye. After the heat treatment of PAAm/Lap, the rate of dye uptake and equilibrium dye uptake were increased. The NC hydrogels may be considered as a good candidate for environmental applications to retain more water and to remove dyes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1786–1798, 2009

Key words: polyacrylamide; nanocomposite; hydrogels; dyes; adsorption

INTRODUCTION

Polymeric hydrogels, consisting of a three-dimensional polymer network and water filling at the interstitial space of the network, have attracted much attention of scientists as functional soft materials. To date, hydrogels have been used in many fields such as soft contact lenses, super adsorbent polymeric gels used in sanitary napkins and disposable diapers, carriers for protein and nucleic acid in gel electrophoresis, amendments in greening and agriculture, medical and food products, etc. Also, many functional, polymeric hydrogels have been investigated for their potential use in glucose-responsive, insulin releasing gels,¹ photoresponsive gels,² enzyme carriers,³ separation devices,⁴ colloid crystals⁵ and cell-cultivation substrates.⁶ Hydrogels loaded

with dispersed clays are a new class of composite materials which combine the elasticity and permeability of the gels with the high ability of the clays to adsorb different substances.^{7–9} Many hydrogel composites such as polyacrylamide (PAAm) with bentonites^{7,10–12} or montmorillonites,¹³ polyacrylic acid¹⁴ or poly (*N*-isopropylAAm)¹⁵ with montmorillonites, etc., have been studied. Among the possible host materials, clays are natural, abundant, and inexpensive minerals that have a unique layered structure, high-mechanical strength as well as high-chemical resistance. It is well known that clays are good adsorbents for removing dye and other contaminants from the wastewater of the textile and dye industries. Many clay minerals are adsorb/desorb organic molecules, and so are widely studied as carriers or supports for pharmaceuticals.

Recently, clay-polymer nanocomposites (NCs) have been the focus of much attention because of their excellent physical properties, such as their toughness, high modulus, heat resistance, transparency, and so on.¹⁶ These properties are much superior to those that would be expected by a simple additive rule. This is partially due to the strong interactions at the clay-polymer interface. Owing to

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the nature of the complex molecules of clay, a variety of chemical reactions can take place at its surface due to its high chemical reactivity, including reactions with a complex chemistry.^{17,18}

With the growing use of a variety of dyes, the pollution from dye wastewater is becoming a major environmental problem. Synthetic dyes represent a relatively large group of organic chemicals having potential toxicity and low biodegradability. In particular, some water-soluble cationic dyes could cause a great deal of damage to natural ecosystems when they are discharged with wastewater. Colored waters are also objectionable on esthetic grounds for drinking and other municipal and agricultural purposes. Many researchers have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions.^{19–21} Although some treatment methods have been developed, the economic and effective removal of these dyes still remains a challenging area.

For the removal of cationic dyes, polymer hydrogels and their composites have employed because of their unique properties, such as their excellent dimensional and adsorption behaviors. Most of these hydrogels are prepared by the copolymerization of AAm with some kinds of acid, to endow them with the ability to remove cationic dyes from the water. The acid, which has negative charges, can interact with the cationic dye. Recently, some researchers used clay-filled hydrogel composites for the removal of cationic dyes.^{22–25} To date, the clays used are all natural and all the hydrogels used for this purpose were crosslinked by an organic crosslinker. Recently, Hara-guchi et al. prepared nanoclay incorporated hydrogels using hectorite clay as a crosslinker in place of the traditional organic crosslinkers.²² It was found that the mechanical properties of the NC hydrogels improved with increasing hectorite content.^{23–25}

Such novel NC hydrogels can obtain with a high content of laponite (Lap) XLS, which is a synthetic hectorite modified by tetrasodium pyrophosphate.²⁶ This clay has many advantages, such as its low viscosity even at a high clay loading, stable dispersion in water and ease of mixing.²⁷ Because there are a lot of negative charges on the clay surface, it can readily interact with cationic dye molecules. Moreover, the polymer chains of NC hydrogels synthesized without an organic crosslinker are more flexible, so the cationic dye molecules can easily interact with the anionic charges present on the surface of modified Lap clay.

The aim of this study is to investigate the swelling properties and dye adsorption characteristics of nanoclay crosslinked PAAm hydrogels. Dynamic swelling studies are important for the swelling characterization of NC hydrogel systems. In this research work, authors have made an attempt to find a con-

venient method of removing water-soluble monovalent cationic dyes from aqueous solutions by adsorption on a novel polymeric adsorbent such as PAAm/Lap XLS clay hydrogels. Water-soluble monovalent cationic dyes, such as Basic Blue 12 (BB 12), Basic Blue 9 (BB 9), and Basic Violet 1 (BV 1), resemble the large molecular weight dyes found in wastewater.

EXPERIMENTAL

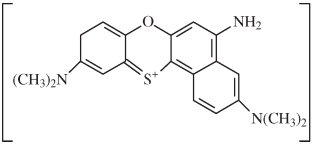
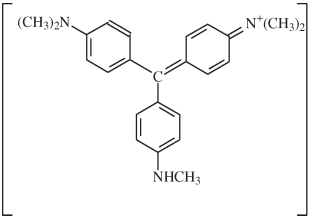
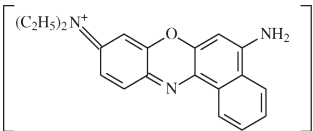
Materials

AAm and the synthetic hectorite, Lap XLS (cation exchange capacity = 104 mequiv/100 g), were obtained from KanTo Chemical Industries, Ltd., Tokyo, Japan and Rockwood Co. (Princeton, NJ), respectively. The composition of Lap XLS is 92.32 wt % $\text{Mg}_{5.34}\text{Li}_{0.66}\text{Si}_8\text{O}_{20}(\text{OH})_4\text{Na}_{0.66}$ and 7.68 wt % $\text{Na}_4\text{P}_2\text{O}_7$. Potassium persulfate (initiator) and *N,N,N',N'*-tetramethylene diamine (TEMED) (catalyst) were obtained from Tokyo Chemical Industry Co. Ltd., Tokyo, Japan and used without further purification. The monovalent cationic dyes namely, Basic Blue 9 (BB-9), Basic Blue 12 (BB-12), and Basic Violet 1 (BV-1) (Merck, Darmstadt, Germany), were of analytical reagent grade and used as received (Table I). Deionized water was distilled for all experiments including the swelling experiments. For the preparation of the hydrogels, nitrogen gas was bubbled through the distilled water for more than 3 h prior to use.

Preparation of polyacrylamide/laponite nanocomposite hydrogels (PAAm/Lap NC hydrogels)

NC hydrogels were prepared using initial solutions consisting of monomer (AAm), crosslinker (clay), solvent (water), initiator (potassium persulfate), and catalyst (TEMED). The molar ratio between the monomer, initiator and catalyst used was 100 : 0.426 : 0.735. The NC hydrogels were prepared by the *in situ* free radical polymerization of AAm in the presence of the water-swollen inorganic clay without using any organic crosslinker.^{19,20} First, a transparent aqueous solution consisting of water (28.5 mL), AAm (3 g), and various amounts of inorganic clay (1–2.5 g) was prepared. Thus, the obtained NC hydrogels are referred to herein as NC10–NC25. The formulations of the prepared NC composites are shown in Table II. The catalyst (TEMED, 24 μL) and subsequently, the aqueous solution of the initiator (0.03-g KPS in 1.5-mL H_2O) were added to the former solution with stirring at freezing temperature. The NC hydrogels were synthesized in airtight glass tubes (interior size: 7.8 mm in diameter and 60-mm long). Then, the polymerization of AAm was allowed

TABLE I
Some Typical Properties of the Dyes

Name	Chemical formula	Molar mass	Color index no.	CAS no.	λ_{\max} (nm)
Basic Blue 9 (BB 9)		320.0	52,015	61-73-4	655
Basic Violet 1 (BV 1)		394.0	42,535	8004-87-3	560
Basic Blue 12 (BB 12)		354.0	51,180	3625-57-8	630

to proceed in a water bath at 30°C for 48 h. The hydrogels were heat treated in an incubator at 60°C for different duration (0–6 days). During the experiments, oxygen was excluded from the reaction mixture by purging it with nitrogen gas.

Characterization

The UV-visible spectra of the dye solution were recorded using a UVS-2100 SCINCO spectrophotometer, Korea. The absorption spectra of the dilute dye solution in water were recorded in the wavelength range of 300–1000 nm using a 3-mL stopper silica cell with a path length of 10 mm. Distilled water was chosen as the reference.

The thermal behavior of the sample was measured using a differential scanning calorimeter (DSC) of thermoanalytical system (TA 2910) USA. About 6–8 mg of the sample was heated in the temperature range of ambient to 250°C at a heating rate of 5°C min⁻¹ under a nitrogen atmosphere. The DSC thermograms were obtained from the second run after

heating to 250°C. Thermogravimetric analysis (TGA) of the NC hydrogels was carried out on a 2100 thermoanalytical system, USA. The TGA scans were recorded in the temperature range of 30–700°C with a heating rate of 10°C/min in air media.

The X-ray diffraction (XRD) patterns of dried gels were recorded on a Rigaku D/max 2500 Diffractometer, Tokyo, Japan at 40 kV, 30 mA, with Cu-K α monochromatic radiation of wavelength 1.5406 Å. The samples were scanned in the 2 θ range of 2–12° at a scanning speed of 4°/min.

Swelling behavior of NC hydrogel

A gravimetric procedure was adopted to monitor the swelling behavior of the NC hydrogels in the different aqueous dye solutions. In brief, a known weight of NC hydrogel was immersed in distilled water at 25°C and taken out at regular intervals of time to measure the change in weight. The measurements were continued until a constant weight was reached for each sample. The swelling percentage

TABLE II
Formulations of the Initial Solutions and the Resulting NC Hydrogels

Hydrogel	Composition (g)		Water/hydrogel (wt %)	Clay/composite (wt %)
	Clay	AAM		
NC10	1.0	3.0	88.2	25.0
NC15	1.5	3.0	87.0	33.3
NC20	2.0	3.0	85.7	40.0
NC25	2.5	3.0	84.5	45.5

(water uptake) (Q) was calculated with the following equation:

$$Q\% = \frac{M_t - M_d}{M_d} \times 100 \quad (1)$$

where M_t is the mass of the swollen hydrogel at time t and M_d is the mass of the original hydrogel (after drying).

Adsorption of cationic dye

For the adsorption kinetics, the adsorptions of cationic dye onto the PAAm/Lap NC hydrogels were examined in batch mode. NC wet hydrogel (1 g) was immersed in 200 mL of dye solutions at 25°C with different concentrations, viz., 4, 10, 15, 20, and 30 mg L⁻¹. During the adsorption process, a small amount of the dye solution was withdrawn from the system at regular intervals of time and the dye concentrations were measured using a UV-visible spectrophotometer. The amount of the dye adsorbed by the hydrogel at time t , q_t (mg g⁻¹ dried hydrogel), was calculated using the following relation:

$$q_t = (C_0 - C_t) \times \frac{V}{M_d} \quad (2)$$

where, V is the volume of the solution (mL), M_d is the weight of the dried NC hydrogel (g), C_0 is the initial dye concentration (mg mL⁻¹), and C_t is the bulk dye concentration at the indicated time, t (mg mL⁻¹).

The PAAm/Lap NC hydrogels were subjected to heat treatment at 60°C for 3 and 6 days. The effects of the heat treatment of the NC hydrogels on their dye uptake behavior were monitored.

The removal efficiency (RE%) of the dye by the PAAm/Lap NC hydrogels was calculated using the following relation:

$$RE\% = \frac{C_0 - C}{C_0} \times 100 \quad (3)$$

where C_0 and C are the initial and equilibrium concentrations of the CV dye solution, respectively. Partitioning of dissolved constituents between an aqueous phase and the adsorbents in water and sediments has commonly been described by an empirical partition coefficient that simply relates the total concentration of the dissolved species to the total concentration of the adsorbed species.

$$K_d = \frac{(C_0 - C)}{C} \quad (4)$$

where K_d is the empirical partition coefficient at equilibrium.

Kinetic models for adsorption

Three different types of kinetic models, including pseudofirst and pseudosecond-order, and intraparticle diffusion models proposed by Mashitah et al.²⁸ were used to analyze the dye adsorption behavior of hydrogels. The first-order rate equation of the Lagergren is given as;

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (5)$$

where q_e and q_t are the amounts of adsorbed dye cations on the hydrogel at equilibrium and at time t respectively, (mg g⁻¹) and k_1 is the first-order adsorption rate constant (min⁻¹).

The pseudosecond-order equation based on the adsorption capacity of the solid phase is given below;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e^2} t \quad (6)$$

where k_2 presents the second-order adsorption rate constant (g mg⁻¹ min) and q_e presents the adsorption capacity calculated by the pseudosecond-order kinetic model (mg g⁻¹).

Considering hydrogel as a porous material, the intraparticle diffusion model was used to describe the behavior of intraparticle diffusion as the rate limiting step in the adsorption, when the diffusion process affect the adsorption process. The intraparticle diffusion equation can be given as;

$$R = K_s t^b \quad (7)$$

where R is the percent dye adsorbed, t is the contact time (min), b is the gradient of linear plots and K_s is the intraparticle diffusion constant.

RESULTS AND DISCUSSION

Uniform PAAm/clay NC hydrogels were prepared by *in situ* free radical polymerization in solutions containing different amounts of clay viz., 25.0, 33.3, 40.0, and 45.5 wt %, without any phase separation or precipitation. In this study, clay crosslinked NC hydrogels with a high clay content (>25%) were prepared with the good dimensional stability and uniform dispersion of all of the constituents. The polymerization yields, calculated from the weight of the dried gels, were nearly 100% for all cases.

Characterization of PAAm/Lap NC hydrogels

The chain flexibility of the polymer component (PAAm) was evaluated by measuring the glass transition temperatures (T_g) of the NC hydrogels in their dried state. The thermograms obtained by DSC

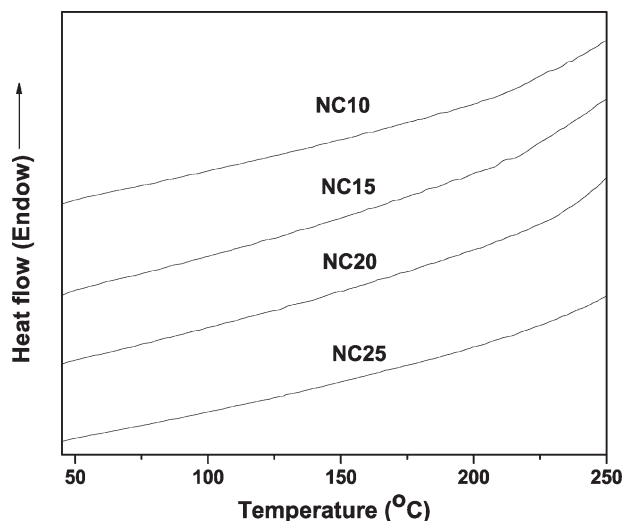


Figure 1 DSC thermograms for dried NC gels with various clay contents (NC10, NC15, NC20, and NC25).

measurements for the NC hydrogels are shown in Figure 1. In the NC gels (as hydrogels), the PAAm chains incorporated in the organic/inorganic networks are highly plasticized by the surrounding

water and adopt random conformations. The DSC thermograms (Fig. 1) show that no glass transition occurred for the NC hydrogels in the investigated temperature range. This means that the PAAm chains in these dried NC gels cannot undergo segment motions within the temperature range examined. This is probably because, (i) these hydrogels have a high clay content (>25% by weight) and (ii) the interactions between the clay sheets and PAAm chains form an intercalated structure in which the thermal molecular motion of the PAAm chains is prevented. A similar observation was made by Haraguchi and Li for clay loaded hydrogels (>20% clay by wt).²⁹

The TGA and derivative thermograms for all of the NC hydrogels are shown in Figure 2. The thermograms obtained during the TGA scans were analyzed to determine the percentage weight loss as a function of temperature. Table III summarizes the T_{10} (temperature of the 10% weight loss), T_{20} (temperature of the 20% weight loss), and T_{50} (temperature of the 50% weight loss) of the NC hydrogels. These results are the main criteria indicating the thermal stability of the NC hydrogels. The T_{50} values of the NC hydrogels increased from 379 to 580°C as

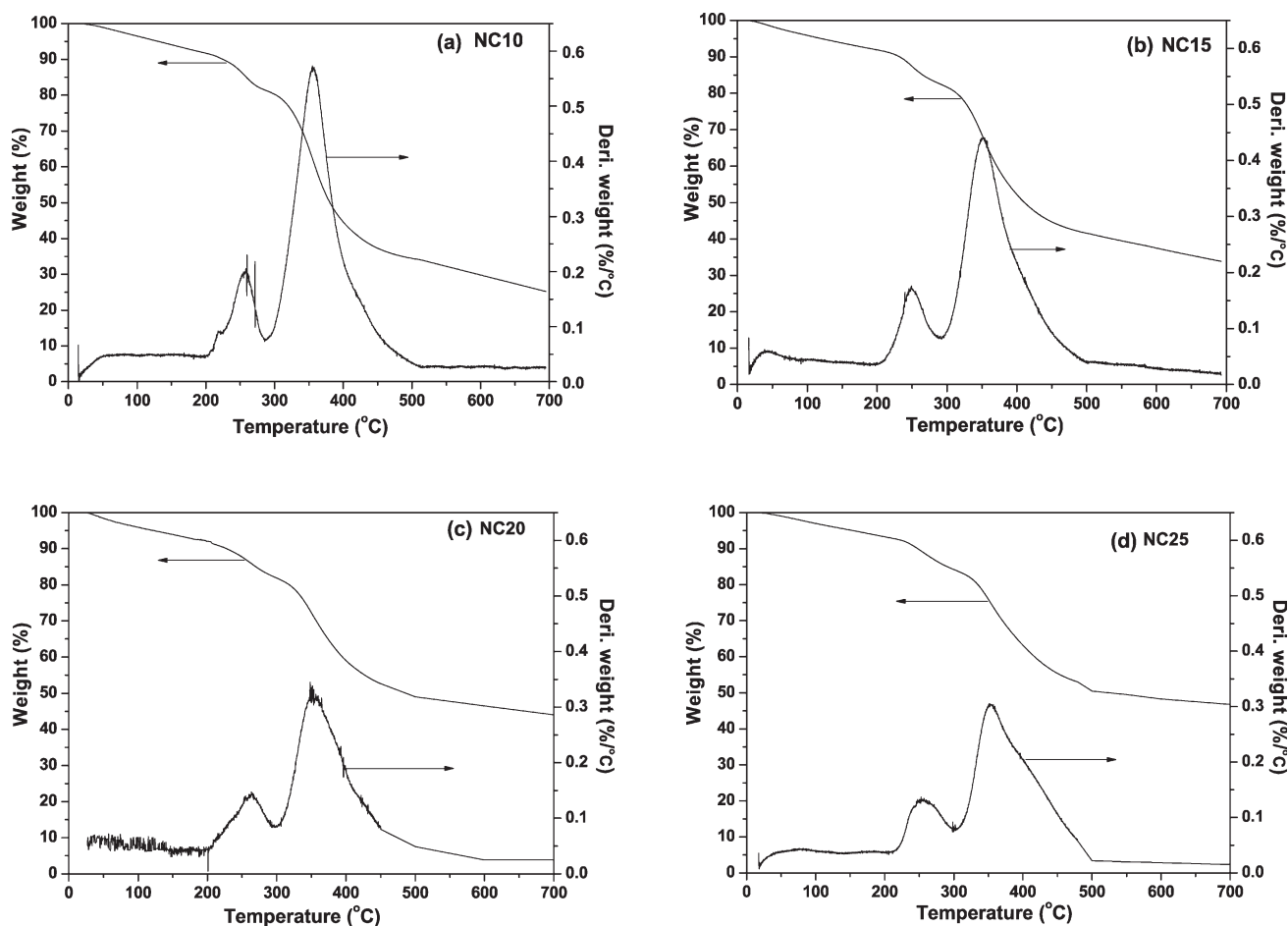


Figure 2 TGA and DTG curves for NC hydrogels containing various amount of clay contents.

TABLE III
Thermal Stability of the TGA Thermograms
for NC Hydrogels

Sample	Transition temperature (°C) up to various weight losses ($\pm 2\%$)		
	T_{10}	T_{20}	T_{50}
NC10	219	302	379
NC15	222	312	410
NC20	226	318	490
NC25	245	334	580

Sample	Process	Temperature range (°C; $\pm 2\%$)	Weight loss (%)
NC10	I	198–288	18.6
	II	288–500	54.9
	Ash	–	27.5
NC15	I	199–291	17.5
	II	291–500	47.6
	Ash	–	34.9
NC20	I	200–298	19.0
	II	298–500	37.0
	Ash	–	44.0
NC25	I	210–300	16.6
	II	300–500	36.6
	Ash	–	46.8

the clay content was increased from 25 to 45%. The nanoclay remarkably increases the thermal stability of the NC hydrogels. This is because the clay is inorganic filler and thermal insulation effect of the exfoliated silicate platelets.^{30,31} The TGA thermograms of the NC hydrogels showed two-step thermal degradation processes. The data obtained from the TGA curves, such as the temperature range of decomposition, the percentage weight loss and the percentage ash, are given in Table III. The NC hydrogels showed a slow initial weight loss of 16.6–19.0% in the temperature range 198–300°C, which was termed as the first stage of the thermal degradation process. The weight loss in this step was attributed to the loss of moisture, oligomers, low molecular weight PAAm, and so forth. The weight loss that occurred in the temperature range 288–500°C was called as the second stage of the thermal decomposition. Major weight loss in the range 36.6–54.9 wt % occurred in this step. The weight loss in this step decreases with increase in clay content. The weight loss in the second step may be assigned to the complete decomposition of the crosslinked PAAm. The weight ratios of clay/polymer in NC gels, evaluated by TG measurements for the corresponding NC dried gels, were in accord with those calculated from the solution composition.

To reveal the state of the clay platelets in the NC hydrogels, XRD measurements were carried out on the dried NC hydrogels with various clay contents.

Figure 3 shows the XRD profiles of the dried NC hydrogels and nanoclay for comparison. The clay shows a strong diffraction peak at around $2\theta = 7.9^\circ$ (d spacing of 1.11 nm), corresponding to the spacing between the clay sheets. In the XRD profiles, no distinct diffraction peak was observed in the 2θ range from 2° to 12° for the dried NC hydrogels, which means that there is no regular stacking of the clay or of the clay/polymer intercalated layers in the dried NC hydrogels.^{19–21} Further, the fact that there is no intense peak indicates that the most of the clay in such dried NC gels with high clay loading is fully exfoliated and well dispersed.

Swelling behavior of hydrogels

The PAAm/Lap NC hydrogels developed in this study were a new kind of hydrogel which shows highly swelling ability. Upon swelling, the hydrogels were strong enough to retain their shape. Some researchers have reported that the swelling properties of hydrogels have some relation with their dye adsorption properties.^{32,33} Therefore, the swelling (water uptake) properties of the PAAm/Lap NC20 hydrogel in different cationic dye solutions were investigated and the results are shown in Figure 4. In general, the equilibrium swelling ratio of a hydrogel depends on structure of dye molecules and the nature of hydrogels. The hydrogels showed similar swelling patterns for all three dye solutions (Fig. 4), but different equilibrium swelling data (water uptake value). A higher water uptake value (275 g g^{-1}) was observed for BB 9 dye solution when compared with the other two dye solutions. The equilibrium water uptake values for different dyes followed the sequence; BB 9 > BB 12 > BV 1. All dyes contain the highly electronegative atoms such as nitrogen and oxygen. These atoms behave like hydrophilic groups and form hydrogen bonds with

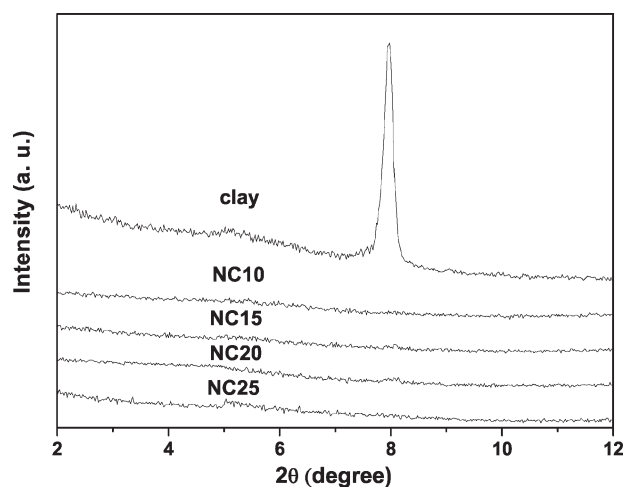


Figure 3 XRD profiles for dried NC gels and clay.

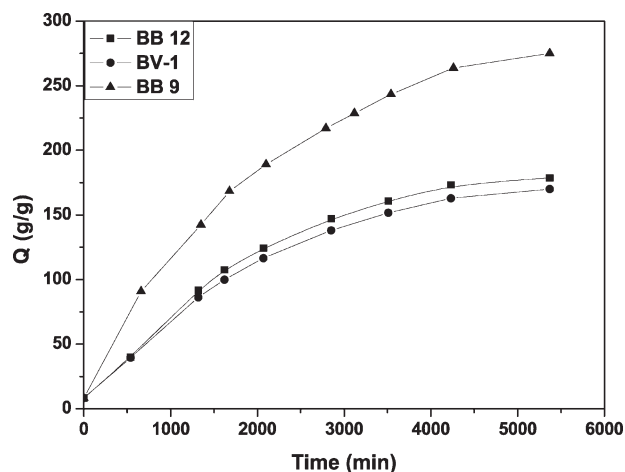


Figure 4 Time-dependent swelling profiles of PAAm/Lap NC20 hydrogel in different dye solutions.

water. Thus, the degree of swelling of the PAAm/Lap composite hydrogels changes as the dyes bring water into them.

The following equation was used to determine the nature of diffusion of water into the hydrogels:

$$F = M_t/M_s = Kt^n \quad (8)$$

where, F is the fractional water uptake at time t , K is the diffusion constant, which is indicative of the characteristic of the hydrogel network system and the penetrant, n is the diffusional exponent, which is indicative of the transport mechanism and M_t and M_s are the mass of water uptake at time, t and at the equilibrium, respectively. eq. (8) is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by $n = 0.5$ and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. This behavior is reflected by n values which lie in the range of 0.5–1.^{34,35} A representative plot of $\ln F$ versus $\ln t$ is shown in Figure 5 for NC20 hydrogel. For the NC hydrogels, the n exponents and K parameters are calculated from the slopes and intercepts of the lines, respectively, and are given in Table IV.

Table IV indicates that the number determining the type of diffusion (n value) is over 0.50. Hence, the diffusion of water into the super water-retaining NC20 hydrogels is generally found to have a non-Fickian character. When the diffusion type corresponds to anomalous behavior, the relaxation and diffusion time are said to be isochronal effective. As the solvent diffuses into the hydrogel, the rearrangement of the chains does not occur immediately. The study of diffusion phenomena in hydrogels with water is of value in that it clarifies the polymer behavior. The complete swelling-time curves for the

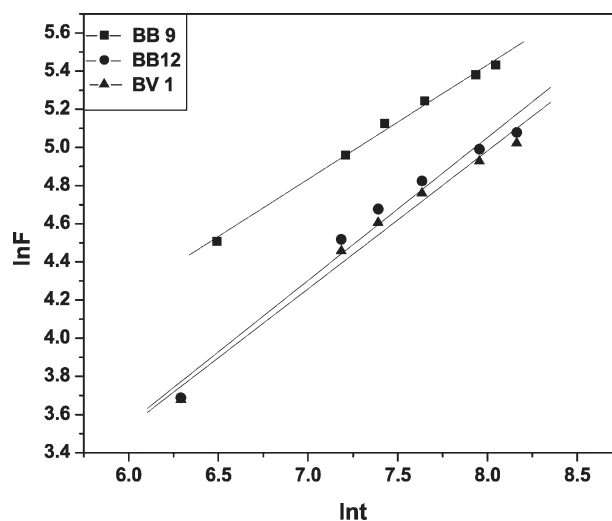


Figure 5 $\ln F$ versus $\ln t$ curves of PAAm/Lap (NC20) hydrogel in the cationic dye solutions.

hydrogels in water are used to calculate the diffusion coefficient (D). The D value of the water was calculated using the following equation;

$$D = \pi r^2 \left(\frac{k}{4} \right)^{\frac{1}{n}} \quad (9)$$

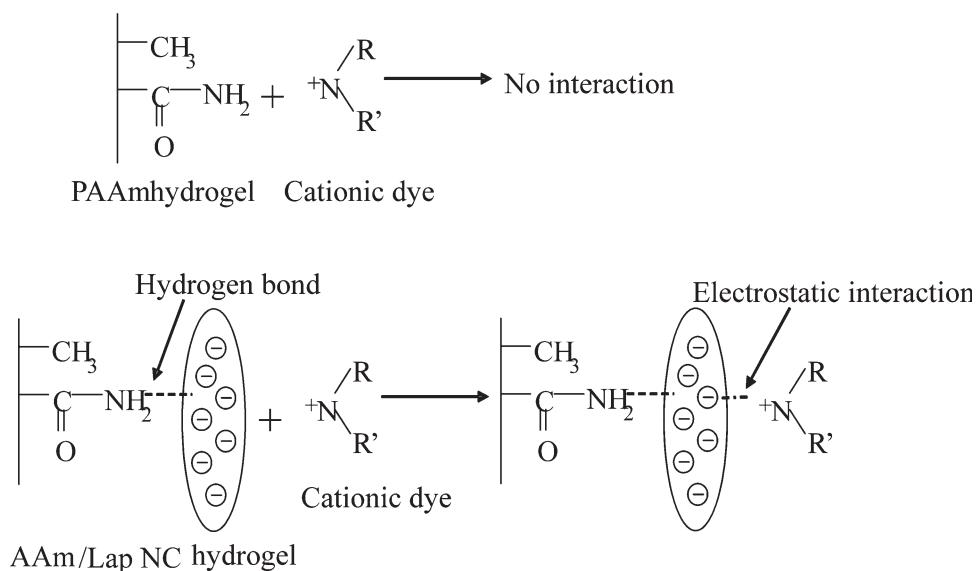
where r is the radius of a cylindrical polymer sample, n is the diffusional exponent and k is a constant incorporating characteristic of the polymer network system and the penetrant. Higher D values ($11.06 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) were noticed for the BB-9 dye solution when compared with the other dye solutions (Table IV). The variation of D depends upon the structural characteristics of the dye molecules in addition to the nature of the hydrogels. Diffusion coefficient decreased with increasing molar mass of the dye molecules. The sequence of variation of D with respect to dyes is, BB 9 > BB 12 > BV 1 and it is reverse trend of molar mass of dyes. Such dependency of D on molar mass of dyes suggested that larger molecules in a related series of dyes occupy larger free volumes, leading to hindered diffusion through the polymer matrix.

Dye adsorption

For the adsorption studies of dyes, the PAAm/Lap NC20 hydrogels were placed in aqueous solutions of the cationic dyes, BB 9, BV 1, and BB 12, and

TABLE IV
Diffusion Parameters of the PAAm/Lap NC20 Hydrogel

Dyes	n	K	$D \times 10^2 \text{ (cm}^2 \text{ s}^{-1}\text{)}$
BB 9	0.60	1.90	11.06
BB 12	0.75	0.45	1.87
BV 1	0.72	0.39	1.75



Scheme 1 A possible mechanism of cationic dye adsorption by PAAm/Lap NC hydrogels.

allowed to equilibrate for 4 days. At the end of the 4 days, the NC20 hydrogels in the solution of all three dyes showed dark colorations of the original dye solutions. The PAAm hydrogel does not adsorb any dye from the solution, since it is a nonionic polymer.³¹ However, the PAAm/Lap NC hydrogels adsorbed the cationic dyes. This is because the modified Lap clay contains anionic charges on its surface and, after the incorporation of the Lap clay into PAAm, the number of anionic groups in the composite is increased. Therefore, the composite hydrogels have many anionic groups that allow for the increased interaction between the cationic groups of the cationic dyes and anionic groups of the NC hydrogels. The mechanism of dye adsorption by the hydrogel is mainly due to the ion exchangability and the physical interactions such as dipole-dipole interactions and hydrogen bond formation between the dye molecules and hydrogels. A typical schematic representation indicating the possible interaction between the cationic dye molecules and NC is shown in Scheme 1.

Figure 6(a) shows the time profiles for the adsorption of the different dyes onto the PAAm/Lap NC20 hydrogel with an initial concentration of 30 mg L^{-1} , and the dye uptakes by the hydrogels at equilibrium are shown in Figure 6(b). As observed, the dye uptake increases with time but the rate of dye uptake decreases with time. The equilibrium dye uptake behavior of hydrogels may be influenced by the size, chemical structure, polarity and solubility parameter of dyes, and the nature of hydrogels. In Figure 6, it is clearly seen that the dye uptake behavior differs for three dyes that have different molecule structures and different hydrogel-dye interactions. Organic cations can bind to the clay in different

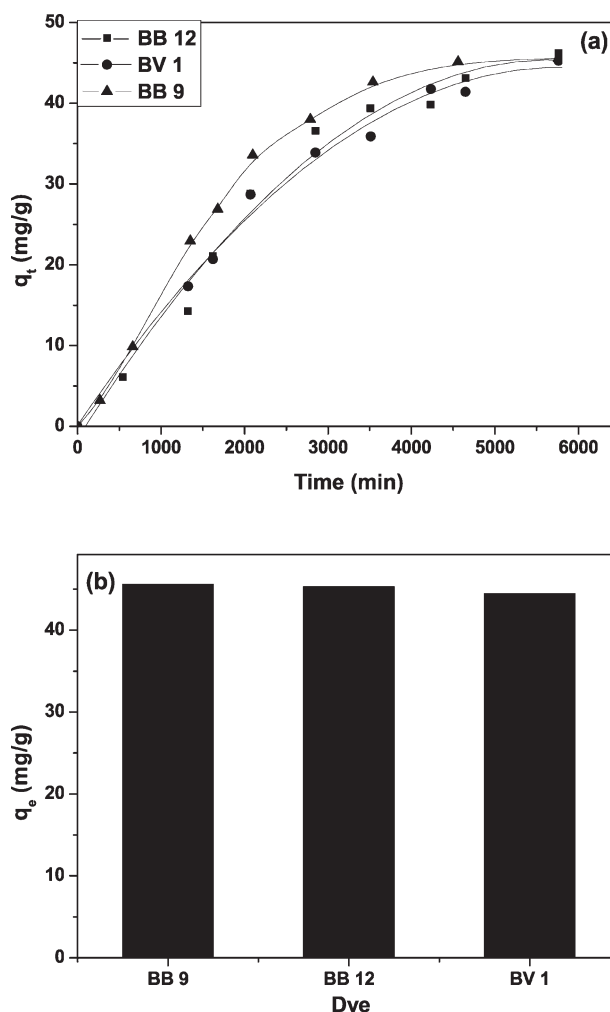


Figure 6 (a) Time profiles for dyes uptake by NC20 hydrogel and (b) equilibrium dye uptake amounts of NC20 hydrogel.

TABLE V
Time Required Reaching 80 and 90% Dye Uptakes
by NC20 Hydrogels

Dyes	Time taken for 80% dye uptake amount by hydrogel (mins)	Time taken for 90% dye uptake amount by hydrogel (mins)
BB 9	2499	3118
BB 12	3239	3750
BV-1	3269	3954

ways. Through ion exchange, the cations (metal ion) on the clay surface can be exchanged by the dye cations, and it results in a neutral complex formed by the binding of a cation of the organic dye to a negative site present on the Lap clay surface. Such an interaction is mainly electrostatic in nature. Though the three dyes show the same trend in Figure 6(a), the uptake speed of BB 9 dye was slightly faster than those of BB 12 and BV 1 and it reached the equilibrium condition earlier than the other two dyes. However, the equilibrium dye uptakes of all the dyes are almost the same [Fig. 6(b)]. To show the differences in the uptake ratio of the three dyes, Table V shows the times taken to reach 80 and 90% of the dye uptake by the hydrogel for the different dye solutions. The results indicate the shorter period was taken by the BB 9 dye to reach 80 and 90% of dye uptake, when compared with the other dyes. This may be due to; (i) the greater physical interaction of the BB 9 dye toward the NC hydrogels than the other dyes and (ii) the molecular mass of BB 9 dye is smaller than other dyes. Also, the result of the equilibrium swelling is parallel to the result of the dye uptake speed. This may be because the swelling ability of the hydrogel can influence the movement of the dye molecules, so as to influence the interaction between the dye molecules and clay.

The calculated dye RE% and empirical partition coefficient at the equilibrium (K_d) values for the different dyes are given in Table VI. From this table, it can be seen that the RE% for all the dyes is above 90%. This result indicates that the PAAm/Lap NC hydrogel is an efficient material for the removal of cationic dyes from water. The K_d values lie in the range of 9.56–12.16 and show an inverse trend to that of the RE% data.

TABLE VI
Removal Efficiency (RE) and Partition Coefficient
at Equilibrium (K_d) of PAAm/Lap NC20
Hydrogel in Different Dye Solutions

Dyes	Removal efficiency (%)	K_d
BB 9	91.13	10.29
BB 12	90.53	12.16
BV-1	92.40	9.56

To analyze the adsorption kinetics of cationic dye onto the hydrogels, the pseudofirst-order, pseudo-second-order and intraparticle diffusion models were tested using experimental data. The corresponding kinetic constants were determined by linear regression analysis and the obtained results were given in Table VII. In the Table VII, it was observed that the pseudosecond-order model was the most suitable for describing the cationic dye adsorption behavior of PAAm/Lap NC hydrogels.

Effect of clay content

The effect of the Lap content in the PAAm/Lap composite hydrogels on the dye adsorption behavior was investigated. PAAm/Lap NC hydrogels containing different amounts of Lap clay were transferred into 50 mL of the aqueous dye solutions with constant concentrations and allowed to equilibrate for 4 days at 25°C in a water bath. Figure 7(a,b) show the time profiles and dye uptakes of BB 9 for the different NC hydrogels, respectively. From these figures, it was observed that the dye uptake speed and equilibrium amount increases significantly with increasing the clay content up to 40% (NC20). This is because, as the clay content increases, the amount of negative charges in the hydrogels increases and, hence, the ion exchangeability and interaction between the cationic dye molecules and anionic groups of the hydrogels is enhanced. The other types of interaction between the swelling hydrogel and the monovalent cationic dyes may be hydrophobic and hydrogen bonding (Scheme 1). In particular, hydrogen bonds would be expected to occur between the amine groups and nitrogen atoms on the dye molecules and the amine and carbonyl

TABLE VII
Kinetic Constants Using Pseudo-First-Order, Pseudo-Second-Order, and Intraparticle Diffusion Models in the
Adsorption of Cationic Dye onto PAAm/Lap NC Hydrogels

Dye solution	Pseudo-first-order		Pseudo-second-order		Intraparticle diffusion	
	$K_1 \times 10^4$ (min ⁻¹)	R^2	$K_2 \times 10^6$ (g mg ⁻¹ min)	R^2	$K_2 \times 10^4$ (g mg min ^{-0.5})	R^2
BB 9	9.58	0.94	64.6	0.97	6.76	0.93
BB 12	5.76	0.97	7.85	0.99	6.37	0.95
BV 1	5.72	0.96	16.5	0.97	4.11	0.95

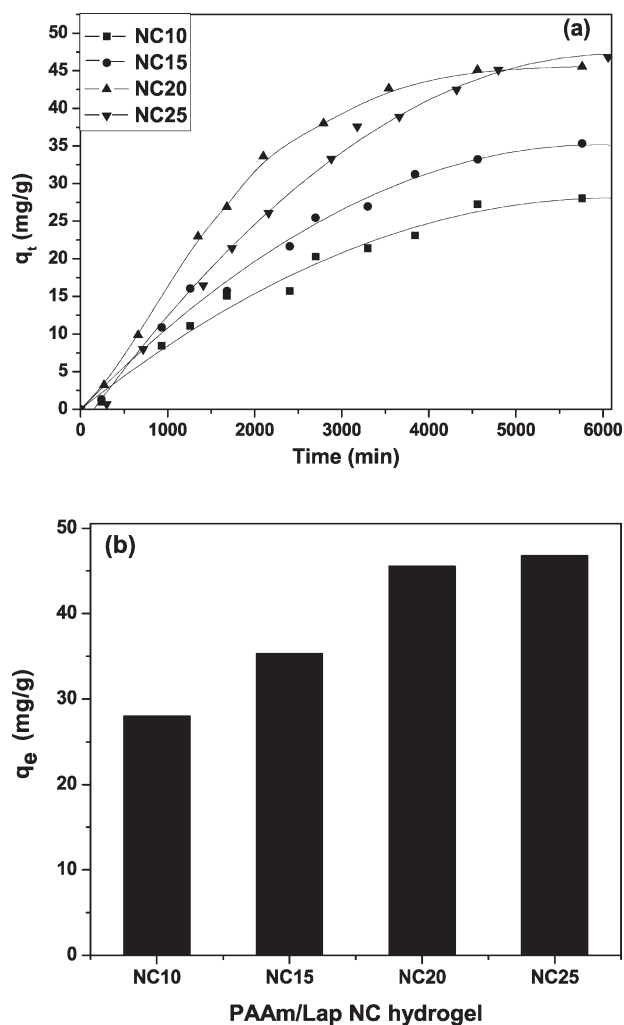


Figure 7 The effect of the clay content in the NC hydrogels on the BB 9 dye uptake: (a) time profiles and (b) equilibrium dye uptakes.

groups on the monomer unit of the polymer. At the same time, as the clay content in the hydrogel increases, the degree of crosslinking increases, which would inhibit the dye adsorption ability. So, there is an optimal content (40%) of clay in the NC hydrogel for effective dye removal. When the clay content is increased above 40%, the equilibrium dye uptake is almost the same as that of NC20 while, at the same time, the dye uptake ratio is decreased. This result indicates that the formulation containing 40% clay (NC20) hydrogel is the optimized system.

The calculated dye RE% and K_d values for the NC20 hydrogels are given in Table VIII. It is noticed that there is a drastic increase in the dye RE% and K_d values as increase in the clay content (up to 40%). Further increase in clay content >40% showed a slight improvement in RE% values. This result clearly indicates the significant influence of the clay content on the dye RE%.

TABLE VIII
Effect of Clay Contents on BB 9 Dye Uptake Behavior of PAAm/Lap NC Hydrogels

Clay content in hydrogel (wt %)	Removal efficiency (%)	K_d
NC10	56.10	1.28
NC15	70.66	2.41
NC20	91.14	10.29
NC25	93.62	14.67

The plot of the quantity adsorbed as a function of dye concentration is shown in Figure 8, to probe the type of adsorption behavior. Figure 8 shows that the adsorption of the BV 1 and BB 12 dyes by the NC20 hydrogel corresponds to S-type while for BB 9 it corresponds to L-type adsorption isotherms in the Giles classification system. In the L-type adsorption isotherm, the initial curvature reflects the fact that as more sites in the substrate are filled, it becomes increasingly difficult for a bombarding solute molecule to find an available vacant site. This implies either that the adsorbed solute molecule is not vertically oriented or that there is an absence of strong competition from the solvent. The types of systems which give this type of curve should fulfill these conditions. Thus, they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition; examples of (ii) are (a) systems with a highly polar solute and adsorbent, and a nonpolar solvent, and (b) systems in which monofunctional ionic substances with very strong intermolecular attractions are adsorbed from water by ion-ion attractions. It is possible that, in these cases, the adsorbed ions may have become associated into very large clusters, and that only adsorption takes place.³⁶

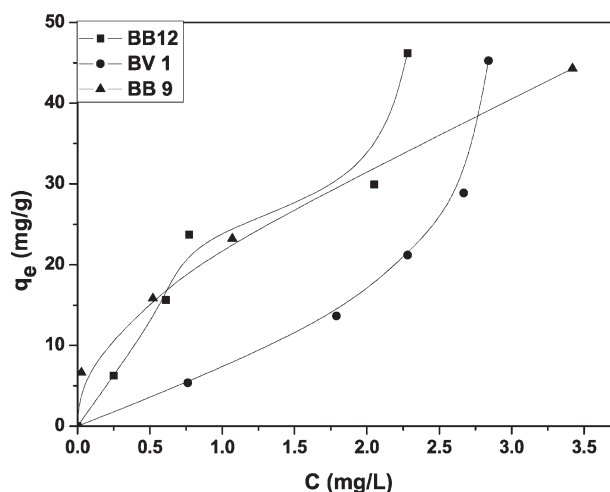


Figure 8 The binding isotherms of the different dye molecules on the PAAm/Lap (NC20) hydrogel.

In the S curves of the Giles classification system, the initial direction of curvature shows that adsorption becomes easier as the concentration rises. In practice, the S curve usually appears when three conditions are fulfilled, viz. the solute molecule, (i) is monofunctional, (ii) has a moderate degree of intermolecular attraction, causing it to pack vertically in a regular array in the adsorbed layer, and (iii) meets strong competition for substrate sites from molecules of the solvent or other adsorbed species.³⁷ The weakness of the adsorbent-adsorbate forces causes the uptake at low concentrations to be small, but once a molecule has become adsorbed, the adsorbate-adsorbate forces promote the adsorption of further molecules (a cooperative process), so that the isotherm becomes convex with respect to the concentration axis. The S-Type isotherms may originate through the adsorption of either nonpolar molecules or polar molecules, always provided that the adsorbent-adsorbate force is relatively weak. Once the hydrogel is covered with a layer of adsorbed water, the adsorbent-adsorbate interaction would be reduced to the weak dispersion energy of water with dyes, so that the system shows S-type isotherm.

Comparing the condition of the different dye adsorption isotherms, we can conclude that the physical interaction between BB 9 and clay is stronger than that of the other two kinds of cationic dyes with clay.

Effect of heat treatment

Figure 9(a) shows the time profiles of BB-9 dye adsorption onto the NC20 hydrogels before and after the heat-treatment of the hydrogels. Table IX shows the effect of heat treatment on the RE% and K_d values of the BB 9–NC20 hydrogel. For the sake of clarity, the effect of heat treatment on the equilibrium dye uptake is shown in Figure 9(b). From Table IX, it is noticed that there is an approximately 5% improvement in the dye uptake for 3 days heat treated hydrogels. A drastic increase in the K_d values was also noticed for 3 days heat treatment of the NC20 hydrogels. The rate of dye uptake also enhanced after the heat treatment of the hydrogels. In our previous study, the FTIR results show that the chemical components of the hydrogels are not altered by the heat treatment and, consequently, the remarkable improvement of the dye uptake and K_d values of the gels must result from the change in the physical structure of the hydrogel network.³⁸ Although the precise nature of the interaction between the polymer and clay is still not completely understood, it is generally regarded as being a combination of hydrogen bonding and ionic interaction.²¹ It is presumed that some repeat units of the

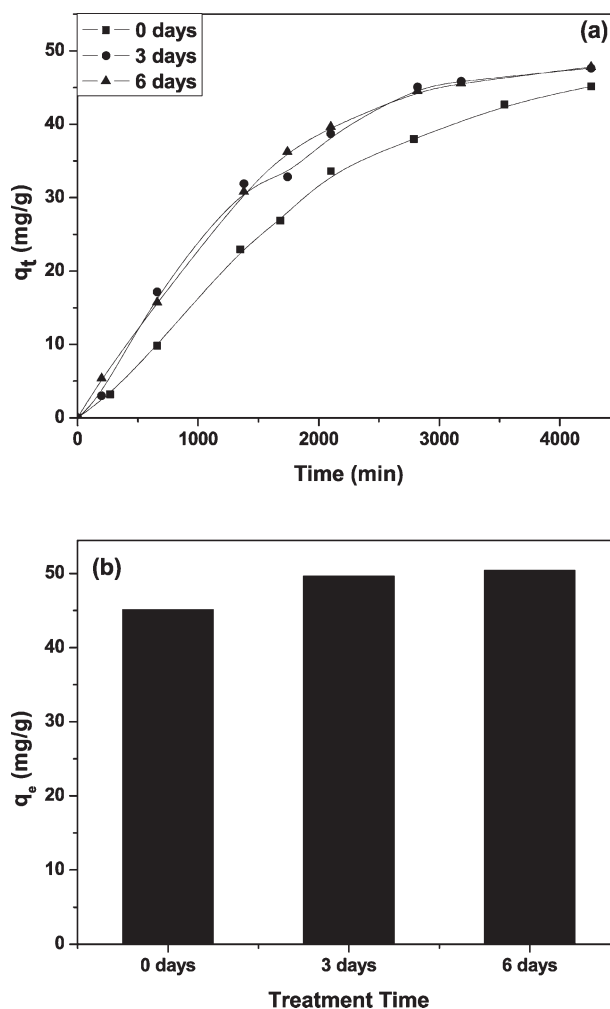


Figure 9 The effect of the heat treatment time of the NC20 hydrogel on the BB 9 dye adsorption behavior: (a) time profiles and (b) equilibrium dye uptakes.

polymer that interacting with the clay platelets became detached from the clay surface during the heat treatment. Thus, the number of repeat units of every PAAm chain that interact with the clay platelets decreases after the heat treatment, and the length of the PAAm chains between neighboring clay platelets increases. This endows the hydrogels with a larger swelling potential and more openings for dye molecule interactions.³⁹ However, the equilibrium dye uptakes of the NC20 hydrogels after 3 and 6 days of heat treatment are nearly the same.

TABLE IX
Effect of Heat Treatment on BB 9 Dye Uptake by PAAm/Lap NC20 Hydrogels

Duration of heat treatment (days)	Removal efficiency (%)	K_d
0	91.14	10.29
3	95.32	20.37
6	95.40	20.74

This may be because the adsorption ability of the clay reaches saturation with the result that further heat treatment has no significant influence on the dye uptake. It can be concluded that 3 days heat treatment is the optimized condition.

Recently, Sema and Yasemin reported the same three kinds of dye uptake properties onto a kind of hydrogel composite prepared using AAm and Saponite clay crosslinked by an organic crosslinker.³² They observed that the best RE% of the hydrogel composite was lower than 50%, when the solution concentration was 15 mg L⁻¹. In the case of the hydrogel studied in this investigation (NC20 hydrogel without an organic crosslinker), the removal efficiencies of all the dyes are more than 90% (Table VI). These data clearly indicate that the PAAm/Lap NC20 hydrogel studied in this investigation show superior dye adsorption behavior. The possible reasons for this are: (i) the presence of more negative charges on the Lap clay surfaces and (ii) the absence of an organic crosslinker in the composites, which allows the polymer chains between the clay layers to be very flexible and homogeneous and the cationic dye molecules to easily enter into the network and interact with the clay.

CONCLUSIONS

On the basis of the XRD measurements, it can be concluded that in the NC gels the clay is extensively exfoliated, and the clay platelets are dispersed uniformly throughout the sample. PAAm/Lap NC hydrogels were used in experiments on the swelling and adsorption of the water-soluble monovalent cationic dyes, BV 1, BB 9, and BB 12. The water uptake of the hydrogels in the different dye solutions followed non-Fickian type diffusion. The effects of the clay contents on the dye uptake behavior were studied. There is optimal clay content in the PAAm/Lap NC hydrogels for the effective removal of cationic dyes. It was found that 40% clay-loaded (NC20) hydrogel is the optimized formulation. The values of the equilibrium swelling degree (Q_e) and diffusion coefficient (D) in the dye solutions follow the order: BB 9 > BB 12 > BV 1. The trend of the cationic dye uptake ratio and RE% of the PAAm/Lap NC hydrogels also follow the same order of Q_e and D . The adsorption rate constants of the dyes were calculated using three kinetic models, and the results showed that pseudosecond-order model was the best suitable for describing the cationic dye adsorption behavior of PAAm/Lap NC hydrogels. The RE% of the NC20 hydrogels for all dyes is found to be more than 90%. The adsorption of BB 12 and BV 1 dyes corresponds to the S-type adsorption isotherms, whereas that of BB 9 dye corresponds to the L-type

adsorption isotherms in the Giles classification system. A significant improvement in the dye uptake speed, RE%, and empirical partition coefficient (K_d) values for the 3 days heat treated NC hydrogels was noticed. This is because of the network of the NC hydrogels crosslinked by the clay platelets is flexible, more homogeneous, and changeable by the heat treatment. Heat treatment for 3 days was found to be a suitable condition for effective dye adsorption. Thus, PAAm/Lap hydrogels can be used as an adsorbent for the treatment of wastewater containing pollutants such as cationic dyes, which is an important problem for the textile industry.

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