Radiation preparation of PVA/CMC copolymers and their application in removal of dyes

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ABSTRACT

Copolymer hydrogels composed of poly(vinyl alcohol) (PVA) and carboxymethyl cellulose (CMC) was prepared by using electron beam irradiation as crosslinking agent. The copolymers were characterized by FTIR and the physical properties such as gelation. The thermal behavior and swelling properties of the prepared hydrogels were investigated as a function of PVA/CMC composition. The factors effecting adsorption capacity of acid, reactive and direct dyes onto PVA/CMC hydrogel, such as CMC content, pH value of the dye solution, initial concentration and adsorption temperature for dyes were investigated. Thermodynamic study indicated that the values the negative values of ΔH suggested that the adsorption process is exothermic. The value of ΔH (38.81 kJ/mol) suggested that the electrostatic interaction is the dominant mechanism for the adsorption of dyes on hydrogel.

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1. Introduction

Dyes have been the subject of many interests in recent years because of increasingly stringent restrictions on the organic content of industrial effluents. The effluents of wastewater in some industries such as dyestuff, textiles, leather, paper, printing, plastic and food, etc. contain various types of synthetic dyestuffs. The treatment of textile wastewater comprising dyestuffs and other non-biodegradable organics and inorganic poses considerable problems in the wastewater treatment industry. However, the increased color intensity is the most serious problem of the wastewater provided by the textile industries because many of the commercial azo dyes can produce hazardous aromatic amines, as well as other highly toxic by-products through metabolic processes in plants and animals or directly after the disposal in lakes, rivers or sea [1–4]. Concerning the reactive dyes which are mainly used for textile dying processes, it is known that 30% of the initial amount of the dye is released in the wastewater due to hydrolysis side reaction, resulting in limited degree of fixation [5]. Moreover, azo dyes which are synthetic products, show rather low biodegradability, firstly because of lack of natural biodegradation paths and secondly because of stereochemical interferences concerning the accession of the reductant or oxidant molecule to the azo-group [6]. As a result, traditional biological processes are not able to fully decolorize azo dye wastewater [7–12]. Most studies have focused on the development of a technique and a method for the treatment of dye wastewater. In general, there are several methods of reducing color in textile effluent streams: coagulation–flocculation, biological treatment, oxidation–ozonation, adsorption and membrane processes. The advantages and disadvantages of each technique have been extensively reviewed. Of these methods, adsorption has been found to be an efficient and economic process to remove dyes, pigments and other colorants [13–15]. In recent years, polymeric adsorbents, due to their wide variations in porosity and surface chemistry, especially regenerability on site and reuse for continuous process, have been increasingly used to remove and recover organic pollutants from waste streams [16,17]

Poly(vinyl alcohol)1 (PVA) has a wide commercial application due to its unique chemical and physical properties. It is a nontoxic, highly crystalline, and water-soluble polymer and has good film forming and high hydrophilic properties. However, PVA as a soluble polymer cannot be used in the treatment of wastewaters. Thus, it has to be converted to a completely insoluble material with high mechanical properties. The structure–property behavior and compatibility of PVA with other polymers have been investigated by many authors. Although extensive research work has been carried out on the synthesis and application of polymeric materials in the field of treatment of waste waters, few authors were concerned with PVA/poly(carboxymethyl cellulose) (CMC) polymer blends. It has been reported that the introduction of 6–16% of CMC Na salt to the PVA matrix leads to an increased sorption capacity with respect to water vapor [18].

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The aim of this study is to focus a synthesized hydrophilic copolymer of poly(vinyl alcohol) (PVA)/carboxymethyl cellulose (CMC) on the retention of anionic dye pollutants such as acid green B, ismative violet 2R and direct pink 3B dyes

2. Experimental

2.1. Materials

Commercial PVA with a molecular weight of about 17,000 was used. CMC of commercial grade was supplied by El Nasr Pharmaceutical Chemicals Co., Egypt. Three types of dyes were used as adsorbates. The dyes used in the experiments were acid (acid green B; λ_{max} = 636 nm), reactive (ismative violet 2R; λ_{max} = 550 nm) and direct (direct pink 3B λ_{max} = 526 nm). The chemical structures of different dyes are depicted in Chart 1. All of dyes were commercial grade and were used without further purification. The other chemicals and phosphate buffers were reagent grade and used as received. In addition, distilled water was used as a solvent. Structure of the dyes is shown below:

2.2. Instrumentation

FTIR spectra were recorded on Mattson 1000, Unicam infrared spectrophotometer Cambridge, England in the range from 400–4000 cm^{-1} using KBr pellets

Thermogravimetric analyzer Shimadzu TGA system of Type TGA-50 was used in this study. The temperature range was from ambient to 500 °C at heating rate of 10 °C/min in nitrogen atmosphere 20 ml/min.

The surface morphology of the copolymer was examined with a Jeol JSM-5400 scanning electron microscopy (SEM) (JEOL, Tokyo, Japan).

Absorbance measurement was carried out on UNICAM UV–vis Spectrometer. 1000 Model spectrophotometer.

2.3. Experimental studies

2.3.1. Preparation of PVA/CMC copolymer

Appropriate weights of dry PVA and CMC–Na were mixed with water at different concentrations, put in peter dish diameter 10 cm and irradiated at different doses using an electron accelerator. Irradiation was carried out on the electron beam facility (1.5 MeV and 25 kW) of the National Center for Radiation Research and Technology, in which the required doses were obtained by adjusting the electron beam parameters and conveyer speed. After irradiation, the prepared polymers were dehydrated by the aid of an ethanol–water mixture (80, 90, and 99%), dried at 378 °C for 24 h, and stored in a vacuum oven at 408 °C for 12 h before use.

2.3.2. Gel content

The gel content of the hydrogels was measured by extraction in hot distilled water at 100 °C for 48 h and dried at 70 °C for 48 h until they reached constant weight. The gel content was defined as in equation below; where W_d is the dried gel weight after extraction, and W_o is the initial weight of the polymer.

$$\text{Gel (\%)} = \frac{W_d}{W_o} \text{X } 100$$

2.3.3. Preparation of buffer solution of different pH's

In all 0.2 M (citric acid/trisodium citrate) and 0.2 M (sodium dihydrogen phosphate/disodium hydrogen phosphate) were used to prepare buffer solution ranged from 3 to 5 and 6 to 8, respectively [19]. 0.2 M HCl was used to prepare solutions of pH 1 and 2.

2.3.4. Swelling studies

Dynamic swelling studies were performed by placing previously weighed dried disks of the gel in 10 ml of the buffer solutions with pH 2, 3, 4, 5, 7, 9 and 11 at 37 °C. The swelling of the PVA/CMC copolymer hydrogel was followed by measuring the weight of the
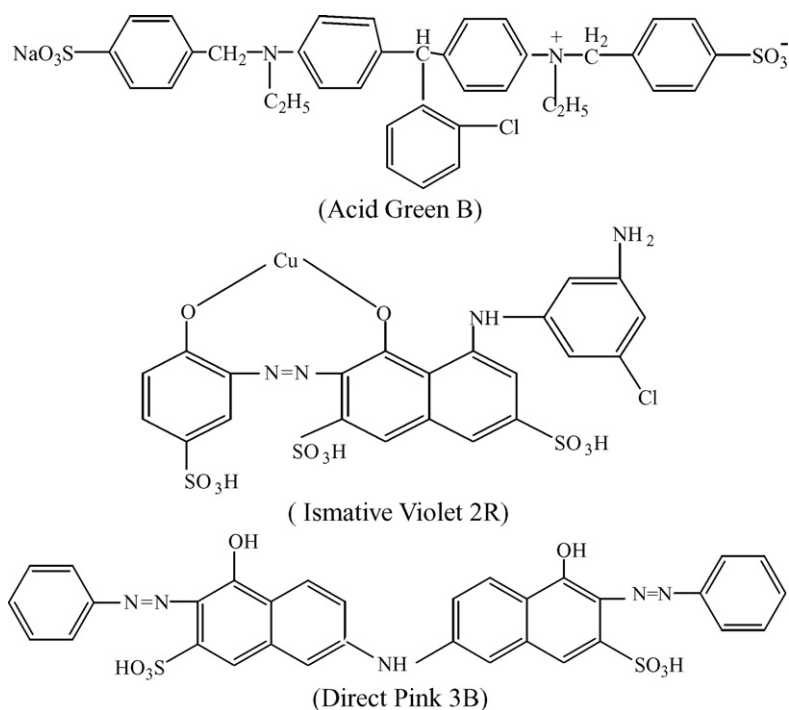

(Acid Green B)

(Ismative Violet 2R)

(Direct Pink 3B)

Chart 1. Chemical structure of dyes.

disk at different times. The degree of swelling could be described as water absorptivity of the hydrogels.

$$Water uptake = \frac{W_s - W_d}{W_d}$$

where W_d and W_s represent the weights of dry and wet hydrogels, respectively.

2.3.5. Adsorption studies

Adsorption isotherms were determined by the batch method for all adsorbents. Accurately weighed dry samples (0.1 g) were placed in a solution of a definite volume (25 mL) and allowed to stand for a period of 4 days at room temperature. Adsorption amount of dye (mg/g) was calculated by using the following equation:

$$q_e = \frac{[(C_0 - C_e) \times V]}{W}$$

where W is the weight of dry hydrogel (PVA/CMC) (g); V is the volume of the aqueous phase (L); q_e is the amount of dye adsorbed onto unit dry mass of the (PVA/CMC) hydrogels (mg g^{-1}), C_0 and C_e are the concentrations (mg/L) of the dye solution before and after adsorption, respectively, that were determined by using an UV–vis spectrophotometer at identical dye's absorbance wavelengths.

The total uncertainly for all experiments ranged from 3–5%

3. Results and discussion

3.1. Gel fraction

CMC is one of the polysaccharides which were able to form hydrogel by radiation crosslinking in so-called "paste-like" status [20], considering the slow increment of gel fraction in the dose range of 5–20 kGy, we can conclude that chain scission took a significant role during gel formation procedure. In previous work, [21] the maximum gel fractions of pure CMC hydrogel in all the above mention cases were reported to be ca. 40–50% To improve the gel properties to meet the demands for many practical applications, PVA which was used to prepared PVA/CMC copolymer. This is due to the higher affinity of PVA to crosslinking through the formation of intra and/or intermolecular hydrogen bonding via –OH groups. The gel fraction on the PVA/CMC compositions and irradiation dose is given in Fig. 1 It can be seen that the gel fraction yield increases with increasing irradiation dose and enhanced PVA content. The high gel fraction of hydrogels; caused by enhanced irradiation dose
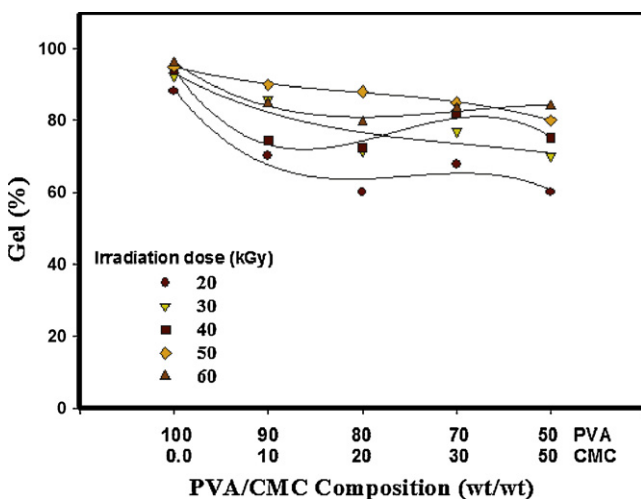

Fig. 1. Effect of various PVA/CMC compositions on the gel (%) of PVA/CMC hydrogel at different irradiation doses. Polymer concentration, 5% (wt/vol).
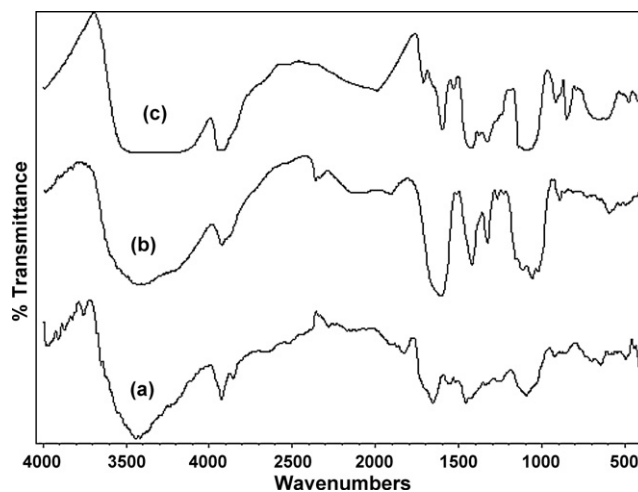

Fig. 2. FTIR spectrum of: (a) PVA, (b) CMC and (c) PVA/CMC (50/50) copolymer.

as a result of higher degree of crosslinking onto polymer network which cause higher gel content.

3.2. FTIR

The IR spectra of pure PVA, CMC homopolymer and crosslinked PVA/CMC copolymer are shown in Fig. 2. The PVA spectra show characteristic broad band at 3340 cm^{-1} corresponding to the O–H stretching vibration of the hydroxyl group of the PVA. The sharp band at 1735 cm^{-1} corresponds to the C=O stretching of the acetate group of PVA. The backbone aliphatic C–H stretching vibrations give sharp bands at 2940 and 2910 cm^{-1}. The strong absorption peak at 1100 cm^{-1} has been assigned to the C–O in stretching mode for PVA and the bands observed at 1335 cm^{-1} have been attributed to combination frequencies of (CH·OH)

The IR spectrum of CMC homopolymer shows the absorption bands due to C–H stretching (2983 cm^{-1}) and that due to C–O stretching of the ether group of the carboxymethylation of cellulose or the ether linkage [1,4-β-D-glucoside] of cellulose at 1187 cm^{-1}. It seems that an overlap has occurred between the C–O bands arising from the two types of ether present in CMC. A strong absorption band can be seen at 3223 cm^{-1} which is due to O–H stretching of the non-substituted hydroxyl groups of cellulose, and a strong absorption band can be seen at 816 cm^{-1}, which is due to the C–O stretching of alcohol. The appearance of the broad absorption bands at 3223 and 3495 cm^{-1} can be attributed to the presence of intramolecular hydrogen bonding in CMC sodium salt molecules [22].

The IR spectra of PVA/CMC copolymer crosslinked by electron beams showed different features, in which some absorption bands had disappeared and others were shown up as shown in Fig. 2c. It seems that the intensity of hydrogen bonding of CMC has been increased as a result of the polymerization of PVA as indicated from the very wide abroad absorption band starting at 3050 and end at 3570 cm^{-1}. This may explain the formation of hydrogen bonding between the carboxylic groups themselves and with the non-substituted hydroxyl groups of cellulose molecule. A series of three bands can be observed within the range 3100–3600 cm^{-1} which can be explained as due to O–H stretching H-bonded hydroxyl groups. Therefore, it may be concluded that the interaction of CMC in the copolymer is through hydrogen bonding.

3.3. Swelling behavior

The influence of comonomer compositions for different PVA/CMC copolymer hydrogels on the swelling ratio at various
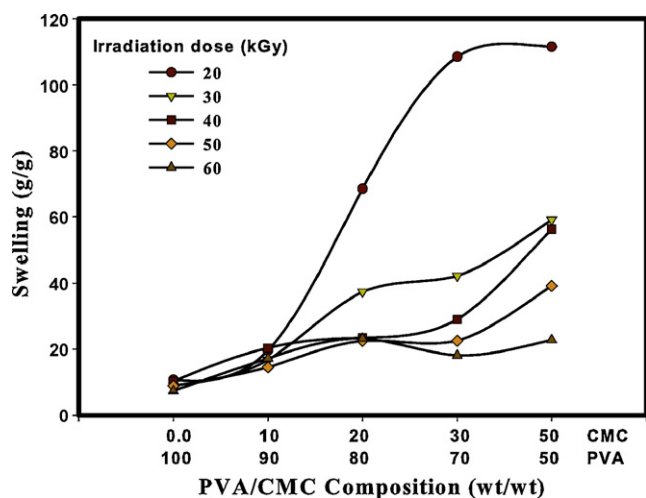
Fig. 3. Effect of various (PVA/CMC) copolymer compositions on the swelling (mg/g) at different irradiation doses. Polymer concentration, 5% (wt/vol).

irradiation doses was investigated and was shown in Fig. 3. As can be seen from this figure, swelling capabilities of all copolymer compositions are increased by increasing the CMC content .CMC is a polysaccharide that contains different type of hydrophilic functional groups. The results revealed that the increase in the CMC content in the initial comonomer feed solution results in a hydrogel with a higher swelling behavior. The increase observed in the swelling could be attributed to the increase in hydrophilic character of each CMC monomeric unit and so, the number of hydrogen bonds formed with water. Furthermore, the results are presented in Fig. 3 which reveals that the swelling ratio continu-

ously decreases with increasing content of PVA in the feed mixture. The results can be explained by the fact that increasing content of PVA in the feed mixture will result to enhancing the crosslinking by intramolecular hydrogen bonding between the PVA chains in the hydrogel network structure which resulting to decrease swelling.

The influence of irradiation dose on the swelling ratio for the hydrogels prepared at different composition is shown in Fig. 3. It can be seen that the higher the irradiation dose, the lower the swelling. This phenomenon is attributed to the enhancement of the crosslinking process at higher doses and, as a consequence, the diffusion and swelling properties are hindered by network structure formation.

The surface morphology of various ratios of PVA/CMC hydrogels was detected by scanning electron microscopy (SEM). The pore size of the polymeric material mainly depends on the irradiation dose and copolymer composition. The copolymer composition affects the hydrogel pore structure as shown in Fig. 4, the PVA/CMC hydrogel of composition (50/50 wt%) shows a larger pore structure compared with the other compositions and this affect on the degree of swelling.

3.4. Effect of pH

CMC is a kind of natural polyelectrolyte, which has many carboxylic groups in its molecular chain. The dissociation degree of carboxyl group is closely related to the pH value of the medium. To investigate the influence of pH value of the medium on the swelling ratios of the hydrogels, the pH range was selected from 2 to 11 in this study. As shown in Fig. 5, in the pH range from 2 to 7, the swelling ratios of the PVA/CMC hydrogels continuously increase with increasing pH values. At lower pH values (below the pKa of carboxylic groups, approximate 4.6), the $-COO^-$ groups in CMC are protonated to $-COOH$ groups, and the hydrogen bonds
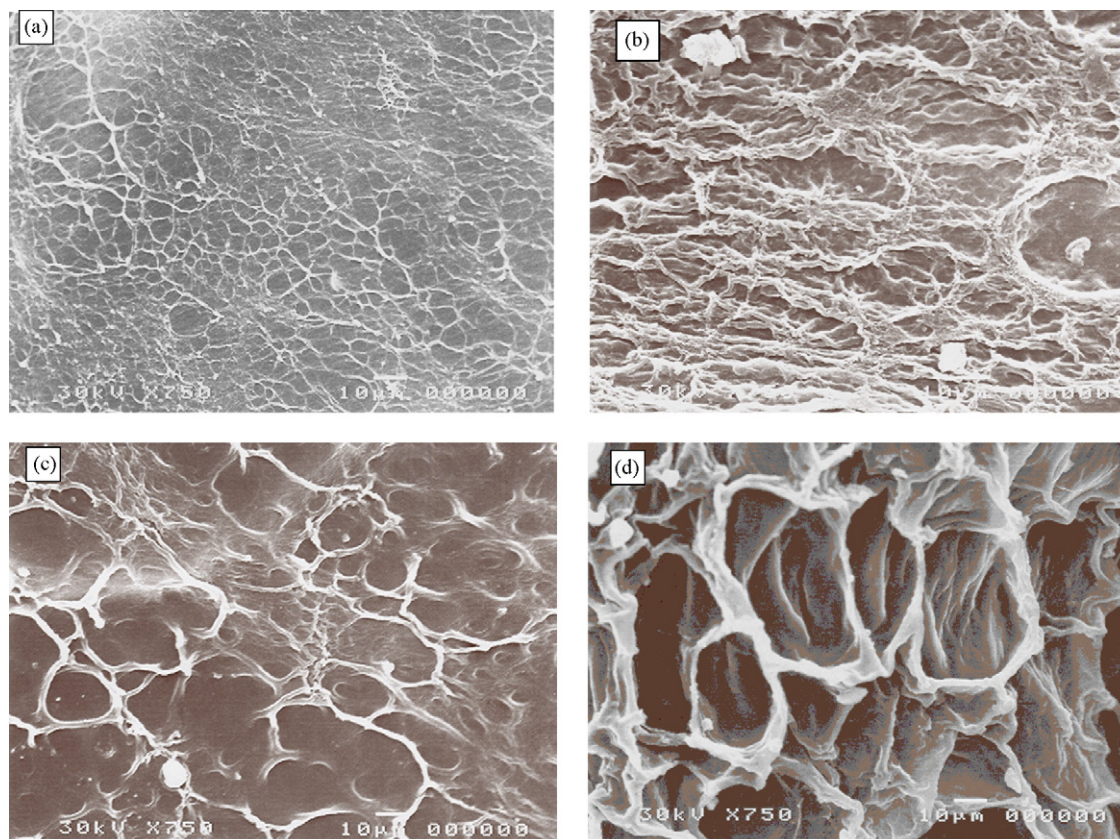

Fig. 4. Morphology of various compositions of PVA/CMC copolymer: (a) 100/0.0, (b) 80/20, (c) 70/30 and (d) 50/50 PVA/CMC wt/wt. Polymer concentration, 5% (wt/vol) and irradiation dose; 20 kGy.
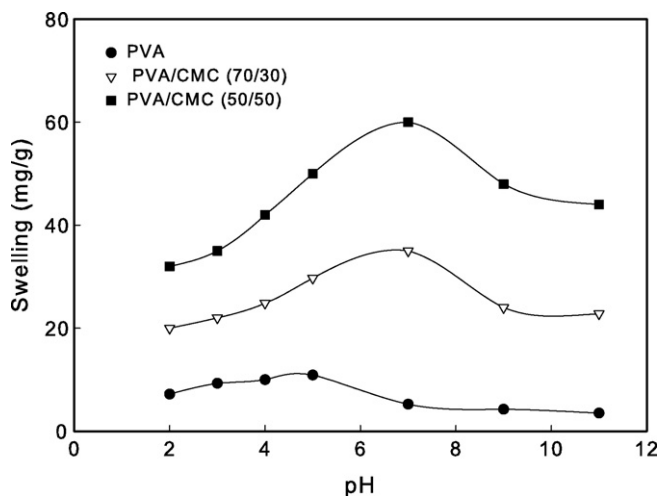
Fig. 5. Effect of pH on swelling capacity of pure PVA and PVA/CMC copolymer compositions. Polymer concentration, 5% (wt/vol) and irradiation dose; 20 kGy.

between –COOH and –OH groups are formed, which result in a decrease of swelling ratios. The lower pH values of the medium, the stronger the hydrogen bonds and thus the smaller the swelling ratios of hydrogels. When pH value is increased to 4.6, the carboxylic groups become ionized and the electrostatic repulsion between the molecular chains is predominated which leads to the network more expanding. There exhibits a maximum swelling ratio at pH 7. Beyond this value, a screening effect of the counter ions, i.e., Na$^+$, shielding the charge of the carboxylate anions may prevents from an efficient repulsion. As a result, a remarkable decrease in equilibrium swelling is observed [23].

3.5. Thermogravimetric analysis (TGA)

The thermal behavior of pure PVA and various PVA/CMC copolymers was investigated by using TGA as shown in Fig. 6. It shows a characteristic three-step thermogram. The first step shows weight loss about 8% within the temperature range of 50–230 °C for pure PVA, and about 20% for the other PVA/CMC compositions. The major weight loss (57%) occurs in the second step (after 230 °C) at a temperature around 350 °C. After this temperature (third step), weight loss of pure PVA and various PVA/CMC copolymers increased with raising temperature but all PVA/CMC copolymers gave more weight
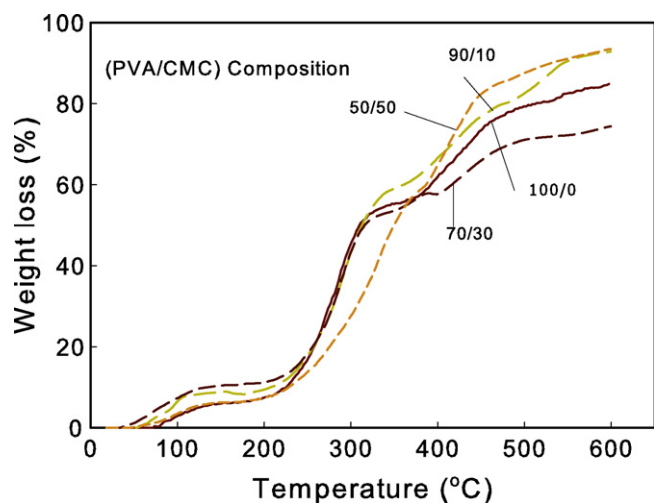

Fig. 6. Thermal stability of PVA/CMC copolymer at various compositions. Polymer concentration; 5% (wt/vol) and irradiation dose; 20 kGy.
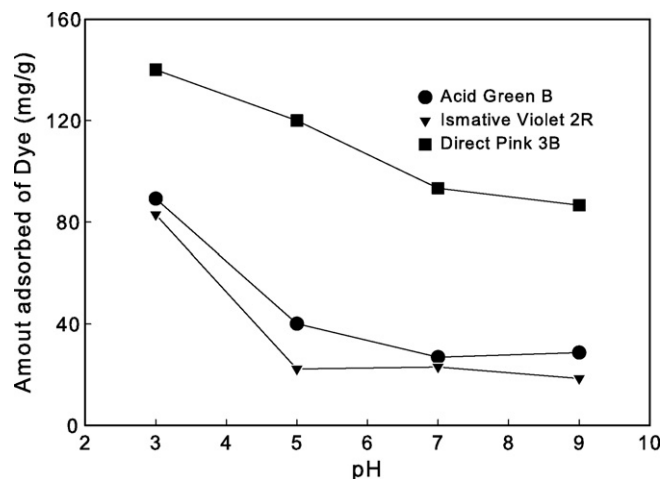

Fig. 7. Effect of pH on adsorption of different type of dyes onto PVA/CMC (50/50) copolymer for equilibrium contact time, initial concentration = 100 mg/L.

loss than the pure PVA except PVA/CMC copolymer with composition; 70/30 wt%. Thus, it is clear that the thermal stability of the most compositions of PVA/CMC copolymer lowers than that of pure PVA except composition; 70/30 wt% which gave high thermal stability at high temperature. This means that the addition of CMC to PVA reduce the thermal stability of the latter.

3.6. Adsorption of dyes

To observe the uptake of some dyes, the prepared hydrogels (0.1 g) were placed in aqueous solutions of anionic dyes (25 mL) and allowed to equilibrate for 4 days at room temperature; thereafter, they showed dark coloration to the colors of the original solutions. The concentration of surrounding solution was monitored by using UV–vis spectrophotometer.

3.7. The effect of pH on the adsorption process

The pH value of the solution, which affects the surface charge of the adsorbent and the degree of speciation of adsorbate was an important controlling parameter in the adsorption process. Fig. 7 shows the effect of pH on the removal of different dyes onto PVA/CMC (50/50) hydrogel from aqueous solution. As can be seen, the adsorption capacity of dyes onto PVA/CMC hydrogel decreases significantly with increasing pH. The high adsorption capacity is due to the strong electrostatic interaction between the PVA/CMC hydrogel and anionic dye molecules. At lower pH, a significantly high electrostatic attraction exists between the positively charged through the chains of copolymer sites (At lower pH values (below the pKa of carboxylic groups, approximate 4.6), the –COO$^-$ groups in CMC are protonated to –COOH groups) and the negatively charged of dyes, thereby causing the increase in dye adsorption [24]. As the pH of the system increases, the adsorbent surface appears negatively charged, which does not favor the adsorption of anionic dye molecules due to the electrostatic repulsion between the negatively charged surface and the dye anions. Also, lower adsorption of dyes at higher pH is also due to the abundance of OH$^-$ ions competing with the anionic dye molecules for the adsorption sites.

3.8. Effect of CMC content

The adsorption of PVA/CMC hydrogels of different composition was investigated towards acid, reactive and direct dyes by the batch equilibrium method. The amount adsorbed of dyes by the different hydrogels is shown in Fig. 8. As can be seen from the figure,
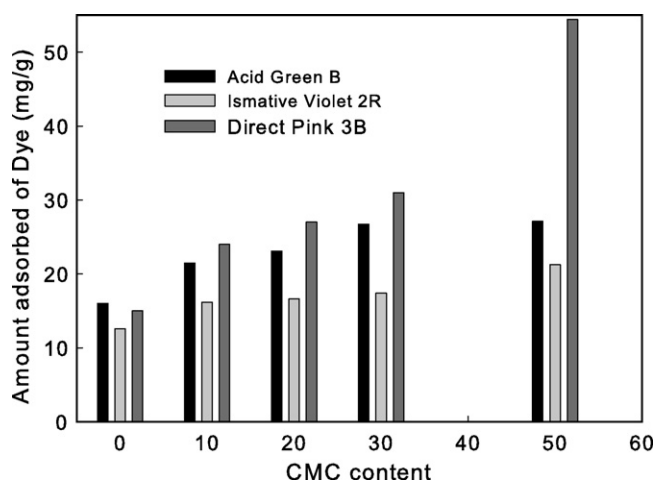
Fig. 8. Effect of CMC content in (PVA/CMC) copolymer on adsorption of different dyes, initial concentration = 100 mg/L.

Fig. 9. Effect of initial concentration on adsorption of different types of dyes onto PVA/CMC (50/50) copolymer, at pH 3.

for all investigated dyes the adsorption increases with increasing CMC content. CMC-rich compositions possess high dye uptake that possess high degree of swelling which increases the diffusion of the dyes inside the hydrogels. These hydrogels contain a large number of hydroxyl groups that can form intermolecular hydrogen bonds between sulfonate groups of dyes and the polymer. The other type of interaction between the hydrogel and anionic dyes may be hydrophobic. *Hydrophobic interaction*: These are specially aqueous solution interaction, which in the present case will involve the aromatic ring on the anionic dye molecules and the methine and methylene groups of on crosslinked polymer chain.

All polymers exhibited higher sorption capacities. However, these polymers exhibit approximately same sorption capacity toward all type of dyes except direct pink 3B which contains more ring and azo-groups than the others. The adsorption capacities varies as direct pink 3B > acid green B > ismative 2R (Fig. 8). The structure of acid and direct dyes is flat and planar and hence the adsorption capacities are higher. The reactive dye is bulkier and no planar which causes the decrease in the rates of adsorption of these dyes on PVA/CMC (50/50) hydrogel as compared to other groups of dyes investigated.

3.9. Effect of initial concentration of dye

Adsorption of dyes on PVA/CMC (50/50) hydrogel dependent on their initial concentration. A representative trend obtained for various initial concentrations of dyes is shown in Fig. 9. The color removal increased with the increasing initial concentrations of dye.

3.10. Adsorption isotherms

The adsorption isotherms of all investigated dyes on PVA/CMC (50/50) copolymer hydrogel are shown in Fig. 10. The adsorption isotherms indicate that the uptake of the investigated dyes increases with increasing equilibrium concentration anions. The isotherm data were analyzed by Freundlich equation. The equilibrium isotherm results were found to be best fitted by Freundlich isotherm model:

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

where q_e is mg adsorbate per gram of dry adsorbent at equilibrium concentration (mg/g), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}) and the Freundlish empirical constants k_F and n referred to the ability of polymer adsorbent and affinity of
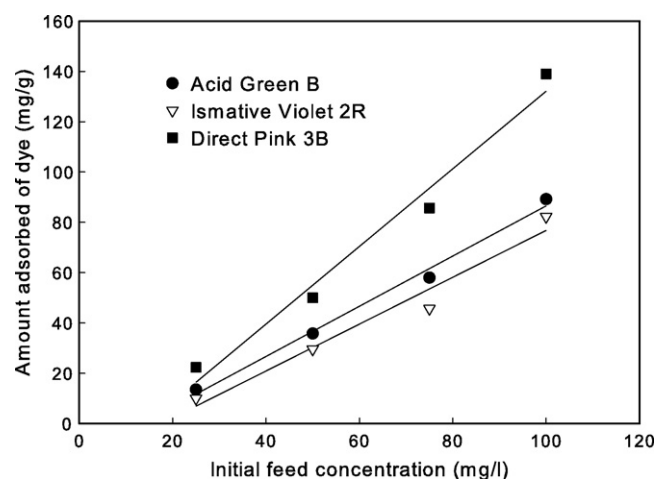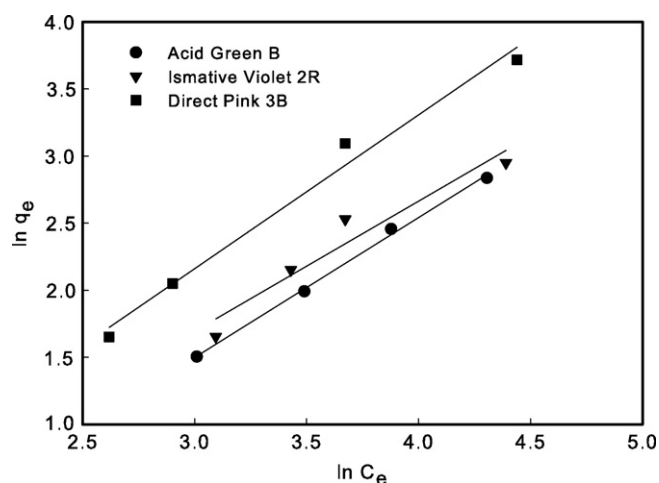

Fig. 10. Adsorption isotherm of different dyes by PVA/CMC (50/50) copolymer at pH 3.0.

adsorbat solution, respectively. The intercept and the slope of the linear plot of $\ln q_e$ versus $\ln C_e$ at given experimental conditions provide the values of k_F and $1/n$, respectively. The Freundlich isotherm constants and R^2 values for different solutions are given in Table 1. Variation in the slopes ($1/n$) and intercepts of the line (K_f) reflects the effect of physico–chemical characteristics of the dyes on the adsorption process and their affinity for adsorption. Consequently, the adsorption parameters (K_f and $1/n$) describe on quantitative basis the adsorption process. Freundlich constant $n > 1$ indicates favorability of adsorption [25,26]. The adsorption rate constant, K_f, represents the adsorption capacity of PVA/CMC (50/50) hydrogel.

3.11. Effect of temperature on adsorption of dye

One of the important parameters which affect adsorption capacity is temperature. The effect of temperature on the adsorption

Table 1
Freundlich and thermodynamic parameter for dye adsorption.

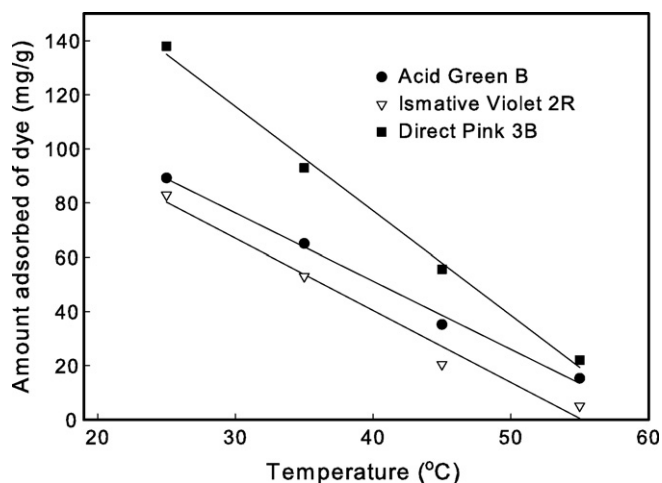| Dye	Freundlich			ΔH (kJ/mol)
	K_f (mg g^{-1})	n	R^2	
Acid green B	0.2780	0.959	0.9973	−38.81
Ismative violet 2R	0.1958	0.8718	0.9431	−34.77
Direct pink 3B	0.2970	1.0314	0.9851	−27.65

Fig. 11. Effect of temperature on adsorption of different type of dyes onto PVA/CMC (50/50) copolymer for equilibrium contact time, at pH 3, initial concentration = 100 mg/L.

of dyes (acid green B, direct pink 3B and ismative violet 2R) on (PVA/CMC) hydrogels is shown in Fig. 11. The adsorption capacity of (PVA/CMC) hydrogels decreases with the increase in the temperature of the aqueous dye solution, suggesting that the adsorption is exothermic in nature.

In order to gain an insight into the adsorption mechanism involved in the adsorption process, thermodynamic parameters for the present system were calculated. To determine the thermodynamic parameters, adsorption experiments are repeated at constant concentration (100 mg/L) at 25 and 35 °C The apparent enthalpy change (adsorption heats) (ΔH) was calculated using the following thermodynamic function:

$$\ln \left(\frac{C_{e2}}{C_{e1}} \right) = \left(\frac{\Delta H}{R} \right) \left[\left(\frac{1}{T_1} \right) - \left(\frac{1}{T_2} \right) \right]$$

where C_{e1} and C_{e2} are the free dye concentrations at absolute temperature T_1 and T_2; respectively. R is the universal gas constant.

Fig. 12 showed $\ln C_e$ versus $1/T$, the slopes of these graphs give $\Delta H/R$ values. Table 1 listed the calculated thermodynamic parameters. The variation of energy (ΔH) for physical adsorption is generally small than that of chemisorption. Typically, ΔH for physical adsorption ranges from 0 to 40 kJ/mol, compared to that of

chemical adsorption ranging from 40 to 800 kJ/mol [27]. As shown in Table 1, the value of ΔH (38.81 kJ/mol) was higher than those corresponding to physical adsorption but near the lower limit of corresponding chemical adsorption. This would suggest that the adsorption process might be considered as physical adsorption in nature. Moreover, the chemical sorption may be involved in PVA/CMC hydrogel adsorption of dyes.

4. Conclusions

PVA/CMC copolymer has been prepared by using electron beam irradiation technique. The prepared of PVA/CMC copolymer is confirmed qualitatively by FTIR. The gel fraction increases with increasing irradiation dose, while the swelling of PVA/CMC copolymer nearly tends to increase with increasing CMC content and reduced with enhanced irradiation doses. The thermal stability of PVA/CMC copolymer reduces with addition of CMC to PVA but of PVA/CMC with compositions; 70/30 wt% gave high thermal stability especially at high temperature. The results indicate that the hydrogels composition is an effective parameter in determining the dyes sorption character. In this regard, the adsorption increases with increasing CMC content. The adsorption capacities varies as direct pink 3B > acid green B > ismative 2R. Freundlich equation and its empirical constants k, n allowed for interpretation of the adsorbent–adsorbate interaction. The adsorption of investigated dyes, decrease with increasing pH value. It was concluded that PVA/CMC copolymer prepared by electron beam irradiation can be use as dye removal materials.

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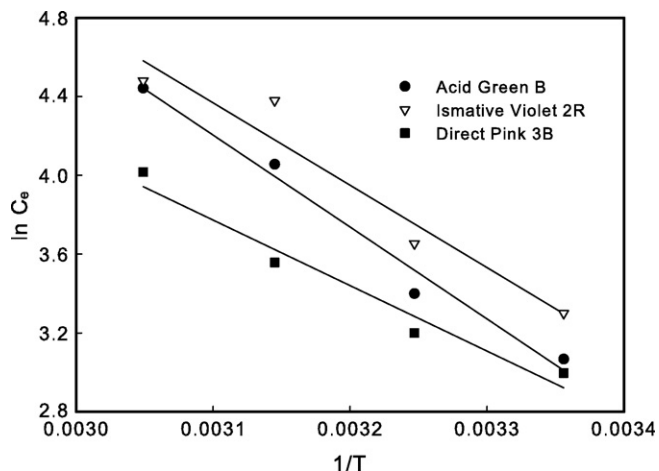
Fig. 12. The variation of ln Ce of PVA/CMC (50/50) copolymer for different dyes with $1/T$ in initial feed concentration: 100 mg/L and pH 3.

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