Preparation, characterization and Cr(VI) adsorption behavior study of poly(acrylic acid) grafted *Ficus carica* bast fiber

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ABSTRACT

In the present study the chemical modification of *Ficus carica* bast fiber with acrylic acid using ceric ammonium nitrate and nitric acid was done in aqueous medium. The raw and modified fibers were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The raw and modified samples were evaluated for swelling behavior in water and chloroform. The chemical resistance was investigated against 0.1N HCl and 0.1N NaOH. The chemically modified *Ficus carica* fiber (CMBF) showed morphological transformations, thermal stability and chemical resistance. The adsorption potential of modified fiber was investigated for Cr(VI) removal from aqueous system. Copyright © 2013 VBRI press.

Keywords: Ficus carica bast fiber; acrylic acid; spectral analysis; swelling behavior; chemical stability; Cr(VI) removal.

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Introduction

In the past decade, bast fibers have drawn more attention from the industrial world as they are abundance in nature, inexhaustible, inexpensive, renewable, biodegradable and modifiable biopolymers [1-5]. Bast fibers mainly composed of cellulose embedded in a matrix of other structural biopolymers like hemicelluloses, lignin, pectin, waxy substances, nitrogen-containing substances, minerals, organic acids etc [6]. Cellulose is a highly functionalized, linear stiff chain homopolymer, characterized by its hydrophilicity, chirality, biodegradability and broad chemical modifying capacity. This heterogeneity makes the natural fibers a potential raw material for many industrial applications [7]. However, the high level of moisture absorption, low bulk density, difficulty in dispersion and insufficient adhesion between fibers and polymer matrix are some drawbacks of natural fibers which become critical issue for industrial applications. Thus, to improve the compatibility between cellulose chains and hydrophobic polymer matrices, various physical or chemical surface treatments have been explored such as corona discharge, plasma treatment, chemical treatment and treatments using fungi, enzymes and bacteria, etc [8]. The cellulosic fibers have hydroxyl groups, so they are amenable to surface treatment which opens up the cellulose matrix, improves surface and molecular retention characteristics. It provides a latent method for reduction of the interfacial free energy and alters the physiochemical and mechanical properties of the natural fibers [9].

Chemical treatment by vinyl monomers using different initiators onto cellulosic fibers has been considered to be a powerful method for producing substantial alteration in physicochemical properties. The chemically modified materials were used as superabsorbents, ion-exchange composites, biofuels etc [10]. The superabsorbents are cross-linked networks of hydrophilic polymers that absorbs water and retain a high volume of aqueous fluids and thus these materials can be used in horticulture, gel actuators, drug-delivery system, water purifier and coal dewatering etc. Various polysaccharides such as cellulose, starch, guar-gum, psylium etc. have been modified for their use in bioplastics and biocomposites engineering applications etc [9-11]. Extensive attention has been given by various workers towards superabsorbent polymers prepared under different conditions through chemical processes [6,12]. Grafting of acrylic acid on natural fibers backbone using ceric ammonium nitrate and nitric acid as redox initiator in aqueous medium enhances the water absorption, cation-exchange property, dye and metal absorption ability without adversely affecting the intrinsic properties of natural fibers [13, 14]. Therefore, efforts have been made to convert the biomass into inexpensive and effective material for industrial purposes.

Ficus carica is a fibrous herbaceous plant with large biomass production and fast growth rate. Different parts of the plant such as bark, leaves, tender shoots, fruits, seeds, and latex are medicinally important [15,16]. Beside the medicinal purposes, the discarded bast of the plant stem has been found to be viable source of fiber.

The grafting of different monomers onto *Ficus carica* bast fibers has not reported in literature. Keeping this in view, the grafting of acrylic acid using ceric ammonium nitrate and nitric acid as redox initiator has been carried out onto *Ficus carica* bast fibers. The raw and grafted fibers have been characterized by FTIR, XRD, SEM, TGA, DTA etc. The materials were subjected to the evaluation of their physico-chemical properties such as moisture resistance, swelling behaviour, thermal stability, surface morphology, chemical resistance behaviour and percent crystallinity. Moreover, both the samples were used as adsorbent for the removal of noxious Cr(VI) from aqueous system.

Experimental

Materials

All the reagents used were of analytical grade and all dilutions have been carried out using double distilled water. Hydrochloric acid (purity>99%, E. Merck, India, Ltd.), sodium hydroxide (purity>99%, E. Merck, India, Ltd.), acrylic acid, AA (purity>99.5%, E. Merck, India, Ltd.), ceric ammonium nitrate, CAN (purity>98.5%, E. Merck, India, Ltd.), nitric acid (S. D. Fine-Chem. Pvt. Ltd, India) were used as received. The pH of the test solution was adjusted with 0.1N HCl and 0.1N NaOH solutions using a pH meter (ELICO model L1-127, India). Stock chromium (VI) solution (1000 mg L^{-1}) was prepared by dissolving 2.828 g potassium dichromate (purity>99.8%, E. Merck, India, Ltd.) in 1000 ml double-distilled water. The solutions of desired concentrations were prepared by diluting the stock solution with double distilled water. Absorbance measurements were recorded on a UV-visible

spectrophotometer (Shimadzu UV-1601, Japan) over the wavelength range 200-800 nm.

Preparation of Ficus carica bast fiber (BF)

Ficus carica fibers were obtained from the bast by water retting process of bark for several days and thereafter washed several times with the double distilled water. The purification of fibers was done by soxhelt extraction using acetone for 72 h. Then the fibers were dried at 50 °C in a hot air oven and stored for further use.

Chemical modification of fiber (CMBF)

Activation of the 0.50 g *Ficus carica* bast fiber (BF) was done by its immersion in 100 ml of distilled water at room temperature for 24h prior to chemical modification. After activation the fiber samples were transferred into a reaction kettle containing 100 mL of distilled water. Predetermined amount of CAN and nitric acid was added to the reaction mixture, followed by the acrylic acid (2.82 x 10^{-1} mol/L) with continuous stirring. The reaction was carried out for definite reaction time at different temperatures. The different reaction parameters such as reaction temperature, time, pH, concentrations of CAN-HNO_3 and acrylic acid (AA) were optimized. The sample was then washed with hot water and dried in hot air oven at 60 ºC. The obtained product was leveled as chemically modified *Ficus carica* bast fiber (CMBF).

Chemical resistance

The chemical resistance of the raw and chemically modified fibers was studied as a function of percentage weight loss of fiber when treated with different chemicals. In this process, a known amount of the raw and chemically modified fibers was separately treated with a fixed volume of hydrochloric acid (0.1N) and sodium hydroxide (0.1N) for 24h. The fibers were then washed with distilled water and finally dried in an oven at 70º C to a constant weight. The percentage of weight loss was determined using the following formula [15]:

$$\% \text{ Weight loss} = (W_i - W_f / W_i) \times 100 \qquad (1)$$

Swelling behavior

The swelling behavior of the BF and CMBF were studied in polar and non-polar solvents such as water and carbon tetrachloride by immersing the known weights of the fibers in different solvents for 24h. After filtration, the surface water on the swollen sample was removed by softly pressing between the folds of filter paper and weighed. The degree of swelling was calculated by using the following relationship [16]:

$$\% \text{ Swelling} = (W_f - W_i / W_i) \times 100 \qquad (2)$$

where, W_f = final weight of the fiber and W_i = initial weight of the fiber.

Fourier transformer infrared spectroscopy

Fourier transformer infrared spectroscopy (FTIR) of the raw and chemically modified fibers was performed using

Perkin Elmer spectrometer (Spectrum 400, USA). The samples were examined in the range 500-4000 cm^{-1} using KBr pellets.

Scanning electron microscopy

A scanning electron microscope (JEOL JSM-6100, Japan) was used to study the surface morphology of the raw and chemically modified fibers. The samples were stocked over a holder, sprayed with about 200 Å gold layers in a vacuum chamber and scanned to identify the surface texture.

XRD diffraction studies

X-ray analysis was carried out on X-ray diffractometer (X'Pert PRO XRD P Analytical, Netherlands), using Cu Kα (1.5418 Å) radiation, Ni-filter and scintillation counter at 45 KV and 40 mA on rotation between 10º to 79º at 2θ-scale.

Thermal analysis (TGA, DTA and DSC)

Thermal analysis of raw and chemically modified samples was performed using Perkin Elmer, (Pyris Diamond) thermal analyzer. A known weight of the each sample was taken into silica crucible for TG-DTA analysis in air with temperature range of 50 ℃ to 700 ℃. The heating rate of the sample was 10º C per min and was scanned for 60 min.

Adsorption studies

The batch adsorption experiments were performed in a set of 250 mL of Erlenmeyer flask containing 50 mL Cr (VI) solution and known weight of adsorbents. The flasks were agitated in an isothermal water-bath shaker at 120 rpm and 30 ºC until the equilibrium was reached. The solution was flittered and Cr(VI) ion concentration in the filtrate solution was determined using atomic absorption spectrophotometer. The percentage removal and amount of dye adsorbed per gram (q_e) of the sample was calculated as follows [**16**]:

$$R = (C_0-C_t) \times 100/ C_0 \qquad (3)$$

$$q_e = (C_0-C_t) \times V/ W \qquad (4)$$

Results and discussion

FTIR analysis

FTIR spectrum of BF was shown in **Fig. 1a**. The broad peak at 614 cm^{-1}, 874 cm^{-1} and 1056 cm^{-1} indicate the presence of –OH bending, (due to β-glycosidic linkage), and C–O stretching, respectively. The appearance of smaller peaks at 1375-1429 cm^{-1} may be due to –CH, –CH$_2$ and –CH$_3$ bending and 1632 cm^{-1} may be due to H–O–H bending of absorbed water. The absorption peak at 3435 cm^{-1} and 2918 cm^{-1} signify the –OH vibration and C–H stretching vibration of aliphatic methylene group. The FTIR spectra of the chemically modified fiber (**Fig. 1b**) showed the characteristic absorption bands at 1725 cm^{-1} and 1581 cm^{-1} due to carbonyl stretching of carboxylic acid group and unsaturated group, respectively [**17,18**].

X-ray Diffraction pattern

Most of the cellulosic natural fibers possess both crystalline and amorphous regions. The existence of dual features in the fiber indicates that ordered and disordered regions coexist in crystalline polymer. In Fig. 3 counter reading of highest peak intensity near 22.68º represents crystalline material and peak near 15º in the halo-pattern corresponds to the amorphous material in BF and CMBF. Percentage of crystallinity, crystallinity index and average crystallite size are given in Table 1. The crystallinity index gives a quantitative measure of the orientation of the cellulose crystals in the fibers. A lower value of percentage crystallinity, crystallinity index and average crystallite size in case of modified fiber showed a marked loss in crystallinity and poor order of cellulose crystals in the modified fiber. This was due to the impregnation of monomer chains, which disturbed the crystalline structure of Ficus carica fibers and increased the amorphous character [**18**]. Moreover, disorientation of the cellulose crystals to the fiber axis led to an increase in surface area and enhanced adsorption capacity [**20-22**].
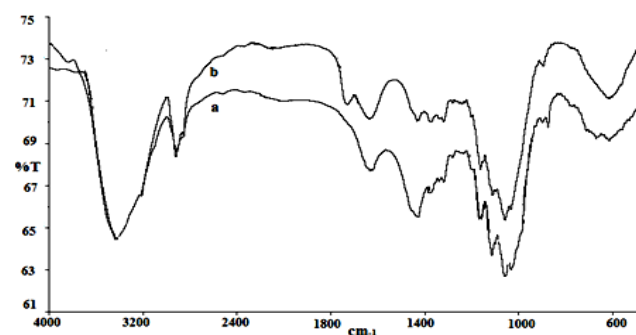

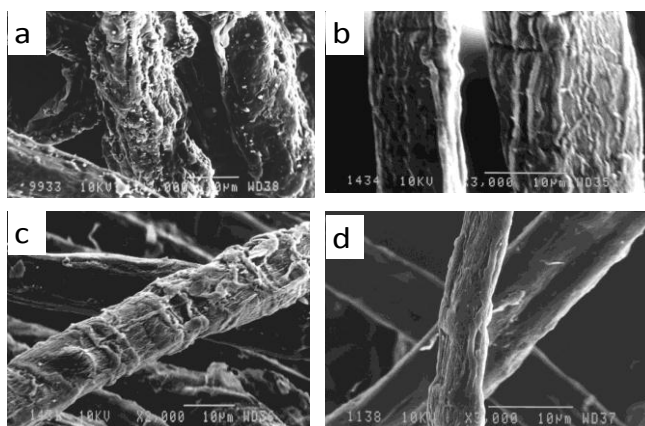**Fig. 1.** FTIR spectrum of (a) BF and (b) CMBF.

Fig. 2. SEM micrograph of BF (a and b) and CMBF (c and d) at different magnification.

SEM analysis

Surface morphology of BF and CMBF samples was studied through scanning electron microscopy and the results were shown in **Fig. 2**(a-d). The comparison of SEM micrographs of both the samples showed that the raw fiber has irregular and porous structure however; modification by AA monomer on the cellulosic chains opens up the matrix of

fiber and changes the morphology of surface due to uniform grafting of AA in the amorphous and crystalline regions of the fiber. This led to physical and chemical cross linking on the surface of fiber to enhance Biosorption [19,20].
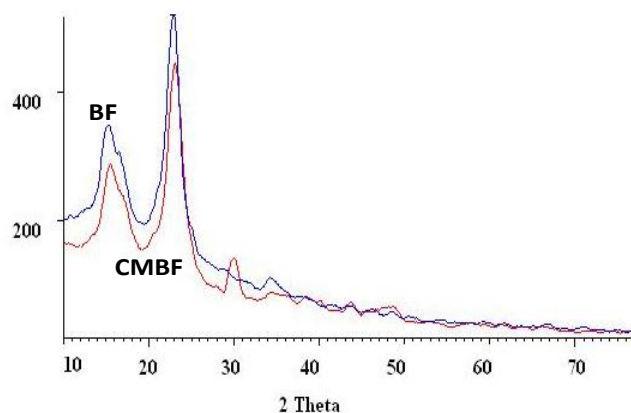

Fig. 3. XRD spectra of BF and CMBF.

Table 1. XRD analysis of natural and modified *Ficus carica* fiber.

Sample	2θ (deg.)	FWHM (deg.)	Intensity		X$_C$%	C.I.	L (Å)
			I$_C$	I$_A$			
FCF	22.87	1.82	526	111	82.58	0.79	44.53
MFCF	23.06	1.9	461	150	75.45	0.68	42.67

Thermal analysis

TGA, DTA, DGA analysis of BF and CMBF were shown in **Fig. 4a** and **Fig. 4b**. In BF depolymerization, and dehydration occur in the temperature range of 25 ºC and 250 ºC and followed by the cleavage of C–H, C–C and C–O bonds [12].The initial decomposition temperature (IDT) was found to be 263.6ºC (12.5 % weight loss) and final decomposition temperature (FDT) to be 379.4ºC (87.4 % weight loss). In the case of CMBF, the IDT and FDT were found to be 254.3ºC (7.3 % weight loss) and 382.8ºC (89.8 % weight loss), respectively. Decrease in IDT of modified fiber was due to decomposition of anhydride (formed due to dehydration of carboxylic acid groups) of poly (AA) chains to carbon dioxide and intermediate species such as ketones, ketenes and unsaturated compounds in the temperature range of 200-275 ºC [22, 23]. Maximum thermal stability (382.8ºC) has been found in case of modified fibers comparised to raw fibers. It was observed that a chemical treatment increases the thermal stability of the fibers. This may due to disturbance in crystalline behavior of BF during grafting of poly(AA) [24].

DTG of raw and modified fibers were studied as a function of rate of weight loss (mg/min) versus temperature. In the case of raw sample the two decomposition peaks are found at 352.4 and 384.1 at the rate of 6.6 and 0.9 mg/min weight loss. The first peak was due to degradation of hemicellulose and second peak is due to cellulose and lignin degradation. The two decomposition peaks of modified sample were found at 344.7 and 382.3 at the rate of 9.61 and 1.17 mg/min weight loss respectively.

The DTG result showed that the decomposition rate of chemically modified fiber was higher than raw fiber [25].

DTA curves showed exothermic peaks at 378.1 (185.2) and 379.5 (197.5) for BF and CMBF (**Fig. 4a,b**). The higher exothermic peak represents the degradation process of the lignocellulosic material in raw fiber and AA chains in modified fiber [26].
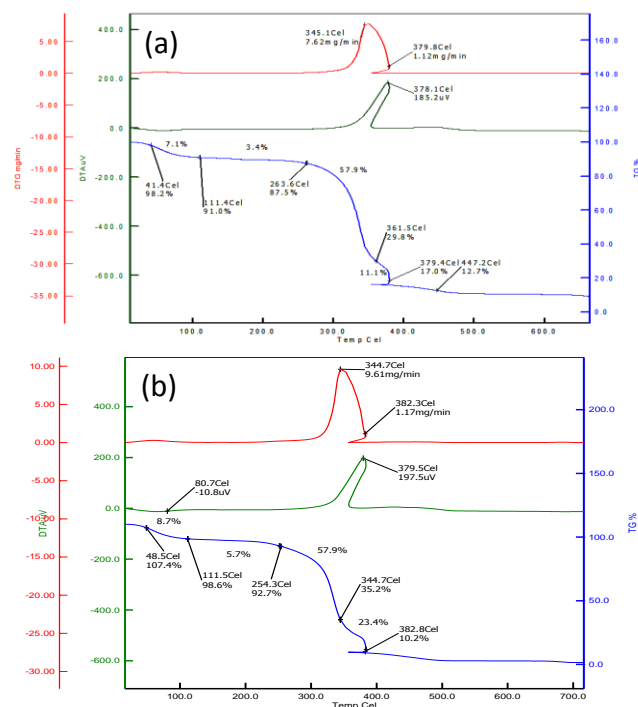

Fig. 4. (a-b) TG, DTA and DTG curves of BF and CMBF.

Swelling behavior

The swelling percentage of BF and CMBF in water and carbon tetrachloride was studied at 30 ºC. A high swelling percentage in water for the chemically modified fiber (57%) than raw fiber (43%) was observed. It was due to the fact that for CMBF more carboxyl groups are available for formation of the hydrogen bond with the water molecules. The chemically modified fibers have high water interaction and molecular retention characteristics and afford efficient adsorbent sites for small molecules and ions [25]. Further dielectric constant (ε) values of different solvents also have great effect on the swelling behaviour of the fiber. Water, having a higher ε value easily enters into H-bonding with the fiber leading to maximum swelling. In case of carbon tetrachloride which has low dielectric constant (ε = 2.24), a lower degree of swelling for the CMBF (11%) than BF (14%) was observed. It was due to lower interaction of CCl$_4$ with carboxyl groups in comparison to hydroxyl groups of the raw fiber.

Acid/base resistance

The chemical resistance has been studied in terms of a weight loss of the fiber with dilute solutions of strong acid and base. It has been revealed that the chemical resistance of lignocellulosic fibers increased with chemical modification. The maximum weight loss of 19.4% and 13.7% were observed for BF and CMBF, respectively in
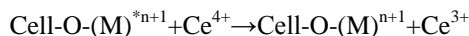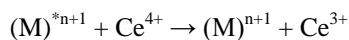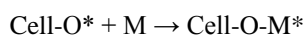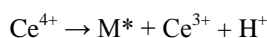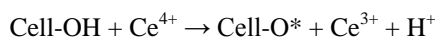
0.1N HCl. It was due to the fact that the most of the reactive sites on the surface of fiber, prone to attack by HCl are blocked by poly (AA) chains. However, the maximum weight loss was found to be 23.18% and 16.9% were observed for BF and CMBF, respectively in 0.1N NaOH. This probably could be due to the formation of sodium salts of acrylic acid and to some extent due to the solubility of poly (AA) chain [27-28].

Reaction mechanism for modification of Ficus carica fiber bast

Ceric ammonium nitrate (CAN) used as source of ceric ion in presence of concentrated nitric acid plays an important role during graft copolymerization. Ceric ion in water reacts in the following manner [**27, 28**]:

$$Ce^{4+} + H_2O \rightarrow [Ce(OH)_3]^{3+}$$

$$[Ce(OH)_3]^{3+} \rightarrow [Ce\text{-}O\text{-}Ce]^{6+} + H_2O$$
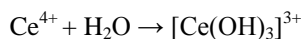
Thus in aqueous medium ceric ion exists as $[Ce\text{-}O\text{-}Ce]^{6+}$. Because of large size, $[Ce\text{-}O\text{-}Ce]^{6+}$ ion is unable to form complex with the fiber whereas, in presence of HNO_3 more of Ce^{4+} and $[Ce(OH)_3]^{3+}$ ions are formed and these ions easily undergo complex formation with the functional groups of fiber. Ceric ion forms the chelate complex with the cellulose molecule through C-2 and C-3 hydroxyl groups of the anhydroglucose unit. Transfer of the electron from the cellulose molecule to Ce (IV) would lead to its reduction to Ce (III), followed by breakage of the bonds at C-2 and C-3, resulting in the formation of the free radical sites. Grafting of vinyl monomer onto polymeric backbone occurs as follows:

$$Cell\text{-}OH + Ce^{4+} \rightarrow Cell\text{-}O\text{*} + Ce^{3+} + H^+$$

$$Ce^{4+} \rightarrow M\text{*} + Ce^{3+} + H^+$$

$$Cell\text{-}O\text{*} + M \rightarrow Cell\text{-}O\text{-}M\text{*}$$

$$Cell\text{-}O\text{-}M\text{*} + nM + Ce^{4+} \rightarrow Cell\text{-}O\text{-}(M)^{*n+1} + Ce^{+3} \quad M \rightarrow (M)^{*n+1}$$

$$(M)^{*n+1} + Ce^{4+} \rightarrow (M)^{n+1} + Ce^{3+}$$

$$Cell\text{-}O\text{-}(M)^{*n+1} + Ce^{4+} \rightarrow Cell\text{-}O\text{-}(M)^{n+1} + Ce^{3+}$$

(Chemically modified Ficus carica fiber)

where, Cell-OH = *Ficus carica* backbone and M = monomer.

Ceric ions forms complexes with carbon chain of polymer back bone as well as from monomer chains and generate free radicals. Free radicals then combine at reactive sites on the polymer backbone to form graft copolymer. On other hand different monomer free radicals combines to form homopolymer free radical. The homopolymer free radical thus formed by the combination of monomers combines with the cellulose chain and forms homopolymer and free radical. On the other hand the ceric ion combines with the free radical to form a stable

poly(AA) chain and terminates the polymerization. Another termination step is the combination of homopolymer free radical and AA free radical [**16,29**]. **Scheme 1** shows the possible structure of chemical modification of *Ficus carica* fiber with acrylic acid using initiator in presence of nitric acid as follows:
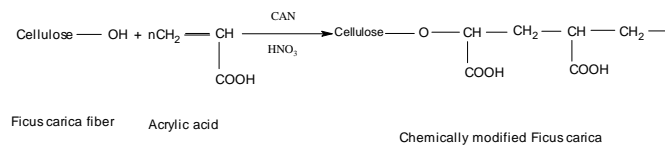
Scheme 1. Chemically modification of *Ficus carica* bast fiber.

Adsorption studies of CMBF

The comparative adsorption behavior BF and CMBF is shown in **Fig. 5**. Adsorption experiments were carried out with initial Cr(VI) concentration of 100 mg/L, 1.0 g of adsorbent and pH 5 at 30°C. It was observed that 40 % and 56 % of adsorption took place in 80 min for BF and CMBF, respectively. The equilibrium was reached after 120 min. The change in rate of adsorption might be due to fact that initially all the adsorbent sites were vacant and solute concentration gradient was very high. Later, the lower adsorption rate was due to decrease in number of vacant site of adsorbent and Cr(VI) concentration. The decreased adsorption rate, particularly, towards the end of experiments, indicates the possible monolayer formation of Cr(VI) ion adsorbent surface. CMBF showed better adsorption capacity for Cr(VI) removal due to introduction of new functionalities in modified bast fiber [**17, 30-32**].
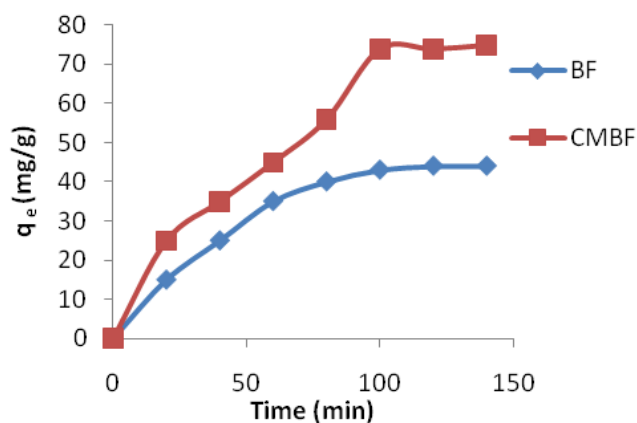
Fig. 5. Adsorption of Cr(VI) onto BF and CMBF.

Conclusion

From present study, it is evident that the chemical modification resulted in the morphological transformation that improved the various physico-chemical properties of the natural cellulosic fiber. Chemical treatment has diminutive effect on thermal stability and crystalline structure of CMBF. Surface of CNBF became smooth on grafting with acrylic acid. CMBF had been found as a potential adsorbent for toxic Cr(VI) removal from aqueous system.

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