Radiation-induced grafting of acrylamide and methacrylic acid individually onto carboxymethyl cellulose for removal of hazardous water pollutants

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ABSTRACT

Carboxymethyl cellulose hydrogels were synthesized by grafting of acrylamide (AAm) and methacrylic acid (MAAc) individually with different concentrations onto carboxymethyl cellulose (CMC) using direct radiation grafting technique. It was found that for both Poly(CMC/AAm) and Poly(CMC/MAAc), the grafting yield and grafting ratio increase with the increasing monomer concentration. Also, it is noted that both grafting ratio and grafting yield of Poly(CMC/AAm) are higher than that of Poly(CMC/MAAc). The effect of different monomer concentrations on gel (%) and swelling behavior was studied. It is found that the increasing monomer concentration increases gel (%). For Poly(CMC/AAm) hydrogels, the swelling behavior decreases with increasing AAm concentration due to high crosslinking hydrogel formation, while as MAAc content increases, swelling behavior increases up to Poly(CMC/MAAc) 1:25 wt%. Swelling kinetics and diffusion mechanism indicate that the water penetration obeys non-Fickian transport mechanism. The structures and properties of the original CMC and the prepared Poly(CMC/MAAc) and Poly(CMC/AAm) were characterized using different analytical tools such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscope (SEM). This study provides a solution to the discharge of different pollutants from wastewater. The adsorption capacity of Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels toward heavy metals, Cu2+ and Co2+, dyes such as acid blue dye and methyl green, and organic contaminants such as 4-chlorophenol and 2,4-Dichlorophenoxy acetic acid has been investigated.

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1. Introduction

Cellulose is regarded as the most abundant and renewable biopolymer in nature. It is one of the promising raw materials used in modern industry due to its use in the preparation of various functional materials.[1,2] Two large categories of commonly used cellulose derivatives, cellulose esters and cellulose ethers, should be mentioned. Among these derivatives, carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups (CH2−COOH) bound to some of the hydroxyl groups of the glucopyranose units of the cellulose backbone.[2]

Industrial waters and even natural waters are often contaminated by toxic or sometimes carcinogenic impurities causing ecological disequilibrium and severe public health problems.[3–6] Despite the considerable advances in the field of water treatment, until now, there is considerably less literature research on the elimination of organic pollutants. Also, in case of the organic compounds, polynephenols, organochlorinated or aromatic, are considered to be the most toxic for both living species and fauna. The origin of these products is multiple such as chemical industry, leaching, and run-off from agricultural and forest land (through the intensive use of pesticides and weed-killers deposition from aerial application and discharge from industrial waste).[7,8] In the absence of any treatment, the organic compounds and the persistent organic pollutants (POP), like certain pesticides, accumulate in water and favor the risk of contamination of underground sources in an irreversible way.[9] This effect is worsened by the fact that the chemical stability of these pollutants is high and even their chemical decomposition can generate very stable products, such as polychlorinated biphenyls (PCB) and dioxins, which are extremely toxic even at very low concentration.

Recently, particular attention has been paid to producing pollutant adsorbents from cellulosic polymers such as carboxymethyl cellulose due to their advantages of being abundant, rapidly renewable, and biodegradable in nature. [10,11] The adsorbent products are usually prepared in the form of hydrogels owing to their three-dimensional
pores, inner structure, readily swelling behavior, and strong adsorption capacity toward heavy metals,[12,13] dyes [14–17], and organic contaminants.[18,19]

Hydrogels are responsive to external stimuli such as pH, temperature, electric field, and external environment and may find applications as artificial muscles, robot actuators, and adsorbers of toxic chemicals.[20]

The aim of our study is to prepare a heavy metal, dye, and organic contaminant adsorbent hydrogels based on CMC which is neither toxic nor expensive. The effect of the type of monomer, AAm and MAAc, on the adsorption capacity toward different types of pollutants was studied. The preparation of different types of the CMC hydrogels was carried out using direct radiation grafting technique.

2. Experimental

2.1. Materials

Methacrylic acid 99%, Sigma–Aldrich, Germany and carboxymethyl cellulose, acrylamide, and N,N-methylene bisacrylamide were provided from Lobachemie PVT. LTD, Mumbai, India. Copper (Cu^{2+}): used as Cuper sulfate pentahydrate was provided from Lobachemie PVT. LTD, Mumbai, India. CuSO_{4}·5H_{2}O, Cobalt (Co^{2+}): used as cobalt sulfate pentahydrate CoSO_{4}·5H_{2}O pink crystals was supplied by Edwic (El-Nasser) Egypt. Acid dye: Xylene blue (Cl acid blue 7), CI number 42080, Molecular formula C_{37}H_{36}N_{2}O_{6}S_{2}Na, Molecular weight 691 and basic dye: Methyl Green Molecular formula C_{16}H_{17}ClN_{4}O_{2}S Molecular weight 364.85 g/mol. (4)-chlorophenol) 98% were provided from Lobachemie PVT. LTD, Mumbai, India., (2,4)-dichlorophenoxy acetic acid 98% was provided from Lobachemie PVT. LTD, Mumbai, India.

2.2. Preparation of Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels

The direct radiation grafting technique was used for the preparation of different hydrogels. Carboxymethyl cellulose's (1%) aqueous solutions were prepared at 60 °C in water bath; then, 10 ml of the stock CMC solution was transferred to glass ampoules and different monomers, acrylamide (AAm) and Methacrylic acid (MAAc), were added separately to CMC solution with polymer to monomer ratios 1:10, 1:15, 1:20, 1:25, and 1:30 wt%. In case of MAAc/CMC hydrogel, n,n-methylene bisacrylamide was added with concentration of 3% wt% of MAAc. The glass ampoules were then sealed and subjected to irradiation dose of 20 kGy at dose rate 0.74 Gy/s.

2.3. Gel percent

The prepared hydrogels were cut into small discs, dried, and weighed. The samples were extracted by hot distilled water at 80 °C for 3 h and then dried at 40 °C until a constant weight was obtained. The gelation percent (G %) was calculated gravimetrically using the following equation:

\[
\text{Gel} \% = \frac{W_g}{W_o} \times 100
\]
where \( W_g \) and \( W_o \) are the weight of dried sample after and before extraction, respectively.

### 2.4. Determination of grafting yield and grafting ratio

Both grafting yield and grafting ratio were determined gravimetrically according to the following equations [10,21]:

\[
\text{Grafting yield} = \frac{W_g - W_o}{W_o} \times 100
\]  
(2)

where \( W_g \) is the weight of grafted hydrogel after extraction and \( W_o \) is the weight of original CMC.

\[
\text{Grafting ratio} = \frac{W_g}{W_o} \times 100
\]  
(3)

where \( W_g \) is the weight of grafted hydrogel after extraction and \( W_o \) is the weight of original CMC.

### 2.5. Swelling studies

#### 2.5.1. Equilibrium swelling

The hydrogels discs were soaked in distilled water at room temperature. Swollen gels were removed from water, dried, and weight several times. The measurements were continued until a equilibrium constant weight was obtained for each sample (160 h). The swelling percent \( (Q) \) at equilibrium was calculated using the following equation:

\[
Q = \text{Equilibrium swelling} = \frac{W_s - W_d}{W_s} \times 100
\]  
(4)

where \( W_d \) is the weight of dried hydrogels and \( W_s \) the weight of the swelling gel at equilibrium.

#### 2.5.2. Kinetic study of swelling

The progress of the water uptake process was monitored by determining the swelling ratio of the hydrogel as increasing at desired time intervals. For kinetic analysis of the results, Fick’s law was applied which was described previously.[22]

The swelling/diffusion kinetic parameters, as diffusion coefficients \( (D) \), swelling rate constant \( (k) \), diffusion constant \( (n) \), and maximum equilibrium swelling ratio, were calculated using the dynamic swelling ratio values for the prepared hydrogels by the following equation:

\[
F = \left( \frac{M_t}{M_\infty} \right) = K t^n
\]  
(5)

In the above equation, \( F \) is a fraction of swelling due to the water uptake, \( M_t \) is the adsorbed water at time \( t \), and \( M_\infty \) is the adsorbed water at equilibrium; \( K \) is the swelling constant and \( n \) is the swelling exponent.

This equation was applied to the initial stages of swellings, and plots of \( \ln(F) \) versus \( \ln(t) \) are shown in Figure 3(a,b); \( n \) and \( K \) were calculated from the slope and intercept of the line, respectively.

Fick’s first and second laws of diffusion adequately describe most diffusion processes. For the prepared hydrogel, the integral diffusion is given in the following equation.

\[
F = M_t/M_\infty = 4 \left( \frac{Dt}{\pi L^2} \right)^{0.5}
\]  
(6)

where \( D \) is the diffusion coefficient and \( L \) is the thickness of the sample. In Equation (4), the slope of linear plot between \( (M_t/M_\infty) \) and \( t^{1/2} \) yields diffusion coefficient \( D \).

### 2.6. FTIR spectroscopic measurements

FTIR-4100 spectrophotometer product of Jasco, Japan was used to determine the functional groups of the original CMC and the prepared Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels. The spectra were recorded from 4000 to 400 cm\(^{-1}\). The Fourier transform infrared (FTIR) analysis was performed in Micro analytical center, Cairo University, Egypt.

### 2.7. Thermogravimetric analysis

TGA-50 Shimadzu, Thermogravimetric analyzer (made in Japan) was used for the measurements of thermogravimetric analysis (TGA) of the original CMC and the prepared Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels. The nitrogen flow rate was 20 ml/min and the heating rate was 10 °C/min from ambient temperature up to 600 °C.

### 2.8. X-ray diffraction

X-ray diffraction (XRD) measurement was conducted for original CMC and prepared Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels at room temperature; XRD operated at CuK at wavelength of 1.54 A, 30 nmA, and 40 keV. The pattern was recorded at scan rate of 0.02, 82 q/sin using ALPHA FTIR Spectrophotometer equipped with X-ray tube (Cu target, 40 kV voltage, 30 mA (current). The X-ray data were recorded in the range from 4° to 80° 2θ with continuous scanning mode and scanning speed 8 (°/min).

From Scherer equation, the average particle size of the prepared hydrogels was calculated.[23]

\[
D = \frac{K \lambda}{\beta_{1/2} \cos \theta}
\]  
(7)

where \( D \) is the particle size, \( K = 0.89 \) is the Scherer constant related to the shape and index of the crystals, \( \lambda \) is
2.11. Adsorption capacity

The removal of different pollutants heavy metals such as CuSO₄·5H₂O, and CoSO₄·5H₂O, dyes such as acid blue dye and methyl green, and organic pollutants such as P-Chlorophenol and 2,4-Dichlorophenoxy acetic acid was investigated. Different pollutants were prepared in lab with concentrations 1000 mg/l for heavy metals, 50 mg/l for dyes, and 200 mg/l for organic contaminant, respectively. 0.1 mg of the prepared Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels were added to 10 ml of solution at room temperature. The adsorption capacities (Q) towards different pollutants were calculated according to the equation:

\[
Q = \frac{(C_i - C_f)V}{W_b}
\]

where \(C_i\) and \(C_f\) are the initial and final concentrations of pollutants, respectively, \(W_b\) is the weight of prepared hydrogel, and \(V\) is the volume of the solution. The concentration of pollutants’ uptake was determined spectrophotometrically using the standard calibration curve.

3. Results and discussion

3.1. Effect of the monomer concentration on gel (%)

The dependence of gel (%) on different monomer concentrations of MAAc and AAm hydrogels was represented in Figure 1. It is noted that for both Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels, the gel (%) increases with increasing the monomer concentration in the hydrogels compositions. This may be due to increase in the free radicals’ concentration, which increases the crosslinking of the hydrogel structures during irradiation copolymerization process, therefore increasing gel percent. The gel (%) of Poly(CMC/AAm) is higher than Poly(CMC/MAAc) hydrogel due to increase in H-bonding interactions among the amide group of AAm with hydroxyl groups of CMC chains within the polymeric matrix.[24–26]

3.2. Determination of grafting yield and grafting ratio

From Table 1, it was found that for both Poly(CMC/AAm) and Poly(CMC/MAAc), the grafting yield and grafting ratio increase with the increasing monomer concentration; this is due to increase in the number of the available free radicals formed by radiation and therefore higher degrees of grafting ratio and yield are obtained. Also, it is noted that higher values of grafting ratio and yield of Poly(CMC/AAm) are higher than that of Poly(CMC/MAAc). This may be due to steric effect of the structure of MAAc than that of AAm thus the diffusion of MAAc is lower than that of AAm; therefore, grafting process of Poly(CMC/AAm) is higher than that of Poly(CMC/MAAc).
3.3. Swelling behavior

The crosslinking can result in a dramatic change in the polymer properties such as the swelling behavior. Swelling is a very important factor for the applicability of the synthetic polymers. Figure 2(a,b) shows the effect of monomers’ concentration on the swelling percent of the prepared Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels’ composition. The equilibrium swelling behavior of Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels is calculated by Equation (4) as a function of time at different monomer concentrations. It was found that the swelling percent is significantly affected by the AAm content in Poly(CMC/AAm) hydrogel, that as AAm content increases in the hydrogel composition, the swelling behavior decreased. This may be due to the increase in the crosslinking density, which resulted in narrowing of the pore size and reducing the free spaces available to water retention, leading to a decrease in the value of osmotic force driving the water into the hydrogel network. Figure 2(a,b) shows the effect of time (h) on the swelling percent of (a) Poly(CMC/AAm) and (b) Poly(CMC/MAAc) hydrogels at different monomer concentrations and irradiation dose 20 kGy.

3.4. Swelling kinetics and diffusion mechanism

Water penetrates into the hydrophilic network of the hydrogel when they come in contact. In this process, water molecules migrate into the network through the free spaces between the polymer chains or spaces during the diffusion process. The relaxation rate and the mobility of the polymer chains which results in the diffusion of water into the network depend on the network structure and the characteristics of the diffuser solvent. The diffusion of water into the hydrogel was classified into three different types based on the relative rates of diffusion and polymer relaxation as mentioned in the experimental part. Figure 3(a–d) shows the relation between time and fraction of swelling due to water uptake. The diffusion constant ($D$) for the different compositions of Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels (1/20 wt%) is obtained from Figure 3(a–d); the apparent diffusion coefficient $D$ is obtained from the slope of the straight line. The $D$ values for the different compositions of Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels

| CMC/monomer ratio | Poly(CMC/AAm) | Poly(CMC/MAAc) |
|-------------------|---------------|----------------|
|                   | Grafting yield | Grafting ratio | Grafting yield | Grafting ratio |
| 1:10              | 808.4         | 908.4          | 638           | 738           |
| 1:15              | 1206.01       | 1306.01        | 1113          | 1213          |
| 1:20              | 1799.9        | 1899.9         | 1553          | 1653          |
| 1:25              | 2294.2        | 2394.2         | 1707.9        | 1807.9        |
| 1:30              | 2624.1        | 2724.1         | 2049.4        | 2149.4        |

Table 1. Effect of monomer ratio on the grafting yield and grafting ratio for both Poly(CMC/AAm) and Poly(CMC/MAAc).
that decreases with the increasing monomer concentration. The swelling exponent \( n \) is found to increase with decreasing diffusion coefficient. The enhancement of swelling exponent value leads to decreases in relaxation rate. It is noted that from the swelling and diffusion kinetic results of the prepared hydrogels, it depends on monomer concentration and the degree of crosslinking where high gelation percent hydrogels with higher monomer concentrations characterized by lower swelling compared to the hydrogels with lower gelation percent of low monomer concentration.[18]

have been analyzed for the prediction of water transport mechanisms. The diffusion constant \( (n) \) values are reported in Table 2 together with other swelling parameters. From the results, it can be concluded that water penetration may occur according to the non-Fickian transport mechanism since the values of the diffusion constant \( (n) \) range between 0.8 and 1.0 and that the anomalous diffusion occurs when the diffusion and relaxation rates are comparable.[14] The swelling/diffusion kinetic data results of the prepared hydrogels strongly depend on hydrogel networks, as well as the diffusion coefficient \( (D) \) that decreases with the increasing monomer concentration. The swelling exponent \( (n) \) is found to increase with decreasing diffusion coefficient. The enhancement of swelling exponent value leads to decreases in relaxation rate. It is noted that from the swelling and diffusion kinetic results of the prepared hydrogels, it depends on monomer concentration and the degree of crosslinking where high gelation percent hydrogels with higher monomer concentrations characterized by lower swelling compared to the hydrogels with lower gelation percent of low monomer concentration.[18]

Table 2. The diffusion parameters for the prepared hydrogels at different monomer concentrations and irradiation dose 20 kGy.

| CMC/AAm          | \( D \)  | \( N \)  | \( K \)  |
|------------------|---------|---------|---------|
| Poly(CMC/AAm)    |         |         |         |
| 1/15             | 0.172   | 0.609   | −2.1    |
| 1/25             | 0.263   | 0.561   | −1.75   |
| 1/30             | 0.120   | 0.675   | −0.6    |
| Poly(CMC/MAAc)   |         |         |         |
| 1/15             | 0.277   | 0.851   | −1.475  |
| 1/20             | 0.250   | 0.909   | −1.675  |
| 1/25             | 0.1     | 0.747   | −1.82   |
| 1/30             | 0.238   | 0.666   | −1.31   |

Figure 3. Variation of fractional swelling \( \ln(F) \) hydrogel with \( \ln(T) \) of (a) Poly(CMC/AAm) and (b) Poly(CMC/MAAc); fractional swelling \( (F) \) hydrogel with \( \ln(T) \) of (a) Poly(CMC/AAm) and (b) Poly(CMC/MAAc); fractional swelling \( (F) \) with \( (T^{1/2}) \) of (c) Poly(CMC/AAm) and (d) Poly(CMC/MAAc) at different monomer concentrations and irradiation dose 20 kGy.
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In case of Figure 4(b) for Poly(CMC/AAm) hydrogel, the presence of a broad absorption band at 3454 cm\(^{-1}\) is due to the overlap between OH stretching and N–H\(_2\) stretching frequency of NH\(_2\) group. A band at 3000 cm\(^{-1}\) is due to the C–H stretching vibrations. A band at 1711 cm\(^{-1}\) was due to the carbonyl group (C=O stretching) of the amide group of AAm, and the band at 1482 cm\(^{-1}\) is due to the bending of NH\(_2\) group. The peaks at 1449 and 1393 cm\(^{-1}\) represent the bending vibration for CH\(_2\) and CH\(_3\) groups; the band at 1267 cm\(^{-1}\) is due to OH bending vibration and the band at 963 cm\(^{-1}\) is due to the presence of C–O stretching. The presence of absorption band at 1176 cm\(^{-1}\) is due to C–C bond. The bands which characterize both CMC and AM bonds. The previous peaks ensure the formation of Poly(CMC/AAm) hydrogel.

In case of Figure 4(c) for Poly(CMC/MAAc) hydrogel, it shows that a broad absorption band at 3436 cm\(^{-1}\) is due to the stretching frequency of the –OH group. The band at 2930 cm\(^{-1}\) is due to C–H stretching vibration. The presence of a strong absorption band at 1652 cm\(^{-1}\) confirms the presence of C=O group, which characterizes both CMC and MAAc. The bands around 1447 and 1424 cm\(^{-1}\) are assigned to CH\(_2\) scissoring and CH\(_3\) bending vibration, respectively. The band at 1168 cm\(^{-1}\) is due to C–O group.

3.5. FTIR analysis

Infrared spectroscopy was carried out to identify the chemical structure of the original CMC and the prepared hydrogels. Figure 4(a,b,c) shows the FTIR spectra of original CMC and the prepared Poly(CMC/AAm) and Poly(CMC/MAAc) respectively.

In case of Figure 4(a) for CMC, it is clear that it shows a broad absorption band at 3443 cm\(^{-1}\) due to the stretching frequency of the −OH group. The band at 2921 cm\(^{-1}\) is due to C–H stretching vibration. The presence of a strong absorption band at 1608 cm\(^{-1}\) confirms the presence of C=O group. The bands around 1424 and 1328 cm\(^{-1}\) are assigned to CH\(_2\) and CH\(_3\) bending vibration, respectively. The band at 1024 cm\(^{-1}\) is due to carboxymethyl ether group > CH–O–CH\(_2\) stretching.[30]

3.6. Thermogravimetric analysis

The remaining weight (%) and the rate of thermal decomposition (dw/dt) were plotted as a function of temperature for original CMC and prepared Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) hydrogels, as shown in Figure 5(a,b). Also the degradation temperature °C of the prepared hydrogels were summarized in Table 3. For CMC, Figure 5(a), the initial weight loss at range 50–173 °C is due to the presence of small amount of moisture in the sample. The second stage of weight loss at range of 173–331 °C represents the degradation of CMC main chain with maximum weight loss at 300 °C attributed to complete decomposition. The rate of weight loss is increased with increase in temperature which corresponds to complete decomposition.

Figure 5(a,b) shows the TGA and the rate of thermal decomposition (dw/dt) curve for Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) hydrogels. It can be noted that there are three decomposition stages. The first stage is in the ranges 50–205 °C and 60–200 °C for both Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) hydrogels, respectively, which is due to the elimination of moisture. The second stage

Table 3. Summarized the degradation temperature °C of the prepared hydrogels.

| Hydrogel    | Maximum degradation temperature °C | Rate of thermal decomposition (mg/min) at maximum degradation temperature |
|-------------|------------------------------------|-----------------------------------------------------------------------------|
| CMC         | 294.2                              | 0.2102                                                                      |
| CMC/AAm     | 366.7                              | 0.1088                                                                      |
| CMC/MAAc    | 405                                | 0.2216                                                                      |
Equation (5) are shown in Table 4. It was found that the intensity of diffraction peaks of prepared hydrogels Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) is higher than original CMC. This is due to an increase in the degree of ordering of chains of the prepared hydrogels that the combination between CMC, AAm and MAAc individually increases the crosslinking of the hydrogels structure during copolymerization process. Also, due to increase in H-bonding interactions among amide group of AAm and carboxylic, methyl groups and hydroxyl groups of CMC chains within the polymeric matrix lead to increase crystallinity of Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels than original CMC.

3.7. X-ray study

Figure 6(a–c) represent the XRD patterns of the original CMC and prepared Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) hydrogels. The characteristic 2θ of original CMC and prepared Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) as well as particle size was calculated by using Scherrer Equation (5) are shown in Table 4. It was found that the intensity of diffraction peaks of prepared hydrogels Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) is higher than original CMC. This is due to an increase in the degree of ordering of chains of the prepared hydrogels that the combination between CMC, AAm and MAAc individually increases the crosslinking of the hydrogels structure during copolymerization process. Also, due to increase in H-bonding interactions among amide group of AAm and carboxylic, methyl groups and hydroxyl groups of CMC chains within the polymeric matrix lead to increase crystallinity of Poly(CMC/AAm) and Poly(CMC/MAAc) hydrogels than original CMC.

3.8. Scanning electron microscope

The SEM images of the cross section of the freeze-dried hydrogel samples of the prepared Poly(CMC/AAm) and Poly(CMC/MAAc) (1/20 wt%) hydrogels were carried out and shown in Figure 7(a,b). The cross sections of the samples exhibited micro-porous structure. Moreover, there was

| Polymers          | 2θ    | θ    | FWHM | Particle size D (Å) | Intensity |
|-------------------|-------|------|------|---------------------|-----------|
| CMC               | 19.7538 | 9.8769 | 1.1520 | 67.997             | 135       |
| Poly(CMC/AAm)     | 22.8333 | 11.4166 | 0.3721 | 223.5937           | 154       |
| Poly(CMC/MAAc)    | 15.8425 | 7.9212 | 0.7326 | 111.5954           | 241       |
3.9. Removal of hazardous water pollutants

3.9.1. Removal of heavy metals

Recently, the complexation–ultrafiltration technique has been shown to be a promising technique for the removal of heavy metals in solution.\[31\] In this study, Poly(CMC/MAAc) and Poly(CMC/AAm) which enhanced ultrafiltration process due to presence of multifunction groups (carboxylic, amide, and hydroxyl groups) are considered as the adsorption sites for heavy metals and have been investigated for removal of heavy metals in solution.\[31\]

Figure 6. XRD for (a) original CMC, and (b) Poly(CMC/AAm) (1/20 wt%) hydrogel, and (c) Poly(CMC/MAAc) (1/20 wt%) hydrogel.

Figure 7. SEM images of swollen (a) Poly(CMC/AAm) (1/20 wt%) hydrogel and (b) Poly(CMC/MAAc) (1/20 wt%) hydrogels.
3.9.2. Removal of dyes

Removal of cationic dyes from industrial effluents is still an important, yet a challenging subject in the field of environmental remediation. Annually, millions of tons of cationic dyes are consumed by the textile, rubber, paper, and plastic industries (in which about 10–20% is discharged in wastewater effluents).[33] These dyes cover thousands of different chemical structures. Most of them exhibit recalcitrant properties, such as high hydrophilicity and stability to light or heat. From the view of industrial application, removal of cationic dyes by adsorption is a promising approach because of its low performance cost and easy technical access.[34] Recently, particular attention has been paid to producing dye adsorbents from cellulosic polymers due to their advantages of being abundant, rapidly renewable, and biodegradable in nature.[11] The adsorbent products are usually prepared in the form of hydrogels owing to their three-dimensional porous inner structure, readily swelling behavior, and strong adsorption capacity of dyes. Many cellulose derivatives such as carboxymethyl cellulose are utilized for this process.[14]

Figure 8(a,b) represents the effect of the time on the adsorption capacity of Poly(CMC/MAAc) and Poly(CMC/AAm) hydrogels toward Cu\textsuperscript{2+} and Co\textsuperscript{2+} ions.

Figure 9(a,b) shows the effect of the time on the adsorption capacities of Poly(CMC/MAAc) and Poly(CMC/AAm) (1/20 wt%) hydrogels toward Cu\textsuperscript{2+} and Co\textsuperscript{2+}, respectively. From the Figure 8(a,b), it is observed that the adsorbed Cu\textsuperscript{2+} and Co\textsuperscript{2+} amount increases markedly with the increase in time. Also, the equilibrium adsorption capacities of the prepared hydrogels toward Cu\textsuperscript{2+} and Co\textsuperscript{2+} for both hydrogels occurred within 5 h. The presence of more chelating groups, carboxyl, hydroxyl, and amide groups, is considered as the adsorption sites for heavy metals.[32] It is observed that the adsorption capacity of Poly(CMC/MAAc) and Poly(CMC/AAm) (1/20 wt%) hydrogels toward Co\textsuperscript{2+} was higher than that of Cu\textsuperscript{2+}. Also the maximum value of metal uptake is very much dependent on the type of metal ions used and the steric effect of this hydrogel complexes.[31] Finally, the adsorption capacities of Poly(CMC/MAAc) hydrogel is greater than that of Poly(CMC/AAm) hydrogel due to the presence of more hydrophilic and chelating carboxylic groups in Poly(CMC/MAAc) hydrogel than amide group in Poly(CMC/AAm) hydrogel.

Figure 9. Effect of time (h) on the adsorption capacity of (a) Poly(CMC/AAm) and (b) Poly(CMC/MAAc) (1/20 wt%) hydrogels toward acid blue and methyl green dyes.
Conclusions

The synthesis of different pollutant adsorbent hydrogels based on CMC which are neither toxic nor expensive was successfully carried out using direct radiation grafting technique. This study will provide a solution to the discharge of different pollutants contaminating water leading to wastewater problem. The results show that the prepared Poly(CMC/MAAc) and Poly(CMC/AAm) (1/20 wt%) hydrogels possess high thermal stability and good hydrophilic properties. Removal of heavy metal ions such as Cu\(^{2+}\) and Co\(^{2+}\), cationic and anionic dyes such as acid blue dyes and methyl green, and organic contaminants such as P-chlorophenol and 2,4 dichlorophenoxy acetic acid from wastewater using adsorbent CMC hydrogel were studied. It is found that the adsorption capacity of the prepared hydrogel is mainly dependent on type of monomer used and chemical structures of the pollutants which are mainly dependent on their polarity and steric effect of these compounds.
Disclosure statement

No potential conflict of interest was reported by the authors.

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