

# Robust Polymeric Hydrogel Using Rod-Like Amidodiol as Crosslinker: Studies on Adsorption Kinetics and Mechanism Using Dyes as Adsorbate

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**ABSTRACT:** Herein, we report the preparation of robust polyacrylic acid hydrogel using rod-like amidodiol as physical crosslinker. Polyacrylic acid–amidodiol hydrogels were characterized for its chemical structure, rheology, swelling, diffusion, and adsorption properties. Kinetics and mechanism of adsorption were investigated by UV–visible spectroscopy using dyes such as rhodamine 6G and methylene blue as adsorbate. Results suggested pseudo second-order kinetics of multilayer adsorption and hydrogel could retain its shape even after swelling. Effect of amidodiol on the adsorption of dyes was investigated. Extent of interaction between adsorbate–adsorbate and adsorbent–adsorbate was studied using Gile’s model. The generated results may provide a low cost simple technology for developing robust polymeric hydrogel adsorbent. The adsorption characteristics results can be exploited for setting up pilot plant adsorbent for the removal of such organic toxic materials. Finally, we have demonstrated its application for the removal of dyes from waste water collected from textile and paper industries. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40908.

**KEYWORDS:** adsorption; crosslinking; dyes/pigments; gels; rheology

Received 14 January 2014; accepted 21 April 2014

DOI: 10.1002/app.40908

## INTRODUCTION

Hydrogels are stimuli responsive three-dimensional networks of flexible polymeric chains which can absorb and retain water and solute molecules. They respond to various stimuli such as temperature, pH, electric field, magnetic field, electrolyte, and so forth. Thus, they are receiving importance in physiological, biological, and chemical systems and find applications in the area of medicine, water treatment, food industry, and agriculture.<sup>1,2</sup> The higher water content and porous structure of the hydrogel network allow solute to diffuse into the interstices of the hydrogel.<sup>3</sup> Various non-covalent interactions include hydrogen bonding,  $\pi$ – $\pi$  stacking, van der Waals interactions are involved during organization of these molecules into 3D architectures that enables the solute molecules to be trapped inside the gel matrix. Polyacrylamide, polyvinyl pyrrolidone, chitosan, polyacrylic acid, and its derivatives are the most commonly used systems for developing hydrogels due to their nontoxicity, flexible long chains, and capacity in preserving their shape. A large number of investigations have been reported for improving the mechanical and chemical properties of these hydrogels through reinforcing with

nanofillers such as inorganic nanoclays, metal nanoparticles, cellulosic particles, carbon nanotubes, and so forth.<sup>4–7</sup>

In this study, we are using a simple organic molecule, amidodiol, which is prepared through aminolysis of lactone at room temperature. It is endowed with two terminal hydroxyl groups and diamide linkage connected through hexamethylene bridge. The liquid crystalline properties attributing from the rigidity of this rod-shaped molecule were earlier reported from our group.<sup>8</sup> The rigidity along with the presence of functional groups such as amide and hydroxyl moieties is expected to adsorb solute molecules through various van der Waals interactions apart from acting as reinforcing agent. The adsorption capability of various adsorbents with respect to various aromatic functional groups was usually tested by checking its adsorption efficiency using dye molecules in aqueous solution. Large amount of dyes and toxic organic molecules are discharged into the aquatic systems from various textile and paper industries. Methylene blue (MB) is a thiazine type cationic dye and rhodamine 6G (R6G) is a cationic amine type fluorescent xanthene dye and are included in the category of hazardous dyes. Removal of dyes is important since they

Additional Supporting Information may be found in the online version of this article.

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affect life due to its carcinogenic and mutagenic effects.<sup>9,10</sup> Moreover, they are not biodegradable and mainly aromatic in structures. Various strategies such as adsorption, chemical oxidation, chemical flocculation, froth flotation, ultrafiltration, reduction, chemical destruction, and membrane filtration have been used for the color removal of water.<sup>11–16</sup> Among these, adsorption process is considered to be highly efficient due to its sludge free clean operation, simplicity of design, and complete removal of dyes. Crini reviewed adsorbents such as activated carbon, clays, siliceous materials, and agricultural wastes for the removal of dyes.<sup>17</sup> Literature showed a number of reports on the adsorptive removal of cationic dyes using various sorbents.<sup>18–24</sup>

Investigations on the mechanism, kinetics of adsorption, swelling, and diffusion process of hydrogels are receiving importance when considering its applications as an adsorbent in a pilot plant scale. Diffusion process of solute particles from water to the hydrogels depends on the relative rate of relaxation of polymeric chain and the rate of diffusion of water. It can be classified as Fickian or non Fickian type of diffusion based on the rate of relaxation process. Hydrogels are also expected to show different swelling index which depend upon the physicochemical interactions established between the solute molecules and polymer networks. The adsorption process can be monolayer or multilayer and it can be studied by applying Langmuir or Freundlich adsorption isotherm. During the diffusion of solute molecules, there may be competition between adsorbate–adsorbent and adsorbate–adsorbate interaction and it can be studied using Gile's model.

Thus, the development of adsorbent based on robust polymeric hydrogel and studies on its adsorption/diffusion characteristics and mechanism is receiving importance. In this work, we have developed robust polymeric hydrogel based on polyacrylic acid physically crosslinked by multifunctional amidodiol by simultaneous polymerization of acrylic acid and cross linking with amidodiol at room temperature using ammonium persulfate as initiator. Thus, the prepared polyacrylic acid–amidodiol (PAG) hydrogels are endowed with hydrophilic groups such as hydroxyl, carboxyl, and diamide groups which can enhance the adsorbate–adsorbent interaction through extensive hydrogen bonding and electrostatic interactions and ionic interactions. The mechanism of swelling and diffusion has been studied. The adsorption efficiency of the hydrogels was monitored by measuring the decrease in absorption intensity using UV–visible spectroscopy and fitted the generated data in different isotherms and kinetic model equations. Effect of amidodiol, pH, and temperature on the adsorption efficiency was studied and also experiments were performed with the mixture of dyes and also with real waste water samples.

## EXPERIMENTAL

### Materials

Hexamethylenediamine, rhodamine-6G (Sigma Aldrich),  $\gamma$ -butyrolactone (Fluka), isopropanol, ammonium persulfate, acrylic acid (E-Merk, India), and methylene blue (Nice Stains) were used without any further purification. Amidodiol was prepared by the aminolysis of  $\gamma$ -butyrolactone and hexamethylene diamine as per the reported procedure<sup>8</sup> and given in Supporting Information (Supporting Information Scheme S1).

### Preparation of PAG Hydrogel

Acrylic acid (1 mL) and 10% amidodiol (1 mL) (in water) were mixed. Two drops of 10% ammonium persulfate were added to the above mixture. The contents were shaken well and kept at 80°C for about 1 h. The gel formed was washed several times with distilled water to remove residual monomers and ions. Experiments were repeated with different compositions of amidodiol and the details of preparation of PAG hydrogel is given in Supporting Information (Supporting Information Table S1).

### Swelling and Diffusion Studies

Experimental details are given in supporting information.

### Adsorption Studies

Aqueous solutions of cationic dyes R6G and MB were prepared in the various concentrations ranging from 20 to 400 mg/L. The uniform size of dried PAG hydrogel (0.1 g) was immersed in 20 mL of each dye solution and stirred for 3 days at room temperature. The pH of the solution is  $\sim 7.5$  and the adsorption experiment is performed at room temperature (30°C). Concentration of the dye present in the filtrate was periodically calculated by measuring absorption intensity from the UV–vis spectra at  $\lambda_{\text{max}} = 665$  nm and 525 nm for MB and R6G, respectively. The absorbance, chemical formula, molar mass, and color index number for these dyes were listed in Supporting Information (Supporting Information Table S2). Adsorption isotherm was studied by calculating the amount of dye adsorbed per gram of the hydrogel using the equation

$$q_e = \frac{(C_0 - C_{\text{eq}})V}{m},$$

where  $C_0$  is the initial concentration of dyes,  $C_{\text{eq}}$  is the equilibrium concentration, and  $V$  is the volume of solution (L), and  $m$  is the mass of the dry hydrogel (g).

Decolorization efficiency of hydrogel was calculated using the equation

$$\text{Decolorization efficiency} = \frac{C_0 - C}{C_0} \times 100,$$

where  $C_0$  is the initial concentration of dye and  $C$  is the concentration of dye at time  $t$ .

The experiments were performed to study the effect of pH (2–10) and temperature (30–70°C).

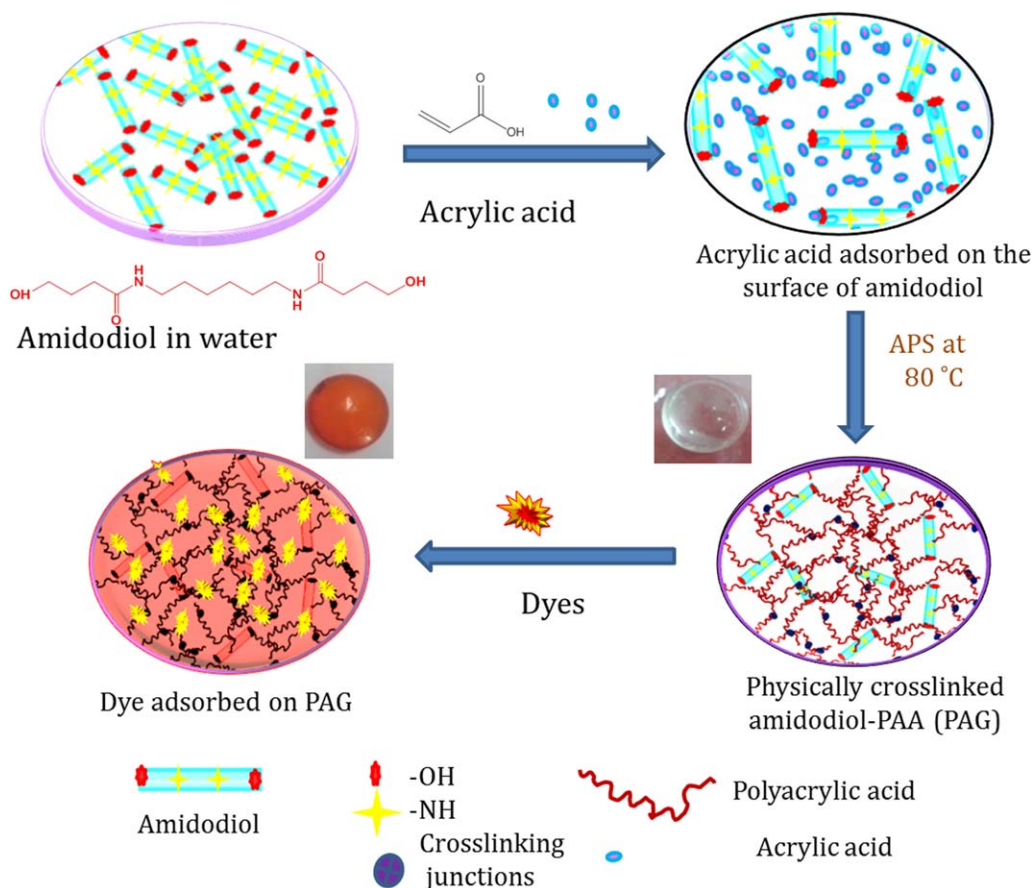
### Characterization Techniques

Optical properties were studied by UV–Vis spectra in the range 300–800 nm using UV–Vis spectrophotometer (Shimadzu model 2100). For SEM measurements, samples were subjected for thin gold and platinum coating using a JEOL JFC-1200 fine coater. The probing side was inserted into JEOL JSM-5600 LV scanning electron microscope. Rheological properties were measured using Anton Paar Rheometer-MCR-150. Experiments were performed with parallel plate sensor under oscillatory mode in the linear viscoelastic region.

## RESULT AND DISCUSSION

### Preparation, Characterization, Swelling, and Diffusion Behavior of PAG

PAG hydrogels were prepared by the simultaneous polymerization of acrylic acid and physical cross-linking with amidodiol



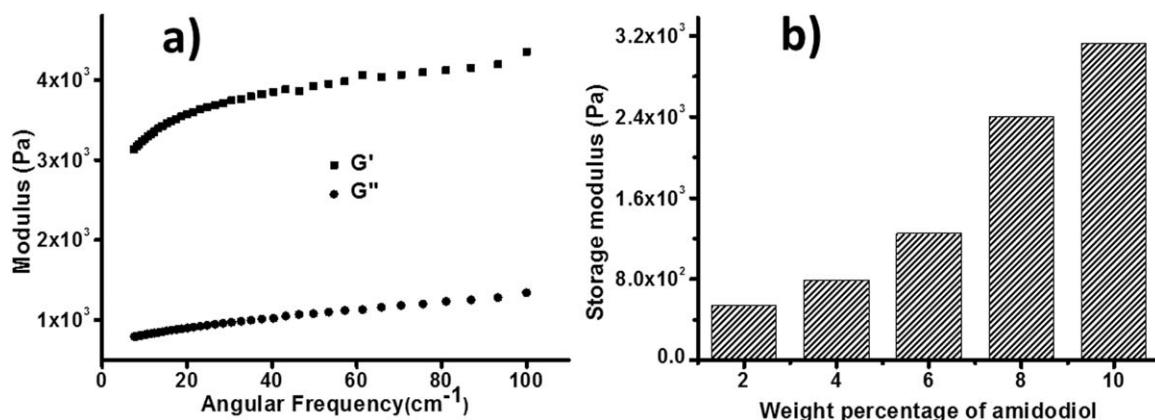
**Figure 1.** Scheme for mechanism of gelation of PAG hydrogel and adsorption of dyes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and obtained as a transparent hydrogel. Various types of interactions among polyacrylic acid–amidodiol were studied by FTIR spectroscopy. FTIR spectra of PAA, PAG, and amidodiol are shown in Supporting Information Figure S1a. FTIR spectra of amidodiol exhibited the characteristic amide band at  $1636\text{ cm}^{-1}$ ,  $1545\text{ cm}^{-1}$ , and the  $\text{—OH}$  stretching frequency at  $3300\text{ cm}^{-1}$ . FTIR spectra of PAA exhibited a broad band at  $3600\text{ cm}^{-1}$  and  $3100\text{ cm}^{-1}$  which is attributed due to the  $\text{—OH}$  and  $\text{—CH}$  stretching. The band observed at  $1714\text{ cm}^{-1}$  corresponds to  $\text{—C=O}$  stretching vibration of the carboxylic acid and band at  $1399\text{ cm}^{-1}$  matches with  $\text{—C—H}$  stretching vibrations which are distinct to the varying micro environments in PAA. The broad band of the hydroxyl group observed at  $3600\text{—}3200\text{ cm}^{-1}$  in PAG revealing the formation of extensive hydrogen bonding among interaction between polyacrylic acid and amidodiol molecules in both compounds. The  $\text{—C=O}$  band shifted to  $1700\text{ cm}^{-1}$  in PAG is also attributed to the formation of hydrogen bonding. The band at  $2930\text{ cm}^{-1}$  in PAG is suggested for stretching vibrations of  $\text{—CH}_2$  group present in the amidodiol moiety. The band at  $1450\text{ cm}^{-1}$  in PAG corresponds to the  $\text{—NH}$  vibrations of the amide group. Thus, the observed shift in the positions of bands in PAG compared to PAA revealed the formation of extensive hydrogen bonding among acrylic acid and amidodiol.

Thus, the PAG hydrogel is endowed with many carboxyl and hydroxyl group which interact with the cationic groups of the

dyes and may enhance the diffusion process. The characteristic band of the hydroxyl group at  $3600\text{—}3200\text{ cm}^{-1}$  of PAG hydrogels adsorbed with R6G and MB is slightly broadened when compared with PAG, revealing the formation of extensive hydrogen bonding between the PAG and the dye molecules and is shown in Supporting Information Figure S1b. These observations confirm the presence of various ionic and hydrogen bonding interactions between the hydrogel and dye molecules. The scheme for gelation of PAG and the adsorption of dyes onto these gels is given in Figure 1.

Further, the visco-elastic property of the gel was measured and the rheogram of the same is given in Figure 2(a). It was observed that in the low frequency region, the variation of  $G'$  and  $G''$  is independent of angular frequency as the applied frequency does not affect considerably the three-dimensional structure of the gels which is the signature for the gel formation. The storage modulus, loss modulus, and complex viscosity of the PAG5 observed as 3130 Pa, 792 Pa, and 427 Pa, respectively. The gap between the storage and loss modulus was measured as 2338 Pa suggesting a solid like behavior. The value of storage modulus increases with increase in the percentage of amidodiol in PAG gel and is shown in Figure 2(b). It is confirmed that rod-like amidodiol molecules possessing both hydroxyl and amide functional group can effectively crosslink with polyacrylic acid and enhances the strength of the gel.



**Figure 2.** (a) Visco-elastic diagram showing storage modulus and loss modulus of PAG5 gel, and (b) variation of storage modulus with increase in concentration of amidodiol.

Equilibrium swelling values of hydrogel in distilled water and dye solutions were evaluated as per the procedure given in the experimental section and the graph showing the variation of percentage of swelling against time is shown in Supporting Information Figure S2. It is observed that swelling percentage increased with time and reached a plateau after a particular time. The observed swelling behavior could be associated with absorption mechanism, which, in turn, is determined by the diffusion process. When PAG hydrogel brought in contact with water, water molecules diffused in to the hydrogel and it swells. The equilibrium swelling percentage of hydrogel was measured as 76% in water, and 120% and 140% in aqueous solutions of MB and R6G, respectively. In dye solutions, PAG exhibited an enhancement in the equilibrium swelling index due to their interaction with the amino group present in the dye molecules which can form hydrogen bond interaction with the functional moieties present in the hydrogel. However, diffusion process depends upon the rate of solvent diffusion ( $R_{diff}$ ) and rate of relaxation ( $R_{relax}$ ) of molecular chains in the polymer. This behavior is classified as Fickian and non-Fickian by Alfrey et al.<sup>25</sup> Fickian diffusion is characterized by a solvent diffusion rate,  $R_{diff}$ , slower than the polymer relaxation rate ( $R_{diff} < R_{relax}$ ). In non Fickian diffusion, the solvent diffusion rate is faster than the polymer relaxation process ( $R_{diff} > R_{relax}$ ), whereas in anomalous diffusion, the solvent diffusion rate and the polymer relaxation are about the same order of magnitude ( $R_{diff} \sim R_{relax}$ ).

The following equation can be used to determine the nature of diffusion rate

$$F = kt^n,$$

where  $F$  is the amount of solvent fraction at time  $t$ ,  $k$  is a constant related to the structure of the network, and  $n$  is called the diffusional exponent which is indicative of the type of diffusion. The plot of  $\log t$  versus  $\log F$  of the PAG gels in water and dye solutions is shown in Figure 3.

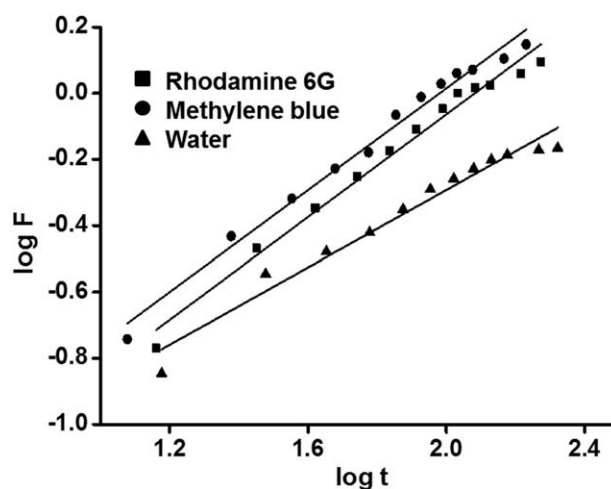
This equation is applied to the initial stages of swelling and plot of  $\log F$  versus  $\log t$  will give straight line. The exponent  $n$  and  $k$  values were calculated from the slope and intercept of the lines, respectively. It was observed that value of  $n$  is 0.54 for water and 0.7 for MB solution and R6G solution suggesting

non-Fickian character<sup>26,27</sup> (when  $n = 0.45-0.50$ —Fickian diffusion, whereas  $0.5 > n < 1$  indicates that diffusion is non-Fickian). When the polymer is in the rubbery state (elastic state), the polymer chains have a higher mobility that allows an easier penetration of the solvent and dye molecules. The high elastic modulus of PAG gel was strengthened by the rheological studies.

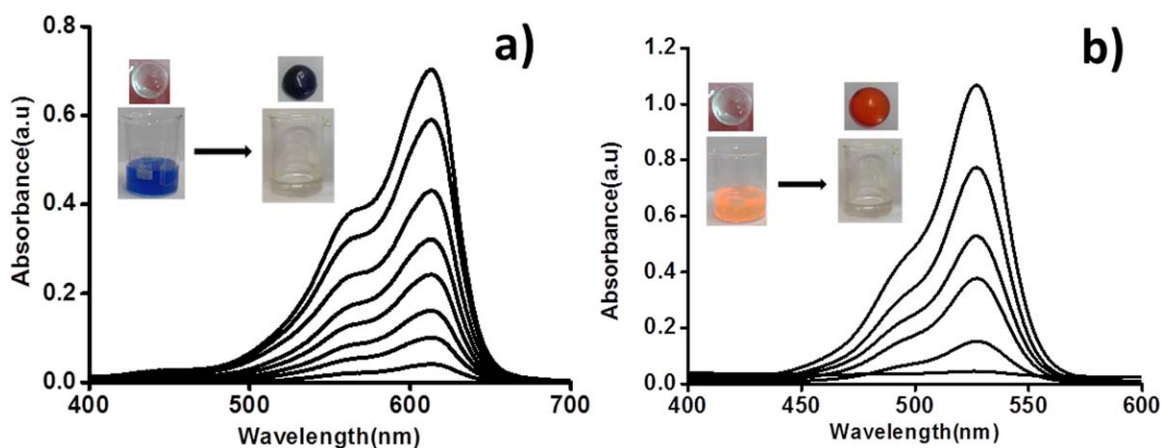
#### Adsorption Studies

Dye adsorption and decolorization efficiency were studied with MB and R6G dye solutions of varying the initial dye concentrations ranging from 20 to 400 mg/L. Experiments were performed with 20 mL of dye solution for 3 days using 0.1 g of PAG hydrogel and the decrease in the UV-visible absorption intensity of the solution was measured at regular intervals of time. The experiment is performed at room temperature (30°C) and the pH of the solution is  $\sim 7.5$ . Representative spectra of dye solutions of R6G and MB at regular intervals of time are shown in Figure 4 (a) and (b), respectively. The photographs of the same before and after adsorption are shown in the inset.

It has been observed that the decrease in the absorption intensity of the band of MB (665 nm) and R6G (525 nm) revealing



**Figure 3.** Swelling kinetic curves of PAG hydrogel in dyes and distilled water with respect to time.



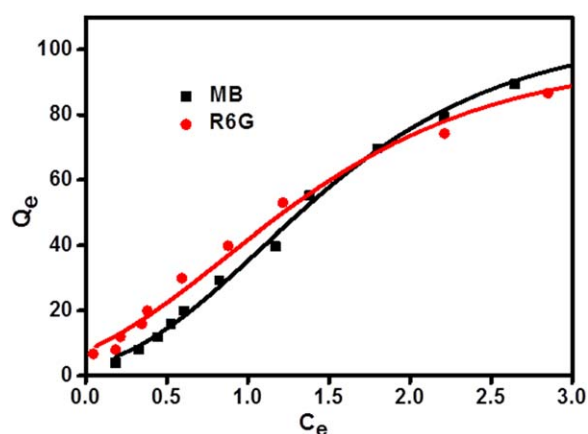
**Figure 4.** UV-visible spectra of aqueous solution of (a) MB and (b) R6G in the presence of PAG recorded periodically (initial dye concentration: 20 mg/L, adsorption time: 3 days, pH: 7). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the adsorption of the dye by PAG hydrogel. It was also observed that as time lapses, gel swelled due to diffusion of water and dye molecules. The functional groups such as carboxyl, amide, and hydroxyl groups present in the PAG hydrogel can interact with the cationic groups of the dyes through electrostatic and hydrogen bonding interaction which leads to the effective adsorption dyes on the hydrogel.

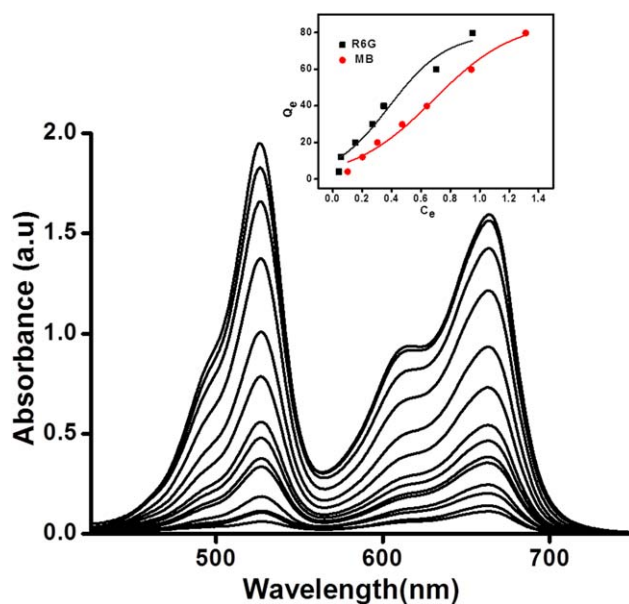
The adsorption of solute from the solution and the adsorbate-adsorbent interaction were studied under Gile's classification system. Amount of MB and R6G adsorbed per dry mass of the hydrogel ( $q_e$ , mg dye/g hydrogel) as a function of equilibrium concentration of dyes ( $c_e$ , mg/L) is shown in Figure 5. Initial direction of adsorption curve shows that adsorption becomes easier with increasing concentration. The type S-isotherm observed may be originating from the relatively weak adsorbate-adsorbent force compared to adsorbate-adsorbate interactions. The weak adsorbate and adsorbent force will cause the slow uptake of dye components initially. However, once the molecule is adsorbed, the adsorbate-adsorbate force will pro-

mote the adsorption of more molecules through a cooperative process where the isotherm becomes convex to the concentration axis. These studies show that the adsorption capacity of the gel increases with increase in concentration of dyes. Gile's curve showed the high absorption capacity of PAG hydrogels which revealed that 1 g of dye can adsorb up to 100 mg of dye.

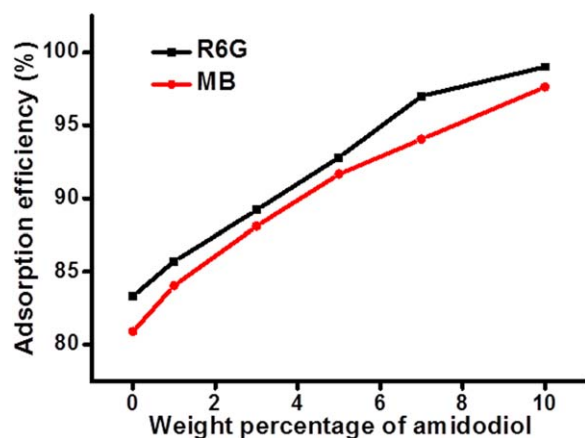
Experiments were performed to study the adsorption capacity of the PAG hydrogel for the mixture of dyes. The experiments were performed with 20 mL of the dye solution at room temperature (30°C) and at pH  $\sim$  7.5. The initial dye concentration varied from 20 to 400 mg/L. The representative UV-visible spectra and the Gile's curve are shown in Figure 6. Same decolorization efficiency for PAG hydrogel was observed in the case of experiments performed with mixture of dyes.



**Figure 5.** Gile's curve for the equimolar mixture of MB and R6G showing S type adsorption (initial dye concentration: 20–400 mg/L, adsorption time: 3 days, pH: 7). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** UV Spectra of mixture of R6G and MB and Gile's curve are shown in the inset (initial dye concentration of R6G and MB: 20 mg/L, adsorption time: 3 days, pH: 7). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Effect of amidodiol in the adsorption of R6G and MB (initial dye concentration: 20 mg/L, adsorption time: 3 days, pH: 7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of amount of amidodiol in PAG on the adsorption efficiency was studied.

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

where  $K_d$  is the empirical partition coefficient which relates the total concentration of the dissolved species to the total concentration of adsorbed species.<sup>28</sup> The decolorization efficiency and  $K_d$  values for PAA and PAGs were listed in Supporting Information Table S3. The  $K_d$  values increased with increasing amidodiol content indicating it as a better adsorbent. The graph showing the adsorption efficiency versus percentage of amidodiol is shown in Figure 7. It has been observed that adsorption efficiency is enhanced with increasing amount of amidodiol due to the presence of higher number of hydroxyl and amide groups which may interact with the cationic groups of dyes. Above 10 wt %, amidodiol forms highly crosslinked networks and reduces the adsorption process. Pure PAA hydrogel showed decolorization efficiency of 83% for R6G and 81% for MB. As the amidodiol content increased, PAG5 exhibited decolorization efficiency of 99% for R6G and 98% for MB.

#### Mechanism of Adsorption

Mechanism of adsorption of dye in hydrogels was studied by Langmuir and Freundlich adsorption isotherms. Langmuir isotherm assumes monolayer adsorption while Freundlich model, the mechanism of adsorption is multilayer sorption. Langmuir model can be represented by the equation<sup>29</sup>

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b}$$

where  $c_e$  is the equilibrium dye concentration in the solution (mg/L),  $b$  is the Langmuir adsorption constant (L/mg), and  $q_m$  is the theoretical maximum adsorption capacity (mg/g).

Langmuir plot of  $c_e$  versus  $(c_e/q_e)$  is shown in the Supporting Information Figure S3 and it exhibited a correlation value of (0.88 for R6G and 0.75 for MB).

The Freundlich adsorption isotherm is mathematically represented by the equation

$$\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n} \log C$$

$$\ln q_e = K_f + \frac{1}{n} \ln c_e,$$

where  $K_f$  is the equilibrium adsorption coefficient and  $n$  is the empirical constant.

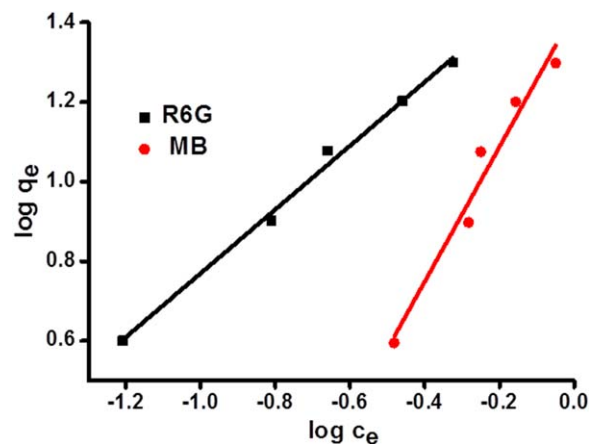
The linear plot of the Freundlich isotherm for R6G and MB is shown in Figure 8. The  $K_f$  and  $n$  values can be calculated from intercept and slope. The values of  $n$  for MB and R6G are 1.7 and 1.1, respectively, and  $K_f$  values are 1.42 and 1.6 for MB and R6G. The value of  $K_f$  for R6G is higher than MB which shows the PAG hydrogel has more affinity towards R6G than MB. The high value of the correlation coefficient obtained in the Freundlich isotherm for MB (0.98) and R6G (0.99) compared with the correlation coefficient of Langmuir isotherm (0.88 for R6G and 0.75 for MB) suggested that Freundlich adsorption isotherm is the best fit for the adsorption of dyes.<sup>30,31</sup>

#### Kinetics of Adsorption

Kinetics of dye adsorption was studied with different model equations. Adsorption of dyes R6G and MB (20 mg/L) onto PAG5 gel as a function of time is given in Supporting Information Figure S4. Kinetics of adsorption was studied by fitting these values in pseudo first-order and pseudo second-order equations. The pseudo first-order kinetics was studied using Lagergren equation<sup>32</sup>

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

where  $q_e$  and  $q_t$  are the amounts of dyes adsorbed at equilibrium and at time  $t$ ,  $k_1$  is the rate constant. Pseudo first-order model was checked by plotting  $\log(q_e - q_t)$  versus time and is given in Supporting Information Figure S5. The rate constant and  $q_e$  were calculated from the slope and intercept and are listed in the Table I. The values calculated from the pseudo first-order model differ considerably from the experimental



**Figure 8.** Freundlich adsorption isotherms of R6G and MB (initial dye concentration: 20 mg/L, adsorption time: 3 days, pH: 7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table I.** Parameters of Pseudo First-Order and Pseudo Second-Order Model

Dye	$q_e$ (mg/g), experimental	Pseudo first-order parameters			Pseudo second-order parameters		
		$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g) calculated	$R^2$	$k_2$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g) calculated	$R^2$
R6G	3.97	$1.69 \times 10^{-6}$	1.05	0.983	$7.78 \times 10^{-3}$	4.05	0.999
MB	3.96	$1.38 \times 10^{-6}$	0.65	0.955	$1.05 \times 10^{-5}$	4.00	0.999

values suggesting that the pseudo first-order model fails to describe the adsorption of dyes.

Then tested for the pseudo second-order equation,<sup>33</sup>

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{1}{q_e},$$

where  $k_2$  is the pseudo second-order rate constant. The plot of  $t/q_t$  versus  $t$  gives a straight line and is shown in Supporting Information Figure S6. The values of  $k_2$  and  $q_e$  can be calculated from the slope and intercept and is presented in the Table I. Here, the calculated value of  $q_e$  matches well with the experimental values. Further, the high value of regression coefficient obtained for pseudo second-order model compared with the pseudo first-order also suggested that the adsorption of dyes onto PAG gel follows pseudo second-order kinetics.

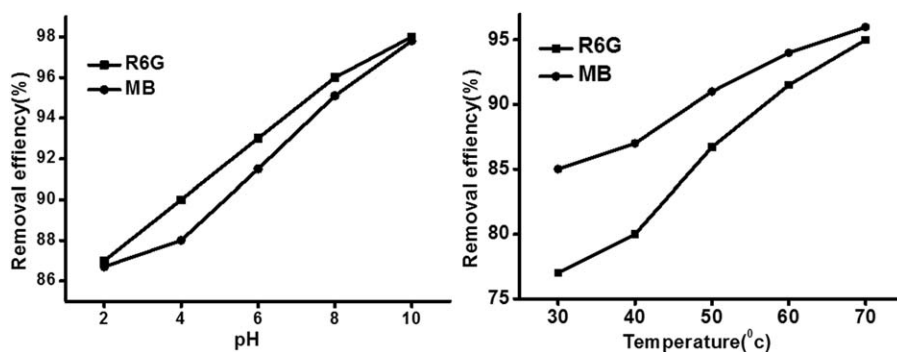
#### Effect of pH and Temperature

The pH of dye solution can change the surface charge of the dye molecule which may suppress or promote the ionization of the adsorbent and dye molecule. Effect of pH on the dye removal efficiency is shown in Figure 9(a). It showed an increase in the removal efficiency with increase in the pH of the dye solution. At lower pH value  $-\text{COOH}$  groups are in the nonionized state. On increasing the pH value,  $-\text{COOH}$  group ionizes and it generates an electrostatic repulsion among the adjacent ionized groups. This causes an expansion of the polymer chain within the hydrogel network.<sup>34</sup> Hence, the decolorization efficiency of the PAG hydrogel increases. For most of the waste water, pH is in the alkaline region and hence PAG hydrogel can be applied effectively in waste water treatment. Figure 9(b) shows the dye removal efficiency of the PAG hydrogel with increase in the temperature. The rate of diffusion increases with increase in temperature and enhances the dye adsorption.

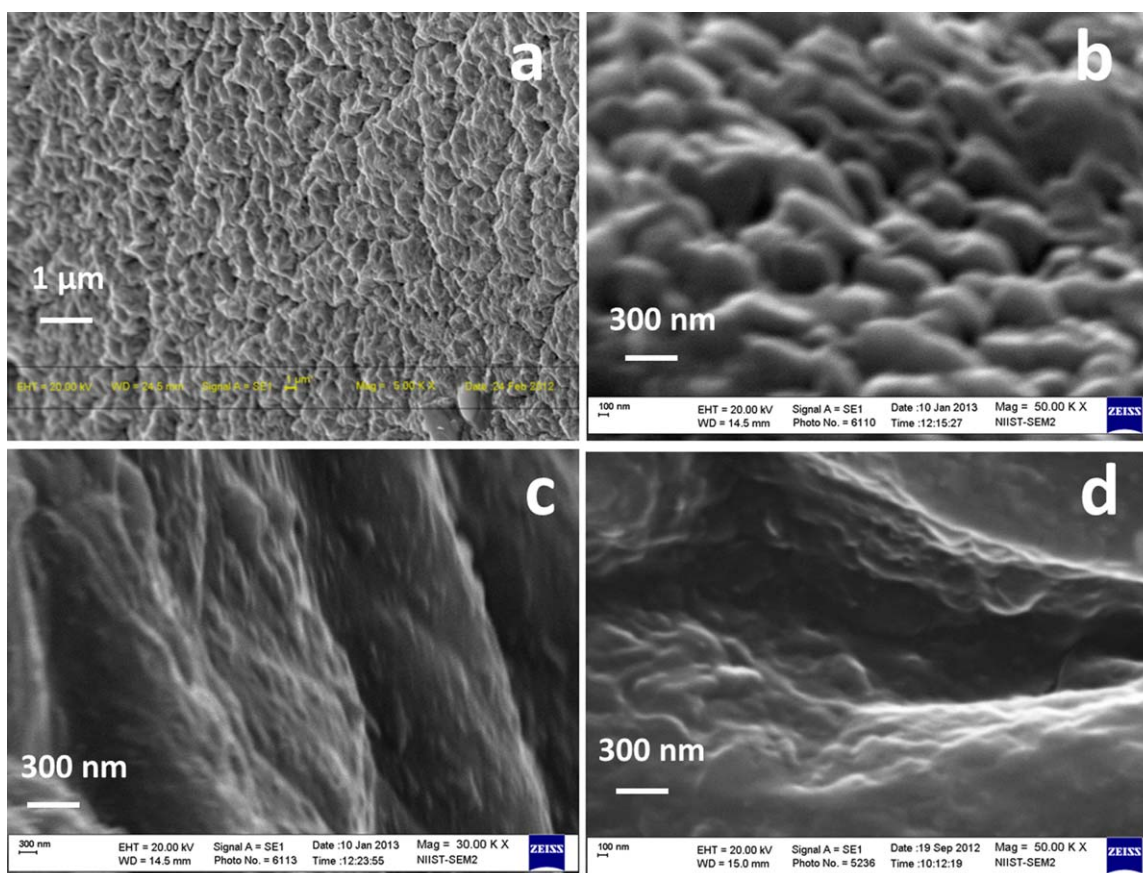
Morphology of the PAG hydrogel was studied by SEM and was observed as cross linked fibrillar networks in the xerogel state as shown in Figure 10(a). During swelling, they will imbibe large amount of water and the SEM image of swelled network is shown in Figure 10(b). A collapsed morphology of swollen gel after the entrapment of dye molecules in the pores of PAG gel networks is shown in Figure 10(c,d). This may be due to the hydrogen bonding interaction between the amine and carboxyl group of the hydrogel and the amine group and oxygen atom of the dye molecules. Thus, it can be inferred from the morphological analysis that PAG hydrogels are porous functional three-dimensional fibrillar network structures which allow the diffusion of solutes and solvent into the interior network.

#### Real Sample Analysis

The suitability of the PAG hydrogel for the dye adsorption in real sample is checked using the mixture of waste water collected from various industries such as food, paper, and textiles. The PAG hydrogel (0.5 g) was dipped in 20 mL of the waste water and stirred for 3 days. The concentration of the dyes present is estimated as  $\sim 20\text{--}30$  mg/L. The pH of the solution was found to be  $\sim 8.5$  and the experiment was performed at room temperature ( $30^\circ\text{C}$ ). The solution became almost colorless indicating the capability of hydrogel to adsorb dyes and other impurities. The extent of adsorption was monitored by recording UV-Vis spectra at regular intervals and is depicted in Supporting Information Figure S7. The photograph of waste water before and after treatment with PAG is given in the inset. The above results suggested that PAG hydrogel could be an excellent candidate for the color removal of waste water and the various kinetic parameters and adsorption mechanism studied can be exploited for the pilot scale waste water purification process. Moreover, desorption of dye was not observed even after few months. Hence, this can be considered as an efficient polymeric



**Figure 9.** (a) Effect of pH (initial dye concentration: 20 mg/L, adsorption time: 3 days, temperature:  $30^\circ\text{C}$ , pH: 2–10) and (b) effect of temperature (initial dye concentration: 20 mg/L, adsorption time: 3 days, pH: 7, temperature:  $30\text{--}70^\circ\text{C}$ ).



**Figure 10.** SEM images of (a) PAG xerogel, (b) swelled PAG gel, (c and d) PAG entrapped with R6G and MB. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

filtration membrane for the removal of dyes from aqueous solutions. These studies can be used for the removal of other aromatic toxic material present in our environment generated from various industries.

## CONCLUSION

A series of robust hydrogels based on acrylic acid (PAGs) have been prepared using rigid rod like functional amidodiol as an efficient physical crosslinker as evident from FTIR spectral results and elastic modulus measured using rheology. Swelling and diffusion studies of PAG showed non-Fickian characteristics and the kinetics of adsorption were observed as pseudo second order. Adsorption was investigated with Langmuir and Freundlich isotherm and suggested multilayer adsorption. The adsorbate–adsorbent interaction studied using Gile’s classification system showed an s type adsorption and better adsorption efficiency of PAG hydrogels. Morphological studies revealed that dye molecules could effectively diffuse to the fibrillar network of the hydrogel and retain its shape even after high percentage of swelling. The adsorption efficiency of the PAG hydrogel showed an enhancement with increase in the amidodiol content, pH, and temperature. Moreover, PAGs are observed to be robust at high pH and temperature and hence it can be used in the real water purification system. Because of the absence of desorption of dyes from the gel, it can be efficiently

used as a polymeric filtration membrane for the removal of dyes from waste water. All these results suggested PAGs as a potential candidate for the water purification and the generated data can be used for pilot plant usage.

## ACKNOWLEDGMENTS

The authors thank CSIR Network project (CSC0101) for the financial support. The authors also would thank Dr. Suresh Das, Director, CSIR-NIIST, and Dr. A. Ajayaghosh, NIIST, Trivandrum. The authors are also thankful Ms. Lucy Paul for SEM analyses. K.N. Rohini also thanks CSIR, Govt. of India for research fellowship.

## REFERENCES

- Kim, B.; La Flamme, K.; Peppas, N. A. *J. Appl. Polym. Sci.* **2003**, *89*, 1606.
- Nho, Y. C.; Park, S.-E.; Kim, H. I.; Hwang, T.-S. *Nucl. Instrum. Methods B* **2005**, *236*, 283.
- Jeon, Y. S.; Lei, J.; Kim, J.-H. *J. Ind. Eng. Chem.* **2008**, *14*, 726.
- Haraguchi, K.; Takehisa, T. *J. Adv. Mater.* **2002**, *14*, 1120.
- Saravanan, P.; Padmanabha Raju, M.; Alam, S. *Mater. Chem. Phys.* **2007**, *103*, 278.



6. Zhou, C.; Wu, Q.; Yue, Y.; Zhang, Q. *J. Colloid Interface Sci.* **2011**, 353, 116.
7. Xia, L. W.; Ju, X. J.; Liu, J. J.; Xie, R.; Chu, L. Y. *J. Colloid Interface Sci.* **2010**, 349, 106.
8. Sudha, J. D. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2469.
9. Wong, Y. X.; Yu, J. *Water Res.* **1999**, 33, 3512.
10. Panswad, T.; Luangdilok, W. *Water Res.* **2000**, 34, 4177.
11. Ong, S. T.; Keng, P. S.; Lee, W. N.; Ha, S. T.; Hung, Y. T. *Water* **2011**, 3, 157.
12. Valdés, H.; Godoy, H. P.; Zaror, C. A. *Water Sci. Technol.* **2010**, 61, 2973.
13. Jian-Xiao, L.; Guog-Hong, X.; Qing-Ling, Y.; Li, Z.; Jian-Min, L.; Ying, C. *Water Sci. Technol.* **2009**, 60, 2329.
14. Wang, S.; Ang, H. M.; Tadé, M. O. *Chemosphere* **2008**, 72, 1621.
15. Zidane, F.; Drogui, P.; Lekhlif, B.; Bensaid, J.; Blais, J. F.; Belcadi, S.; Kacemi, K. E. *J. Hazard. Mater.* **2008**, 155, 153.
16. Wong, Y. C.; Szeto, Y. S.; Cheung, W. H.; McKay, G. *J. Appl. Polym. Sci.* **2008**, 109, 2232.
17. Crini, G. *Bioresour. Technol.* **2006**, 97, 1061.
18. Liu, Y.; Zheng, Y.; Wang, A. *J. Environ. Sci.* **2010**, 22, 486.
19. Mahdavinia, G.; Massoumi, B.; Jalili, K.; Kiani, G. *J. Polym. Res.* **2012**, 19, 1.
20. Zhu, X.; Jiang, X.; Cheng, S.; Wang, K.; Mao, S.; Fan, L. *J. Polym. Res.* **2010**, 17, 769.
21. Solpan, D.; Sen, M.; Kolge, Z.; Torun, M.; Guven, O. *Hacet-tepe J. Biol. Chem.* **2009**, 7, 233.
22. Saraydin, D.; Karadağ, E.; Güven, O. *J. Appl. Polym. Sci.* **2001**, 79, 1809.
23. Rosa, S.; Laranjeira, M. C. M.; Riela, H. G.; Fávere, V. T. *J. Hazard. Mater.* **2008**, 155, 253.
24. Zendehtdel, M.; Barati, A.; Alikhani, H.; Hekmat, A. *Iran. J. Environ. Health Sci. Eng.* **2010**, 7, 431.
25. Alfrey, T.; Gurnee, E.F.; Lloyd, W.G. *J. Polym. Sci. Part C: Polym. Symp.* **1996**, 12, 249.
26. Mendizábal, E.; Katime, I. *Mater. Sci. Appl.* **2010**, 1, 162.
27. Hu, D. S.G.; Chou, K. J. N. *Polymer* **1996**, 37, 1019.
28. Li, P.; Siddaramaiah; Kim, N. H.; Heo, S. B.; Lee, J. H. *Composites Part B* **2008**, 39, 756.
29. Al-Qodah, Z. *Water Res.* **2000**, 34, 4295.
30. Akpomie, G. K.; Ogbu, I. C.; Osunkunle, A. A.; Abuh, M. A.; Abonyi, M. N. *J. Emerg. Trends Eng. Appl. Sci.* **2012**, 3, 354.
31. Mahdavinia, G. R.; Zhalebaghy, R. *J. Mater. Environ. Sci.* **2012**, 3, 895.
32. Perju, M. M.; Dragan, E. S. *Ion Exch. Lett.* **2010**, 3, 7.
33. Ho, Y. S.; McKay, G. *Process Biochem.* **1999**, 34, 451.
34. Paulino, A. T.; Guilherme, M. R.; Reis, A. V.; Campese, G. M.; Muniz, E. C.; Nozaki, J. *J. Colloid Interface Sci.* **2006**, 301, 55.