ORIGINAL ARTICLE

Adsorptive removal of chromium(VI) from aqueous solution using binary bio-polymeric beads made from bagasse

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Abstract

In this study, bio-polymeric gel beads were made from synthetic and laboratory-made CMC (bagasse). Calcium chloride cross-linked with sodium alginate (Na-Alg) added to CMC displayed great affinity for the removal of hexavalent chromium (Cr(VI)) ions present in an aqueous solution. Activated carbon obtained from bagasse was also used for adsorptive removal of Cr(VI) ions from aqueous solution. The effect of different adsorption parameters such as pH, contact time and adsorbent dosage was studied. Bio-polymeric gel beads and activated carbon were prepared and characterized by SEM, FTIR and XRD. The maximum percentage removal for synthetic and bagasse bio-polymeric gel beads reaches 94.56% and 98.42% values at a pH of 4.0 at 25 °C and for activated carbon 64.79% value at a pH of 6.0 at 25 °C. Higher degree of substitution results in an increase in the percentage removal of Cr(VI) ions due to the increase in the surface area and the binding sites of the adsorbent. Our study suggests that bio-polymeric gel beads made from laboratory-made CMC (bagasse) can be used in a more cost-effective and efficient way for the removal of harmful chromium ions.

Keywords Carboxymethyl cellulose (CMC) · Sodium alginate · Gel beads · Activated carbon

Introduction

Heavy metals, widely used in industrial wastewater, are extremely toxic to human kidneys, liver, lungs and intestines. Discarded chromium (Cr) is a general toxic heavy metal pollutant present in wastewater, where it basically exists in two stable oxidation states, i.e., trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Chromium is widely used in industries like electroplating, leather tanning, ceramics, pigment manufacturing, ceramics, wood preservation and manufacturing of paper. Chromium is used in leather tanning process in large quantity to stop water diffusion inside leather pores. Cr(VI) is primarily present in the form of chromate (CrO_4^{2-}) and dichromate (CrO_7^{2-}) ions. On the other hand the Cr(VI) is also 500 times more toxic than the trivalent form (Garg et al. 2007; Fahim et al. 2006). Cr(VI) is a very soluble and toxic chromate anion and is a distrusted carcinogen and mutagen. The conventional physical and chemical methods used for the chromium removal from wastewater include reduction, solvent extraction, precipitation, ion exchange, membrane filtration, reverse osmosis and adsorption (Sathish et al. 2015). Precipitation process is favored, but the major drawback is sludge formation. Ion exchange is a better technique, but its operating cost is high. Cellulose is a linear and high molecular weight polymer, and due to the presence of inter- and intra-molecular –OH bond, it neither melts nor dissolves easily in common solvents and it can be chemically modified to increase its metal-binding ability (Yang et al. 2011; Selvi et al. 2001; Khezami and Capart 2005). Cellulose is highly crystalline in nature, and this high crystallinity results in low adsorption capacity for heavy metal ions such as chromium. Adsorption on bio-polymeric adsorbent made from CMC which is extracted from cellulose is an extremely effective way for the removal of heavy toxic metals because of low cost and high feasibility. Activated carbon is also efficient in the removal of heavy metals because of its low cost and easy regeneration of the carbon. Cr(VI) adsorption

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is dependent on pH, and maximum removal takes place between pH 5 and 6 for activated carbon. It is an amorphous solid involving of microcrystallites with a graphite lattice, and they are nonpolar, highly porous, usually equipped in powder form (Abdulrazak et al. 2017; Fahim et al. 2006). Natural bio-polymeric beads offer number of advantages such as nontoxic, inexpensive, renewable, biodegradable, modifiable, etc. This is an efficient method for the removal of heavy metals from wastewater. In this study, we focus on bio-polymeric gel beads made from carboxymethyl cellulose (CMC). CMC is a water-soluble polysaccharide formed by mercerization and etherification process. CMC displays alkaline solubility when the degree of substitution is about 0.3 and displays water solubility when the degree of substitution is above 0.4 (Kumar et al. 2018). CMC is highly amorphous in nature and has high adsorption capacity for heavy metal ions removal. CMC is widely used in oil exploration, detergents, cosmetics, paper products, food and textile industries. Synthetic CMC obtained directly from market offers 0.51 degree of substitution (DS), and laboratory-made CMC from bagasse has a DS of 0.65 (Gulati et al. 2014; Joshi et al. 2015; Mohkami and Talaeipour 2011). This higher DS of laboratory-made CMC results in better use in the commercial products (Yeasmin and Mondal 2015). Na-Alg is a natural polysaccharide biopolymer mainly composed of mannuronic and guluronic acid and contains free carboxyl groups which make it attractive addition to CMC. Alginate can be cross-linked with several divalent and trivalent cations (i.e., Ca, Ba and Fe) to form a stable gel (Pourjavadi et al. 2006; Ren et al. 2016). The main objective of the current study is to calculate the adsorption capacity of bio-polymeric gel beads made from synthetic CMC and laboratory-made CMC (bagasse) and activated carbon obtained from bagasse waste for the efficient removal of Cr(VI) from the aqueous solution by varying the pH, adsorbent dosage and contact time. The bio-polymer gel beads obtained were characterized and analyzed by infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction analysis.

Materials and methods

Raw material

The chemicals used to make bio-polymeric beads were synthetic CMC having high molecular weight ($M_w = 10,000$ Da, DS = 0.51) that was obtained from Molychem. We manufactured the CMC from bagasse (DS = 0.65). All the other chemicals used were of analytical grade.

Cellulose isolation from bagasse waste

Removal of moisture and reduction in size

First, half kilogram of bagasse was dry in distilled water for 24 h to eliminate water-soluble extractives and dried in an oven at 75 °C for 2 days. Afterward, bagasse was grind to pass through a 60-mesh size screen.

Acid hydrolysis

Dilute sulfuric acid (4% v/v) can lead to the enzymatic biomass hydrolysis to eliminate hemicelluloses sugars through stirred at the temperature of 80 °C for 2 h. The treated fibers were washed with Millipore water to attain pH 7. The filtered bagasse fibers were dried in an oven at 70.0 °C temperature.

Alkali treatment

2% NaOH was fed to the reactor at 80.0 °C to temperature for 2 h to enhance the swelling of the inner surface and reduces crystallinity and lignin structure disturbance. The treated fibers were filtered and washed with Millipore water to attain pH 7. The filtered bagasse fibers were dried in an oven at 70.0 °C temperature.

Bleaching

Whiteness was obtained by using sodium chlorite (4% w/v) at 80.0 °C for 4 h. The pH maintained during bleaching process was within 3–4 adjusted by adding acetic acid drop by drop. After washing, cellulose fibers were dried in an oven at 70 °C temperature.

Production of CMC from cellulose

The cellulose produced from bagasse was dried in an oven for 1 h at 70.0 °C temperature, and after that, it was placed in the desiccator to avoid moisture. There are two steps for the production of CMC mercerization followed by etherification.

Mercerization

In total, 100 ml isopropanol in 100 ml of 20% w/v NaOH solution was mixed with 10 grams of cellulose sample that helps to break the inter- and intra-molecular –OH bonding. The mixture was stirred for 2.5–4 h and increased the temperature from 50.0 to 60.0 °C. The washed alkali cellulose

fibers were filtered and dried in an oven for 3–4 h s at 70.0 °C, and then, it was sent for etherification process.

Etherification

In total, 100 ml of 20% MCA (monochloroacetic acid) solution was mixed with mercerized cellulose and stirred for 2.5–4 h from 50 to 60 °C to support and substitute the –OH groups with the CH_2COOH groups. After etherification reaction, it was filtered and washed with HCl and ethanol mixture (mixed in equal volume). HCl causes neutralization of any NaOH remaining, and ethanol removes salt formed during the side reaction. The remaining residue on filter paper was the CMC produced which was then dried in an oven at 60.0 °C temperature for 12 h (Gulati et al. 2014; Kumar et al. 2009). The complete schematic representation of synthesis of carboxymethyl cellulose from cellulose is displayed in Scheme 1.

Preparation of bio-polymeric beads

The polymer beads were prepared by using both CMCs (synthetic and laboratory made) and sodium alginate (0.5 g each) by mixing in 100 ml of distilled water. To form granular beads 0.05 M $CaCl_2$ was added in the mixture which acted as cross-linking agent, thus helping in the formation of gelting beads with constant slow stirring. After 24 h, gelatin beads were removed and washed with distilled water with number of times to make it free from several unreacted ions. Afterward the polymeric beads were stored in distilled water at room temperature. The whole process of preparation of bio-polymeric gel beads from laboratory-made CMC is shown in Fig. 1.

Preparation of activated carbon from bagasse waste

Activated carbon was prepared from sugarcane bagasse waste under nitrogen atmosphere. The pyrolysis of waste was done at 800 °C. After pyrolysis, the char was soaked with potassium hydroxide (KOH) and mixture was dried overnight at 90 °C. The produced activated carbon was transferred to a beaker containing hydrochloric acid (0.1 mol/l) (to remove inorganic compounds), stirred for 1 h and then washed with warm deionized water to remove residual HCl, until the pH of the solution neutralized and then filtered. The filtered activated carbon was dried in an oven at 90 °C overnight (Eslami et al. 2018).

Preparation of the chromium solution

Chromium solutions of 1000 mg/dm^{-3} were prepared by dissolving 0.245 mg $K_2Cr_2O_7$ in 1000 ml of double-distilled water. The required operational solutions of different concentrations were prepared by proper dilution of the stock
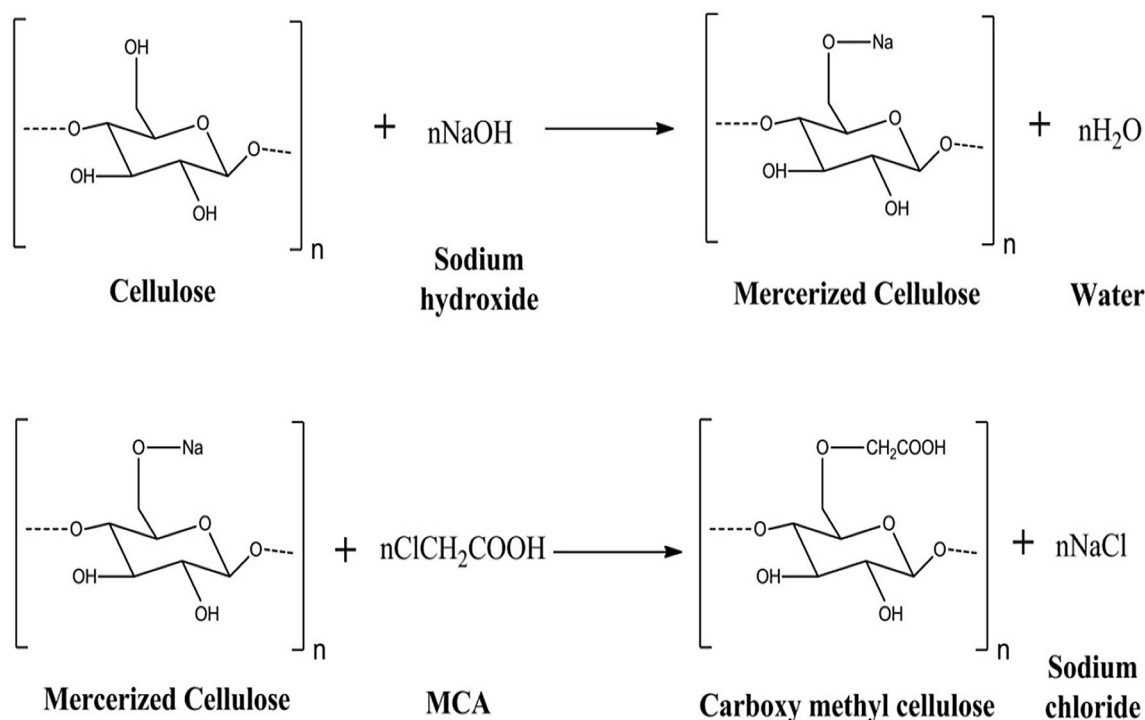
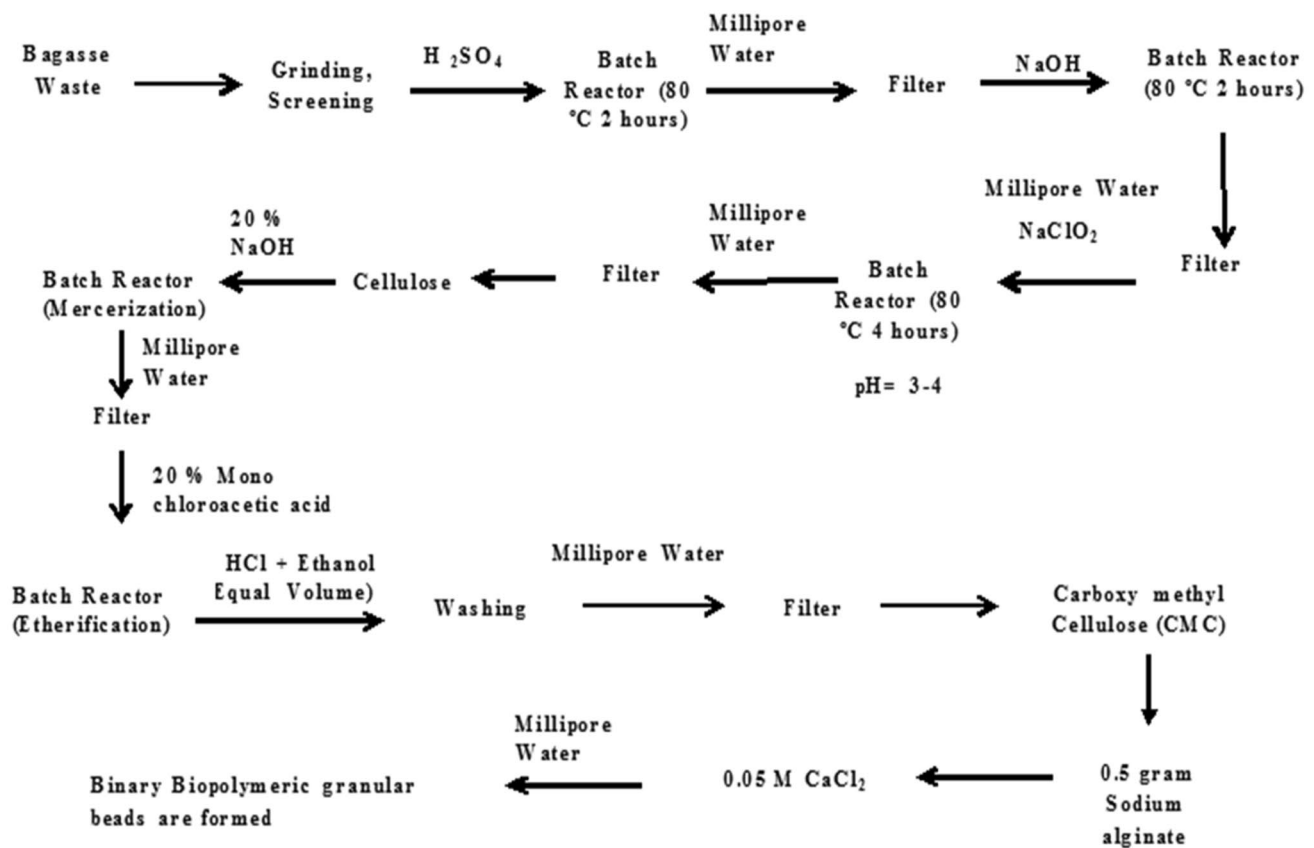**Scheme 1** Synthesis of carboxymethyl cellulose from cellulose

Fig. 1 Preparation of bio-polymeric beads from laboratory-made CMC

solution. The reagent was prepared by dissolving 0.2 g diphenyl carbazide in ethyl alcohol and sulfuric acid (1:2) concentration. After that the reagent was stored in amber bottle to avoid light.

Batch mode adsorption studies

For each experiment 0.2 g bio-polymeric gel beads and 0.3 g activated carbon quantity of the adsorbent were introduced into 100-ml stoppered conical flasks in which 20 ml of the potassium dichromate solution was added. The desired pH values (2, 4, 6, 8, 10) were maintained by the addition of 0.01 M hydrochloric acid (HCl) and NaOH solution. The solution was kept in a temperature-controlled shaker at a steady speed of 150 rpm for a period of (5, 10, 15, 20, 25) min at room temperature to achieve the equilibrium. After the required time, samples were taken from the incubator and the adsorbent was separated by filtration and the supernatant was centrifuged for 5 min. The residual chromium ion concentration was determined by diphenyl carbazide method. After that, the absorbance was calculated with the help of UV–Vis spectrophotometer (PerkinElmer, Shimadzu, Japan). The purple-violet color complex solution recorded a peak at 540 nm. The quantity of chromium

adsorbed per unit weight of adsorbent, q_e (mg/g), was calculated by following Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where V is the volume (L) of Cr(VI) solution, C_0 and C_e are the initial and equilibrium concentrations (mg/L) of Cr(VI) in solution, respectively, and W is the weight (g) of adsorbent.
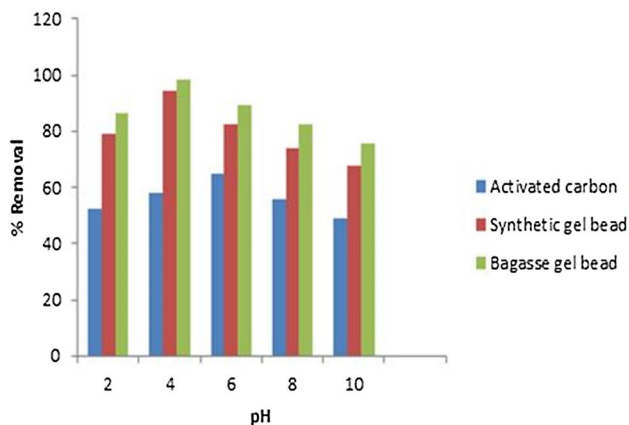
Characterization of adsorbent

Fourier Transform infrared spectroscopy (FTIR) indicates chemical occurring in the bio-polymer. For analysis the samples were crushed with KBR to make pellets, and spectra were taken on PerkinElmer B_X 11-FTIR Spectrophotometer, in the range of 4000–400 cm^{-1}. The surface morphology of the bio-polymeric beads and activated carbon was examined using scanning electron microscopy (SEM). The dried samples were layered with a thin layer of palladium gold alloy after mounting on a twice sided carbon tape (Zeiss 1555 VP). The dried samples were compressed into the disks and then measured with an X-ray diffractometer models recorded

with Rigaku D/MAX-2400 X-ray diffractometer system using a Cu Ka radiation (1 ¼ 1.5406 Å) in the 2*q* range from 5° to 70°, operated at 40 mA and 40 kV, and a scanning speed of 10°/min.

Results and discussion

Effect of pH on removal

The pH plays an important role in the removal of heavy metal ions present in an aqueous solution. The pH also affects the degree of ionization of the adsorbent, solubility of metal ions and charge present on the adsorption sites. To determine the effect of pH in the removal of chromium ions, it was varied from 2 to 10. The maximum adsorption of Cr(VI) ions occurred at pH 4, and adsorption decreased at higher or lower pH (2 and 6). At pH 2 the adsorption removal of the metal ion was lower as compared to pH 4 due to the acidic nature of chromium solution, because at pH 2 protonation increases H^+ ions which results in decrease in the adsorption capacity due to elimination of electrostatic repulsive forces. With an increase in pH from 4 to 7, de-protonation occurs and it results in decrease in electrostatic repulsive forces. There are many carboxylic groups present in bio-polymeric gel beads that increase the adsorption efficiency at pH 4 (Yang et al. 2011; Dewangan et al. 2011). In activated carbon with an increase in pH from 4 to 10 degree of protonation decreases resulting in electrostatic forces elimination (Murugesan et al. 2012). The percentage removal of Cr(VI) ions for synthetic and sugarcane bagasse bio-polymeric gel bead reaches maximum 94.56% and 98.42% values at a pH of 4.0 at 25 °C and for activated carbon 64.79% value at a pH of 6.0 at 25 °C as shown in Fig. 2.

Effect of time on removal

The adsorption experiments were monitored at different time intervals (0–25 min) at pH 4 and 6 for bio-polymeric gel beads and activated carbon using a constant concentration of chromium ions. In Fig. 3, it was found that as the time increases from 5 to 20 min adsorption removal increases and is almost constant after 15 min for bagasse and synthetic gel beads due to difference in the degree of substitution (DS) of bagasse (0.65) and synthetic gel beads (0.51). Higher degree of substitution (DS) increases the percentage removal of Cr(VI) ions due to an increase in the surface area and the binding sites of the adsorbent. In activated carbon the rate of removal increases
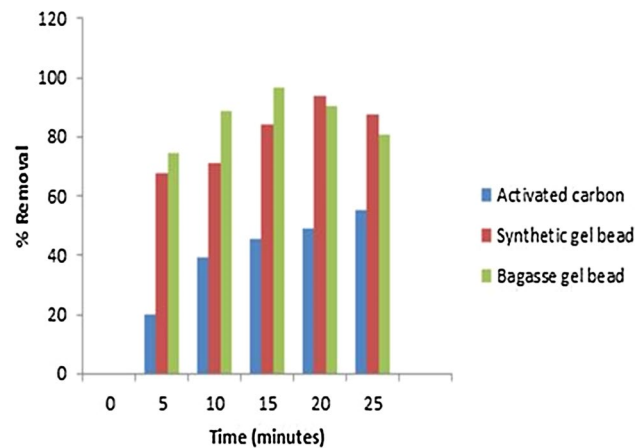
Fig. 3 Effect of time on the adsorption of chromium ions onto bio-polymer beads and activated carbon = 0.2, 0.3 g, pH = 4.6, temperature = 25 °C

Fig. 2 Effect of pH on the adsorption of chromium ions onto bio-polymer beads and activated carbon = 0.2, 0.3 g, pH = 4.6, temperature = 25 °C
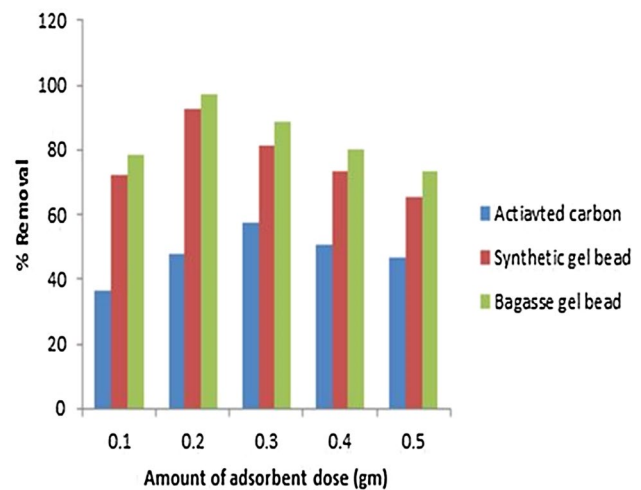
Fig. 4 Effect of adsorbent dose on the adsorption of chromium ions onto bio-polymer beads and activated carbon = 0.2, 0.3 g, pH = 4.6, temperature = 25 °C

as the time increases from 5 to 25 min due to availability of large number of free void sites of adsorbent for chromium ion adsorption (Murugesan et al. 2012; Dewangan et al. 2011).

Effect of adsorbent dosage

The adsorbent dosage is also an important parameter for the heavy metal ions adsorption. Variation in adsorption dosage of bio-polymeric gel beads affects active sites of the adsorbent. As mentioned in Fig. 4, maximum Cr ions adsorption occurs at 0.2 g adsorption concentration in case of bio-polymeric gel beads. The adsorption capacity decreases after 0.2 g due to reduction in active sites on gel beads. Bagasse bio-polymeric gel beads show higher percentage removal and then synthetic bio-polymer gel beads and activated carbon because laboratory-made CMC (sugarcane bagasse) has high degree of substitution that increases surface area and porosity, hence increasing active sites for
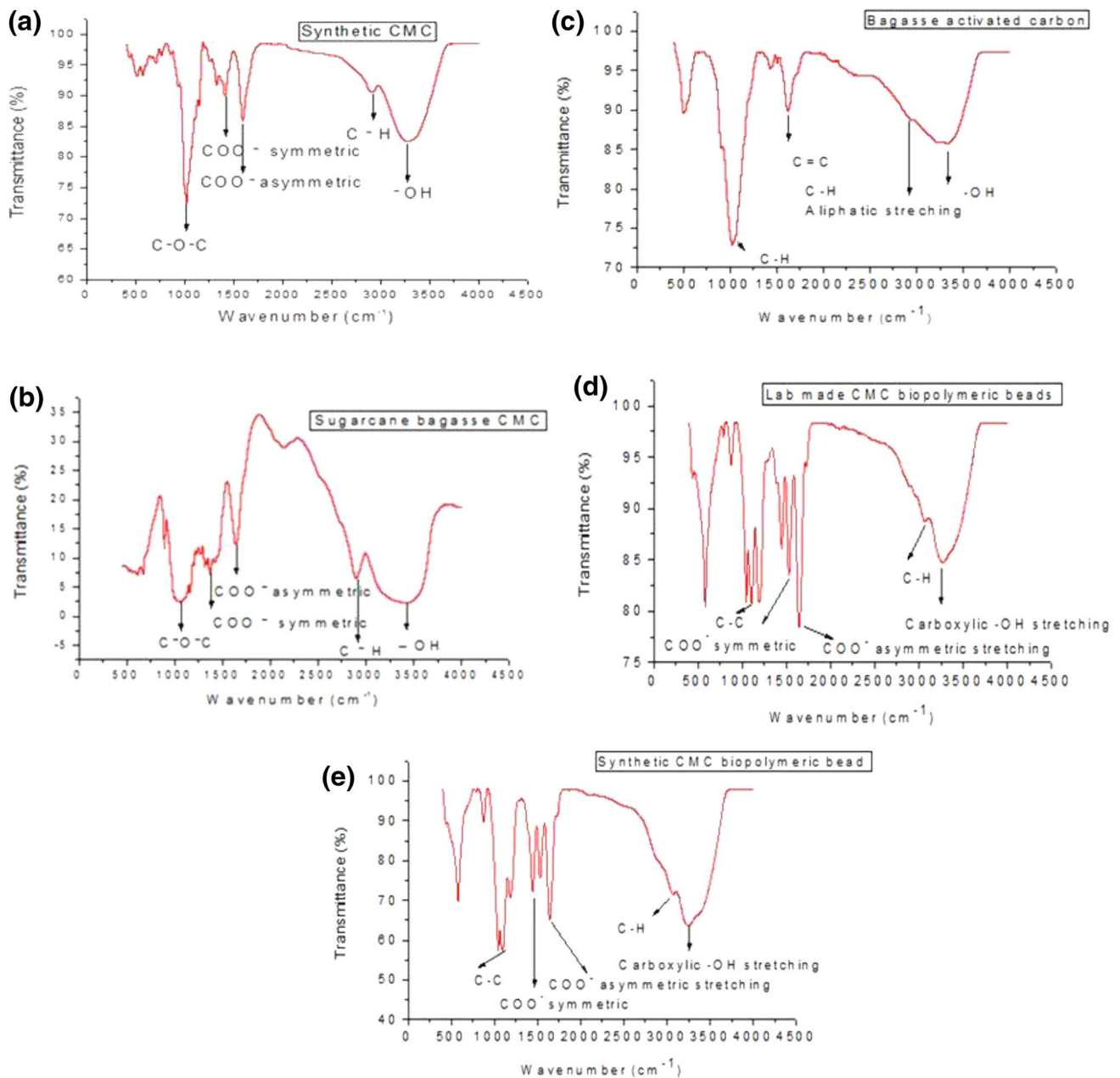
Fig. 5 **a** FTIR spectra of synthetic CMC, **b** FTIR spectra of bagasse CMC, **c** FTIR spectra of bagasse activated carbon, **d** FTIR spectra of bio-polymeric beads of bagasse CMC and **e** FTIR spectra of bio-polymeric beads of synthetic CMC

adsorption (Dewangan et al. 2011). In activated carbon chromium ions adsorption increases from 0.1 to 0.3 g and after that it starts decreasing because the number of availability of the exchangeable binding sites for adsorption decreases (Murugesan et al. 2012).

FTIR spectroscopy

Figure 5a–e shows the FTIR spectrum of CMC (Rachtanapun and Rattanapanone 2011; Saputra et al. 2014), bio-polymeric gel beads (Dewangan et al. 2011) and activated carbon (Hesas et al. 2013; Takahata et al. 2009). The distinct difference is observed between CMC, bio-polymeric gel beads and activated carbon. The band at range 3300–3400 (cm^{-1}) is assigned to the -OH stretching vibrations. The band observed at range 2700–2900 (cm^{-1}) in the spectrum of CMC, bio-polymeric gel beads and activated carbon indicates the –CH aliphatic stretching. It can be seen from the spectrum that the band at range 1500–1650 (cm^{-1}) indicates the C–O stretching, asymmetrical stretching –COO$^-$, C=C stretching for CMC, bio-polymeric gel beads and activated carbon. The band observed at range 1300–1500 (cm^{-1}) indicates the –CH$_2$ bonding, symmetrical stretching, –C–H aliphatic bending for CMC, bio-polymeric gel beads and activated carbon. The band at 1000–1150 (cm^{-1}) indicates the C–O–C stretching, C–O–C stretching, O–H stretching for CMC, bio-polymeric gel beads and activated carbon. The band observed at 833,856,865 indicates the β-glycoside linkage, C–C stretching, C–C stretching for CMC, bio-polymeric gel beads and activated carbon. The functional groups present on the surface of adsorbent identified by FTIR are summarized in Table 1.

XRD analysis

X-ray diffraction (XRD) was performed to investigate the crystallinity of CMC, bio-polymeric gel beads and activated carbon shown in Fig. 6a–c. In CMC structure XRD-type peak's height and width were significantly changed due to breaking of the –OH bond that maintained the crystalline arrangement by replacing hydrogen atoms of -OH by carboxymethyl groups (Gulati et al. 2014). The
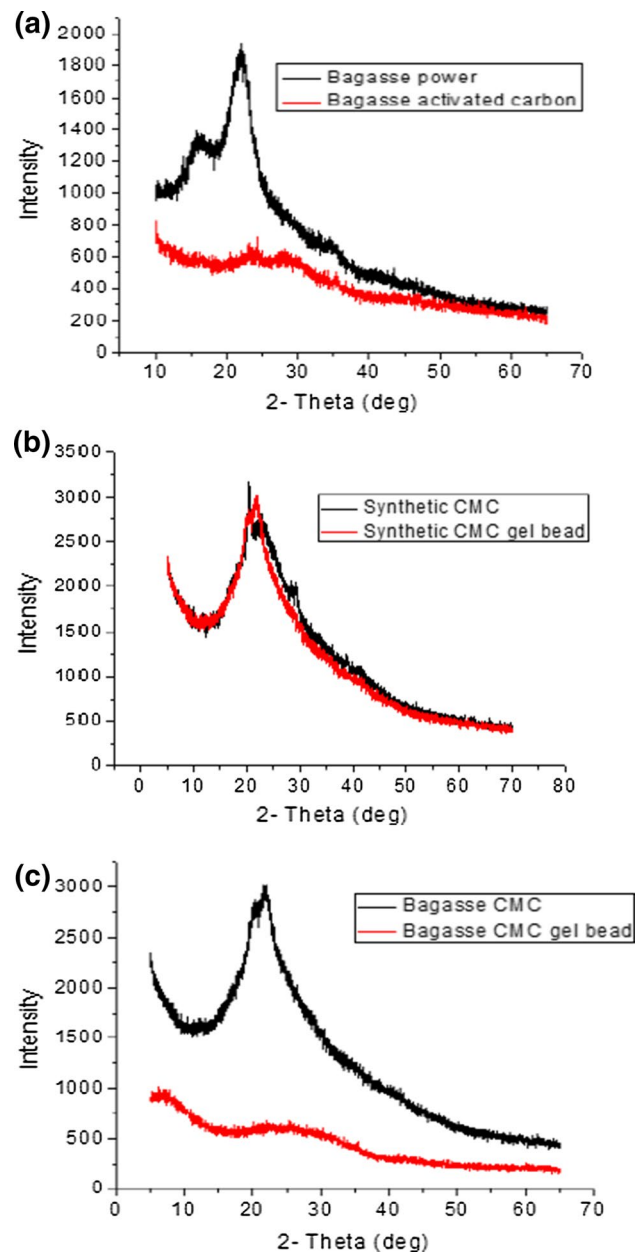

Fig. 6 **a** XRD spectra of bagasse powder and activated carbon, **b** XRD spectra of synthetic CMC and synthetic CMC bio-polymeric gel bead and **c** XRD spectra of bagasse CMC and bagasse CMC bio-polymeric gel bead

Table 1 Functional group of CMC, polymeric gel bead and activated carbon

Wave number (cm^{-1})	Bands indication of CMC	Bands indication of polymeric gel	Bands indication of activated carbon
3300–3400 (cm^{-1})	O–H stretching	Carboxylic –OH stretching	O–H stretching
2700–2900 (cm^{-1})	–CH aliphatic stretching	–CH aliphatic stretching	C–H aliphatic stretching
1500–1650 (cm^{-1})	C–O stretching of carboxyl group	Asymmetrical stretching –COO$^-$	C=C stretching band
1300–1500 (cm^{-1})	CH$_2$ bonding	Symmetrical stretching –COO$^-$	–C–H aliphatic bending
1000–1150 (cm^{-1})	C–O–C stretching	C–O–C stretching	C–O carboxylic acid, alcohols, esters

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decrease in crystallinity is significant in many applications, like manufacturing of hydrogels, enhanced ability of CMC to absorb water due to an increase in the amorphous

region (Spychaj et al. 2013). Crystalline peak in XRD spectra of CMCs gets shifted due to the breakage of β-1, 4 glycosidic bonding which is responsible for increase in

(a)

(c)

(b)

(d)

(e)
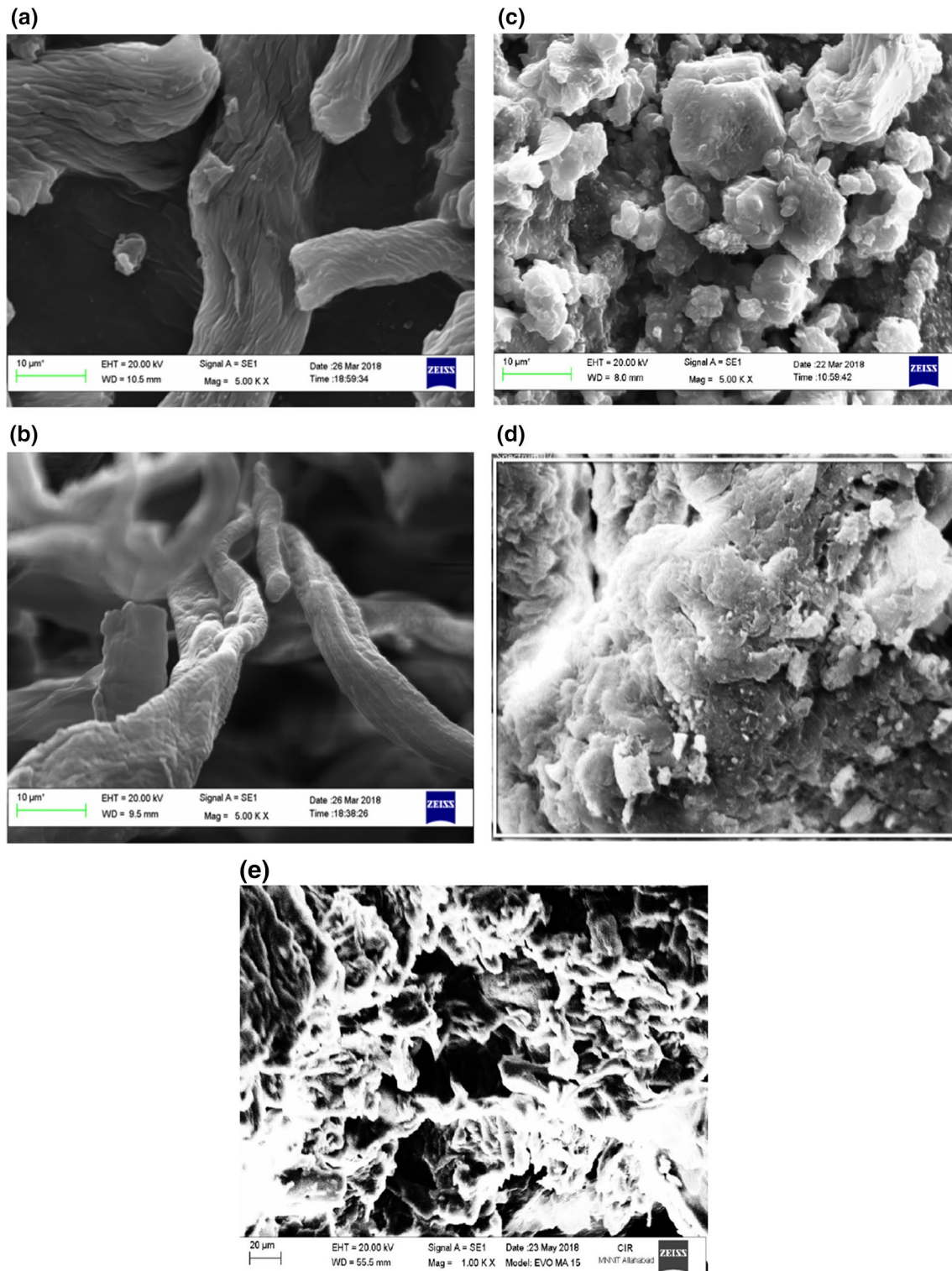
Fig. 7 **a** SEM of synthetic CMC, **b** SEM of laboratory-made CMC (bagasse), **c** SEM of bio-polymer gel bead made from laboratory-made CMC (bagasse), **d** SEM of bio-polymer gel bead made from synthetic CMC and **e** SEM of bagasse activated carbon

the gap among cellulose molecules. Bio-polymeric gel bead diffraction signals at $2\theta = 15°$, $17.8°$, $22.8°$ were not observed in the XRD spectra, because of the presence of cross-linking between the sodium alginate, and calcium chloride could destroy the crystallinity and increase the amorphous region. Due to the lack of crystallinity, metal ions could easily penetrate into the gel beads and hence increase in adsorption capacity occurs (Yang et al. 2011). The diffraction peak at the position of $2\theta = 23°$ shows the amorphous region of the activated carbon because KOH activation increases the specific surface area of porous carbon materials and decreases the crystallinity of the structure (Takahata et al. 2009).

Morphological analysis

The SEM image was employed to investigate the surface morphology of CMC, bio-polymer gel beads and activated carbon structures as shown in Fig. 7a–e. The higher concentration of NaOH during mercerization hydrolyzed the remaining hemicellulose that increases the surface area for better contact during etherification process (MCA) (Gulati et al. 2014). The higher the DS values more cracks will appear because during the carboxymethylation reaction disruption of the outer layer of the cellulose fibers occurs (Gu et al. 2012). Bio-polymeric gel beads surface was moderately rough surface and exhibited more porosity. This porosity is due to the electrostatic repulsions among the carboxylate anions (COO$^-$) which increases the size of pores in the gel beads (Pourjavadi et al. 2006). Therefore, metal ions can simply disperse in and out and hence increases the adsorption capacity of the adsorbent. The bagasse raw material was fairly smooth with few cracks or voids. After the activation with KOH carbonization increases the size of the pores and also decomposition of the volatile organic matters happens (Eslami et al. 2018).

Conclusion

In this study bio-polymeric gel beads manufactured from synthetic and laboratory-made CMC (bagasse) and sodium alginate show great promise as an adsorbent for the removal of chromium ions. The pH also affects degree of ionization of the adsorbent, solubility of metal ions and charge present on the adsorption sites. An increase in pH hikes the adsorption capacity due to de-protonation (reduction of H$^+$ ions) of the metal-binding sites. Activated carbon made from bagasse also displays high chromium percentage (64%) removal, but it is much lower than synthetic gel beads and bagasse gel beads (94.56%) and (98.45%). Gel beads concentration also effects the Cr(VI) removal. Bagasse bio-polymeric gel

bead shows higher percentage removal than synthetic biopolymer gel bead and activated carbon because laboratory-made CMC (bagasse) has higher degree of substitution that increases surface area and porosity and hence provides more active sites for adsorption. This porosity is due to the electrostatic repulsions among the carboxylate anions (COO$^-$) which increases the size of pores in the gel beads. This study provides an economical, easily available adsorbent for the removal of chromium ions from the aqueous solutions.

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