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Anionic natural graft copolymer used in removal of hazardous dye water pollutants

Arti Srivastava*[,1], Pratibha Mandal[1] & Rajesh Kumar[2]

[1*]Department of Chemistry, Guru GhasidasVishwavidyalaya, Bilaspur-495 009, India
[2] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221 005, India
E-mail: artifeb@gmail.com

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The carboxymethyl cellulose (CMC), guar gum, sodium alginate and chitosan etc. are natural polysaccharides. This paper presents the synthesis and characterization of natural polymer carboxymethyl cellulose (CMC) and synthetic monomer acrylic acid (AA) based graft copolymer (CMC–g–AA) and its applications in removal of Methylene blue dye from industrial effluents. CMC–g–AA has been synthesized using free radical initiator and characterized by FTIR, TGA, and SEM analysis. The AA concentration has been varied from 5.5 x 10^{-2} to 35.5 x 10^{-2} mol dm^{-3} to get maximum grafting of AA monomer onto CMC. The FTIR spectral analysis proves the successful grafting. The synthesized graft copolymer (CMC–g–AA) has been applied in adsorption of a water soluble monovalent cationic dye such as Methylene Blue.

Keywords: Acrylic acid, Carboxymethyl cellulose, Dye removal, Graft copolymer, Redox pair.

The removal of synthetic dyes from industrial effluents is a significant environmental issue of global concern due to the challenges in treating industrial waste water using conventional methods[1]. In surface water environments presence of dyes even at very low quantities, it is undesirable. Additionally these pigments can hinder photosynthesis and inhibit the growth of aquatic plants by attenuating transmission of sunlight in aqueous environments. Synthetic dyes are usually organic compounds which are refractory in nature with changeable toxicity. Therefore various techniques have been recently reviewed and used for the treatment of dye–containing waste waters. These include solvent extraction, chemical oxidation, coagulation and flocculation, electrochemical, and adsorption based methods[2-8]. Among all these techniques, adsorption is attractive method because it is relatively low cost, technological simplicity, easy of operation, and good mechanical stability[9].

Methylene blue is a widely used organic dye in the chemical industry due to its high water solubility with various applications in dyeing of cottons, wools, and coating for paper stock, temporary hair colorants and coloring paper[10]. Methylene blue is hazardous when ingested through dermal contact, digestion, and breathing. Acute exposure to Methylene Blue will cause increased heart rate, shock, vomiting, quadriplegia, cyanosis, jaundice, Heinz body formation, and tissue necrosis in humans. Adsorptive removal of Methylene blue with activated carbon is effective due to its high adsorptive capacity, high surface area, microporus structure and its high degree of surface reactivity. However, commercial activated carbon is generally expensive and difficult to regenerate after usage[11].

Now a day, there is a great attention in the development of new adsorbents having high adsorption capacity and fast adsorption rate for wastewater treatment. Hydrogels possessing different functional groups have been investigated in the preceding literature for this purpose[12-15]. Chemical cross-links through N,N–methylene bis acrylamide (covalent bonds) or physical junctions (e.g., secondary forces, crystallite formation and chain entanglements) provide the hydrogels unique swelling behavior and three dimensional structure[16,17]. These materials are of great interest due to their promising applications such as heavy metal adsorption[18,19], wound dressing,[20] super absorbent,[21,22] adsorbent for dye removal[23] and drug-delivery systems[24,25]. Hydrogels can be prepared by graft copolymerization and crosslinking of one or more monofunctional and one multifunctional monomer or by crosslinking of a homopolymer or copolymer in solution. In recent years, considerable researches have been done on the characterization and swelling behavior of synthetic hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent[26-31]. They can also show stimuli-responsive properties to the various external parameters such as temperature, *p*H, solvent composition and salt composition depending on the type of functional groups in the structure[32,33]. The present work was aimed to synthesize polymeric hydrogels based on acrylic acid (AA) and carboxymethyl cellulose (CMC) using N,N–methylenebis acrylamide (MBAAm) as crosslinking agent. In this work, it has been aimed to study a convenient method for removing the water soluble monovalent cationic dye such as Basic Blue 9 (Methylene blue) from aquous solutions by adsorption on novel polymeric adsorbent such as AA/CMC/MBAAm hydrogels.

Carboxymethyl cellulose (CMC) is the most important anionic water–soluble linear polysaccharide and it is prepared by the partial substitution of the –OH groups of glucose repeating unit of cellulose molecular chain by introducing carboxymethyl group (–CH_2COOH) (Fig. 1 shows the structure of carboxymethyl cellulose. It has received much attention due to its exclusive properties such as low cost, hydrophilicity, transparency, high viscosity, non-toxic, biodegradability, biocompatibility, good film forming ability[34-36]. Carboxymethyl cellulose is useful in which hydrophilic colloids are indicated. The basic properties that enhance its commercial value are its abilities to thicken water, suspend solids in aqueous media, stabilize emulsions, and absorb moisture from the atmosphere. These properties have been, utilized widely in divergent applications such as, textile processing industries, formulation agents for the controlled release of pesticides and drugs,[37] paper industry,[38] tissue engineering,[39] food industry,[40] cosmetics,[41] pharmaceuticals,[42] tablet excipients,[43] adhesives,[44] water treatment through oil recovery, detergents, and oil well drilling operations[45,46]. In current years, the chemical modification of carboxymethyl cellulose by the grafting of hydrophilic vinyl monomers (nonionic, cationic or anionic), such as acrylonitrile, acrylamide,[47] acrylic acid,[48] and trimethyl allyl ammonium chloride has gained extensive attention for preparing new polymeric materials with extraordinary properties. The graft copolymerization of carboxymethyl cellulose and its derivatives with hydrophilic monomers has received considerable attention during the past decades as a convenient way of introducing ionizable or other polar groups into the cellulose backbone.

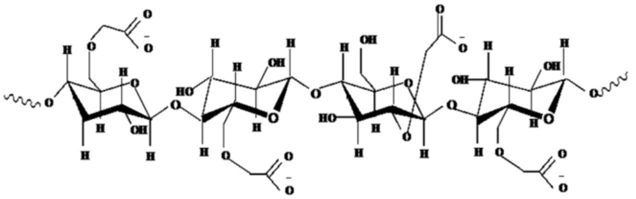

Fig.1 — Structure of Carboxymethyl Cellulose

Experimental Section

Materials

Acrylic acid (AA) was purchased from Sigma Aldrich Chemicals (USA) and used after distillation, and it is distilled under vacuum at 9 mm Hg pressure and at 40˚C. Carboxymethyl cellulose (CMC) and N,N–methylenebis acrylamide (MBA) (Fig. 2) were purchased from Hi Media Chemical, Mumbai, India. Potassium Bromate, Thiourea and Methylene Blue were supplied by Merck Chemicals. Triple distilled water was used for polymerizations, swelling and adsorption experiments. All the chemicals are analytical grade.

Synthesis of (CMC-g-AA) copolymer

For synthesis of graft copolymer, carboxymethyl cellulose (CMC) solution was prepared by adding the calculated amount of CMC in required amount of triple distilled water. The calculated amount of acrylic acid, sulphuric acid and thiourea and N,N–methylenebis acrylamide solutions were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium bromate solution was added to initiate the reaction. The reactions were performed under a continuous flow of oxygen free nitrogen gas.

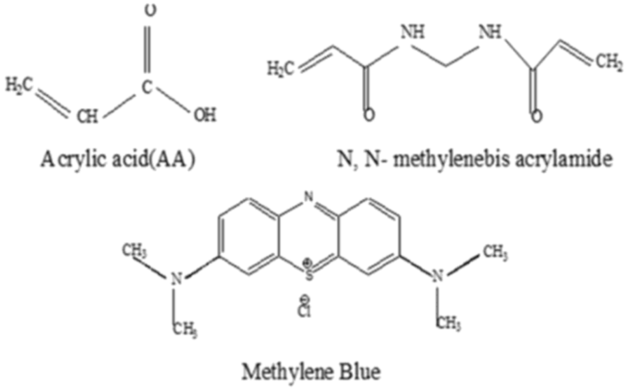

Fig. 2 — Structure of acrylic acid, N,N–methylenebis acrylamide, methylene blue

After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample was precipitated by pouring the reaction mixture into water methanol mixture. The precipitate was dried and weighed.

Swelling studies

The swelling behaviors of weighed dried hydrogel samples were carried out by immersion in distilled water at room temperature. The graft copolymeric gels were gently wiped and weighed to determine the water absorbed at various time intervals. The swollen gels were weighed by an electronic balance with an accuracy ± 0.0001 g. The effect of *p*H on the swelling properties was studied using buffers solutions. All swelling studies were carried out in 150 mL of swelling medium. The swelling studies were carried out until equilibrium in swelling was reached. Swelling measurements were done two or three times. The total uncertainty for all experiments ranged from 3 to 5 %. The swelling ratio was calculated using the following equation:

$$\% S = \frac{M_t - M_0}{M_0} \times 100 \qquad \ldots (1)$$

where, M_t and M_o refer to the weight of swollen hydrogel at time t and at time 0, respectively.

The equilibrium degree of swelling S_{eq}, after hydrogels had swollen to equilibrium in the swelling media was calculated using the following equation:

$$\% S_{eq} = \frac{M_{eq} - M_0}{M_0} \times 100 \qquad \ldots (2)$$

Here, M_{eq} is the mass of the swollen hydrogel sample at equilibrium.

The water absorbed by CMC–g–AA polymeric hydrogels is quantitatively represented by the equilibrium water content (EWC),[28, 29] where

$$EWC = \frac{M_{eq} - M_0}{M_{eq}} \qquad \ldots (3)$$

Characterization techniques

The synthesized hydrogel was characterized by various type of characterization method.. FTIR spectra of CMC and CMC–g–AA were recorded on FTIR-4100 spectrophotometer product of Jasco, Japan. TGA–50 Shimadzu, Thermogravimetric analyzer was used for the measurement of thermal analysis. The nitrogen flow rate was 20 ml/min and the heating rate was 10°C/min from ambient temperature up to 800°C. JEOL–JSM–5400 scanning electron microscope (SEM) was used for investigating the porous structure and morphology of the prepared CMC–g–AA polymeric hydrogel. UV–Vis spectra of dye solution were recorded on a Shimadzu UV 1800 spectrophotometer using a 10 mm path length quartz cuvette.

Results and Discussion

FTIR Analysis

Infrared spectroscopy was carried out to identify the chemical structure of the original CMC and the prepared hydrogels. Figure 3 shows the FTIR spectra of original CMC and the prepared

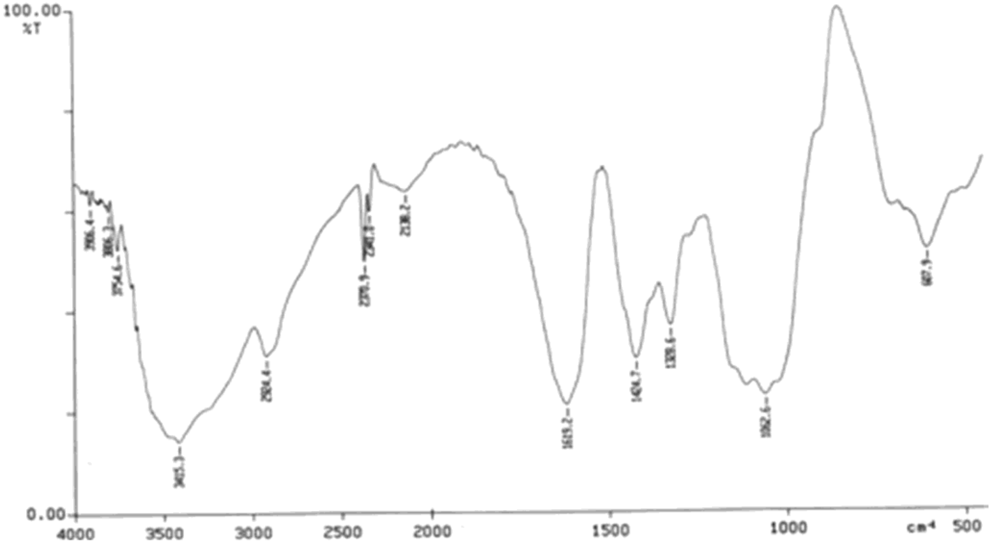

Fig. 3 — FTIR of Carboxymethyl cellulose (CMC)

AA/CMC/MBAAm hydrogel respectively. In case of Fig. 3 for CMC, it is clear that it shows a broad absorption band at 3415 cm^{-1} due to the stretching frequency of the –OH group. The band at 2924 cm^{-1} is due to C–H stretching vibration. The presence of a strong absorption band at 1619 cm^{-1} confirms the presence of –COO 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.

In case of Fig. 4 for CMC-g-AA graft polymeric hydrogel, the presence of a broad absorption band at 3404 cm^{-1} is due to the overlap between –OH stretches and NH_2 stretching frequency of NH_2 group. A band at 2927 cm^{-1} is due to the C–H stretching vibrations. A band at 1732 cm^{-1} was due to the carbonyl group (C=O stretching) of the carboxylic acid group of AA, The band at 1096 cm^{-1} is due to OH bending vibration and the band at 792 cm^{-1} is due to the presence of C–O stretching. The presence of absorption band at 1096 cm^{-1} is due to C–C bond, the bands which characterize both CMC and AA molecule. The previous peaks ensure the formation of CMC–g–AA graft polymeric hydrogel.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a procedure in which a material is decomposed by heating, which causes bonds within the molecule to be broken. TGA plays an important role in determining thermal stability of the materials. The TGA curves have been recorded on TGA–50 Shimadzu, thermal analyzer within a temperature range 0–900°C and with a heating rate of 10°C per minute in an atmosphere of Nitrog°en. Figure 5 shows the degradation of sodium

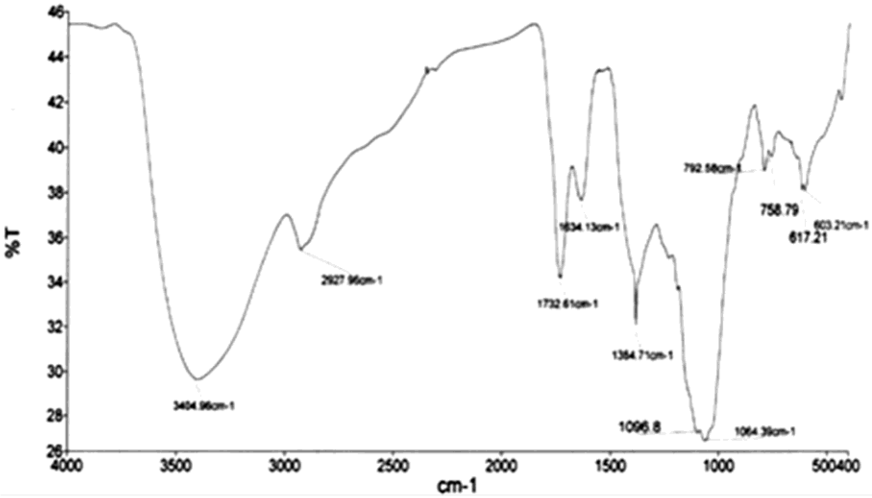

Fig. 4 — FTIR of CMC-g-AA

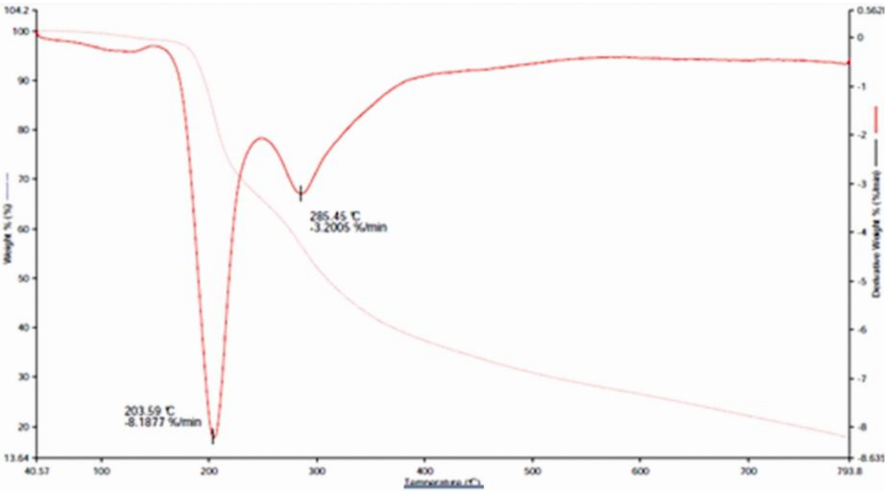

Fig. 5 — TGA of Carboxymethyl cellulose

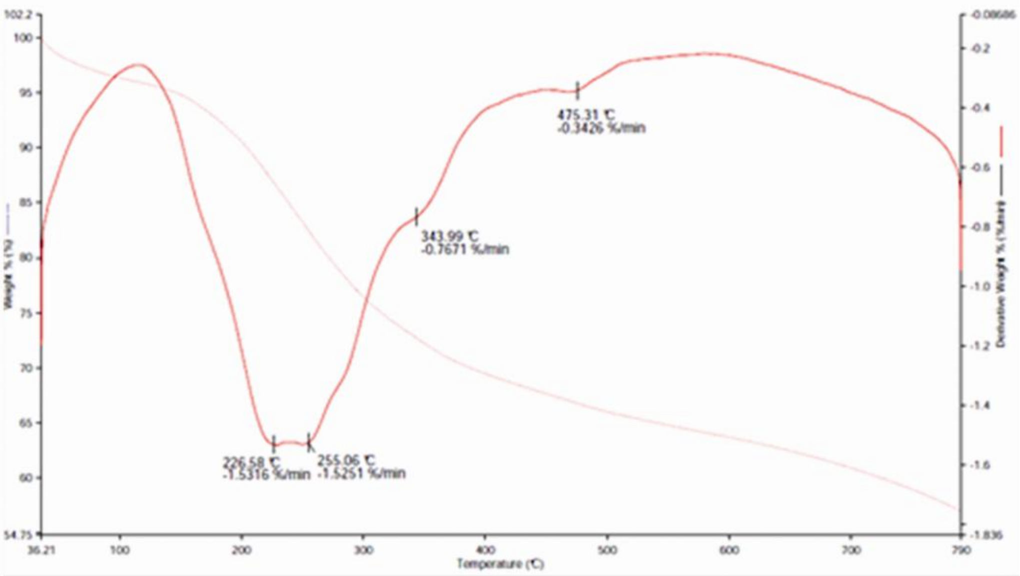

Fig. 6 — TGA of CMC-g-AA

carboxymethyl cellulose starts at about 140°C. The degradation occurs in two stages, that is, from 140 to 288°C and from 288 to 500°C. The polymer decomposition temperature (PDT) and final decomposition temperature (FDT) have been found as 140 and 385°C respectively, and temperature at which maximum degradation occurs which is called T_{max} has been found at 280°C and it is due to the loss of CH_2COO group from CMC. The char yield was found to be 20 % at 800°C.

TGA curve of graft copolymer show Fig. 6 that the thermal stability of the CMC–g–AA due to the grafting of AA and graft copolymer of carboxymethyl cellulose began to degrade at about 150°C. About 1.5 % mass loss observed at 200°C and it might be due to the loss of absorbed water. The degradation of CMC–g–AA occurs in three stages. The PDT was found to be 110°C, and it is due to elimination of groups from grafted polymer chain. The first T_{max} found to be 215°C and it is due to the loss of $-CH_2COO$ group from parental backbone. The second and third T_{max} were found at 343°C due to the elimination of water and CO_2 respectively. The higher value of FDT and char yield that are 580°C and 35% at 800°C respectively than CMC which prove the high thermal stability of graft copolymer.

Scanning Electron Microscopy (SEM) analysis

SEM micrographs of ungrafted and AA grafted carboxymethyl cellulose are shown in Fig. 7 By comparing the surface morphology of grafted carboxymethyl cellulose Fig. 7(b) with that of ungrafted carboxymethyl cellulose Fig. 7(a), found that the grafted chains drastically changed the morphology of carboxymethyl cellulose. As shown in Fig. 7(b), the surface of the CMC–g–AA copolymer was more uneven than that of Carboxymethyl cellulose, and this is another proof of grafting. A closure inspection of micrographs reveals that there is large difference in the morphological appearance of the native natural polysaccharide and the graft

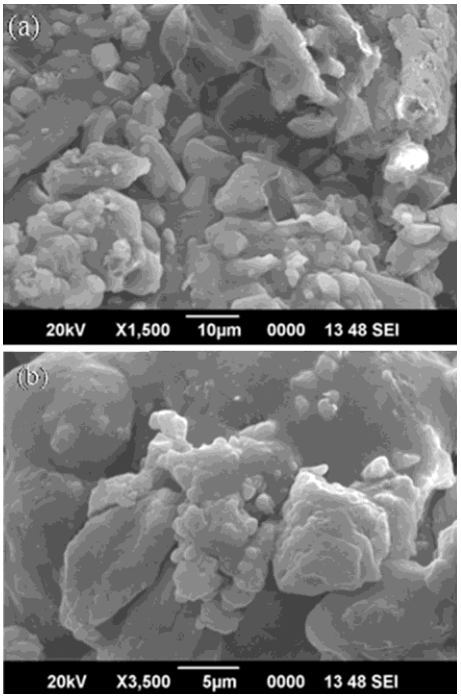

Fig. 7 — SEM images (a) CMC (b) CMC-g-AA

copolymer. Carboxymethyl cellulose has granular morphology. After grafting, the granular appearance of the native CMC was distorted and transferred smooth morphology, as the grafted AA chains got agglomerated. This observation implies of AA affects the morphological characteristics of carboxymethyl cellulose.

Swelling studies

The swelling behaviors of the AA/CMC/MBAAm hydrogels in pure water, at 45°C is plotted in Fig. 8. All the hydrogels swelled rapidly, reaching equilibrium within 3 hour. Sample AA/CMC/MBAAm 3 showed the highest swelling ratio for the time – dependent swelling behavior and AA/CMC/MBAAm 1 the lowest. AA was found to be more hydrophilic. Since AA/CMC/MBAAm 3 contained more hydrophilic groups within its structure, its swelling ratio should be the highest of the hydrogels prepared. Figure 8 also shows the temperature-dependent swelling behavior of the AA/CMC/MBAAm random copolymer hydrogels in pure water. The swelling ratios of the hydrogels increased with increasing the temperature. The thermo sensitive hydrogel could be described as either a positively or a negatively temperature sensitive system. In a positively temperature-sensitive system, hydrogels with an upper critical solution temperature (UCST) shrink by cooling below the UCST, while hydrogels with a lower critical solution temperature (LCST) contract by heating above the LCST in a negatively temperature sensitive system. In an aqueous system, the temperature dependence of swelling of a hydrogel is closely related to the temperature dependence of the polymer–water and polymer–polymer interaction. The AA/CMC/MBAAm hydrogels exhibited a temperature-responsive swelling behavior, due to the association/dissociation of the hydrogen bonding of the carboxyl groups in the AA and the amide groups in the MBAAm of the hydrogels. Hydrogel samples at low temperature swell through a diffusion process only, because hydrogen bonds may not be destroyed at low temperature. Meanwhile, hydrogel samples at a high temperature adsorb more water than at low temperature, because the dissociation of hydrogen bonding at higher temperatures generates carboxylate ions which cause ionic repulsion.

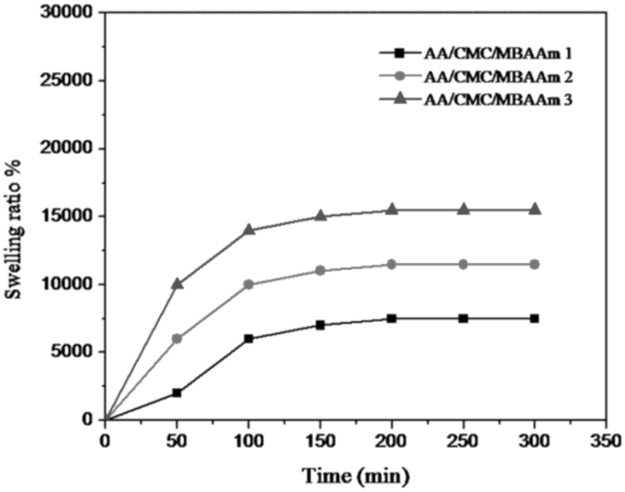

Fig. 8 — Swelling behavior of AA/CMC/MBAAm

Removal of dyes

The effect of contact time on the adsorption of MB onto the prepared hydrogel at an initial concentration of 100 ppm from 0 to 500 min was investigated to identify the rate of dye removal. As depicted in Fig. 9 the adsorption increases with the increasing contact time and rapid adsorption of MB was observed during the initial 250 min. The amount of MB adsorbed increased rapidly in the early stage and then increased more slowly over extended periods, gradually approaching adsorption equilibrium (Fig. 10). This is due to approaching adsorption equilibrium. This is due to availability of active binding sites on the sorbent at the initial stage. With gradual occupancy of binding sites, the sorption became slower in the later stage. A contact time of 8 hour was sufficient to reach equilibrium. Therefore sorption experiments were conducted for 8 hour.

Adsorption experiments

For the dye adsorption, accurately weighed hydrogels (12 mg) were immersed in water for at least 12 h to achieve the swelling equilibrium. Adsorption

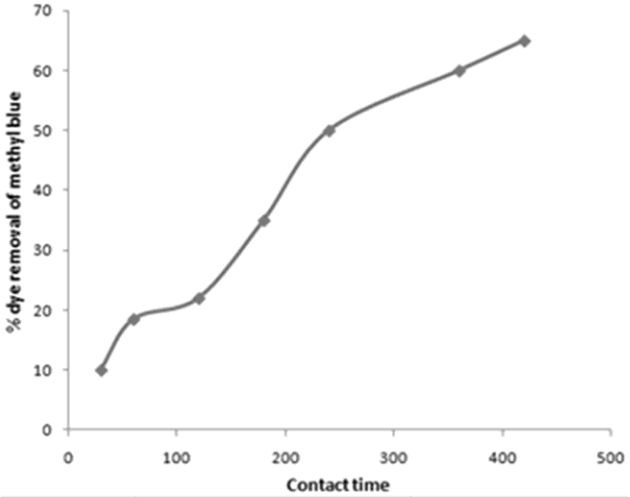

Fig. 9 — Effect of contact time on dye adsorption

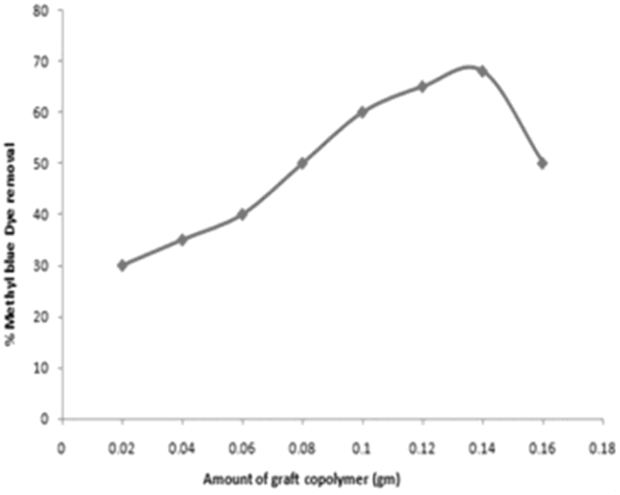

Fig. 10 — Effect of amount of graft copolymer

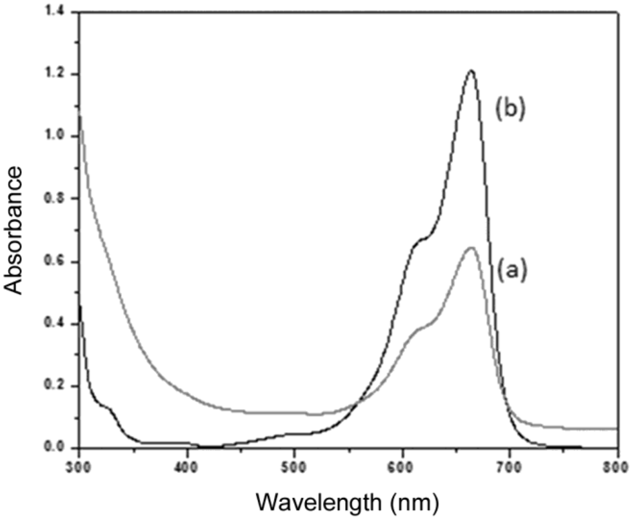

Fig. 11 — UV Spectra (a) after adsorption (b) before adsorption

experiments were carried out at room temperature, in cylindrical glass vessels, by using batch conditions. In these experiments, the swollen samples of the prepared hydrogels were immersed in MB dye solutions (10 mL) with concentration of 100 mg/L. The amount of residual dye in the solution was determined at regular time using a UV–Vis spectrophotometer (Fig. 11). All of the experiments were performed in triplicate and the average was used in this work. The influence of *p*H on MB removal was investigated in detail. The influence of *p*H on MB removal was studied by adjusting MB solutions (100 mg/L) to 8 *p*H values using a pH meter.

The amounts of adsorbed dye per unit mass of adsorbent at time t (Q_t, mg g^{-1}) and at equilibrium (Q_e, mg g^{-1}) were calculated by using the following expressions:

$$Q_t\,(\text{mg/g}) = \frac{(C_i - C_t)\,V\,(L)}{m\,(g)} \qquad \dots (4)$$

$$Q_t\,(\text{mg/g}) = \frac{(C_i - C_e)\,V\,(L)}{m\,(g)} \qquad \dots (5)$$

where C_i and C_e are the initial and equilibrium concentrations of dye (mg/L), respectively and Ct is dye concentration at time t, V is the volume of the solution added (L) and m is the amount of polymer (g).

Conclusion

The synthesis of dye adsorbent copolymers based on CMC which are neither toxic nor expensive has been successfully carried out using free radical polymerization technique. The results show that the prepared CMC–g–AA polymeric hydrogel possessed high thermal stability and good hydrophilic properties. It is found that the adsorption capacity of the prepared graft copolymeric 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. The copolymer is used in adsorption of the MB dye from aqueous solutions.

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References

1 Forgacs E, Cserháti T & Oros G, *Environ Int*, 30 (2004) 953.
2 Tünay O, Kabdasli I, Eremektar G & Orhon D, *Water Sci Technol*, 34 (1996) 9.
3 Pandit P & Basu S, *Environ Sci Technol*, 38 (2004) 2435.
4 Kim T H, Park C, Yang J & Kim S, *J Hazard Mater*, 112 (2004) 95.
5 Papis S, Koprivanac N, Bozic A L & Metes A, *Dyes Pigments*, 62 (2004) 291.
6 Moghaddam S S, Alavi Moghaddam M R & Arami M, *J Hazard Mater*, 175 (2010) 651.
7 Martinez Huitle C & Brillas E, *Appl Cataly B Environ*, 87 (2009) 105.
8 Garg V K, Gupta R, Yadav A B & Kumar R, *Bioresour Tech*, 89 (2003) 121.
9 Sanghi R & Bhattacharya B, *Color Technol*, 118 (2002) 256.
10 Kumar K, Ramamurthi V & Sivanesan S, *J Colloid Interf Sci*, 284 (2005) 14.

11 Ozcan A & Ozcan A, *J Colloid Interf Sci*, 276 (2004) 39.

12 Salama A, Shukry N & El-Sakhawy M, *Int J Biol Macromol*, 73 (2015) 72.

13 Vesna V P, Madzarevic Z P, Volkov-Husovic T & Velickovic S J, *Chemical Eng J*, 217 (2013) 192.

14 Bhattacharyya R & Ray S K, *J Indus Eng Chem*, 20 (2014) 3714.

15 Hosseinzadeh H & Khoshnood N, *Desalin Water Treat*, 57 (2015) 1.

16 Hoffman A S, *Adv Drug Deliv Rev*, 54 (2002) 3.

17 Garcia D M, Escobar J L, Noa Y, Bada N, Hernaez E & Katime, *Euro Polym J*, 40 (2004) 1683.

18 Li Z, Wang Y, Wu N, Chen Q & Wu K, *Environ Sci Pollu. Res*, 20 (2013) 1511.

19 Hui B & Ye L, *J Ind Eng Chem*, 35 (2016) 309.

20 Kanarat N, Nantarat S, Chinanat W & Robert M, *Chiang Mai J Sci*, 34 (2007) 183.

21 Hosseinzadeh H, *Curr Chem Lett*, 2 (2013) 153.

22 Thakur S, Pandey S & Arotiba O A, *Carbohydr Polym*, 153 (2016) 34.

23 Fang F, He W, Xue H & Chen W, *Reac Funct Polym*, 102 (2016) 1.

24 Hong K H, Jeon Y, Chung D J & Kim J, *Macromol Res*, 18 (2010) 204.

25 Atta S, Khaliq S, Islamb A, Javeria I, Jamil T, Athar M M, Shafiq M I & Abdul Ghaffar, *Intern J Biological Macromol*, 80 (2015) 240.

26 El Hamshary H, *Euro Polym J*, 43 (2007) 4830.

27 Mohan Y M, Murthy P S K & Raju K M, *Reac Funct Polym*, 63 (2005) 11.

28 Gundogan N, Okay O & Oppermann W, *Macromol Chem Phys*, 205 (2004) 814.

29 Caykara T & Akcakaya I, *Euro Polym J*, 42 (2006) 1437.

30 Thakur A, Wanchoo R K & Singh P, *Chem Biochem Eng Q*, 25 (2011) 181.

31 Mittal H, Jindal R, Kaithb B S, Maity A & Ray S S, *Carbohydr Polym*, 115 (2015) 617.

32 Ohmine I & Tanaka T, *J Chem Phys*, 77 (1982) 5725.

33 Katayama S, Hirokawa Y & Tanaka T, *Macromol*, 17 (1984) 2641.

34 Togrul H & Arslan N, *Food Hydrocolloids*, 18 (2004) 215.

35 Butun S, Gul Ince F, Erdugan H & Sahinner N, *Carbohydrate polymer*, 86 (2011) 636.

36 Yai H, Songkhla, *Inter Food Research J*, 15 (2008) 237.

37 Barkhordari S & Yadollani M, *Appl Clay Sci*, 121 (2016) 77.

38 Joshi G, Naithani S, Varshney V K, Bisht S S, Rana V & Gupta P K, *Carbohydr Polym*, 38 (2015) 33.

39 Sainitya R, Sriram M, Kalyanaraman V, Dhivya S, Saravanan S, Vairamani M, Sastry T P & Selvamurugan N, *Intern J Biological Macromol*, 80 (2015) 481.

40 Mondal M I H, Yeasmin M S & Rahman M S, *Intern J Biological Macromol*, 79 (2015) 144.

41 Ullah H, Santos H A & Khan T, *Cellulose*, 23 (2016) 2291.

42 Liu J, Zhan X, Wan J, Wang Y & Wang C, *Carbohydr polym*, 121 (2015) 27.

43 Wang C, Huang H, Jia M, Jin S, Zhao W & Cha R, *Carbohydr polym*, 130 (2015) 275.

44 Dekina S, Romanovsha I, Ovsepyan A, Tkach V & Muratov E, *Carbohydr polym*, 147 (2016) 208.

45 Bakry A M, Fang Z, Ni Y, Cheng H, Chen Y Q & Liang Li, *Food Hydrocolloids*, 60 (2016) 559.

46 Ladeira S A, Cruz E, Delatorre A B, Barbosa J B & Martins M L L, *Electro J Biochem*, 18 (2015) 56.

47 Ogbeifun D E & Okieimen F E, *J Science*, 15 (2004) 53.

48 Tulain U R, Ahmad M, Rashid A, Malik M Z & Iqbal F M, *Adv Polym Tech*, 37 (2018) 290.