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Ultrasonically prepared poly(acrylamide)-kaolin composite hydrogel for removal of crystal violet dye from wastewater

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ABSTRACT

In the present study, synthesis of poly(acrylamide)-kaolin (PAAm-K) hydrogel nanocomposite has been carried out via ultrasound assisted in situ emulsion polymerization. Kaolin was used as a cross-linker and use of ultrasound during synthesis helps in uniform dispersion of kaolin in the hydrogel matrix increasing the strength and stability of hydrogel leading to improved adsorption of an organic pollutant. The viability of the synthesized PAAm-K hydrogel nanocomposite was studied for the removal of crystal violet (CV) dye. The adsorption studies were performed under different pH, temperature, initial dye concentration, kaolin clay content and cavitation conditions. The % dye removal efficiency is higher for higher pH and temperature. Also the adsorption process is highly favorable at the lower dye concentration and higher quantity of hydrogel where the maximum removal efficiency of dye was obtained. The obtained data are processed using adsorption kinetics, isotherm models and the thermodynamic behavior of the cationic dye adsorption is studied. It is found that the formation of network of cross-linked polymer hydrogel shows a good swelling behavior due to the presence of kaolin. The combined effect of hydrogel and ultrasound demonstrate a higher percent removal of the dye as compared to hydrogel alone. Pseudo-second-order kinetic model provided a better correlation for the experimental data in comparison to the pseudo-first-order kinetic model. The experimental error observed is less than 5%. The negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process. The positive ΔH° suggests the endothermic nature of the adsorption.

Introduction

Wastewater effluents released from different types of industries generally contain several organic pollutants and toxic substances which are harmful to aquatic life. The effluent discharged from various industries such as leather, paint, pulp mills, textiles and dyestuff manufacturing are highly colored wastewater which creates severe ecological concerns all over the world [1–3]. The use of different synthetic dyes in these industries produces large volumes of colored wastewater. The dyes are generally classified as an anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes). Most of the dyes are designed and manufactured for their chemical stability and do not undergo biochemical degradation readily [4]. Consequently, this dye containing wastewater must be treated before being discharged into the receiving body of water. In order to remove dyes from wastewater various treatment processes like ozonation [5], coagulation [6], ultrafiltration [7], oxidization [8], electrochemical [9], photocatalytic degradation [10] and adsorption [11,12] have been extensively studied. Adsorption processes are quite accepted because of its simplicity and higher efficiency with the availability of a wide range of adsorbents. Though adsorption using activated carbon is attractive due to its high efficiency, but it is a high-cost adsorbent. Hence, the natural clay materials such as bentonite, fly ash, kaolin and montmorillonite are preferred as adsorbents [13–15]. However, these adsorbents have the tendency to generate secondary waste which again creates a disposal problem ultimately leading to environmental pollution. Gupta et al. [16] have prepared a novel extremely efficient and recyclable catalyst based on Fe@Ag bimetallic nanoparticles involving *p*-aminothiophenol (ATP) functionalized calcium alginate (Fe@Ag-ATP-CA) beads. The

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catalytic reduction of 4-nitrophenol (4-NP) and 2-nitrophenol (2-NP) has been reported using Fe@Ag-ATP-CA catalyst synthesized in the presence of sodium borohydride ($NaBH_4$).

As per their report, the Fe@Ag-ATP-CA catalyst has excellent catalytic activity and it was found to be efficiently recyclable. Yola et al. [17] have synthesized a new composite containing silver nanoparticles (AgNPs) and colemanite ore waste (COW) and used this composite in adsorption and photocatalysis to remove Reactive Yellow 86 (RY86) and Reactive Red 2 (RR2) from aqueous solution in single and binary dye systems. The prepared composite has been reported to be a good material for dye adsorption. Further Olgun and Atar [18], in their study, have reported the adsorption characteristics of Basic Yellow 28 (BY 28) and Basic Red 46 (BR 46) onto boron waste (BW). The results indicated that the BW has high-adsorption capacity for basic dyes and the capacity slightly decreased with increasing temperature. The kinetics of the adsorption of BY 28 and BR 46 onto BW followed a pseudo-second-order model.

Recently, several researchers have explored smart materials such as hydrogels, which are used for the removal of dyes by the process of adsorption [19,20]. Hydrogels are the three dimensional cross-linked polymer networks of flexible chains that are able to absorb and retain water and solute molecules because of the presence of different functional hydrophilic groups [21–25]. Change in volume of hydrogel (swelling) occurs in response to a small change of external parameters such as temperature, pH, solvent composition and electrical stimuli. The characteristics and adsorption capability of hydrogels generally depend on the presence of the functional groups such as —OH and —COOH [26,27]. The presence of these functional groups makes the hydrogel hydrophilic and diffusion of water into the hydrogel takes place because of the capillary action and the difference in the osmotic pressure. The presence of functional groups, the nature of cross-linking agents and the polymerization method are important parameters that control the swelling ability of the hydrogel [28]. Some of these materials are not proving to be good adsorbents due to limitations in their cation exchange capacity and lower adsorption rate, etc. [29]. The improvement in the adsorption capability can be achieved by using hybrid nanocomposites, changing cation exchange capacity and use of cavitation during the synthesis [30]. In recent years, attempts have been made to modify the properties of polymeric hydrogels by the incorporation of nano- and micro-particles of inorganic materials/clays into the polymer networks without decreasing their absorption ability. The resulting hydrogel composites can combine the elasticity and permeability of polymeric hydrogels with the high ability of the clays to absorb different substances. The existing problem of the present waste water treatment methods (ion exchange, adsorption, and wet air oxidation, etc.) could be overcome by nanocomposite hydrogels.

Ultrasound assisted in situ emulsion polymerization has been effectively used for the preparation of polymer nanocomposites [31–34] in which the initiation of the emulsion polymerization to form polymer was done through the generation of free radicals [35,36]. Use of ultrasonic irradiations during the hydrogel synthesis helps to control the molecular weights which are attributed to the high shear gradients generated by cavitational events.

The loading of the different types of clays like bentonite, laponite, sepiolite in the polymer matrix of hydrogels is facilitated by the ultrasound. The use of ultrasound improves the dispersion of these clays with enhancement in the mechanical properties and adsorption capacity of hydrogels. Further high molecular weight polymers have often been used as flocculants for colloidal suspensions to separate and dewater solid/water systems. Polyacrylamide and its derivatives are among the most common and extensively used flocculants for kaolin in aqueous media [37]. Shirsath et al. [38] have studied the removal of Brilliant Green dye from wastewater using a poly(acrylic acid) hydrogel composite (PAA-K hydrogel) which was reported to be prepared by incorporation of kaolin clay. The positive effects of ultrasound have been reported during the synthesis of hydrogel and its use for the removal of the dye. The dye removal efficiency has been found to be increased with an increase in the contact time and initial dye concentration.

In earlier studies [39] it has been reported that the incorporation of amide groups in polymer backbone gives more sorption sites and it results into more sorption of the dye molecules from the waste water. In view of this it was thought imperative to combine the beneficial effects of acrylamide, kaolin clay and ultrasound. With this aim, an attempt was made to synthesize PAAm-K hydrogel nanocomposite in the presence of ultrasound. The modification of polyacrylamide hydrogel through the uniform dispersion of kaolin clay has been suggested as a means to improve the polymer performance [40,41] by using ultrasound assisted in situ emulsion polymerization method. The feasibility of the synthesized PAAm-K hydrogel for the removal of crystal violet dye has been studied. The adsorption equilibrium studies were carried out under different pH, temperature, dye initial concentration and kaolin clay content conditions. The combined effect of hydrogel and ultrasound was also studied. The data obtained is processed using the adsorption kinetics, isotherm models and the thermodynamic behavior of the cationic dye adsorption is also evaluated.

Experimental

Materials

Acrylamide (AAm), tetramethylethylenediamine (TEMED), ammonium persulfate (APS), sodium dodecyl sulfate (SDS) and crystal violet dye (CV) were of analytical grade and procured from M/s CDH, India. Natural kaolin clay was obtained from MD Chemicals, Pune, India.

Synthesis of poly(acrylamide)-kaolin nanoclay (PAAm-K) hydrogel

Nanocomposite hydrogels were prepared using initial solutions consisting of monomer (AAm), cross-linker (kaolin clay), solvent (water), initiator (ammonium persulfate), surfactant (SDS) and catalyst (TEMED). The synthesis procedure used for the formation of the hydrogel was simple and versatile. Initially, a transparent aqueous solution consisting of water (50 mL), inorganic kaolin clay (0.3 g) and AAm (8.6 g) were prepared in one beaker. Then, 3 mL TEMED and an aqueous solution of the initiator (0.03 g APS in 1.5 mL water) with 0.2 g of SDS were added to the former solution. The entire mixture was then transferred to the reactor equipped with an ultrasound probe (Dakshin make, 22 mm probe diameter operating at 22 kHz frequency and rated power of 120 W). Then, the emulsion polymerization was allowed to proceed in a water bath at room temperature for 45 min. The polymerized hydrogel was then dried in oven for 48 h at 85 °C. During the experiments, the reaction medium was purged with nitrogen gas in order to remove oxygen from the system.

Sample characterization

UV–vis spectrophotometer (CHEMITO 2600 model) was used to measure the concentration of CV dye. The wavelength of maximum absorbance (λ_{max}) of CV dye was 591 nm. Deionized water was used as a reference. FTIR spectra of the hydrogel samples were recorded on a PerkinElmer FTIR spectrometer (Paragon 1000 PC) in the wave number range of 500–4000 cm^{-1}. Transmission electron microscopy (TEM, magnification 750,000×) image was taken with a Philips Tecnai 20 model.

Swelling behavior of PAAm-K hydrogel

The equilibrium swelling of prepared PAAm-K hydrogels in deionized water was studied at 25 °C by direct weighing method [20]. The measured quantity of PAAm-k hydrogel was kept in the deionized water and the weight of swollen PAAm-K hydrogel was measured at regular intervals of time after gently wiping the excess water on the surface with tissue paper. This was continued till equilibrium swelling and the swelling ratio, *S* has been estimated using Eq. (1)

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

where W_s is the weight of swelled hydrogel in water at equilibrium and W_d is the initial dry weight of the PAAm-K hydrogel.

Adsorption of CV dye

In order to investigate the effects of various experimental parameters like pH, temperature, dye initial concentration, quantity of hydrogel and kaolin clay content in hydrogel on the adsorption kinetics of CV dye onto PAAm-K hydrogel the following procedure was used. In the typical experiment, 100 mL of the dye solution of desired concentration and 1 g PAAm-K hydrogel were taken in a 200 mL beaker. Buffer solutions were used to get the desired pH of the CV dye solution. The effect of initial dye concentration was studied by preparing CV dye solutions of various concentrations from 10 to 50 mg/L. The effect of hydrogel loading was studied by using different amounts of PAAm-K hydrogel (0.5–2.0 g). Constant temperature was maintained using a water bath except the experiments where the effect of temperature was studied (15, 25 and 35 °C). Additionally the combined effect of hydrogel and cavitation environment was also investigated. The percentage of CV dye removal was estimated using the following equation:

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

where, C_0 and C_e are the initial and the equilibrium concentrations of CV dye (mg/L), respectively. Further the amount of dye adsorbed per unit mass of PAAm-K hydrogel (mg/g) was estimated using the following equation,

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

where C_t refers to the concentration of CV dye (mg/L) at any time *t*, *V* is the volume of the dye solution in L and *M* is the mass of dry hydrogel in g.

Results and discussion

It is well known that the extreme environment created by acoustic cavitation generated by ultrasound is responsible for facilitating the incorporation of inorganic materials like $CaCO_3$, kaolin clay into the polymer like hydrogel matrix [33,34,42,43]. The details of the procedure for the dispersion of kaolin clays through the polymer are well described in the literature [44,45]. During the polymerization in the presence of ultrasound, exfoliation of the kaolin clay platelets takes place which is a result of shearing effect of acoustic cavitation. Fig. 1 shows the TEM images of kaolin nanoparticles dispersed in the PAAm hydrogel matrix by ultrasound assisted in-situ emulsion polymerization process. In Fig. 1(a) and (b) it can be seen that the kaolin nanoparticles are evenly distributed in the hydrogel matrix. TEM images clearly indicate the beneficial effects of ultrasound, resulting in the uniform dispersion of kaolin nanoparticles in the hydrogel matrix. The particle size of kaolin was found to be around 50 nm.

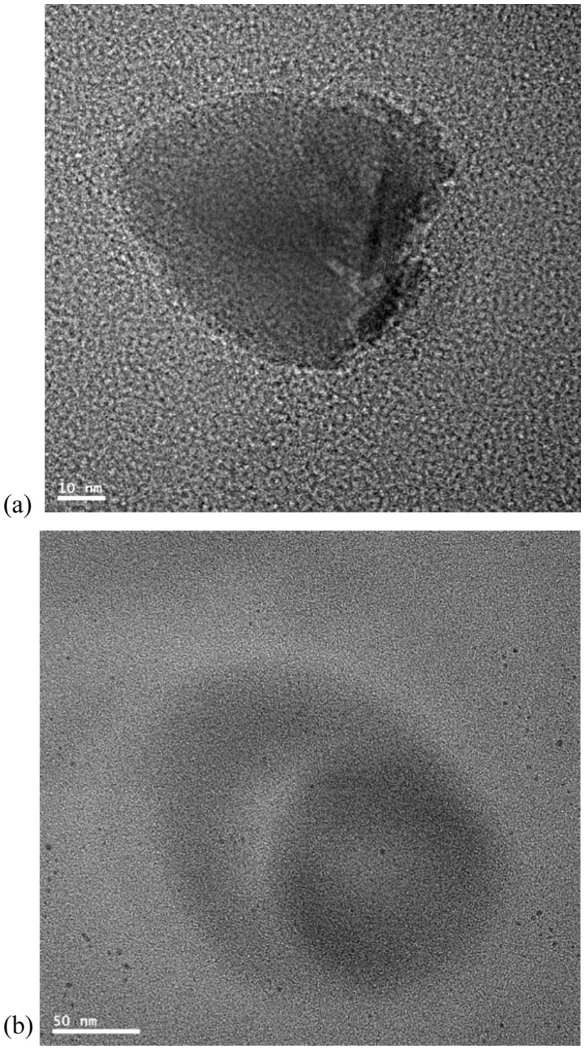

Fig. 1. Transmission electron microscopic images of PAAm-K hydrogel.

Swelling behavior of hydrogel

A fundamental relationship exists between the swelling of a polymer in a solvent and the natures of the solvent and the polymer. The swelling of a hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. Swelling involves larger scale segmental motion resulting in an increased distance of separation between the hydrogel chains. Whereas the diffusion involves migration of water into pre-existing or dynamically formed spaces between hydrogel chains. When the weighed quantity of PAAm-K hydrogel was kept in a large volume of water for a long time, the compact network structure of the polymer matrix tries to get relaxed and swollen due to the diffusion of water molecules inside the matrix, until equilibrium stage is reached.

It was observed that when the pure PAA hydrogel (without kaolin) was put in water for studying its swelling behavior it was dissolved due to absence of cross-linking agent, however the dissolution of the composite PAAm-K hydrogel does not take place in water. This is attributed to the presence of the cross-linker, such as kaolin clay which resists the dissolution of PAAm-K hydrogel as against pure PAA hydrogel in water. In the presence of kaolin clay cross-linker the mechanical strength and dissolution properties are changed [25,46].

In recent years, extensive efforts have been made to understand the mechanisms of water diffusion through hydrogel matrices [46–48]. The time dependent swelling behavior of the hydrogel is calculated by Eq. (4) [49,50].

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

where, F is the fractional uptake at time t, K is the diffusion constant, M_t is the mass of water uptake at any time t, M_s corresponds to the mass of water uptake at equilibrium and n is the characteristic exponent which relates to the transport mode of the penetrating molecule.

Eq. (4) is applicable to the initial stages of swelling and plots of $\ln F$ vs $\ln t$ yield straight lines up to almost 60% increase in the mass of hydrogel. The swelling exponent n was calculated from the slope of the line. A graph of $\ln(M_t/M_s)$ against $\ln t$ can be used to evaluate the swelling exponent n as depicted in Fig. 2.

According to the classification of the diffusion mechanism, the value of $n = 0.5$ corresponds to Fickian diffusion where the rate of diffusion is slow compared to the relaxation rate of hydrogel. When $n = 1$ the rate of diffusion is fast compared to relaxation rate. Values of n for non-Fickian diffusion is between $0.5 < n < 1$ [50]. In the present case the value of n is found to be 0.75 indicating that the transport mode of water in the gel is non-Fickian diffusion. The diffusion constant 'K' can be calculated from the intercept of the line, which is 0.014.

Effect of pH on dye adsorption

The adsorption process is greatly affected by the change in the pH of the solution. The effect of solution pH generally depends on the ions present in the reaction mixture and electrostatic interactions with the adsorption surface [51,52]. It also affects the degree of ionization of the material present in the solution, the surface charge of the adsorbent as well as the dissociation of functional groups on the active sites of the adsorbent.

The influence of pH on the removal of CV dye by PAAm-K hydrogel nanocomposite was studied to gain further insight into the adsorption process. The experiments were performed by adjusting the pH from 4 to 11 using acid/base buffer solutions. Fig. 3 shows the effect of pH on the CV dye adsorption with an initial concentration of 30 mg/L in the presence of 1 g of PAAm-K hydrogel nanocomposite for 5 h of equilibrium time. The maximum dye removal (more than 80%) was observed in the pH range of 8–11. At lower pH values, more protons are available to protonate the amino groups of PAAm, hence, the positively charged cationic dye molecules are not attracted. Additionally, below a pH of 7, the kaolin surface acquires a positive charge hence there seems to be an electrostatic repulsion of positively charged cationic dye molecules from the surface of kaolin. Above a pH value of 8 surface of kaolin is more negative, hence there are more negative sites on the external surface of PAAm-K hydrogel and a complex may form by the interaction between one dye cation and one of these negative sites of kaolin clay. Therefore, electrostatic interactions between the dye molecules and hydrogels are dominant at higher pH. However, at pH 11 the % removal of dye decreased, which suggest that the chemical structure of a dye molecule and its behavior at alkaline pH can affect the results. Hence, for further experiments, pH 10 was used as the solution pH.

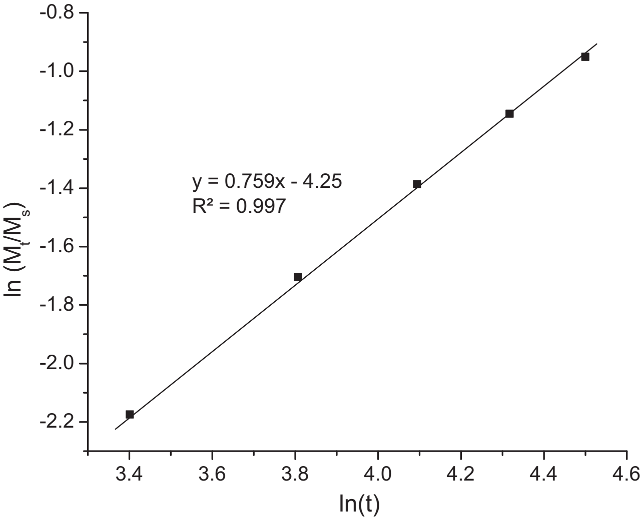

Fig. 2. Plot of $\ln(M_t/M_s)$ against $\ln(t)$ of water in PAAm-K hydrogel.

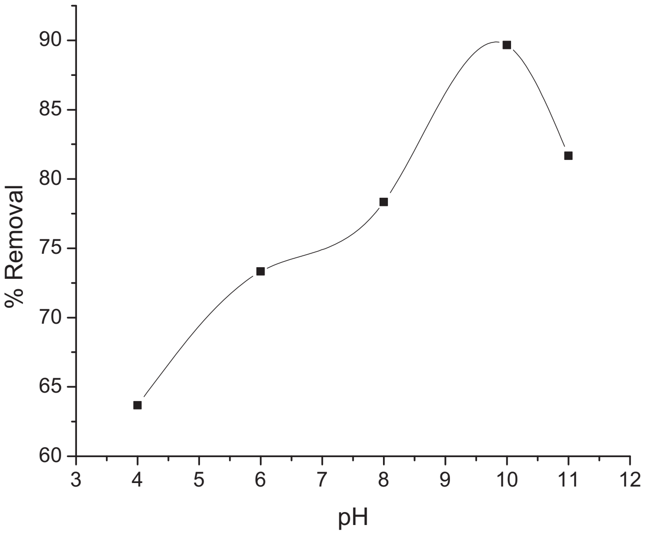

Fig. 3. Effect of pH on adsorption of CV dye in PAAm-K hydrogel at 35 °C, equilibrium time 5 h.

Effect of temperature on dye adsorption

To study the adsorption behavior of the synthesized hydrogel at different temperatures, the temperature was varied from 15 to 35 °C for 1 g hydrogel with 30 mg/L initial dye solution.

From Fig. 4 it is found that the adsorption of the CV dye increases with an increase in temperature indicating that the removal of CV is favored at high temperatures. This is attributed to a result of an increase in the mobility of the dye molecules with an increase in the temperature. More number of molecules may acquire sufficient energy to undergo an interaction with active sites on the hydrogel surface. Additionally, the higher temperature may produce a swelling effect within the internal structure of the hydrogel providing an easy passage for dye molecules in the hydrogel matrix. It is observed that at 35 °C maximum 89% dye removal takes place, hence the rest of the experiments were performed at 35 °C. The highest temperature of 35 °C was used in the experiments to avoid possible collapse of hydrogel matrix due to heat effects.

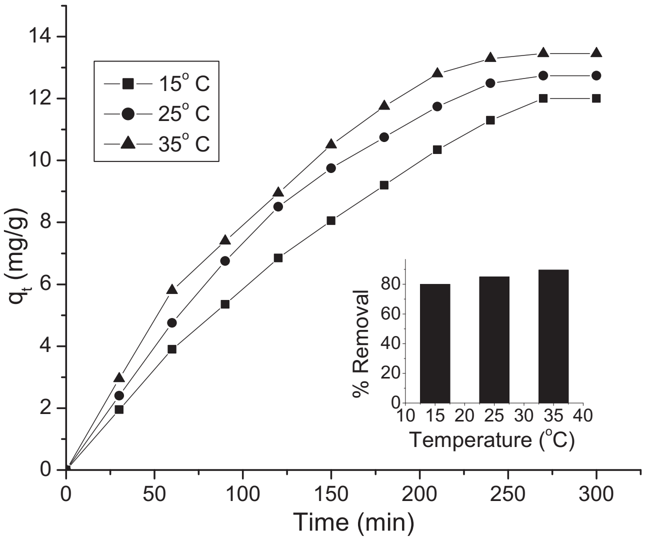

Fig. 4. Effect of temperature on adsorption of CV dye in PAAm-K hydrogel at pH 10.

Comparing the results of this work with previous work [38], where poly(acrylic acid)-kaolin hydrogel composite was used, it is found that with poly(acrylic acid)-kaolin hydrogel 12.8 mg/g of Brilliant Green dye removal was achieved for 30 mg/L initial dye concentration, at 35 °C temperature and optimized pH of 7. Whereas in the present work poly(acrylamide) was used instead of poly(acrylic acid) and 13.4 mg/g of Crystal Violet dye removal has been achieved for 30 mg/L initial dye concentration, at 35 °C temperature and pH of 10. Thus the use of poly(acrylamide) resulted in better performance though the increase in the sorption capacity was marginal.

Effect of initial dye concentration

An equilibrium adsorption study has been performed in order to determine the adsorption capacity of PAAm-K hydrogel at different CV dye concentrations ranging from 10 to 50 mg/L with 1 g of PAAm-K hydrogel at pH 10 and 35 °C temperature. From the obtained results it is found that as the initial dye concentration increases the dye uptake (mg/g) by PAAm-K hydrogel increases as shown in Fig. 5. This is attributed to the higher initial concentration of the dye which offers more number of dye molecules that can diffuse easily through PAAm-K hydrogel. As more number of CV molecules are present in the initial solution there exists a higher concentration gradient at the hydrogel–solvent interfaces which causes an enhancement in the CV dye absorption. Conversely, the CV dye removal efficiency was found to be reduced at high initial dye concentrations indicating the saturation of hydrogel and that the active sites on the surface of hydrogel are covered. These results highlight the fact that removal of cationic dyes from wastewater by using PAAm-K hydrogel may find prospective application in the industry. Fig. 6 shows the picture of the change in color of the hydrogel and the dye solution after 5 h immersion of hydrogel in the dye solution. The hydrogel shows dark blue coloration after adsorbing CV dye compared to the original white color of the hydrogel and simultaneously fading of the color of the dye solution is also observed.

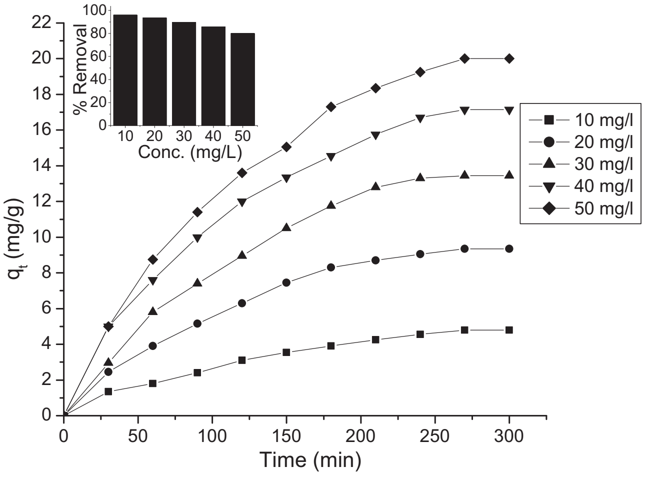

Fig. 5. Effect of initial concentration on adsorption of CV dye in PAAm-K hydrogel at pH 10 and 35 °C.

Effect of quantity of hydrogel and kaolin clay loading

Various amounts of PAAm-K hydrogel (0.5–2.0 g) have been used in 30 mg/L concentration of 100 mL CV dye solution in order to study the effect of hydrogel quantity on adsorption, i.e., % removal of CV dye for 5 h of equilibrium time and is depicted in Fig. 7. It is observed from Fig. 7 that the % removal of the CV dye increases with an increase in the quantity of PAAm-K hydrogel. Maximum 96% of CV dye removal is observed when 2 g PAAm-K hydrogel was kept in the solution. This shows that the presence of higher quantity of PAAm-K hydrogel provides a large number of negatively charged adsorption sites on the surface of hydrogel to adsorb more amounts of positively charged CV dye molecules due to electrostatic attractions [20].

The amount of kaolin clay content in the hydrogel is an important factor which can affect CV dye adsorption. Generally, an appropriate amount of kaolin clay content can improve the polymeric networks and contribute to higher the adsorption. Hence, the effect of kaolin clay loading in PAAm hydrogel on dye adsorption has been investigated. PAAm-K composite hydrogels containing different amount of kaolin (0.3 and 0.6 g) were transferred into 100 mL of the aqueous dye solutions of different concentrations ranging from 10 to 50 mg/L and equilibrated for 5 h at 35 °C in a water bath. Plots of % removal of CV dye values against the concentrations are depicted in Fig. 8. It shows that the percentage of dye removal from solutions increased with the increase of the content of kaolin clay in PAAm-K composite hydrogel. The possible reason for the higher dye removal corresponding to higher kaolin loading can be attributed to the enhanced quantum of active adsorption sites offered with an increase in the kaolin content. However, there is not a substantial difference in the removal between 0.3 and 0.6 g kaolin loading hence it can be concluded that 0.3 g kaolin loading is sufficient for getting reasonable removal.

Effect of ultrasound in dye removal

The combined effect of ultrasound and hydrogel adsorption was investigated and compared. In these experiments, 100 mL CV dye solutions of different concentrations were used and 1 g of PAAm-K hydrogel (0.3 g kaolin loading) was added to the prepared solutions. The removal efficiencies for hydrogel alone and the combined effect of hydrogel and ultrasound are shown in Fig. 9. It is to be noted that all the readings corresponding to the combined effect of hydrogel and ultrasound are for 30 minutes, whereas for hydrogel alone the readings are for 5 h. The obtained results clearly show that the combined effect of hydrogel and ultrasound gives higher dye removal compared to hydrogel adsorption alone. When PAAm-K hydrogel composite was used alone, 80% removal of CV

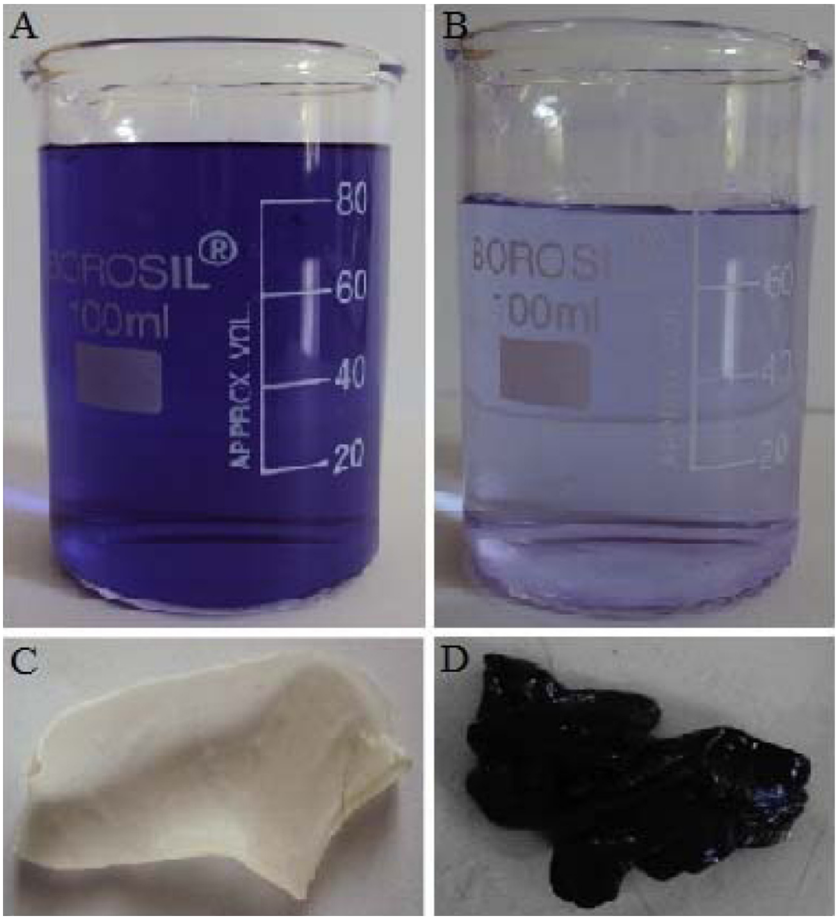

Fig. 6. Color change of CV dye and hydrogel before (A), (C) and after adsorption (B), (D) respectively.

dye was achieved in 5 h, whereas 89% of CV dye was removed in the case of the combination of hydrogel and ultrasound in only 0.5 h for 50 mg/L concentration.

Ultrasound has been recently used as an advanced oxidation process (AOP) for the removal of dyes in waters. Application of ultrasound generates $OH^{\bullet}$ radicals through acoustic cavitation, which is defined as the formation, growth and collapse of microbubbles. In the final stage of the collapse, the temperature inside the bubble or in the surrounding liquid is considered to be above 2000 K. Under such extreme environment, entrapped molecules of dissolved gases, vaporized water and solutes inside the bubbles can be brought to an excited state and dissociate to generate $OH^{\bullet}$ radicals as per the following reactions [53].

$$H_2O \rightarrow H^{\bullet} + OH \quad (5)$$

$$O_2 \rightarrow 2O \quad (6)$$

$$H + O_2 \rightarrow HO_2^{\bullet} \quad (7)$$

$$O + H_2O \rightarrow 2OH^{\bullet} \quad (8)$$

$$H^{\bullet} + O_2 \rightarrow OH^{\bullet} + O \quad (9)$$

In the present work when the ultrasound was used with the combination of hydrogel, the removal of CV dye may have occurred through the reaction with $OH^{\bullet}$ radicals in the bulk solution [53] in addition to the adsorption of CV dye onto the surface of hydrogel. There could be the synergistic effect of both processes which may have resulted in drastic reduction in the time duration as well as higher removal of CV dye.

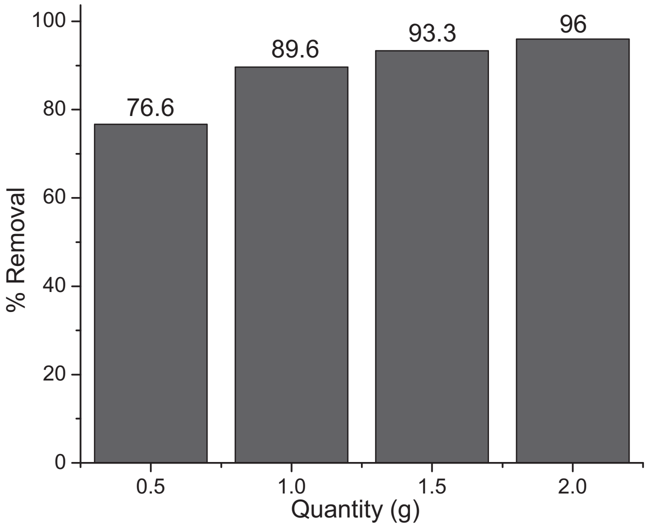

Fig. 7. Effect of initial quantity of PAAm-K hydrogel on removal of CV at pH 10, temperature 35 °C and equilibrium time 5 h.

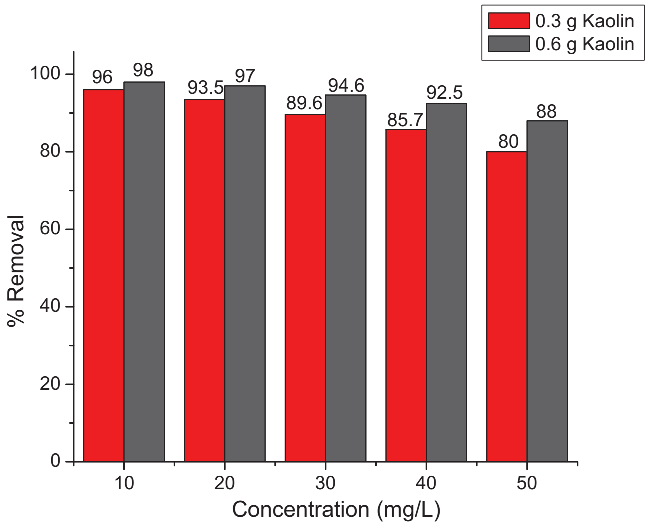

Fig. 8. Effect of clay loading in PAAm-K hydrogel for the adsorption of CV dye at pH 10, temperature 35 °C and equilibrium time 5 h.

FTIR Study of PAAm-K hydrogel before and after adsorption

FTIR (Fourier transform infrared spectroscopy) is a useful technique for identifying the chemical structure of a substance. This technique is widely used to investigate the structural arrangement in hydrogels. Information on the interaction between the dye molecules and the PAAm-K hydrogel was obtained from the FTIR spectra. Fig. 10 shows the FTIR spectra of PAAm-K hydrogel prior to and after adsorption of the CV dye. The FTIR spectra of the PAAm-K hydrogel (Fig. 10a) show the peak at 1000 cm^{-1}, which is the characteristic peak of Si—O stretching of kaolin clay in PAAm-K hydrogel. The strongest peak at 1750 cm^{-1} is attributed to $\nu_{C=O}$, and the characteristic peak at 2922 cm^{-1} can be assigned to ν_{CH_2} [54]. The characteristic peak at 1350 cm^{-1} corresponds to C—N stretching of PAAm group. The FTIR data showed the expected characteristic groups in the prepared hydrogels. After the adsorption of CV dye (Fig. 10b), the vibration band of the carboxyl groups was shifted from 1750 to 1680 cm^{-1} and new peaks appeared at 1500 and 1108 cm^{-1} which were attributed to the phenyl group of CV dye.

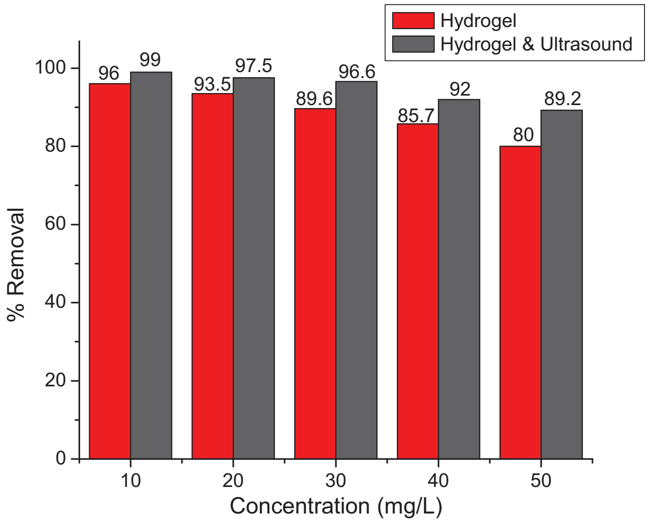

Fig. 9. Comparison of hydrogel & hydrogel with ultrasound on adsorption of CV at pH 10 with temperature 35 °C.

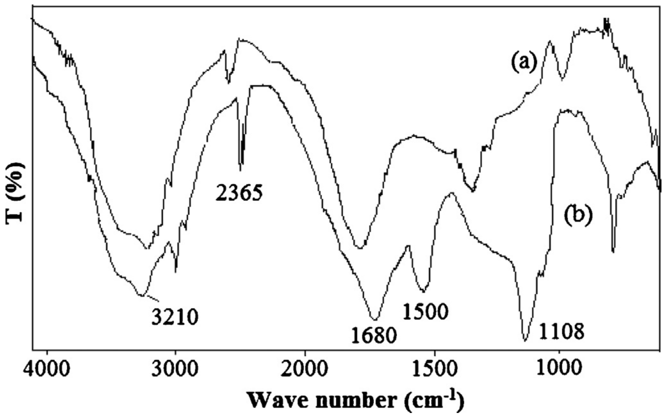

Fig. 10. FTIR spectra of PAAm-K hydrogel (a) before and (b) after adsorption of CV dye.

Adsorption kinetics and adsorption isotherm models

Various available models in the literature can be used to express the mechanism of solute adsorption onto an adsorbent. In order to examine the mechanism of adsorption, the characteristic constants of adsorption were determined using a pseudo-first and second-order equation of the Lagergren model. Linear form of pseudo-first order model is:

$$\frac{dq}{dt} = K_1(q_e - q) \tag{10}$$

where, q_e and q are the amounts of adsorbed dye onto the hydrogel at equilibrium and at time t, respectively. K_1 is the rate constant of first-order adsorption. The integrated form of Eq. (10) is given as follows:

$$\log(q_e - q) = \log q_e - K_1\left(\frac{t}{2.303}\right) \tag{11}$$

The plot of $\log(q_e - q)$ against t for the pseudo-first-order equation gives a linear relationship. K_1 and q_e values can be determined from the slope and intercept of this equation, respectively. Fig. 11 shows the plot of the linearization form of the pseudo-first-order equation. The kinetic parameters of the

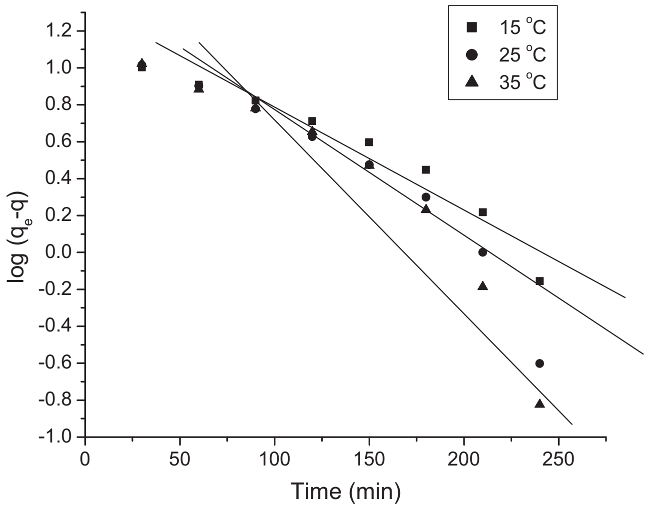

Fig. 11. Adsorption kinetics of CV at different temperatures for pseudo-first-order.

Table 1
Constants for the first-order and second-order kinetics for the CV dye adsorption on the PAAm-K hydrogel.

Temperature (K)	First-order kinetics		
	K_1 (min^{-1})	q_e (mg/g)	R^2
288	0.011	17.94	0.94
298	0.013	23.38	0.90
308	0.018	28.51	0.89

Temperature (K)	Second-order kinetics		
	K_2 (g mg^{-1}/min) × 10^4	q_e (mg/g)	R^2
288	2.01	23.25	0.96
298	1.60	25.00	0.95
308	2.30	30.30	0.97

first-order kinetic model are shown in Table 1 along with the corresponding correlation coefficients.

Further, if the adsorption rate is pseudo-second-order, the kinetic rate equation can be expressed as [14,55]:

$$\frac{dq}{dt} = K_2(q_e - q)^2 \tag{12}$$

where, K_2 is the rate constant of second-order adsorption. After integrating Eq. (12), the following equation is obtained:

$$\frac{t}{q} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \tag{13}$$

By plotting t/q against t for the different temperatures, straight lines were obtained which are depicted in Fig. 12. The values of K_2 and q_e were calculated and shown in Table 1. From Table 1 it can be observed that the correlation coefficients for second order kinetics are higher than the correlation coefficients for first order kinetics for all the temperatures involved. This suggests a strong relationship between the parameters and the process followed the pseudo-second-order kinetics better than pseudo-first-order model.

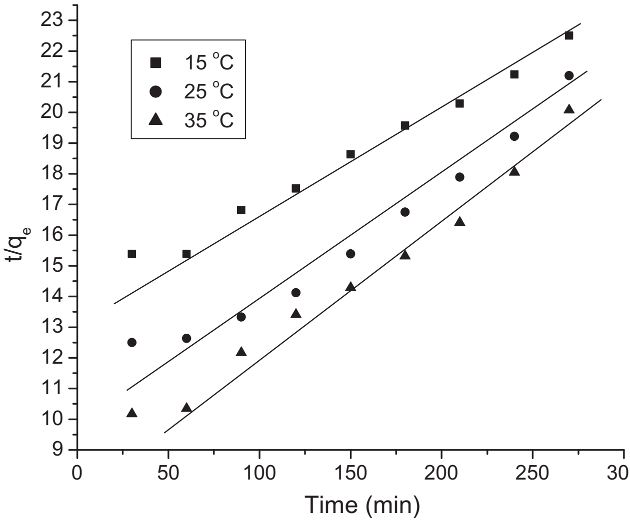

Fig. 12. Adsorption kinetics of CV at different temperatures for pseudo-second-order.

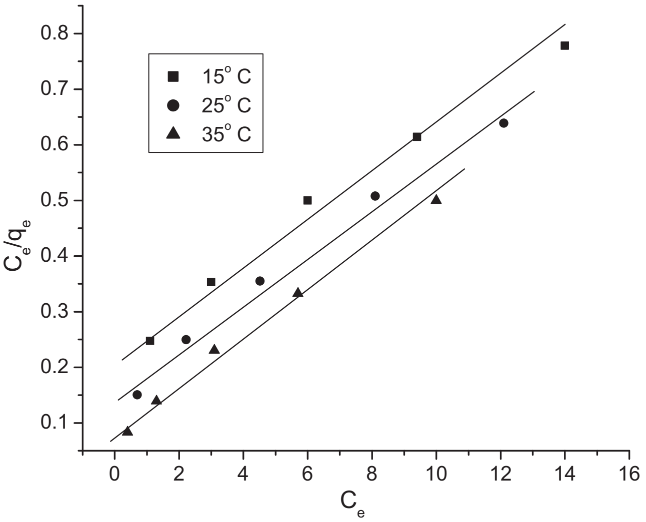

Fig. 13. Plot of C_e/q_e vs C_e for Langmuir isotherm.

The equilibrium data and adsorption isotherms are important parameters that describe the interaction between the pollutants and the adsorbent material which is helpful in design and optimization of the adsorption system. The equilibrium removal of CV dyes can be mathematically expressed in terms of Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm is valid for monolayer adsorption of the adsorbate molecules on the adsorbent surface [56]. The Langmuir isotherm is based on the assumption of adsorption homogeneity and no interaction between adsorbed species. The Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{(\alpha Q_m)} + \frac{C_e}{Q_m} \tag{14}$$

where C_e is the equilibrium concentration of the dye in solution (mg/L), q_e is the amount of adsorbed dye on the adsorbent surface (mg/g). Q_m and α are the Langmuir constants related to the maximum binding at the complete saturation of adsorbent binding sites and energy of adsorption, respectively [55]. The values of Q_m and α can be calculated from the slope and intercept of the linear plot of C_e/q_e vs C_e (Fig. 13), respectively. The estimated values of Q_m and α along with the correlation coefficients are given in Table 2. It can be clearly seen that the Langmuir model was found to be suitable to describe the adsorption process of the CV dye.

This Freundlich isotherm model is an empirical equation employed to explain heterogeneous systems with a non-uniform distribution of heat of adsorption over the surface. This model proposes that the adsorption energy exponentially decreases on completion of the adsorption sites of adsorbent [14,55,56]. The Freundlich isotherm is given by the equation:

$$q_e = K_F \times \log {C_e}^{\left(\frac{1}{n}\right)} \tag{15}$$

Table 2
Langmuir and Freundlich isotherm constants of CV dye adsorption on PAAm-K hydrogel at different temperatures.

Temperature (K)	Langmuir constants		
	Q_m (mg/g)	α	R^2
288	23.80	0.17	0.98
298	23.80	0.28	0.98
308	25.00	0.51	0.99

Temperature (K)	Freundlich constants		
	K_F	n	R^2
288	4.39	1.81	0.99
298	5.75	2.03	0.99
308	7.72	2.24	0.98

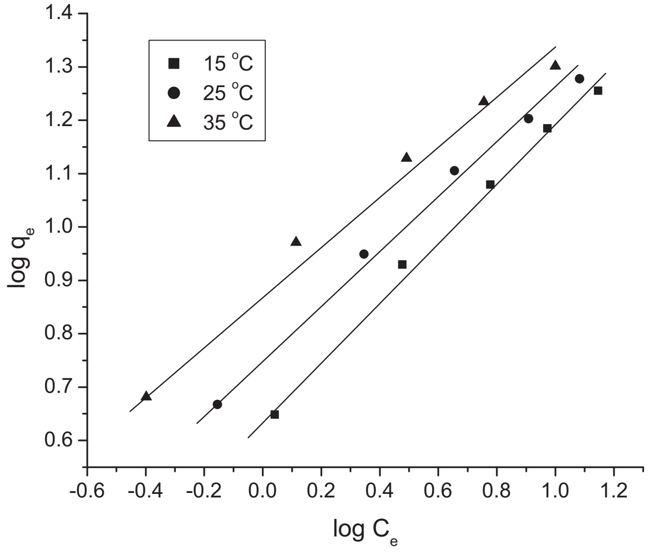

Fig. 14. Plot of $\log q_e$ vs $\log C_e$ for Freundlich isotherm.

Taking log on both sides:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{16}$$

where, K_F and n are the constants of the Freundlich isotherm which are indicators of adsorption capacity and adsorption intensity of the sorbents, respectively. The values of K_F and n are found from the slope and intercept of the linear plot of $\log q_e$ vs $\log C_e$ (Fig. 14). Values $1/n$ indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) or unfavorable ($1/n > 1$) [14,55,56]. The Freundlich constants and correlation coefficients are reported in Table 2. The obtained results suggest that the Freundlich isotherm is also an appropriate model for describing the adsorption phenomenon of CV dye on PAAm-K hydrogel.

Evaluation of thermodynamic parameters

The feasibility and the effect of temperature for CV dye adsorption onto PAAm-K hydrogel was evaluated by estimating thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) [57,58].

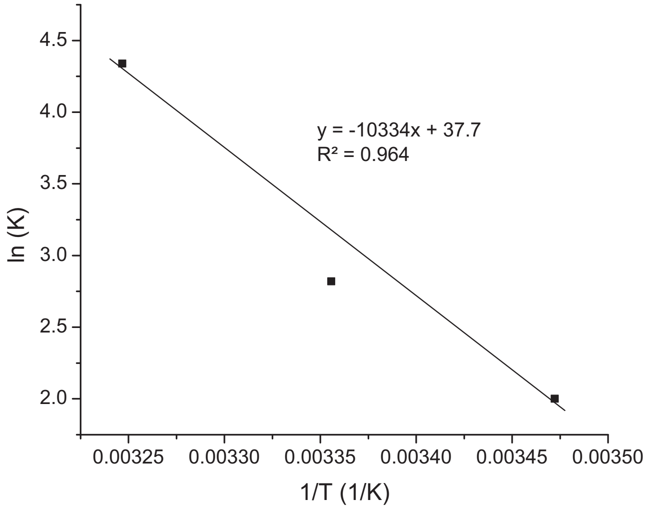

Fig. 15. Plot of $\ln K$ vs $1/T$ for values of thermodynamic parameters at different temperatures.

Table 3
Thermodynamic parameters for the adsorption of CV dye on the dye PAAm-K hydrogel.

Temperature (K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/(mol K))
288	−4472.93	85,916.88	313.8535
298	−7611.47		
308	−10,750.00		

The Gibbs free energy change of the adsorption process was evaluated with the use of the following equations:

$$\Delta G^\circ = -RT\ln K \tag{17}$$

where, K is the thermodynamic equilibrium constant. Further the effect of temperature on the thermodynamic equilibrium constant is determined by the following equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}t} = \frac{\Delta H^\circ}{RT^2} \tag{18}$$

Integrating Eq. (13) and rearranging we get

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{19}$$

where $K = (q_e/C_e)$ and Gibbs free energy is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{20}$$

where ΔG° is the free energy change (J/mol), R is the universal constant (8.314 J/mol K) and T is the absolute temperature (K).

The ΔH° and ΔS° values were estimated from the slope and the intercept of the linear plot of $\ln K$ vs $1/T$ which is depicted in Fig. 15. The values of the standard enthalpy and the entropy changes were determined as 85,916.88 J/mol and 313.85 J/(mol K) respectively. The obtained thermodynamic parameters are reported in Table 3. The positive value of ΔH° shows that the adsorption process is endothermic in nature [48,59]. The positive value of ΔS° suggests increased randomness at the solid/solution interface during the adsorption process [60]. ΔG° values studied at all temperatures were negative that indicates the adsorption process led to a decrease in Gibbs free energy. Negative ΔG° values confirm the feasibility and spontaneity of the adsorption process. The change in free energy for physical adsorption is between −20 and 0 kJ/mol and it is in the range from −80 to −400 kJ/mol for chemisorption [61]. The values of ΔG obtained in this study are within the range of −20 and 0 kJ/mol, indicating that the physical adsorption is the dominating mechanism.

Conclusions

This study investigated the potential use of PAAm-K hydrogel for the removal of CV dye from aqueous solution. PAAm-K hydrogel was synthesized using ultrasound assisted in situ emulsion polymerization of AAm and cross-linked by kaolin. The FTIR spectrum confirms the presence of the amide group in all hydrogel samples and TEM images indicated the fine distribution of kaolin clay in PAAm matrix. The formed cross-linked network of polymer hydrogels exhibited an excellent swelling behavior due to the presence of kaolin. The % dye removal efficiency is higher for higher pH and temperature. Further the adsorption process is more favorable at the lower dye concentration and higher quantity of hydrogel where the maximum removal efficiency of dye was obtained. Also ultrasound plays an important role in the removal of the CV dye. The synergistic effect of ultrasound and hydrogel adsorption resulted in drastic reduction in the time required for dye removal as well as higher amounts of dye removal was achieved as compared to hydrogel alone. The equilibrium data for adsorption shows good agreement with both Langmuir and Freundlich isotherms. The pseudo-first order and the pseudo-second order models were used to describe the kinetics data. Pseudo-second-order kinetic model provided a better correlation for the experimental data studied in comparison to the pseudo-first-order kinetic model. The positive value of ΔH° shows that the adsorption process is endothermic in nature and the negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process. The physical adsorption is found to be the dominating mechanism.

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