Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.904822

54 (2015) 3114–3121
June

Taylor & Francis
Taylor & Francis Group

Modification of *Hibiscus cannabinus* fiber by graft copolymerization: application for dye removal

Gaurav Sharma[a,*], M. Naushad[b], Deepak Pathania[a], Alok Mittal[c], G.E. El-desoky[b]

[a] *School of Chemistry, Shoolini University, Solan 173212, Himachal Pradesh, India, email: gaurav8777@gmail.com*
[b] *Department of Chemistry, College of Science, Building #5, King Saud University, Riyadh, Saudi Arabia*
[c] *Department of Chemistry, Maulana Azad National Institute of Technology, Bhopal 462052, India*

Received 2 January 2014; Accepted 10 March 2014

ABSTRACT

Hibiscus cannabinus fiber was modified by graft copolymerization with vinyl monomer acrylic acid (AAc) and binary mixture of AAc and acrylamide (AAm). The different reaction parameters were optimized to get maximum grafting yield. The optimized percent grafting for AAc and binary mixture (AAc + AAm) was found to be 93.6 and 74.6%, respectively, at the molar concentration of 0.35 M for AAc and 0.4 M for AAm. The raw AAc grafted *H. cannabinus* fiber *(Hcf-g-polyAAc)* and AAc + AAm grafted *H. cannabinus* fiber *(Hcf-g-poly-AAc + AAm)* were characterized by FTIR and scanning electron microscopy. The modified *H. cannabinus* fibers were used as potential candidate for the removal of dye from aqueous system.

Keywords: Acrylic acid; Acrylamide; *Hibiscus cannabinus*; Graft copolymerization; Dye adsorption

1. Introduction

The use of natural fiber has been reported in different fields as they possess high mechanical strength and stiffness. There are various advantages which provide importance to natural fiber over the synthetic fiber, such as low cost, low density, non-abrasive character, high toughness, biodegradability, strength, reduced dermal, and respiratory irritation which make them potential eco-friendly materials [1–8]. But the utility of these natural fibers is restricted because of their poor properties such as their less thermal stability, prone to degrade in acidic and basic medium [9–11]. To overcome these limitations and to introduce desired functionality in natural fibers, they are grafted with different synthetic monomers [12–15]. This leads to increased application of modified fibers in diverse fields including drug delivery systems, temperature sensitive coatings, flocculating agents, smart catalysis packing, and construction industries [16–19].

Among the various treatments used to improve the properties of fiber, the graft copolymerization of vinyl monomer into natural backbone is an interesting method to improve mechanical properties and to reduce aging hence ultimately increasing their durability. Many techniques of graft copolymerization of various monomers onto cellulosic backbone have been developed. These surface modification techniques include free radical polymerization, ring-opening polymerization, nitroxide-mediated polymerization,

---

*Corresponding author.

1944-3994/1944-3986

atom transfer radical polymerization, microwave radiation induced polymerization, pressure induced graft copolymerization, X-ray, UV light, and by chemical methods [20–27]. The formation of copolymers of cellulose and various synthetic polymers via graft copolymerization has been extensively studied [28,29]. Different monomers and their binary mixtures have been reported which have been grafted on various natural fibers such as methyacrylate, acrylonitrile, acrylic acid (AAc), methyl methacrylate, 4-vinyl pyridine [30–34].

Keeping in view the versatility of graft copolymerization, it has been worthwhile to graft copolymerize principal monomer AAc and binary mixture of AAc and acrylamide (AAm) onto *Hibiscus cannabinus* to improve the properties. The modified *H. cannabinus* fibers were used as potential candidate for the removal of dye from water system.

2. Experimental

2.1. Reagents

AAc (SD fine, Mumbai), AAm (SD fine, Mumbai), ceric ammonium nitrate (CAN) (CDH, Delhi), sodium hydroxide (CDH, Delhi), acetone (RANKEM, Faridabad), benzoyl peroxide (CDH, Delhi), nitric acid (CDH, Delhi), and methylene blue were used, which were of analytical grade.

2.2. Methods

2.2.1. Graft copolymerization of AAc and binary monomer mixture (AAc + AAm) onto peroxide treated Hibiscus cannabinus fiber

Reactive sites onto *H. cannabinus* fibers were activated by pre swelling in 100 mL of distilled water at room temperature for 24 h prior to carrying out graft copolymerization. The graft copolymerization of principal monomer, that is, AAc is carried out for optimization of different reaction parameters such as temperature, time, pH, monomer, and initiator concentration to get maximum graft yield. After the optimization of reaction conditions, further graft copolymerization of binary mixture was done at optimized conditions. About 0.5 g fiber was pre-activated and optimized amount CAN and nitric acid was added to the reaction flask, followed by the drop wise addition of definite ratio of binary mixture (AAc + AAm) monomer with continuous stirring of the reaction mixture. The reaction was carried out at 60˚C for 120 min with continuous stirring. Homopolymers and comonomers formed during the graft copolymerization were removed by extraction with different solvents such as acetone, hot water and methanol and ethanol. The grafted samples were then dried in a hot air oven at 60˚C to a constant weight. The percent graft yield (G%) of grafted sample was calculated using the following formula:

$$\%\,\text{Grafting} = \frac{W_g - W}{W} \times 100 \tag{1}$$

where W_g and W are the weight of grafted and raw fiber, respectively.

2.2.2. Physio-chemical behavior of graft copolymer

2.2.2.1. Swelling behavior. Swelling behavior of raw materials and grafted copolymers was studied in water. For this study, 0.5 g sample was suspended in 20 mL water. Weight of sample was noted at different intervals of time at room temperature. The excess of water was removed by softly pressing the samples between the folds of filter paper. Percent swelling (%, S) was calculated as follows:

$$\%\,\text{Swelling} = \frac{W_F - W_I}{W_I} \times 100 \tag{2}$$

W_F and W_I are final and initial weight of fibers after and before swelling, respectively.

2.2.2.2. Chemical resistance. Chemical resistance studies were done by immersing the known weight of raw and grafted samples in the different molarities solution of HNO_3 and NaOH for 5 h. The samples were then taken out and dried in hot air oven. The percent weight loss was calculated as follows:

$$\%\,\text{Weight loss} = \frac{W_1 - W_2}{W_1} \times 100 \tag{3}$$

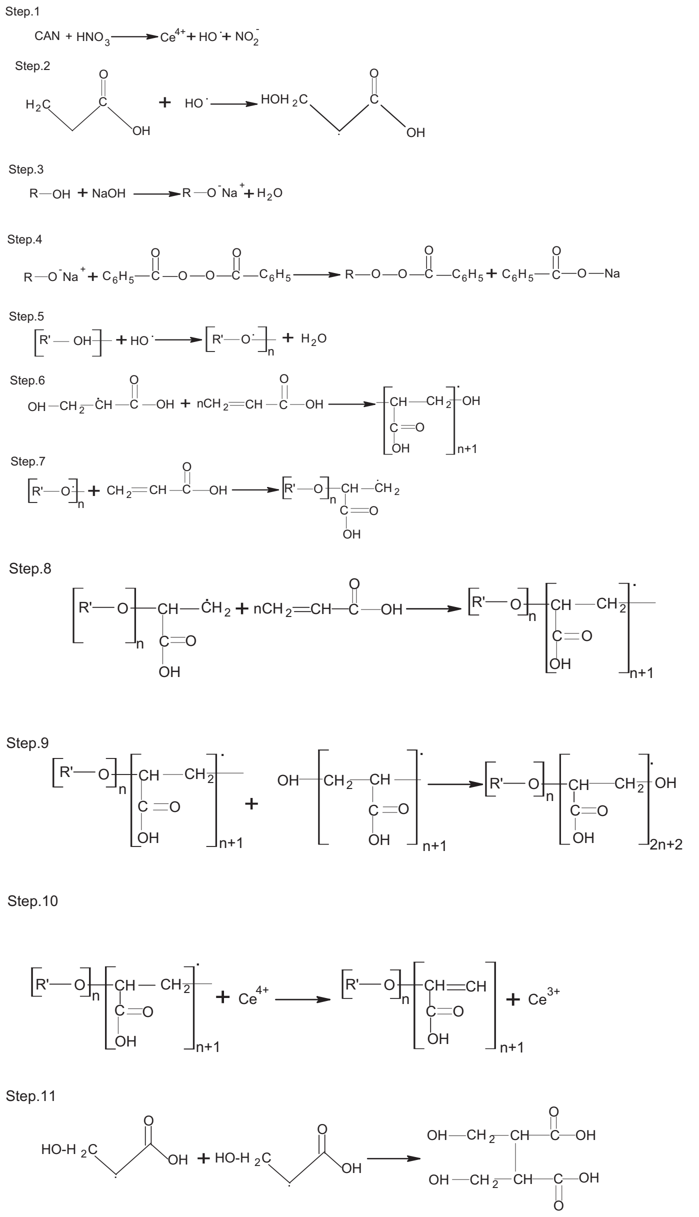
where W_1 and W_2 are the initial and final weight of the samples, respectively.

2.3. Characterization

The FTIR study of raw fiber, grafted, and binary copolymer was recorded by PerkinElmer FTIR spectrophotometer, USA, by using KBr disk method. A disk was formed by applying a pressure of 80,000 psi in a moisture free atmosphere. FTIR absorption spectra were recorded between 400 and 4,000 cm^{-1}. The surface morphologies of the raw fiber, grafted, and binary *H. cannabinus* copolymers were studied using scanning electron microscopy (SEM). They samples were gold sputtered in order to make them conducting before focusing electron beam on the samples SEM studies were made on scanning electron microscope (SEM Qant-250, model 9393).

2.4. Application for dye removal

The adsorption of methylene blue dye on raw fiber, grafted, and binary fibers was carried out by batch mode. About 30 mL of methylene blue dye solution of specified concentrations was treated with 30 mg fibers in a stopper cork conical flask in temperature controlled water bath shaker at 25°C for 120 min. The adsorption measurements were made in triplicate and average values were reported. The amount of methylene blue adsorbed, q_e (mg g^{-1}), was calculated by mass balance relationship, which can be expressed as:



Where R is the cellulose ring in the mechanism and R' is the benzoylated cellulose ring in the mechanism.

Fig. 1. Proposed mechanism of the grafting.
Note: Where R is the cellulose ring in the mechanism and R' is the benzoylated cellulose ring in the mechanism.

$$q_e = \frac{C_0 - C_e V}{m} \tag{4}$$

where C_0 and C_e are the initial and equilibrium dye concentrations in solution (mg L^{-1}), respectively, V is the volume of solution (mL), and m is the mass of the fibers (g).

3. Results and discussion

The maximum grafting of 93.54% was obtained at optimized reaction temperature of 60˚C (shown in Fig. 2(a)), reaction time 120 min (shown in Fig. 2(b)), at pH 10.5 (shown in Fig. 2(c)), monomer concentration of 0.35 mol L^{-1}(shown in Fig. 2(d)), and initiator concentration of 0.45 mmol L^{-1} (shown in Fig. 2(e)). The proposed mechanism of the grafting is shown in Fig. 1. The various reaction parameters that have been optimized to get the maximum graft yield include temperature, pH, time, initiator, and monomer concentration. The effect of reaction temperature on percent grafting of AAc onto *H. cannabinus* fiber was observed. The behavior of variation of percent grafting with temperature could be attributed to the fact that with the initial rise in temperature, the kinetic energy of the molecules increased and more radicals drifted at faster rate onto the backbone of fibers, resulted in the increase in grafting yield [21,35]. Thus, with the initial increase in temperature, graft yield increased which reached up to the optimum value at 60˚C and started to decrease when further reaction temperature increased (Fig. 2(a)). At higher temperature, the percent of grafting decreased because the rate of termination reaction increases. The kinetic energy of free radicals increases due to rise in temperature. This enhances the probability of self-coupling of free radicals or growing chains of monomers with each other leading to termination [35]. With the initial increase in time, graft yield increased and reached up to the optimum value at 120 min and decreased with further increase in reaction time (Fig. 2(b)). This variation of percent graft yields with time can be explained on the basis that as the reaction time increased, more and

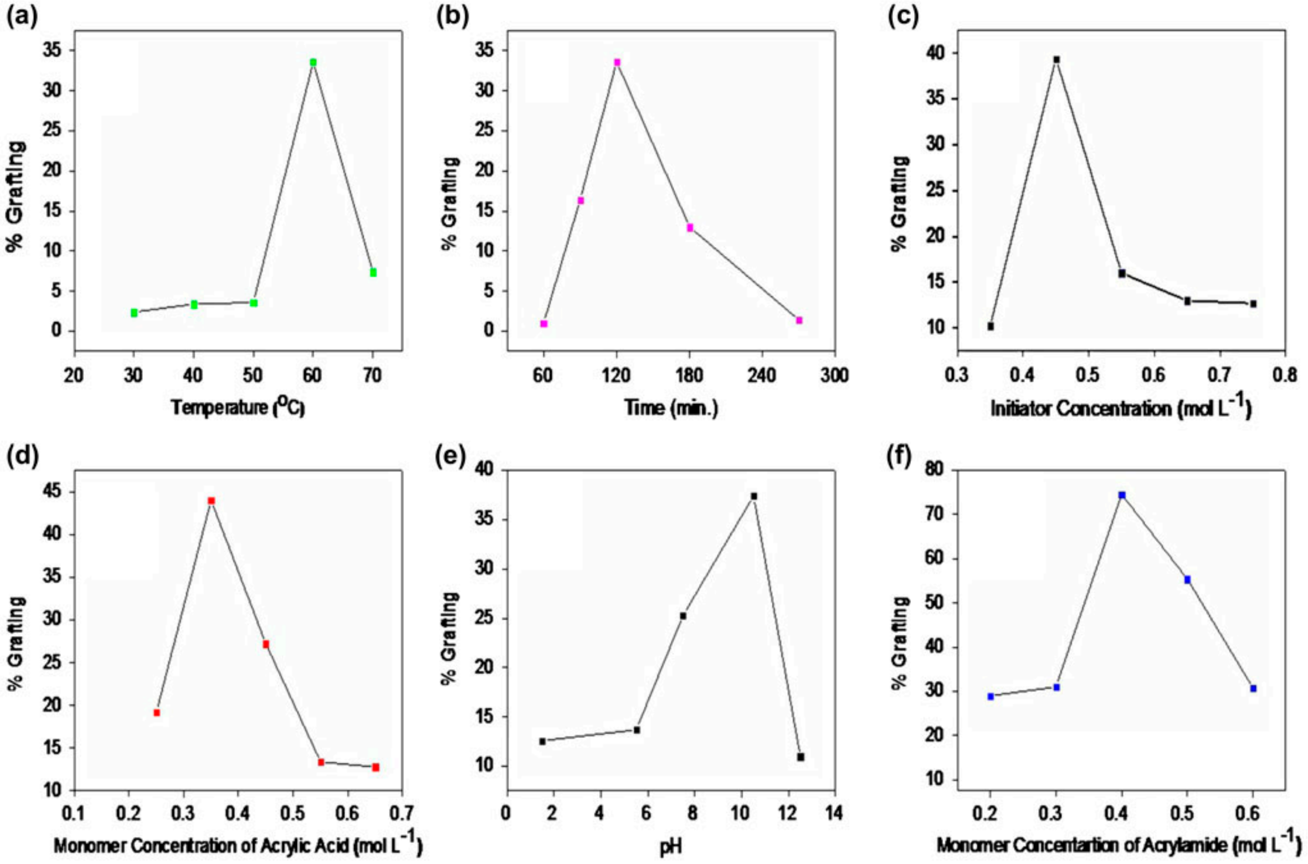


Fig. 2. Variation of grafting % with (a) Temperature (b) Time (c) Initiator concentration (d) Monomer concentration (d) pH and (e) AAm monomer concentration with fixed concentration of AAc (0.35 M).

more radicals move onto the backbone, resulted in the increase in graft yield. After reaching the optimum value, as the reaction time further increased, most of the active sites on the backbone are occupied by the radicals and the formation of the homopolymer dominated the graft copolymerization [36]. The Fig. 2(c) shows the effect of initiator concentration on grafting. The ceric ions from CAN ($0.45\,\text{mmol}\,\text{L}^{-1}$) complexed with carbon chains on the backbone and generated active sites. Also ceric ions generated free radicals in the monomer chains as the concentration of initiator increased, more and more radicals are generated, which resulted in the increase in grafting. After reaching the optimum value, the graft yield decreased with further increase in the initiator concentration. The increase in initiator concentration, chain termination reactions dominated the graft copolymerization, which leads to premature decay of the monomer radicals [37]. The graft yield also depends on monomer concentration. With initial increase in monomer concentration, the percent grafting increased and reached up to the optimum value at $0.35\,\text{mol}\,\text{L}^{-1}$ and then decreased with further increase in the monomer concentration (Fig. 2(d)). The behavior of the monomer concentration may be explained on the basis that more and more radicals reached onto the backbone, resulted in the increase in graft yield. Further increase in the monomer concentration, homopolymerization dominated over graft copolymerization, leading to decrease graft yield [38]. The graft yield increased with the increase in pH up to 10 and then started to decrease as the pH was further increased (Fig. 2(e)) [39]. The effect of monomer concentration on the percent graft yield with fixed concentration of 0.35 M AAc and different concentration of AAm for *H. cannabinus-g-(AAc)* was studied. It was found that with the increase in AAm monomer concentration up to 0.4 M, the graft yield increased and then started to decrease with further increase in the concentration. The maximum percent graft yield was found to be 74.6% at $0.4\,\text{mol}\,\text{L}^{-1}$ of AAm (Fig. 2(f)).

The FTIR spectra in Fig. 3(a) of *H. cannabinus* fiber showed broad peaks at $3{,}410\,\text{cm}^{-1}$ which may be due to the presence of the hydrogen bonded –OH stretching of the cellulose structure, $2{,}918\,\text{cm}^{-1}$ was due to asymmetric stretching of $-CH_2$ group, 2,198 cm^{-1} due to –OH stretching of absorbed moisture, $1{,}642\,\text{cm}^{-1}$ due to H–O–H bending of absorbed water and for C–H deformation, $1{,}502\,\text{cm}^{-1}$ due to aromatic vibration and stretching, $1{,}427\,\text{cm}^{-1}$, $1{,}379\,\text{cm}^{-1}$, $1{,}337\,\text{cm}^{-1}$ were due to –CH, $-CH_2$, and CH_3, respectively. The peaks at 1,161 and $1{,}055\,\text{cm}^{-1}$ were due to antisymmetric stretching vibration of C–O–C and C–O of saccharide structure. The peaks at $898\,\text{cm}^{-1}$ were due to β–glycosidic linkage and $602\,\text{cm}^{-1}$ due to out of plane –OH bending. In case of *H. cannabinus-g-(AAc)* shown in Fig. 3(b), additional peaks were found at $1{,}726\,\text{cm}^{-1}$ due to C=O of AAc and $1{,}248\,\text{cm}^{-1}$ due to –C–O of AAc. The FTIR spectra of *H. cannabinus-g-poly (AAc + AAm)* fiber shown in Fig. 3(c) the additional peaks were observed at 1,656 and $3{,}420\,\text{cm}^{-1}$, which were due to C=O of amide and due to stretching of NH_2 of amide group [40–43].

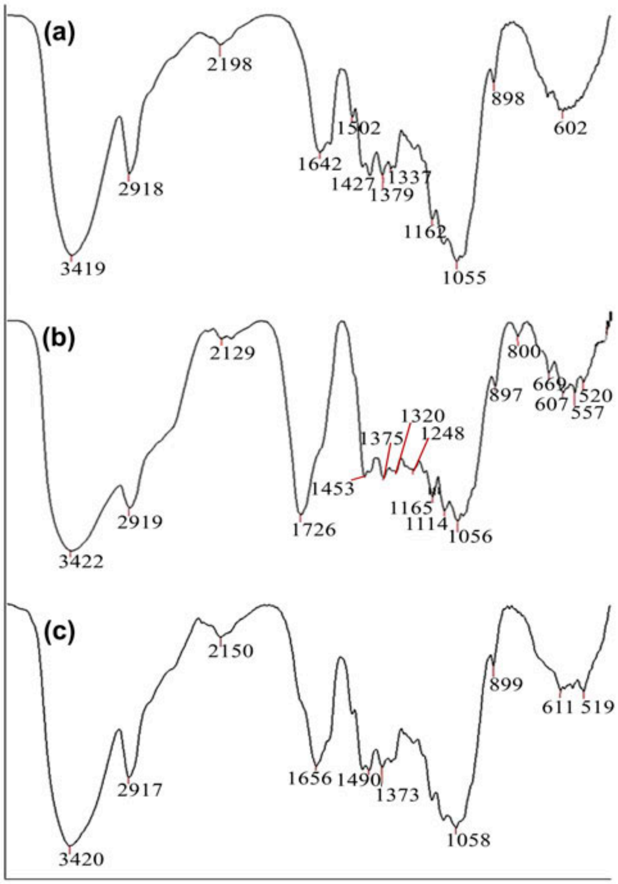


Fig. 3. FTIR spectra of (a) *H. cannabinus* (b) *H. cannabinus-g-poly(AAc)* (c) *H. cannabinus-g-poly(AAc + AAm).*

The changes in the topography and morphology of fiber surfaces are studied by SEM. It is observed that the surface of grafted fibers (Fig. 4(b) and (c)) is highly rough in comparison with the raw fiber, as shown in Fig. 4(a). This is attributed to the high graft density. It was observed that the adhesion of the grafted fiber to other materials to form composites such as phenol formaldehyde, urea improves with an increase in the roughness of its surface. This results in increased surface area for bonding and mechanical interlocking. Hence, the adhesion power of raw fiber is increased by graft copolymerization.

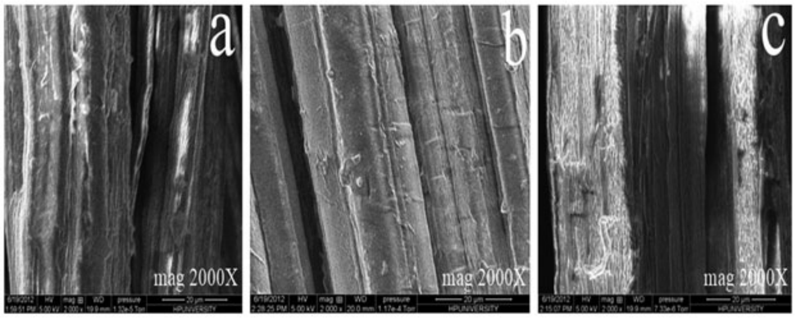


Fig. 4. SEM micrographs of (a) *H. cannabinus* (b) *H. cannabinus-g-poly(AAc)* (c) *H. cannabinus-g-poly(AAc + AAm).*

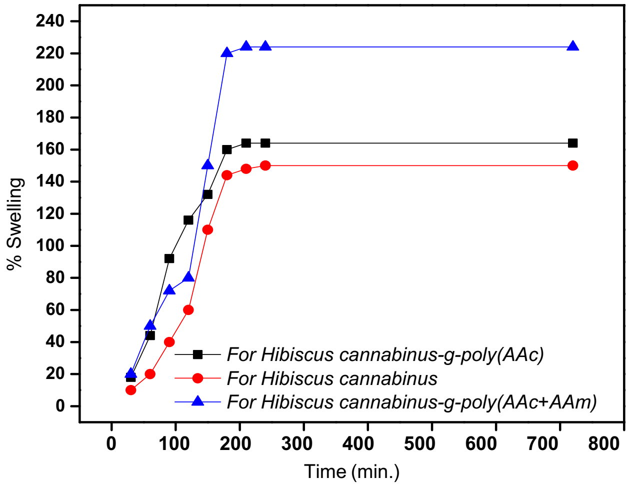


Fig. 5. Swelling behavior for *H. cannabinus, H. cannabinus-g-poly(AAc), H. cannabinus-g-poly(AAc + AAm)* fibres in demineralised water.

Swelling behavior of fibers as shown in Fig. 5 was mainly affected by the structural and the environmental factors. Structural factors can be tailored by synthetic conditions those determines swell ability of fibers as hydrophilicity in fibers was due to the presence of –OH, –COOH, and $–CONH_2$ groups. The grafted fiber showed more swelling behavior as compare to the raw fiber due to the presence of –OH and –COOH groups. The binary fiber showed maximum swelling behavior due to the presence of $–CONH_2$ group, which is hydrophilic in nature. The maximum swelling of 224% was found for *H. cannabinus-g-poly (AAc + AAm)* fibers.

The chemical resistance of raw, grafted, and binary grafted fiber was studied by keeping the different fiber samples in acid (1 and 5 N HNO_3) and base (1 and 5 N NaOH) for a period for 5 h. For given strength of acid and base, raw fibers showed

Table 1
Chemical resistance of raw and grafted samples in HNO_3 and NaOH solutions

Fiber	1 N HNO_3 (%)	5 N HNO_3 (%)	1 N NaOH (%)	5 N NaOH (%)
Hibiscus cannabinus-g-poly(AAc+AAm)	68	42.23	72.12	54.89
Hibiscus cannabinus-g-poly(AAc)	79.23	67.51	78.72	66.10
Raw Hibiscus cannabinus	90.11	72.3	89.61	69.71

Table 2
Adsorption of dye

Initial concentration of dye (mg L^{-1})	*H. cannabinus-g-poly(AAc)* (q_e)	*Raw H. cannabinus* (q_e)	*H. cannabinus-g-poly(AAc+AAm)* (q_e)
4.8	2.88	2.27	2.82
6.4	3.55	3.18	3.46
8.0	4.67	3.72	5.185
9.6	6.17	4.35	6.11
11.2	7.11	4.38	6.988
12.8	7.04	5.64	6.226

maximum weight loss. The weight loss of grafted and binary grafted fiber was less which indicated that grafting increased the chemical resistance of fiber and the results are shown in Table 1. The results for dye removal by grafted and raw fibers are shown in Table 2. The maximum q_e values of 7.11 mg g^{-1} were observed for *H. cannabinus-g-poly(AAc)* and 6.98 mg g^{-1} for *H. cannabinus-g-poly(AAc + AAm)* were higher than for *H. cannabinus* fiber, that is, 5.94 mg g^{-1}. The adsorption is a mass transfer process that can generally be defined as the accumulation of material at the interface between two phases. The initial dye concentration is one of the most important factors controlling the adsorption of dye on to the adsorbent. The amount of the dye adsorbed onto material increased with an increase in the initial dye concentration of solution if the amount of adsorbent was kept unchanged. This was due to the increase in the driving force of the concentration gradient with the higher initial dye concentration. The adsorption of dye by fibers was very intense and reaches equilibrium very quickly at low initial concentration. At a fixed fibers dosage, the amount of dye adsorbed increased with increasing concentration of solution, but the percentage of adsorption decreased. In other words, the residual dye concentration will be higher for higher initial dye concentrations in the solution. The higher values of q_e show more number of functional active groups was present on the surfaces of grafted fibers as compared to raw fibers.

4. Conclusion

H. cannabinus fiber was modified through graft copolymerization of AAc in air. The different reaction parameters were optimized to get maximum % grafting yield, that is, 93.6%. The binary mixture (AAc + AAm) was graft copolymerized on *H. cannabinus* fiber and maximum grafting was found to be 74.6% at molar concentration of 0.35 M for AAc and 0.40 M for AAm. It was concluded from the evaluation of physical properties of binary grafted polymer that incorporation of poly(AAc + AAm) chains on the surface of the cellulosic fiber through graft copolymerization increased the affinity of cellulosic fibers with water. By modification through grafting, the chemical resistance of fiber increased. The FTIR spectrum of modified fiber showed characteristics peaks for desired functionalities. The AAc grafted and AAc + AAm binary grafted fiber showed better q_e values then raw fiber. Thus, grafted and binary grafted fiber could be potential candidate for the removal of pollutant organic dye.

Acknowledgment

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

References

[1] J. Chen, J. Yi, P. Sun, Z.-T. Liu, Z.-W. Liu, Grafting from ramie fiber with poly(MMA) or poly(MA) via reversible addition-fragmentation chain transfer polymerization, Cellulose 16 (2009) 1133–1145.
[2] I. Hutton, H. Azizi, N. Naeimian, Rheological behavior of polypropylene/kenaf fiber/wood flour hybrid composite, Iran Polym. J. 17 (2008) 191–198.
[3] C. Baley, Analysis of the flax fibers tensile behavior and analysis of the tensile stiffness increase, Compos. Part A 33 (2002) 339–348.
[4] C. Baley, Mechanical properties of flex fiber/polypropylene composites. Influence of fiber matrix modification and glass fiber hybridization, Compos. Part A 36 (2002) 1637–1644.
[5] S. Zakaria, K.L. Poh, Polystyrene benzoylated EFB reinforced composites, Polym. Plast. Technol. Eng. 41 (2001) 951–962.
[6] A.K. Mohanty, A. Wibowo, M. Misra, L.T. Drzal, Effect of process engineering on the performance of natural fiber reinforced cellulose acetate biocomposites, Compos. Part A 35 (2004) 363–370.
[7] A.K. Mohanty, A. Wibowo, M. Misra, L.T. Drazal, Effect of process engineering on the performance on natural fiber reinforced cellulose acetate biocomposites, Compos. Part A 35 (2003) 363–370.
[8] P. Akkas, O. Güven, Enhancement of uranyl ion up take by pre-structuring of acrylamide-malic acid hydrogels, J. Appl. Polym. Sci. 78 (2000) 284–289.
[9] M.J. John, R.D. Anandjiwala, Recent developments in chemical modification and characterization of natural fiber-reinforced composites, Polym. Comp. 29 (2008) 187–207.
[10] E.A.M. Mohd, H.M. Akil, B. Azhar, M.I.Z. Ariffin, Chemical modification of kenaf fiber, Mater. Lett. 61 (2007) 2023–2025.
[11] B.V. Voorn, H.H.G. Smit, R.J. Sinke, B. de Klerk, Natural fibre reinforced sheet moulding compound, Compos. Part A 32 (2001) 1271–1279.
[12] B.S. Kaith, A.S. Singha, S.K. Sharma, Synthesis of graft copolymers of binary vinyl monomer mixtures and flax fiber using FAS-KPS redox system, Int. J. Chem. Sci. 2 (2004) 37–43.
[13] B.S. Kaith, A.S. Singha, S.K. Sharma, Graft copolymerization of flax fibers with binary vinyl monomer mixtures and evaluation of swelling, moisture absorbance and thermal behavior of the grafted fibers, J. Polym. Mater. 20 (2003) 195–199.
[14] V. Kumar, Y.K. Bhardwaj, K.P. Rawat, S. Sabharwal, Radiation-induced grafting of vinylbenzyltrimethyl ammonium chloride (VBT) onto cotton fabric and study of its anti-bacterial activities, Radiat. Phys. Chem. 73 (2005) 175–182.
[15] A.S. Singha, B.S. Kaith, S. Kumar, Evaluation of physical and chemical properties of FAS—KPS induced graft co-polymerization of binary vinyl monomer mixtures onto mercerized flax, Int. J. Chem. Sci. 2 (2004) 472–478.

[16] J.S. Lee, R.N. Kumar, H.D. Rozman, B.M.N. Azemi, Pasting, swelling and solubility properties of UV initiated starch-graft-poly(AA), Food Chem. 91 (2005) 203–211.

[17] V. Singh, D.N. Tripathi, A. Tiwari, R. Sanghi, Microwave synthesized chitosan-graft-poly(methylmethacrylate): An efficient Zn^{2+} ion binder, Carbohydr. Polym. 65 (2006) 35–41.

[18] A.S. Singha, R.K. Rana, Enhancement of hydrophobic character of lignocellulosic fibers through graft-copolymerization, Adv. Mater. Lett. 1 (2010) 156–163.

[19] A.V.R. Prasad, K. Rao, K.S. Gupta, B.V. Reddy, A Study on flexural properties of wildcane grass fiber-reinforced polyester composites, J. Mater. Sci. 46 (2011) 2627–2634.

[20] M. Meng, X. Gao, J. Zhang, J. Yun, Y. Zhang, Graft copolymer prepared by atom transfer radical polymerization (ATRP) from cellulose polymer, Cellulose 50 (2009) 447–454.

[21] B.N. Mishra, A. Bhattacharya, Grafting: A versatile mean to modify polymers: Techniques, factors and applications, J. Appl. Polym. Sci. 29 (1980) 767–814.

[22] L. Zhen, J. Hao, M. Yuan, X. Deng, Ring opening polymerization of adipic anhydride initiated by dibutylmagnesium initiator, Eur. Polym. J. 39 (2003) 313–317.

[23] B.L. Lee, T.F. Walsh, S.T. Won, H.M. Patts, Penetration failure mechanism of armour grade fiber composite under impact, J. Appl. Polym. Sci. 35 (2001) 1605–1633.

[24] A.S. Singha, R.K. Rana, Microwave induced graft copolymerization of methyl methacrylate onto lignocellulosic fibers, Int. J. Polym. Anal. Charact. 15 (2010) 370–386.

[25] F. Khan, Photoinduced graft-copolymer synthesis and characterization of methacrylic acid onto natural biodegradable lignocelluloses fiber, Biomacromolecules 5 (2004) 1056–1067.

[26] F. Khan, S.R. Ahmad, F. Kronfki, γ-Radiation induced changes in the physical and chemical properties of lignocelluloses, Biomacromolecules 7 (2006) 2302–2309.

[27] H.D. Rozman, K.R. Ahmadhilmi, Polyurethane (PU)—Oil palm empty fruit bunch (EFB) composites: The effect of EFBG reinforcement in mat form and isocyanate treatment on the mechanical properties, Polym. Test. 23 (2004) 559–565.

[28] A. Bessadok, S. Marais, S. Roudesli, C. Lixon, M. Metayer, Influence of chemical modifications on water-sorption and mechanical properties of Agave fibres, Compos. Part A 39 (2008) 29–45.

[29] P. Lanthong, R. Nuisin, S. Kiatkamjornwong, Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents, Carbohydr. Polym. 66 (2006) 229–245.

[30] C. Xiao, L. Wu, S. Ren, Study on graft copolymerization of acrylic acid onto ramie fibers with cromic acid initiation system, J. Nat. Sci. 3 (1998) 316–320.

[31] M.G. Samal, M.G. Kumaran, S. Thomas, Effect of fiber surface modification on water sorption characteristics of oil palm fiber, Compos. Sci. Technol. 34 (1994) 67–78.

[32] T. Sun, P. Xu, Q. Liu, W.M. Xie, Graft copolymerization of methacrylic acid onto carboxy methyl chitosan, Eur. Polym. J. 39 (2003) 189–192.

[33] D.S. Varma, V. Narasimhan, Physical properties of natural and modified cotton cellulose grafted with acrylate monomer, J. Appl. Polym. Sci. 18 (1974) 3745–3759.

[34] A. Nagaty, S.E. Shakra, S.T. Ibrahim, O.Y. Mansour, Properties of grafted cellulose with vinyl polymers, Cell. Chem. Technol. 14 (1980) 177–189.

[35] X. Yuan, Jing Sheng, F. He, Y. Tang, X.S. Ning, Surface modification of acrylonitrile copolymer membranes by grafting acrylamide. II. Initiation by Fe^{2+}/H_2O_2, J. Appl. Polym. Sci. 69 (1998) 1907–1915.

[36] N.C. Nayak, H.K. Das, B.C. Singh, Influence of glycine on the kinetics of the graft copolymerization of acrylonitrile onto jute fibers initiated by ceric ion, J. Appl. Polym. Sci. 42 (1991) 2391–2396.

[37] L. Rahman, S. Silong, M.Z. Wan, A. Zaki, A. Mansor, H. Jelas, Graft copolymerization of methyl acrylate onto sago starch using ceric ammonium nitrate as an initiator, J. Appl. Polym. Sci. 76 (2000) 516–523.

[38] Y. Huang, B. Zhao, G. Zheng, S. He, J. GaO, Graft copolymerization of methyl methacrylate on stone ground wood using the H_2O_2–Fe^2 method, J. Appl. Polym. Sci. 45 (1992) 71–77.

[39] D.J. Mcdowall, B.S. Gupta, V.T. Stannett, Grafting of vinyl monomers to cellulose by ceric ion initiation, Progr. Polym. Sci. 10 (1984) 1–50.

[40] J. Prachayawarakorn, K. Boonsawat, Physical, chemical, and dyeing properties of bombyxmori silks grafted by 2-hydroxyethyl methacrylate and methyl methacrylate, J. Appl. Polym. Sci. 106 (2007) 1526–1534.

[41] A. Biswas, J.L. Willet, S.H. Gordon, V.L. Finkenstadt, H.N. Cheng, Complexation and blending of starch, poly(acrylic acid), and poly(N-vinyl pyrrolidone), Carbohydr. Polym. 65 (2006) 397–403.

[42] Z. Zhu, M. Li, E. Jin, Effect of an allyl pretreatment of starch on the grafting efficiency and properties of allyl sta(rch-g-poly(acrylic acid), J. Appl. Polym. Sci. 112 (2009) 2822–2829.

[43] Y. Zheng, S. Hua, A. Wang, Adsorption behavior of Cu^{2+} from aqueous solutions onto starch-g-poly (acrylic acid)/sodium humate hydrogels, Desalination 263 (2010) 170–175.