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Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study

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ABSTRACT

The present work deals with the removal of Brilliant Green dye from wastewater using a poly(acrylic acid) hydrogel composite (PAA-K hydrogel) prepared by incorporation of kaoline clay. The composite has been synthesized using ultrasound assisted polymerization process as well as the conventional process, with an objective of showing the better effectiveness of ultrasound assisted synthesis. It has been observed that the hydrogel prepared by ultrasound assisted polymerization process showed better results. The optimum conditions for the removal of dye are pH of 7, temperature of 35 °C, initial dye concentration of 30 mg/L and hydrogel loading of 1 g. The extent of removal of dye increased with an increase in the contact time and initial dye concentration. A pseudo-second-order kinetic model has been developed to explain the adsorption kinetics of dye on the PAA-K hydrogel. Thermodynamic and kinetic parameters indicate that the adsorption process is spontaneous in nature and the PAA-K hydrogel prepared by ultrasound process is a promising adsorbent compared to conventional process. The obtained adsorption data has also been fitted into commonly used adsorption isotherms and it has been found that Freundlich as well as Langmuir adsorption isotherm models fits well to the experimental results.

1. Introduction

Effluent streams generated by different industries such as textile, tannery, food, printing, pulp and paper, etc. contain dyes as one of the most commonly observed component imparting obnoxious color to the effluent streams [1–3]. Discharge of effluent streams containing dyes into the natural streams is harmful to the aquatic life and also in long run to the human beings. Removal of dyes from wastewaters is a complex problem because of the significant difficulty in treating the dye containing wastewaters using the conventional treatment schemes. In the past, various attempts have been made to develop effective treatment technologies for dye bearing wastewaters, but no single solution has been found to be satisfactory [4]. Different physicochemical processes like adsorption, electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation, and photo-catalytic degradation processes have been attempted in treating these wastewaters [5–10]. Each technique has its own limitations such as generation of secondary effluent, hazardous intermediate products and slow rates of degradation. Thus, it is need of time to research into cleaner techniques for the effective removal of dyes from the effluent stream. The present work deals with adsorption of dyes on hydrogel synthesized using ultrasonic irradiations and by conventional technique as adsorption using hydrogel is one of the important approaches for the effective removal of dyes. Hydrogel are superior as compared to other adsorbents due to their characteristic properties such as adsorption–regeneration, economic feasibility and environmental friendly behavior, and hence lot of research is done on the use of hydrogels in pollution control studies. The hydrogels are made of porous structure networks and allow solute diffusion through their structure. They possess ionic functional groups which can be helpful for trapping ionic dyes. The model dye selected in the work is Brilliant Green, which is a odorless cationic dye used for various purposes, e.g. biological stain, dermatological agent, veterinary medicine, and an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus [11]. It is also extensively used in textile dying and paper printing. Brilliant Green causes several effects on human beings including irritation to the gastrointestinal tract, nausea and vomiting, irritation to the respiratory tract and irritation to skin [12]. Brilliant Green

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may form hazardous products like nitrogen oxides, and sulfur dioxides due to decomposition on heating [13].

In the past some studies for the removal of dye have been based on the use of hydrogel, a class of cross-linked polymeric materials, which have played an important role in the treatment of wastewater for the removal of different water pollutants like dyes [14–16], phenolic compounds [17], heavy metals [18], ammonia [19], boron [20,21], etc. In addition, hydrogel are extensively used in many fields, such as molecular filters, super absorbents, and contact lenses [22–26]. Mechanical stability of hydrogel is an important issue for their effective use in wastewater treatment. Recently, some attempts have been made to modify the mechanical properties like elasticity and permeability of the gels to adsorb different substances by the incorporation of the clays or inorganic materials, such as montmorillonite, kaolin, mica, bentonite into the polymer networks [27–30]. Many hydrogel composites such as polyacrylamide with bentonites or montmorillonites, polyacrylic acid or poly(N-isopropyacrylamide) with different clays have been synthesized and studied in terms of mechanical properties and swelling behavior [27–32]. Clays as compared to the other adsorbents are natural, abundantly available and inexpensive minerals that have unique structure and high mechanical strength. Clay minerals are good adsorbents for removing contaminants from textile and dye industry wastewater [20,33–37].

Ultrasonic irradiation has been used for intensification/improvement of different physical and chemical processing applications and one of the applications has been in the polymer synthesis through the generation of free radicals and activation of free radical initiators. Ultrasound has been found to be an effective method for the polymerization of monomers and production of hydrogel in the absence of a chemical initiator [38]. Due to the cavitation effects such as formation of micro-jets and turbulence, which are higher in the case of heterogeneous systems [39], uniform particle size distribution of the composite can be obtained. Similarly uniform dispersion of clay into the polymer matrix can be effectively achieved. Further, clay acts as a cross-linking agent and uniform cross-linking can be achieved due to the cavitation effects. During the adsorption studies when the hydrogel is immersed in water for adsorbing the dye molecules from the wastewater, hydrophilic polymer chains of the hydrogel does not dissolve into the aqueous phase because of the uniform cross-linking. The degree of cross-linking in the polymer network structure is critical as it dictates the mechanical strength, swelling ratio, and many other properties of the polymer gel by influencing the molecular weight between cross-links [40].

In the present work, poly(acrylic acid) hydrogel loaded with the Kaolin clay was synthesized using ultrasound induced polymerization and conventional process and the feasibility of these hydrogels for the removal of Brilliant Green (BG) dye has been investigated. The adsorption equilibrium studies were carried out and the effect of various parameters such as pH, temperature, initial dye concentration, quantity of hydrogel and clay loading on the extent of removal of dye has been investigated.

2. Experimental methodology

2.1. Materials

Acrylic acid (AA), ammonium persulfate (APS), sodium dodecyl sulfate (SDS) and Brilliant Green dye (BG) were of analytical grade and procured from M/s CDH, India. Kaolin (China clay) clay was obtained from MD Chemicals Pune, India and used without any further purification. Deionized water was used for dilution in all the experiments.

2.2. Synthesis of poly(acrylic acid)-Kaolin (PAA-K) hydrogel using insitu ultrasound assisted emulsion polymerization and conventional process

PAA-K hydrogel has been synthesized from acrylic acid (monomer), APS (initiator), and SDS (surfactant). Initially, the reactor was flushed using argon to maintain inert atmosphere. In the actual synthesis process, 36 g of acrylic acid with 100 mL water was loaded into the ultrasound polymerization reactor. In other beaker, SDS–kaolin solution was prepared using 0.5 g of SDS and 0.36 g kaolin in 20 mL water (corresponding to 1.0% (wt.%) of acrylic acid). The mixture was then homogeneously mixed using ultrasound bath and added into a polymerization reactor. Then the solution was irradiated for 5 min using ultrasonic horn (Dakshin make, 22 mm probe diameter) operating at 22.5 kHz frequency and rated power of 120 W. The total acoustic power dissipated into the sample was calculated using calorimetric method. The total power dissipated into polymerization reactor was 12.5 W. The objective of using the ultrasonic irradiation was to form uniform small size emulsion droplets which will remain stable and hence, will give uniform final polymer particle size. APS solution was prepared by mixing 0.1 g of APS in 10 mL water and it was added into the reactor as initiator. Reactor temperature was maintained at 60 °C for 30 min. Argon gas was used for blanketing of the polymerization reactor to avoid the contact with atmosphere. The presence of ultrasonic environment in the polymerization reactor assisted the uniform distribution of kaolin platelets through hydrogel network. Another hydrogel containing 2% (wt.%) kaolin was also prepared to study the effect of kaolin loading. Fig. 1a shows the experimental setup for the synthesis of hydrogel by ultrasound assisted method and Fig. 1b shows the schematic representation of the process of the formation of PAA-K hydrogel. Similar procedure was used for conventional synthesis in which the temperature of the polymerization reactor was maintained at 60 °C and the reaction was carried out for 60 min under mechanical stirring instead of using ultrasound probe. In both the preparation methods, the formation of thick solution was initially observed which then transformed into a sticky suspension. However during the ultrasonic synthesis less time was required for the formation of the gel. The reduction in time compared to conventional synthesis is due to the cavitational effect. Further, the rapid micromixing and implosive collapse of bubbles in a liquid solution could have resulted in extremely high temperature which accelerated the reaction.

2.3. Water uptake of hydrogel

To confirm the swelling behavior of synthesized hydrogel, 1 g of PAA-K hydrogel was allowed to swell in 100 mL of deionized water at 30 °C for 3 h. At predetermined time intervals, the hydrogel was taken, wiped with filter paper to remove excess water and was weighed to find the water content [16]. The swelling ratio, S, was calculated using Eq. (1).

$$S = \frac{W_s - W_d}{W_d} \tag{1}$$

where W_s and W_d are the swollen and dry weights of the hydrogel respectively.

2.4. Adsorption of BG dye

The adsorption experiments were carried out in a batch mode to study the effect of different parameters like pH, temperature, initial dye concentration, quantity of hydrogel and clay content on the extent of adsorption. PAA-K hydrogel (1 g) was added to

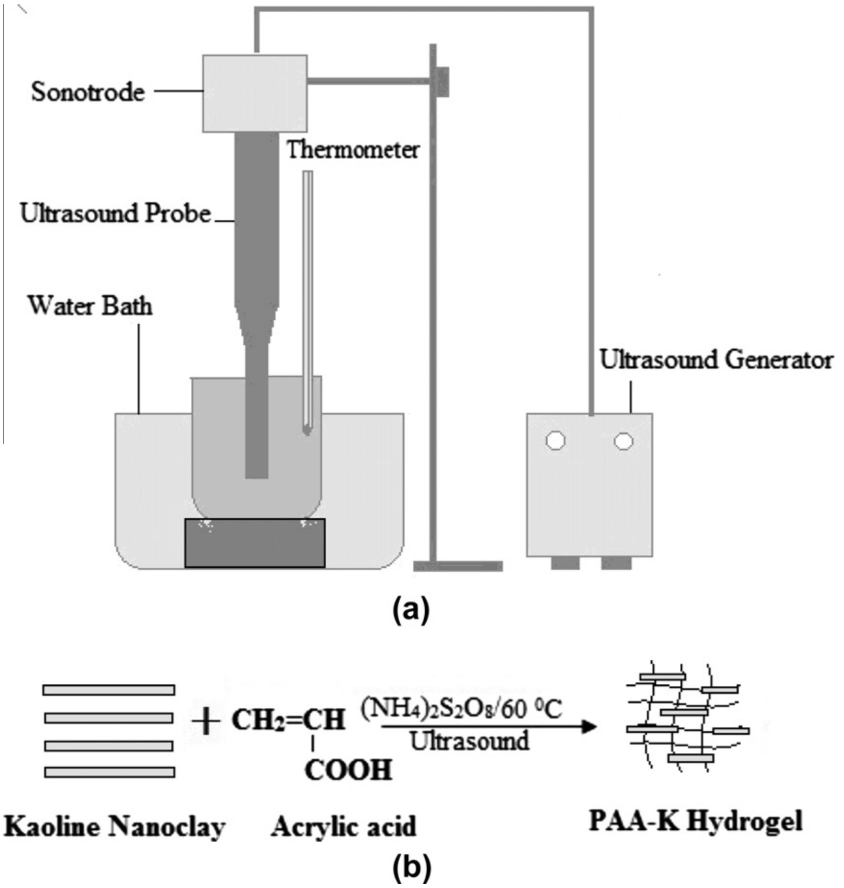

Fig. 1. (a) Experimental set up for synthesis of hydrogel by ultrasound assisted method, (b) schematic representation of the formation of hydrogel.

100 mL of aqueous dye solution of known concentration and pH of the solution was adjusted using buffer solution. The effect of initial BG dye concentration was investigated over the concentration range of 10–50 mg/L. The effect of hydrogel loading was investigated using different quantities of PAA-K hydrogel over the range 0.5–2 g. Temperature was maintained constant throughout the duration of experiments using water bath. The percentage dye removal has been calculated using the following equation:

$$\text{Percentage removal} = (C_0 - C_e)/C_0 \times 100 \tag{2}$$

where, C_o and C_e are the initial and equilibrium concentrations of BG dye (mg/L).

Amount of dye adsorbed per unit mass of hydrogel (mg/g) has been determined using following equation.

$$q_t = (C_0 - C_t)V/M \tag{3}$$

where V is volume of the dye solution in L and M is the mass of dry hydrogel in g, t refers to the time of treatment.

2.5. Analysis and characterization

The concentration of Brillient Green (BG) dye was measured using UV–vis spectrophotometer (SHIMADZU 160A model). The wavelength of maximum absorbance ($\lambda_{\max}$) of BG dye was found to be 624 nm. Deionized water was used as a reference. FTIR Spectra of the hydrogel samples were recorded on Perkin Elmer FTIR spectrometer (Paragon 1000 PC) in the wave number range of 500–4000 cm^{-1} with resolution of 1 cm^{-1}. FTIR of the sample was taken after partially drying the hydrogel in an oven at 60 °C for 180 min. Transmission electron microscopy (TEM, magnification 750,000×) image was taken on a Philips Tecnai 20 model.

3. Results and discussion

3.1. Morphology of poly(acrylic acid) and nanocomposite hydrogel

With an objective of investigating the efficacy of dispersion of kaolin clay in the PAA hydrogel matrix, transmission electron microscope (TEM) images of the dried PAA-K hydrogel (0.36 g clay) prepared by conventional as well as ultrasound method have been obtained and shown in Fig. 2. Fig. 2a shows the TEM image of poly(acrylic acid). Hydrogel with kaolin prepared by conventional method whereas Fig. 2b gives the image for the ultrasonically prepared hydrogel. The presence of dark-spots in both the figures confirms the occurrence of kaolin clay in the hydrogel matrix however it can be observed in the case of Fig. 2a that the kaolin particles are not uniformly distributed through the hydrogel matrix and aggregation of kaolin particles can be seen at different locations. In contrast, it can be clearly established from the depicted image for the ultrasound assisted synthesis (Fig. 2b) that the clay platelets are substantially exfoliated and dispersed homogeneously throughout the polymer matrix. Thus, fine and homogeneous clay dispersion was achieved in the hydrogel matrix due to the presence of ultrasound. The complete exfoliation of clay platelets and insertion of poly(acrylic acid) chains into the gallery spacing of clay is due to the shear and turbulence effects of the cavitation phenomena occurring during the emulsion polymerization. The particle size of kaolin clay was measured from the TEM images, where the black

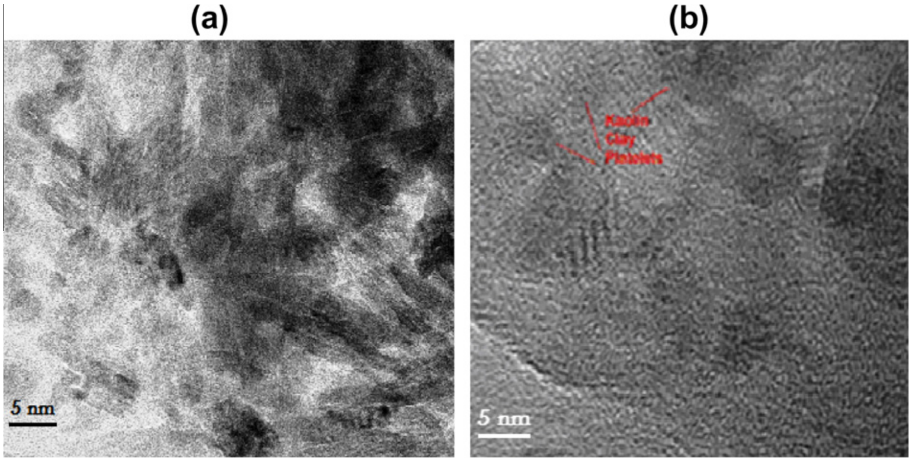

Fig. 2. Transmission electron microscopic images of PAA-K nanocomposite hydrogel (a) conventional method, (b) ultrasound assisted method.

spots in Fig. 2b indicates the presence of clay. The particle size of the kaolin clay was found to be in the range of 20–50 nm.

3.2. Swelling behavior of PAA-K hydrogel

In recent years, considerable efforts have been made to understand the mechanism of water diffusion through hydrogel matrices [20,32,33]. The time dependent swelling behavior of hydrogels has been described by a power-law function [32,33] as shown in Eq. (4).

$$F = M_t/M_s = Kt^n \tag{4}$$

where, F is the fractional uptake at time t, K is a constant depending on the type of the diffusion system, and 'n' is related to the transport mode of the penetrate. M_t and M_s are the mass uptake of water at time t and equilibrium respectively. Eq. (4) is valid for the initial 60% of the fractional uptake. The plot of $\ln(M_t/M_s)$ against $\ln(t)$ depicting the swelling behavior of PAA-K hydrogel synthesized using conventional method and ultrasound assisted method has been shown in Fig. 3. For the diffusion of water in the hydrogel, value of 'n' in Eq. (4) has been found to be 0.39 for hydrogel prepared by conventional method as against 0.87 for the ultrasound assisted method. The diffusion of solvent into a polymer is a combination of two different processes: the diffusion of the solvent into the swollen matrix, and the advancement of the swollen–unswollen boundary as a result of the stress induced in the polymer. When the first mechanism is the rate determining step there is a linear dependency between the solvent uptake and time and the system exhibits Fickian behavior. Also the value of n is a characteristic of the mode of transport of the penetrating molecule and it actually indicates the type of diffusion inside the hydrogel. The values of n for Fickian diffusion and case II transport are 0.5 and 1, respectively whereas for the n value between 0.5 and 1, it is usually described as the non-Fickian diffusion, which is considered the intermediate between Fickian diffusion and case II transport. In the present investigation, from the obtained values of n, we can conclude that for conventionally synthesized hydrogel the Fickian behavior was observed while for ultrasonically synthesized hydrogel non fickian behavior was observed indicating that the advancement of the swollen–unswollen boundary was slower than the diffusion of the solvent in the swollen polymer indicative of zero-order kinetics. As a result, the water uptake increased linearly with the sorption time [10,14,41]. The value of n varied significantly as a result of change in the method of preparation and therefore different diffusion behaviors are expected. Similar type of change of behavior related to diffusion is reported by Li et al. [16] for PAAm/Laponite clay nanocomposite hydrogel as a result of heat treatment to the hydrogel.

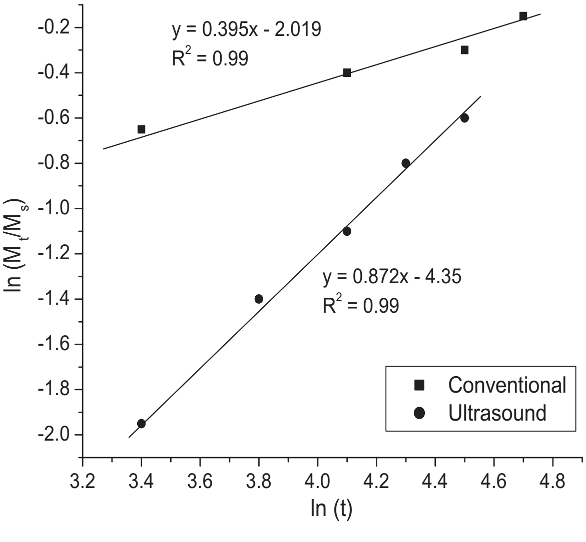

Fig. 3. Plot of $\ln(M_t/M_s)$ against $\ln(t)$ of water in PAA-K hydrogel.

3.3. Effect of pH on the responsive adsorption of BG dye

The initial pH of the dye solution is an important parameter, which controls the adsorption process, especially the adsorption capacity. The operating pH of the solution changes the surface charge of the adsorbent, the degree of ionization of the adsorbate molecule and the extent of dissociation of functional groups on the active sites of the adsorbent. The influence of solution pH on the extent of removal of the dye was investigated over the pH range of 4–9 using acidic and basic buffer solutions. The percentage dye removal for the initial dye concentration of 30 mg/L and 1 g hydrogel at different operating pH has been shown in Fig. 4. For both preparation methods it has been observed that the maximum adsorption takes place at pH value of 7. The extent of removal of dye increases with an increase in the pH till an optimum value of 7, beyond which it gradually decreases. The observed results can be attributed to the fact that the pH value affects the structural stability of Brilliant Green molecules [13]. For kaolin, the point of zero charge (ZPC) is 7.0 [11]. Below this range, the kaolin surface acquires positive charge and there would be an

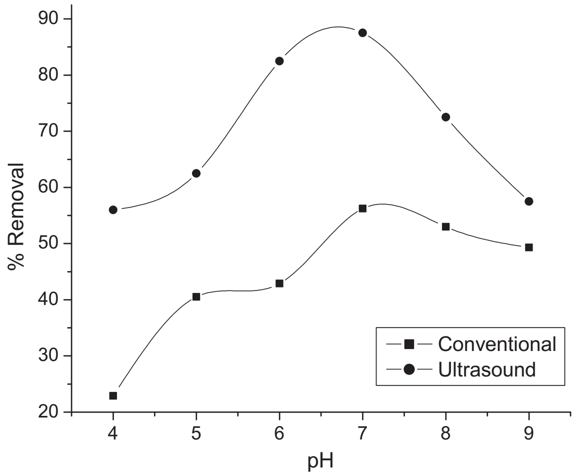

Fig. 4. Effect of pH on adsorption of BG dye on PAA-K hydrogel at 35 °C.

electrostatic repulsion between cationic dye molecules and kaolin. Above a pH of 7, the kaolin particle acquires a negative surface charge. This should lead to higher cationic dye adsorption, however, this behavior has not been observed in the present investigation as seen in Fig. 4. The observed trends can be attributed to the chemical structure of a dye molecule (ionic or molecular) and its behavior under alkaline conditions [34]. Nandi et al. [11] have reported similar existence of the optimum pH of 7 for the removal of Brilliant Green dye from aqueous medium using kaolin. Based on these results, all the further experiments were carried out at pH value of 7.

3.4. Effect of operating temperature on the responsive adsorption of dye

The influence of operating temperature on the adsorption process has been studied at three different temperatures as 15, 25 and 35 °C and the obtained results have been shown in Fig. 5. It can be seen from the figure that the adsorption of the dye increased with an increase in the operating temperature. The maximum extent of removal obtained at 35 °C was 56.24% for the conventional method and 88.3% for ultrasonic method (Fig. 5). The observed results can be attributed to the relaxing of the hydrogel network at higher temperatures, due to which the dye molecules can diffuse more easily through the matrix resulting into more adsorption. However it should be noted that the temperature cannot be increased indefinitely as collapse of hydrogel matrix may take place due to heat effects. It has been demonstrated that many hydrogel show continuous volume transition with change in the temperature and highly swollen gel network can collapse at high temperatures [17]. Based on these results and related discussion, the operating temperature was fixed at 35 °C for all the further experiments.

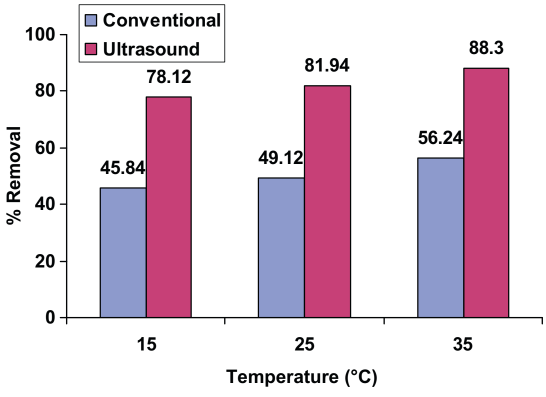

Fig. 5. Effect of temperature on adsorption of BG dye in PAA-K hydrogel at pH 7 for conventional method and ultrasound assisted method.

3.5. Effect of initial concentration of dye

The effect of initial concentration of dye on the extent of removal has been investigated by varying the initial concentration of BG dye over the range 10–50 mg/L. The solution of dye was mixed with 1 g of PAA-K hydrogel at pH 7 and 35 °C temperature and then equilibrated for 5 h. The obtained results indicate that the dye uptake by hydrogel increases sharply with an increase in the initial dye concentration for both the preparation methods as shown in Fig. 6. The obtained trends can be attributed to the fact that with increasing concentration of BG dye in the initial solution, higher concentration gradient at the hydrogel–solvent interface exists resulting in an enhancement in the BG dye removal rate. Similar results have been reported for the adsorption of metal ions on chitosan-2-acrylamido-2-methyl propane sulfonic acid (AMPS) hydrogel [18]. It is also seen that for the hydrogel prepared by ultrasonic method the extent of removal was increased by almost 30% as compared to conventional method. This may be attributed to the cavitational effects such as formation of micro-jets and

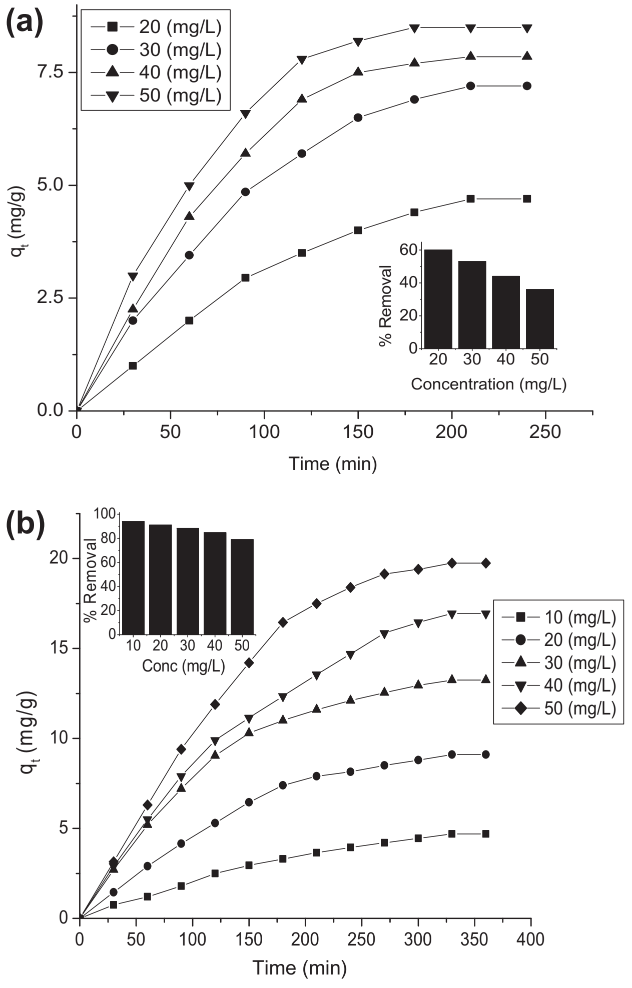

Fig. 6. Effect of initial concentration on adsorption of BG dye in PAA-K hydrogel at pH 7 and 35 °C (a) conventional method, (b) ultrasound assisted method.

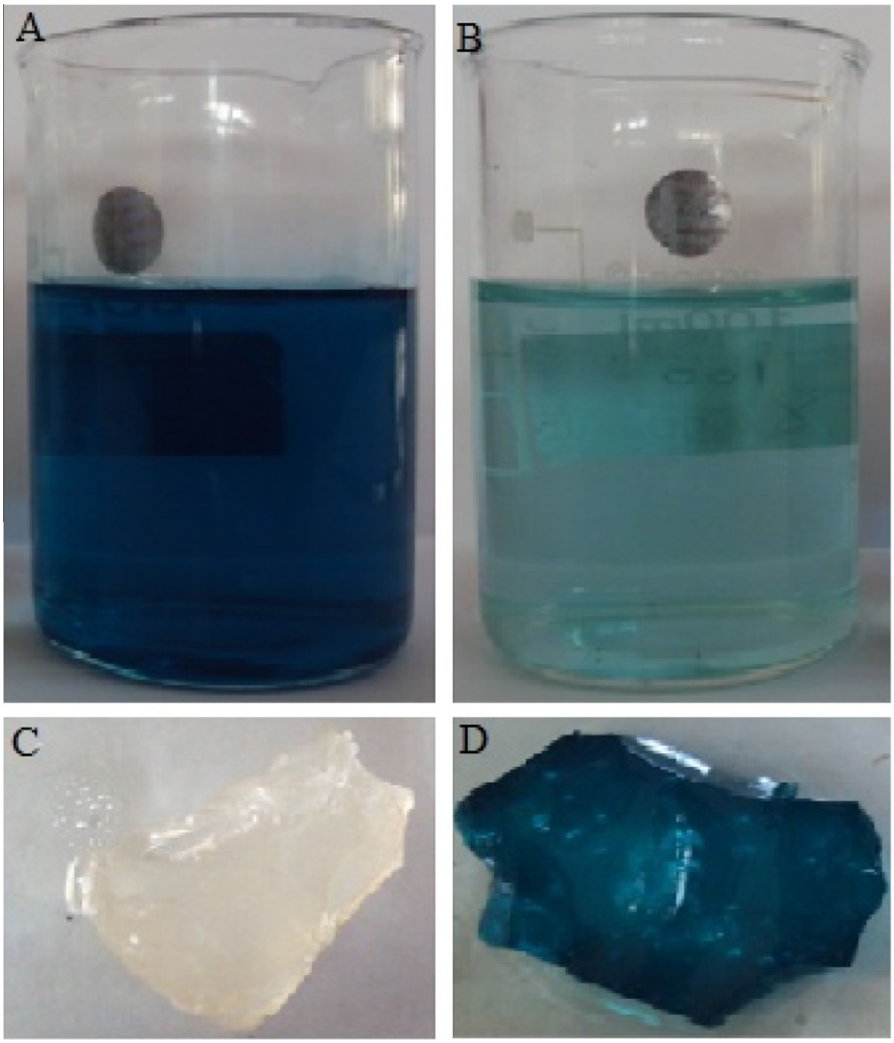

Fig. 7. Colour changes of BG dye and hydrogel before (A, C) and after adsorption (B, D), respectively.

turbulence during polymerization resulting in uniform distribution of kaolin clay throughout the hydrogel matrix. The change in color of both the hydrogel and dye solution before and after the adsorption has been shown in Fig. 7.

3.6. Effect of quantity of hydrogel and kaolin loading

The effect of hydrogel loading on the extent of removal of dye was studied by using different amounts of hydrogel (0.5, 1, 1.5, 2 g) in 100 mL of fixed concentration (30 mg/L) BG dye solution. Fig. 8 shows that the percent removal of the dye increases with an increase in the quantity of hydrogel. The higher dye removal, close to 100%, was reached when 2 g of ultrasonically synthesized hydrogel was used. This indicates that the presence of higher quantity of hydrogel provides large number of active adsorbent sites for removal of enhanced quantum of the pollutant. At the same time when the conventionally synthesized hydrogel was used, 2 g hydrogel was able to remove only 63% dye.

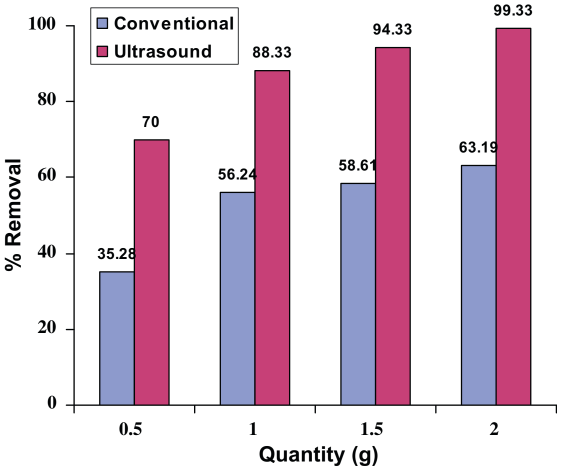

Fig. 8. Effect of initial quantity of PAA-K hydrogel on removal of BG at pH 7 and 35 °C.

Effect of the clay content on BG adsorption was investigated for PAA-K hydrogel prepared by both methods. For this purpose, PAA-K hydrogel was loaded with two different amounts viz. 0.36 g (1 wt.% of monomer) and 0.72 g (2 wt.% of monomer) of the kaolin clay. The PAA-K hydrogels containing different amounts of kaolin were added to 100 mL solutions of BG dye with different concentrations (10–50 mg/L) at 35 °C in a water bath. The removal efficiency (RE%) of the dye by the PAA-K hydrogel containing different amounts of clay has been shown in Fig. 9. Fig. 9a shows the dye removal for conventional method and Fig. 9b shows the same for ultrasound assisted synthesis method. It can be seen from

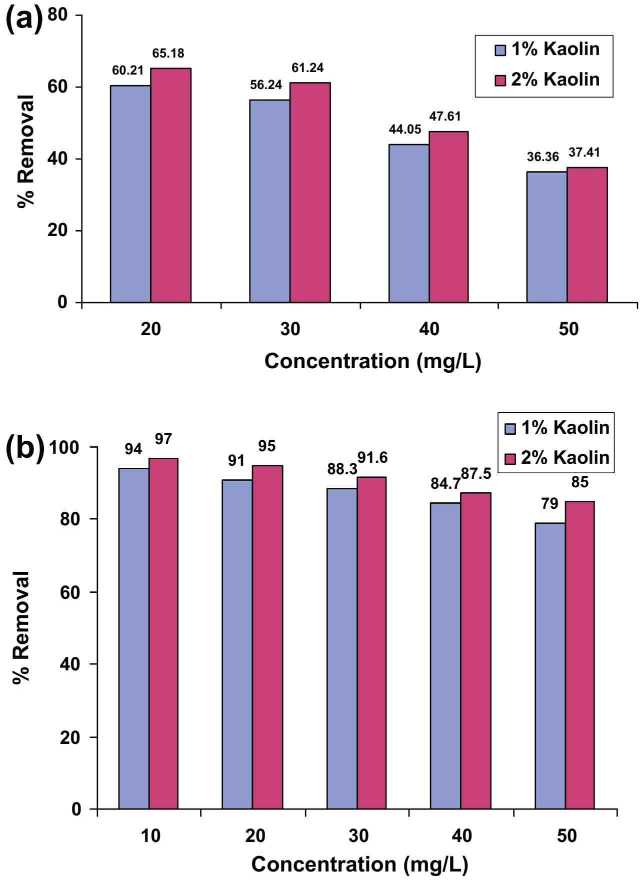

Fig. 9. Effect of clay loading in PAA-K hydrogel for the adsorption of BG dye at pH 7 and 35 °C (a) conventional method, (b) ultrasound assisted method.

both the figures that the dye uptake increases with increasing clay content. The obtained results can be explained on the basis of the fact that enhanced adsorbent active sites are available with an increase in the kaolin content. However there was not a major enhancement in the removal efficiency with the increase in the quantity of kaolin from 1% to 2% (wt.% monomer).

3.7. FTIR study of hydrogel nanocomposite before and after adsorption

The characterization of hydrogel was obtained using FTIR analysis to study the interaction between the dye molecules and the PAA-K hydrogel and to confirm the presence of carboxyl group of acrylic acid. Fig. 10 shows FTIR spectra of PAA-K hydrogel (synthesized by ultrasonic method), before (curve a) and after adsorption (curve b) of the dye. It can be seen from the spectra that before adsorption, the FTIR spectra of the PAA-K hydrogel shows a peak at 1700 cm^{-1}, which is characteristic peak of the C=O stretching due to the presence of carboxyl groups in poly(acrylic acid). After the adsorption of the dye, the band is shifted to 1625 cm^{-1}. Also, after the adsorption of dye, the FTIR spectra shows a peak at 3350 cm^{-1} which originates due to the formation of hydrogen bond between hydogel and the dye. The presence of band at 1010 cm^{-1} indicates the Si–O stretching vibration of kaolin clay. The presence of band at 3500 cm^{-1} is due to some quantity of moisture in the hydrogel. There are small bands originating at 2850 and 2950 cm^{-1} which are due to the –CH$_3$ groups of the dye molecules.

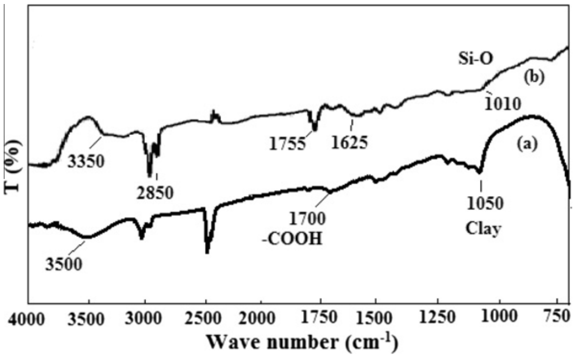

Fig. 10. FTIR spectra of pure PAA-K hydrogel before and after adsorption of BG dye (ultrasound assisted method).

3.8. Adsorption kinetics and adsorption isotherm models

Based on the studies related to the effect of different operating parameters on the adsorption of BG dye by hydrogel prepared by both the methods it was observed that the hydrogel prepared by ultrasound assisted polymerization process proved to be superior as compared to the hydrogel prepared by conventional method. Therefore for studying the adsorption kinetics the results obtained with hydrogel prepared by ultrasound assisted polymerization process were analyzed in greater details.

In order to find out the rate-controlling step of the adsorption process, it is necessary to establish well defined kinetic models. Pseudo-second-order kinetic model was used to fit the experimental data at different initial concentrations and temperatures. The kinetic rate equation is expressed as follows [42,43].

$$dq/dt = K_2(q_e - q)^2 \tag{5}$$

where, K_2 (g/mg min) is the pseudo second-order rate constant of adsorption. After integrating Eq. (5), the following equation is obtained:

$$t/q = 1/(K_2 q_e^2) + t/q_e \tag{6}$$

The plot of t/q_e against t for the different temperatures gives a characteristic straight line fit as shown in Fig. 11. The obtained values of second-order rate constants K_2 and q_e values are reported in Table 1. The results indicate that the correlation coefficients for the second-order kinetic model were close to 1.0 for all the cases indicating a good fit of the models to the experimental data sets. Therefore, the adsorption of BG dye by the PAA-K hydrogel can be approximated more favorably by the pseudo-second-order model.

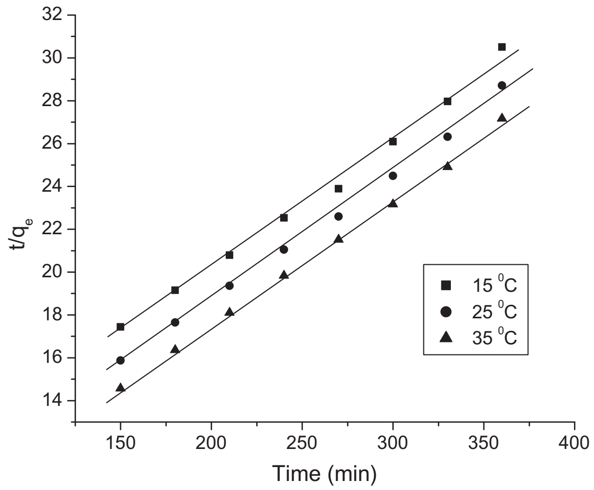

Fig. 11. Adsorption kinetics of BG dye at different temperatures for pseudo-second-order kinetic model.

Table 1
Second-order kinetic constants for the BG adsorption on the PAA-K hydrogel.

Temperature (K)	Pseudo-second-order kinetic constants		
	K_2 (g/mg min) × 10^4	q_e (mg/g)	R^2
288	3.39	17.30	0.98
298	4.12	17.54	0.99
308	5.37	17.85	0.99

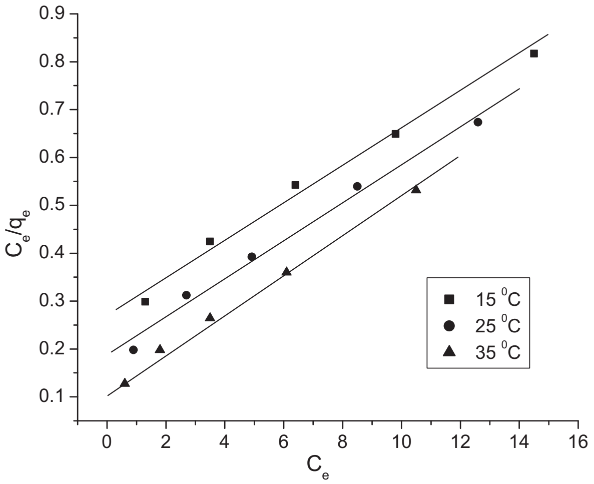

Fig. 12. Plot of C_e/q_e vs C_e for Langmuir isotherm.

There are several isotherm models available for analyzing the experimental data and for describing the equilibrium of adsorption. The more commonly used Langmuir and Freundlich isotherm have been used in this work to determine equilibrium relationships between sorbent and sorbate. The Langmuir equation is given as [43,44].

$$C_e/q_e = 1/(\alpha Q_m) + C_e/Q_m \tag{7}$$

where, C_e (mg/L) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye adsorbed at equilibrium, Q_m is the maximum adsorption capacity and α is the Langmuir constant. Q_m and α values were obtained from slope and intercept of the linear plot of C_e/q_e vs C_e (Fig. 12) respectively. The values of Q_m and α are given in Table 2.

Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [43,44]. The Freundlich isotherm is described by equation

$$q_e = K_F \times \log C_e^{(1/n)} \tag{8}$$

Taking log of Eq. (8)

$$\log q_e = \log K_F + (1/n) \log C_e \tag{9}$$

where, K_F and n are the physical constants of the Freundlich adsorption isotherm indicating sorption capacity (mg/g) and intensity respectively. The slope and intercept of the linear plot of log q_e vs log C_e gives the values of n and K_F (Fig. 13). The Freundlich constants are given in Table 2. Values of $1/n$ indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) or unfavorable ($1/n > 1$). Results showed that n was greater than unity, indicating the dye was adsorbed favorably by the hydrogel at all the temperatures studied. The regression correlation coefficients of both the models were close to 1.0 suggesting that both the isotherms could satisfactorily explain the adsorption of the dye molecules on the hydrogel.

Table 2
Langmuir and Freundlich isotherm constants.

Temperature (K)	Langmuir constants		
	Q_m (mg/g)	α	R^2
288	24.90	0.13	0.99
298	25.60	0.20	0.98
308	26.31	0.33	0.98
	Freundlich constants		
	K_F (mg/g)	n	R^2
288	3.82	1.69	0.99
298	4.96	1.85	0.99
308	6.47	1.95	0.98

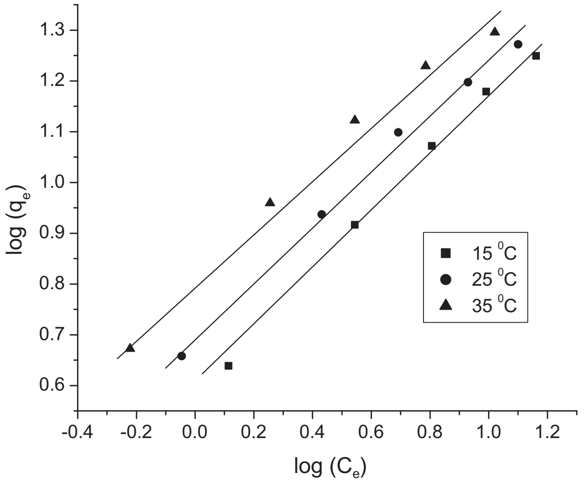

Fig. 13. Plot of log q_e vs log C_e for Freundlich isotherm.

3.9. Evaluation of thermodynamic parameters

Temperature dependence of the adsorption process is associated with several thermodynamic parameters such as Gibbs free energy change ΔG^o, standard enthalpy change ΔH^o and standard entropy change ΔS^o. Thermodynamic considerations of a sorption process are necessary to determine whether the process is spontaneous or not. The value of ΔG° can be determined from the following equation:

$$\Delta G^{\circ} = -RT \ln K \tag{10}$$

where K is the thermodynamic equilibrium constant.

The effect of temperature on thermodynamic constant is determined by

$$d \ln K/dt = \Delta H^{\circ}/RT^2 \tag{11}$$

Integrating and rearranging Eq. (11) we get

$$\ln K = -(\Delta H^{\circ}/RT) + \Delta S^{\circ}/R \tag{12}$$

and Gibbs free energy is also given by

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{13}$$

The equilibrium constant K has been determined by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero as shown in Fig. 14 [44,45]. The ΔH^o and ΔS^o values were calculated from the slope and intercept of linear plot of $\ln K$ versus 1/T (Fig. 15). The calculated values of the thermodynamic parameters are reported in Table 3. The negative value of ΔG^o indicates that the dye adsorption process is

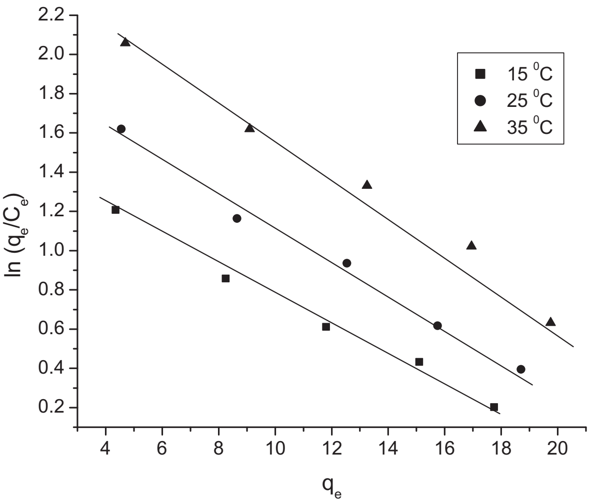

Fig. 14. Plot of ln (q_e/C_e) vs q_e for K values at different temperatures.

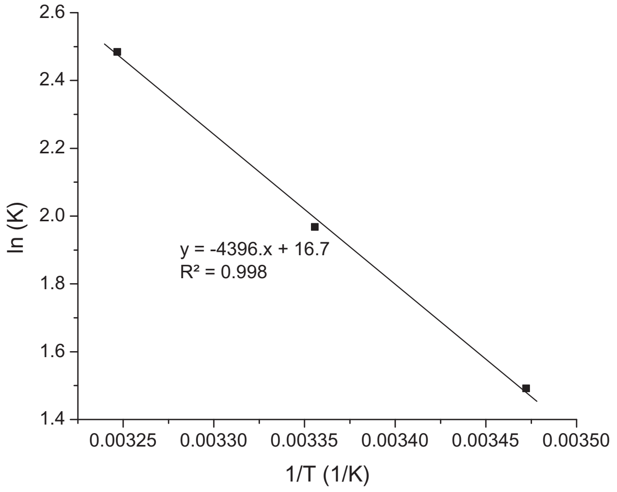

Fig. 15. Plot of ln K vs $1/T$.

Table 3
Thermodynamic parameters of adsorption of dye onto PAA-K hydrogel.

Temperature (K)	ln K	ΔG^o (J/mol)	ΔH^o (J/mol)	ΔS^o (J/mol K)
298	1.49	−3532.61	36,548.34	139.17
308	1.96	−4924.31		
318	2.48	−6315.92		

feasible and positive value of ΔH^o shows that the adsorption process is endothermic in nature.

4. Conclusions

The present work has clearly established the utility of hydrogel synthesized using ultrasound induced polymerization for dye adsorption. The use of ultrasound during polymerization reaction has been shown to uniformly disperse the kaolin clay in the polymer matrix enhancing its adsorption properties considerably for the removal of Brilliant Green from aqueous solution as compared to hydrogel prepared by conventional method. The extent of Brilliant Green removal has been observed to increase with an increase in pH (till optimum value), temperature, adsorbent and adsorbate concentrations as well as the kaolin clay content in the hydrogel. It has been observed that the maximum BG dye removal by PAA-K hydrogel was achieved for the initial dye concentration of 30 mg/L at a temperature of 35 °C and pH 7. Adsorption kinetics investigation revealed that the pseudo-second-order model fits the experimental data well. Also the Freundlich and Langmuir adsorption isotherm models explain the experimental results satisfactorily. The negative value of ΔG^o indicates the feasibility and spontaneity of the adsorption process and the positive value of ΔH^o indicate the endothermic nature of the adsorption process.

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