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Amputation of congo red dye from waste water using microwave induced grafted *Luffa cylindrica* cellulosic fiber

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ABSTRACT

The present study deals with the surface modification of *Luffa cylindrica* fiber through graft copolymerization of methyl acrylate/acrylamide (MA/AAm) via microwave radiation without the use of initiator. Various reaction parameters effecting grafting yield were optimized and physico-chemical properties were evaluated. The grafted *Luffa cylindrica* fiber showed morphological transformations, thermal stability and chemical resistance. The adsorption potential of modified fiber was investigated using adsorption isotherms for hazardous congo red dye removal from aqueous system. The maximum adsorption capacity of dye onto grafted *Luffa cylindrica* fiber was found to be 17.39 mg/g with best fit for Langmuir adsorption isotherm. The values of thermodynamic parameters such as enthalpy change, ΔH^0 (21.27 kJ/mol), entropy change, ΔS^0 (64.71 J/mol K) and free energy change, ΔG^0 (−139.52 kJ/mol) were also calculated. Adsorption process was found spontaneous and endothermic in nature.

1. Introduction

Recently, the surface modification of natural polymers has received great consideration with new developments in science and technology. Lignocellulosic materials developed with substantial alteration in physicochemical properties have been mainly employed as electrical insulators, thermal insulators, vacuum sealants, adsorbents and matrix materials for composites. The desirable and targeted physico-chemical properties can be added to natural polymers through various physico-chemical methods in order to meet the specialized applications (Bhattacharya & Misra, 2004; Gupta, Jain, & Varshney, 2007; Gupta, Singh, Al Khayat, & Gupta, 2007; Goyal, Gupta, & Chatterjee, 2008).

Polysaccharides of vegetable origin are unique raw materials as they are abundant in nature, inexpensive, biodegradable, renewable, stable, hydrophilic and modifiable biopolymers. The dried fruit of *Luffa cylindrica* (Lc) has been used as good source of lignocellulosic fiber. Luffa sponge contains about 60% of cellulose, 30% hemicelluslose and 10% lignin (Rowell, James, & Jeffrey, 2002). The heterogeneity makes the fibers a potential raw material for many industrial applications. 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 (Pathania & Sharma, 2012a,b; Zhenping, Xiulin, Mingchen, Chen, & Zhang, 2003). Thus, to improve the compatibility between cellulosic chains and hydrophobic polymer matrices, various physical or chemical surface treatments have been explored (Clasen & Kulicke, 2001; Gupta, Pathania, Agarwal, & Sharma, 2012; Gupta, Ali, Saleh, Nayak, & Agarwal, 2012; Gupta, Agarwal, & Saleh, 2011). Graft copolymerization has been considered to be a powerful method for surface modification of lignocellulosic fibers (Gupta, Pathania, Sharma, Agarwal, & Singh, 2013). The improvement in dyeing, printing, chemical resistance, water repelling, fiber strength and abrasion resistance are the some advantages of graft copolymerization (Singha & Rana, 2010).

The grafting under the influence of microwave radiation is rapid, efficient, clean, cheap, convenient, energy saving and green method (Gupta, Pathania, Sharma, & Singh, 2013). Microwave heating is an alternative to conventional heating techniques as the microwave energy can easily penetrate and all particles can be heated simultaneously, thus reducing heat transfer problems (Bogdal, Penczek, Pielichowski, & Prociak, 2003; Hou, Wang, & Wu, 2008). Recently, microwave radiation has been used in the grafting of monomers onto natural fiber without the use of initiator (Jocob, Chia, & Boey, 1997; Singh, Tiwari, Tripathi, & Sanghi, 2004). In the presence of

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microwave radiation the oxidative reactions are initiated and free radicals are produced, which leads ultimately to graft reactions.

The environment pollution due to toxic compounds discharged from the industrial effluent has been increased with advancement of life. Dyes are the most important constituents among the toxic compounds present in the effluent (Gupta, Agarwal, Pathania, Kothiyal, & Sharma, 2013; Gupta & Ali, 2008; Gupta, Pathania, Agarwal, & Singh, 2012; Gupta, Pathania, Kothiyal, & Sharma, 2013). Due to the toxicity of organic dyes to human health, their removal from water system was of great concern. Many methods have been used for the removal of organic dyes from water (Bhattacharyya & Sharma, 2005; Gupta & Ali, 2008; Wang & Zhu, 2007). However, due to disadvantages associated with conventional methods, adsorption process has been used for the removal of organic dye. Adsorption is one of the most effective methods, economically viable, technically feasible and socially acceptable method employed for the treatment of waste water containing dye (Gupta & Rastogi, 2009; Pathania & Sharma, 2012a,b; Pathania, Sharma, Kumar, & Kothiyal, 2014; Rathore, Gupta, Pathania, Sharma, 2014).

Cellulosic fibers modified with different monomers have been used as adsorbents for the removal of organic impurities from water system due to of their good selectivity, favorable physicochemical stability, remarkable functionality, enhanced surface area and porosity (Gadhari, Sanghavi, & Srivastava, 2010). The grafting usually increased the adsorption sites and hence enhance the sorption selectivity of different organic pollutants (Gupta, Agarwal, Singh, & Pathania, 2013; Gupta, Pathania, Sharma, et al., 2013).

In view of above facts, the present work deals with the evaluating the viability of using microwave radiations for grafting of binary monomer onto the cellulosic *Luffa Cylindrica* fiber without using initiator. The functional and surface chemistry of the grafted fibers were analyzed. The adsorption capacity of the sample was tested for removal of congo red dye from aqueous system. Moreover, adsorption equilibrium isotherms and thermodynamic studies were also investigated. Thus, efforts have been made to convert this biomass into inexpensive and effective material for industrial purposes.

2. Experimental

2.1. Materials

Methyl acrylate (MA), acrylamide (AAm) and congo red dye were purchased from E. Merck Pvt. Ltd., India. Sodium hydroxide, potassium bromide, ethanol and benzene were received from CHD Ltd., India. Acetone (Rankem Pvt. Ltd., India), nitric acid and dimethyl formamide were obtained from SD Fine Pvt. Ltd., India. All chemicals in this study were used as received.

2.2. Instrumentation

X-ray diffraction (XRD) was carried out on X-ray diffractometer (Bruker D8 Advance). Infra red spectra were recorded on FT-IR spectrophotometer (Perkin Elmer Spectrum 400) using KBr pellets. The morphology study of surface was performed by scanning electron microscope (JEOL, JSM-6610LL, Japan). Perkin Elmer (Pyris Diamond, USA) Thermal Analyzer was used to determine the thermal analysis. The concentrations of dye were determined using UV-vis spectrophotometer (Systronics 117).

2.3. Extraction and purification of Luffa cylindrica fiber (LcF)

Luffa cylindrica fibers (LcF) were obtained from dried and ripe fruit collected from the local fields. The fiber was first extracted from the fruit by soaking in water for 24 h and washed with 2% detergent solution. The fibers were subjected to soxhlet extraction with acetone for 12 h in order to remove the impurities. Then the fibers were washed thoroughly with distilled water.

2.4. Mercerization of Luffa cylindrica fiber

In this process, *Luffa cylindrica* fibers were pre-treated with 5% sodium hydroxide for 30 min to increase its hydrophilicity. The alkali treated fibers were washed thoroughly with distilled water until the pH of wash water come close to neutral. The fibers were then dried in oven at 50 °C for 12 h.

$$\text{Fiber-OH} + \text{NaOH} \rightarrow \text{Fiber-O}^{-}\text{Na}^{+} + \text{H}_2\text{O}$$

2.5. Graft copolymerization of methyl acrylate (MA)/acrylamide (AAm) onto Luffa cylindrica fiber under microwave irradiation

0.5 g of mercerized *Luffa cylindrica* fiber was immersed in 100 mL double distilled water for 24 h prior to graft copolymerization in order to activate the reaction sites on the fiber surface. Then the known amount of methyl acrylate/acryl amide binary monomer in definite ratio was added with constant stirring for definite time. Different reaction parameters such as monomer concentration, temperature and microwave exposure time were optimized. The homopolymer formed during the graft copolymerization was removed with hot distilled water followed by methanol. The grafted *Luffa cylindrica* fibers (*Lc-g-poly(MA/AAm)*) thus obtained were dried at 50 °C for 12 h in a hot air oven. The percentage grafting yield (*G*%) of grafted sample was calculated as follow:

$$\text{Grafting yield} = \frac{W_3 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 is the initial weight of the raw fiber and W_3 is the final weight of the grafted fiber after extraction of homopolymer. The general grafting reaction of binary monomer onto *Luffa cylindrica* cellulosic fiber has been shown as follow:

$$\underset{\text{(L. cylindrica fiber)}}{\text{Cellulose----OH}} + \underset{\text{(binary monomer)}}{\text{MA/AAm}} \xrightarrow{\text{MW}} \underset{\text{(Poly-g-copolymer)}}{\text{Cellulose----(MA/AAm)}_n}$$

2.6. Characterization of grafted fiber

2.6.1. Fourier transform infrared (FTIR)

Fourier transform infrared spectra of raw and grafted samples were recorded by Perkin-Elmer FTIR spectrophotometer (model 400, USA) using KBr pellets. FTIR spectra of the sample were analyzed in the range of 400–4000 cm^{-1}.

2.6.2. Thermal analysis (TGA/DTA)

Thermo gravimetric and differential thermal analysis of raw and grafted samples were carried out in nitrogen atmosphere at a heating rate of 10 °C/min using Perkin Elmer (Pyris Diamond, USA) thermal analyzer.

2.6.3. X-ray diffraction studies (XRD)

X-ray diffraction studies of raw and grafted sample were performed on Bruker D8 Advanced X-ray diffractometer, using Nickel-filtered Cu Kα radiation (λ = 0.15406 nm) and scanned from 2 to 60 °C at a scan speed of 20/min. Finely powdered samples of raw and grafted fibers were used to study the crystallinity of the samples.

2.6.4. Morphological studies

Morphological analysis of *LcF* and *Lc-g-poly(MA/AAm)* were carried out on scanning electron microscope (JEOL JSM-6100, Japan).

2.7. Physico-chemical behavior

2.7.1. Swelling behavior

The swelling studies of *LcF* and *Lc-g-poly(MA/AAm)* were performed in water, dimethyl formamide (DMF) and benzene. In this, 0.5 g sample was immersed in 100 mL solvent for 24 h. The excess of solvent was removed with filter paper. The final weight of sample was noted and percentage swelling was calculated by following formula:

$$\%\ \text{swelling} = \frac{W_f - W_i}{W_i} \times 100 \quad (2)$$

where W_i is the initial weight of the fiber and W_f is the weight after swelling of fiber.

2.7.2. Water uptake study

The water uptake capacity of *LcF* and *Lc-g-poly(MA/AAm)* was studied using concept of capillary action. In this method, the wicks of different sample of same diameter were prepared and initial ink mark is drawn at one end. These wicks were dipped into beakers containing water for 24 h. The rise in water level in each wick was noted with the help of the scale.

2.7.3. Moisture absorbance studies

0.5 g dry weight of *LcF* and *Lc-g-poly(MA/AAm)* were placed in the humidity chamber for 2 h under 40% humidity level. The final weights of the samples were noted after taking out the sample immediately. The percentage moisture absorbance (M_{abs}) was calculated by following formula:

$$\%\ \ M_{abs} = \frac{W_2 - W_1}{W_1} \times 100 \quad (3)$$

where W_1 is the initial weight of the fiber and W_2 is the weight after moisture absorbance.

2.7.4. Chemical resistance studies

Chemical resistance of samples was determined in term of percentage weight loss. In this, known weight of *LcF* and *Lc-g-poly(MA/AAm)* samples were immersed in aqueous solution of 1 N NaOH and 1 N HNO_3. Then samples were taken out and dried in hot air oven to constant weight. The final weights of the samples were noted and percentage weight loss was calculated by following formula:

$$\%\,\text{wt loss} = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

where W_1 is the initial weight of the sample and W_2 is the weight after action of acid and base.

2.8. Dye adsorption experiments

The adsorption of congo red (CR) onto grafted sample was performed using batch experiments. In this process, 0.2 g of adsorbent was added to 100 mL of dye solution of different concentrations (50–500 mg/L) and the mixture was agitated in a thermoshaker at a speed of 100 rpm for a given time at 30 °C. The suspensions were centrifuged equilibrium concentration of dye in the supernatant liquor was analyzed by double beam UV–vis spectrophotometer (Gupta, Agarwal, Singh, et al., 2013). The experiment conditions were optimized at different concentration, temperature, pH, adsorbent amount and contact time. The amount of dye adsorbed per unit mass of adsorbent, q_e, (mg/g) was obtained using following equations:

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (5)$$

where q_e (mg/L) is amount of dye adsorbed, C_0 is the initial concentration of congo red solution (mg/L), C_e is the concentration at equilibrium, V is the volume of dye solution and W is the weight of the grafted fibers. The study of isotherms was carried out by varying the concentration of CR dye (50–500 mg/L), volume (100 mL), adsorbent dose (0.50 g), pH (7), time interval (120 min) and temperature (30 °C). For thermodynamics studies, observations were made under optimized conditions at different temperatures (20–50 °C).

3. Results and discussion

3.1. Graft copolymerization of methyl acrylate/acrylamide (MA/AAm) onto Luffa cylindrica fiber

The major component of the *Luffa cylindrica* fiber is cellulose. The presence of active hydroxyl group at positions C_2, C_3 and C_4 of cellulose are responsible for graft copolymerization. Before the treatment of fiber with binary monomers it was mercerized with 5% sodium hydroxide to increase the hydrophilicity.

3.1.1. Optimization of grafting parameters

3.1.1.1. Optimization of MA concentration in MA/AAm binary monomer. The results of effect of MA concentration on grafting yields were shown in Table 1. It has been observed the grafting yield decreased with increase in the concentration of MA. It was due to dominance of homopolymerization onto cellulosic fiber with increase in monomer concentration. The maximum grafting yield (49%) was observed at 1.12×10^{-3} mol/L concentration of MA in MA/AAm binary monomer by keeping AAm concentration constant.

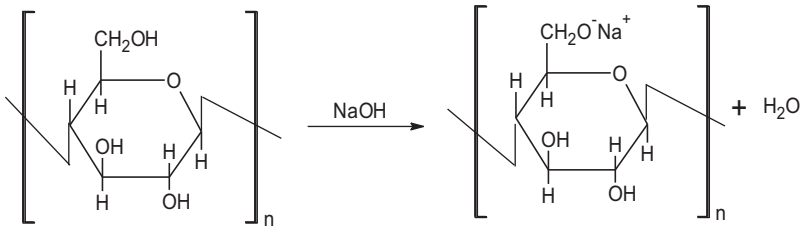
3.1.1.2. Optimization of AAm concentration in MA/AAm binary monomer. The effect of AAm concentration on grafting yields was shown in Table 1. It has been observed that grafting yield initially increased with increase in the concentration of AAm and then decreased further with increase in the concentration. The maximum grafting yield (51.08%) was observed at 2.81×10^{-3} mol/L concentration of AAm in binary monomer by keeping MA concentration constant.

3.1.1.3. Effect of microwave exposure time. Table 1 shows the variation of grafting yield with time. It is evident that with increase in the microwave irradiation time up to 2 min the grafting yield increases to 48%. Further, increase in reaction time resulted in decrease in grafting yield due to homopolymer formation and may be degradation of the cellulosic backbone of fiber (Mishra & Sen, 2011).

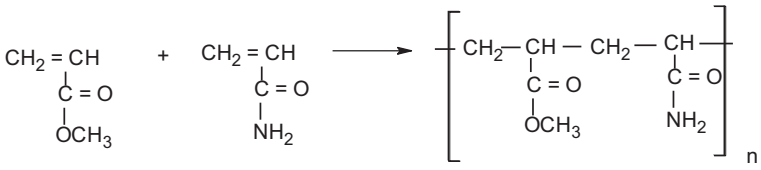
3.2. Mechanism of grafting of MA/AAm on to raw fiber of Luffa cylindrical

Cellulose is a large molecule with many —OH groups attached at different positions. It has been observed that in microwave region the resulting dielectric of cellulose molecule may cause an increase in the rate of reaction at these groups. The dielectric heating results rapid energy transfer from these groups to neighboring molecules (MA, AAm and water) as it is impossible to store the energy in specific part of the molecule. The dielectric heating results in bond breaking and creating radical sites at oxygen. Moreover, microwaves also resulted in lowering of Gibbs energy of activation of the reaction (Galema, 1997; Ibrahim, Shuy, Ang, & Wang, 2010). The proposed steps for the mechanism of grafting reactions are as follow (Mishra & Sen, 2011; Singh et al., 2004; Singha & Rana, 2010):

Step 1: Mercerization

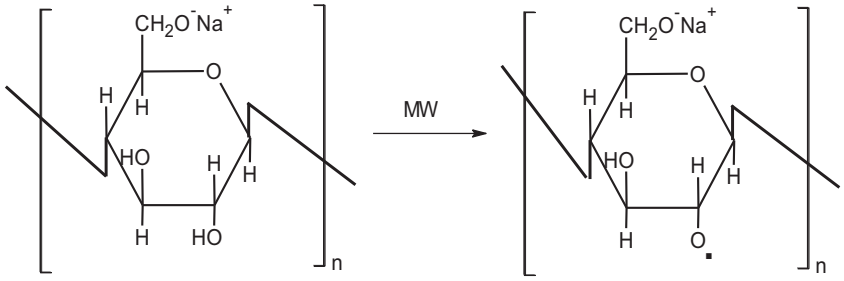


Step 2: Formation of binary monomer

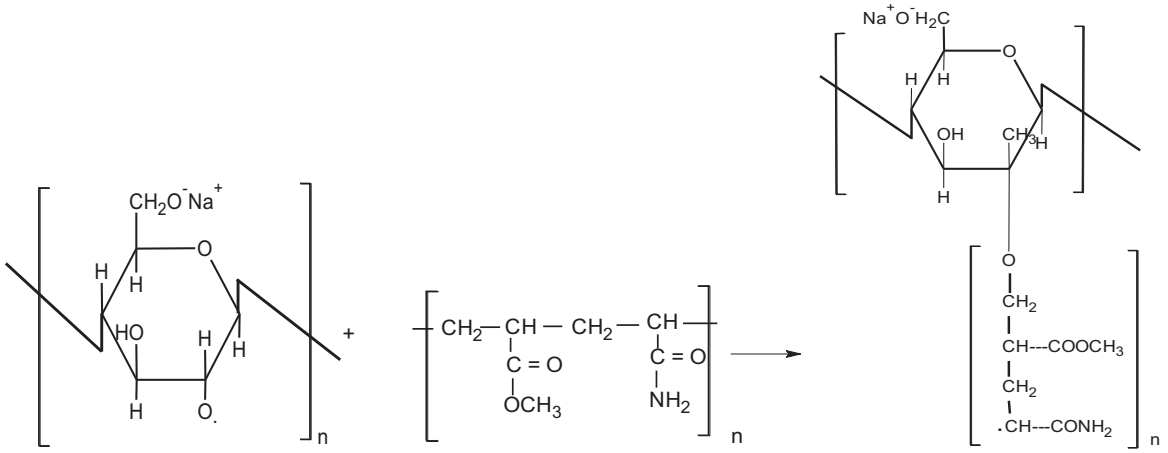


(MA) (AAm) binary (MA/AAm) copolymer

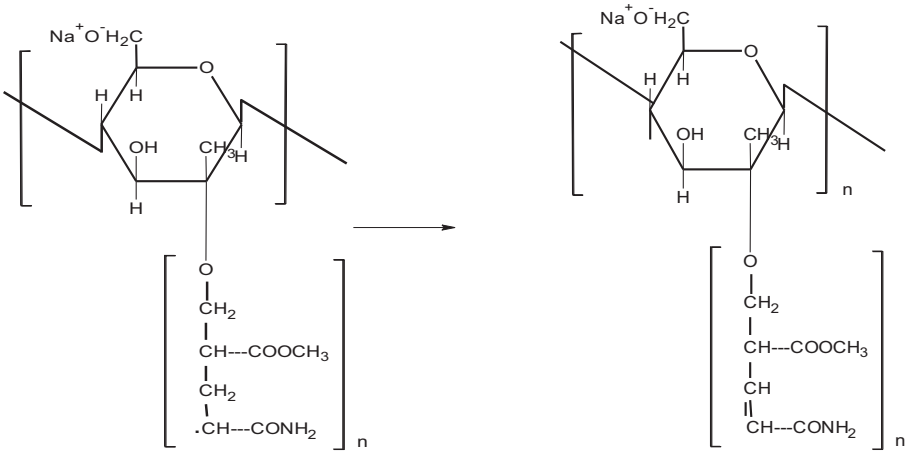
Step 3: Initiation



Step 4: Propagation

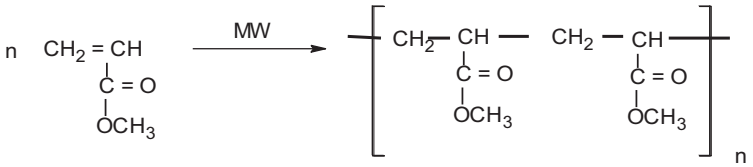


Step 5: Termination

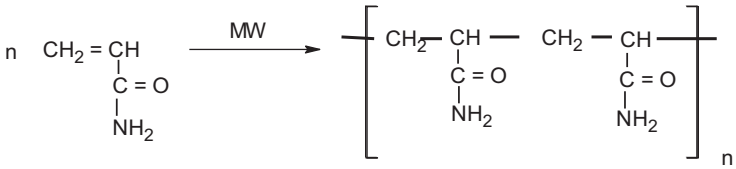


Step 6: Formation of homopolymers

(i) Homopolymer of MA



(ii) Homopolymer of AAm



3.3. Characterization of LcF and Lc-g-poly(MA/AAm)

3.3.1. X-ray diffraction (XRD)

The XRD pattern of *LcF* and *Lc-g-poly(MA/AAm)* were shown in Fig. 1(a) and (b). The *LcF* at 2θ scale showed peaks at 22.35° and 15.48° with relative intensities of 779 and 442, respectively. Similarly, *Lc-g-poly(MA/AAm)* showed peaks at 24.23° and 16.40° with relative intensities of 546 and 352, respectively. The percentage crystallinity (X_c %) and crystallinity index (C.I.) was calculated as follow (Kalia, Kumar, & Kaith, 2010; Sanghavi, Mobina, Mathur, Lahiri, & Srivastava, 2013):

$$X_C\% = \left\{ \frac{I_C}{I_A + I_C} \right\} \times 100\% \quad (6)$$

$$\text{C.I.} = \frac{I_C - I_A}{I_C} \quad (7)$$

where I_C is peak intensity of crystalline phase, I_A is peak intensity of amorphous phase.

The percentage crystallinity of *LcF* and *Lc-g-poly(MA/AAm)* fiber was observed as 63.80 and 60.80, while the crystallinity index as 0.43 and 0.35. It was observed that the intensity of the peak in *Lc-g-poly(MA/AAm)* decreased on grafting. The decrease in intensity of peak during grafting indicated decreased crystallinity of *Lc-g-poly(MA/AAm)*. However, the *Lc-g-poly (MA/AAm)* showed broadening of the peak after grafting due to convergence of the fibers toward more disordered system (Sanghavi, Kalambate, Karna, & Srivastava, 2014).

It has been observed that (Table 2) a slight decreased in percentage crystallinity of the fiber on graft copolymerization resulted in increase in randomness or disorder in the crystal lattice of cellulose fiber. This was due to incorporation of *poly(MA/AAm)* chains on the active sites of backbone during grafting and fibers became more amorphous and resulted in impaired crystalline structure (Sharma, Pathania, & Singh, 2013; Wang, Dong, & Xu, 2006).

3.3.2. Fourier transform infra red spectroscopy (FTIR)

The IR spectra of *LcF* and *Lc-g-poly(MA/AAm)* were shown in Fig. 1(c) and (d). The peak at 899 cm^{-1} may be due to C—C stretching vibration and β-glycosidic linkage (Kaur, Kumar, & Sharma, 2010). The peaks at 2856 cm^{-1} and 2925 cm^{-1} were due to symmetric and asymmetric stretching of C—H bond of —CH_2 (Mishra & Sen, 2011). The broad peak at 3401 cm^{-1} was due to stretching vibration of —OH (Singh et al., 2004). Peaks observed at 1376 cm^{-1}, 1427 cm^{-1} and 1456 cm^{-1} may be due to —CH, —CH_2, and —CH_3 bending, respectively (Singha & Rana, 2010). The additional peaks for grafted sample at 1052 cm^{-1}, 1505 cm^{-1}, 3400 cm^{-1} and 1111 cm^{-1} were due to C—O—H deformation of raw fiber, C—O of amide group of acryl amide, N—H stretching of amide group and C—O groups, respectively (Wan et al., 2011). A sharp peak at 1736 cm^{-1} was

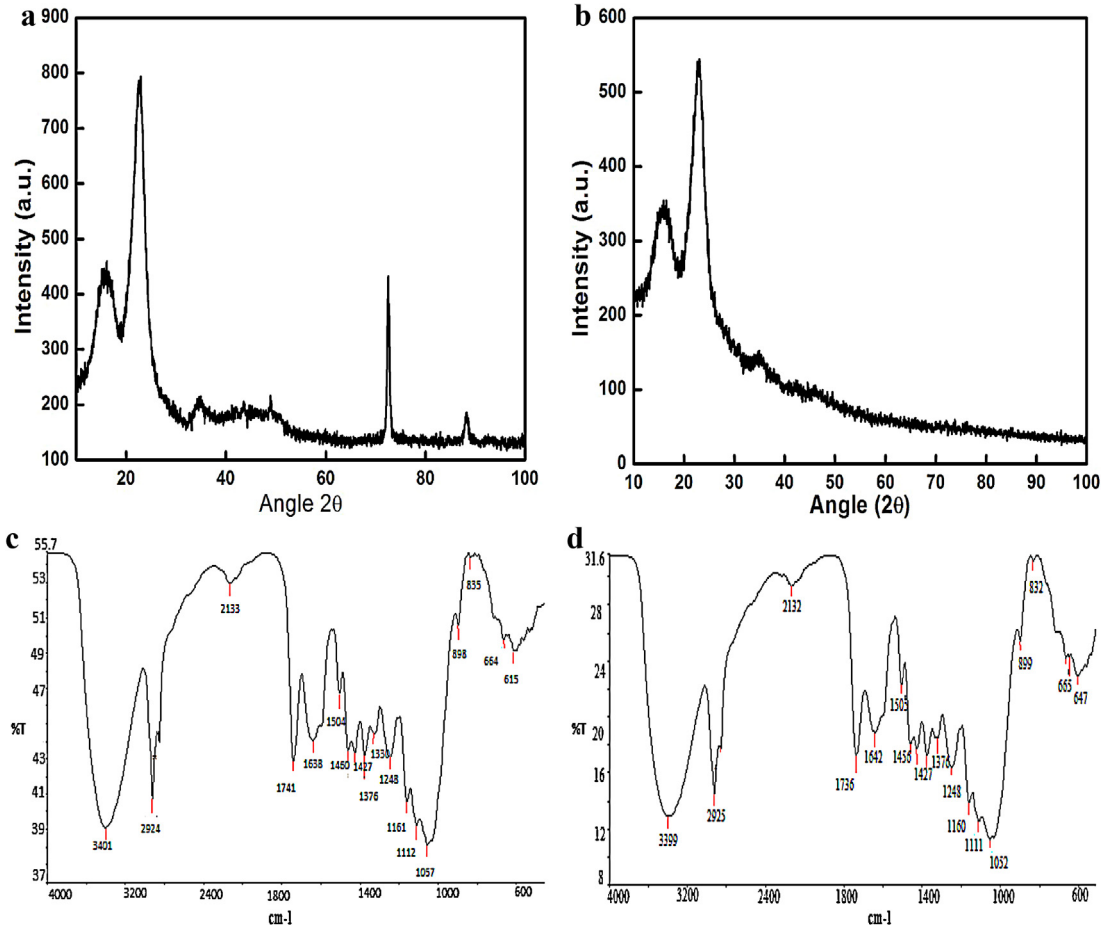


Fig. 1. (a and b) X-ray diffraction pattern of LcF and Lc-g-poly(MA/AAm) and (c and d) FTIR spectra of LcF and Lc-g-poly(MA/AAm)FTIR spectra of (a) LcF (b) Lc-g-poly(MA/AAm).

observed due to C=O group of ester (methylacrylate) (Kalia et al., 2010; Oei, Ibrahim, Wang, & Ang, 2009). The additional peaks observed in the grafted sample confirmed the grafting of MA/AAm binary monomer onto *Luffa cylindrica* fiber.

3.3.3. Thermal analysis (TGA/DTA)

Thermogravimetric analysis of *LcF* and *Lc-g-poly(MA/AAm)* was carried out as a function of weight loss verses temperature as shown in Fig. 2(a) and (b). The degradation may occur in various forms such as deacetylation, dehydration, decarboxylation and chain scissions. In TGA curve of *LcF*, two stage decomposition was observed, with maximum weight loss of 59.5% between 86.1 °C and 332.5 °C in first stage and maximum weight loss of 30.8% between 332.5 °C and 503.2 °C in second stage of decomposition. The first stage decomposition was due to loss of moisture and second stage decomposition was due to cellulosic and lignin degradation (Ibrahim, Fatimah, Ang, & Wang, 2010; Kalia et al., 2010).

The TGA curve of *Lc-g-poly(MA/AAm)* also showed two stage decomposition. The first stage decomposition was observed with 15.7% weight loss between 49.8 °C and 277.6 °C and second stage decomposition with 73.2% weight loss between 277.6 °C and 363.2 °C. This was attributed due to the strengthening of fibers due to increase in covalent bonds in the *Lc-g-poly(MA/AAm)* (Pathania, Kumar, & Bhatt, 2009; Tiwari & Singh, 2008).

Differential thermogravimetric (DTG) curve indicated the decomposition peak at 319.8 °C for *LcF* and 334.7 °C for *Lc-g-poly(MA/AAm)*. Thus DTG studies confirmed the improved thermal resistance of grafted copolymer due to incorporation of covalent bonding through inclusion of *poly(MA/AAm)* (Sanghavi, Sitaula, et al., 2013).

3.3.4. Scanning electron microscopy (SEM)

Fig. 3(a) and (b) shows the SEM micrographs of *LcF* and *Lc-g-poly(MA/AAm)*. It was revealed that the grafting results in change in morphology of the fibers. The surface of the fibers became rough

Table 1
Optimization of MA, AAm concentration and microwave exposure time.

S. no.	MA/AAm ratio ($\times 10^{-3}$ mol/L)	% grafting	MA/AAm ratio ($\times 10^{-3}$ mol/L)	% grafting	Time (min)	% grafting
1	1.12:2.81	49.0	2.23:1.40	30.21	1	43
2	2.23:2.81	48.1	2.23:2.81	51.08	2	48
3	3.36:2.81	47.8	2.23:4.21	29.22	3	38
4	4.48:2.81	43.6	2.23:5.62	27.83	4	24
5	5.60:2.81	39.8	2.23:7.03	25.74	5	21

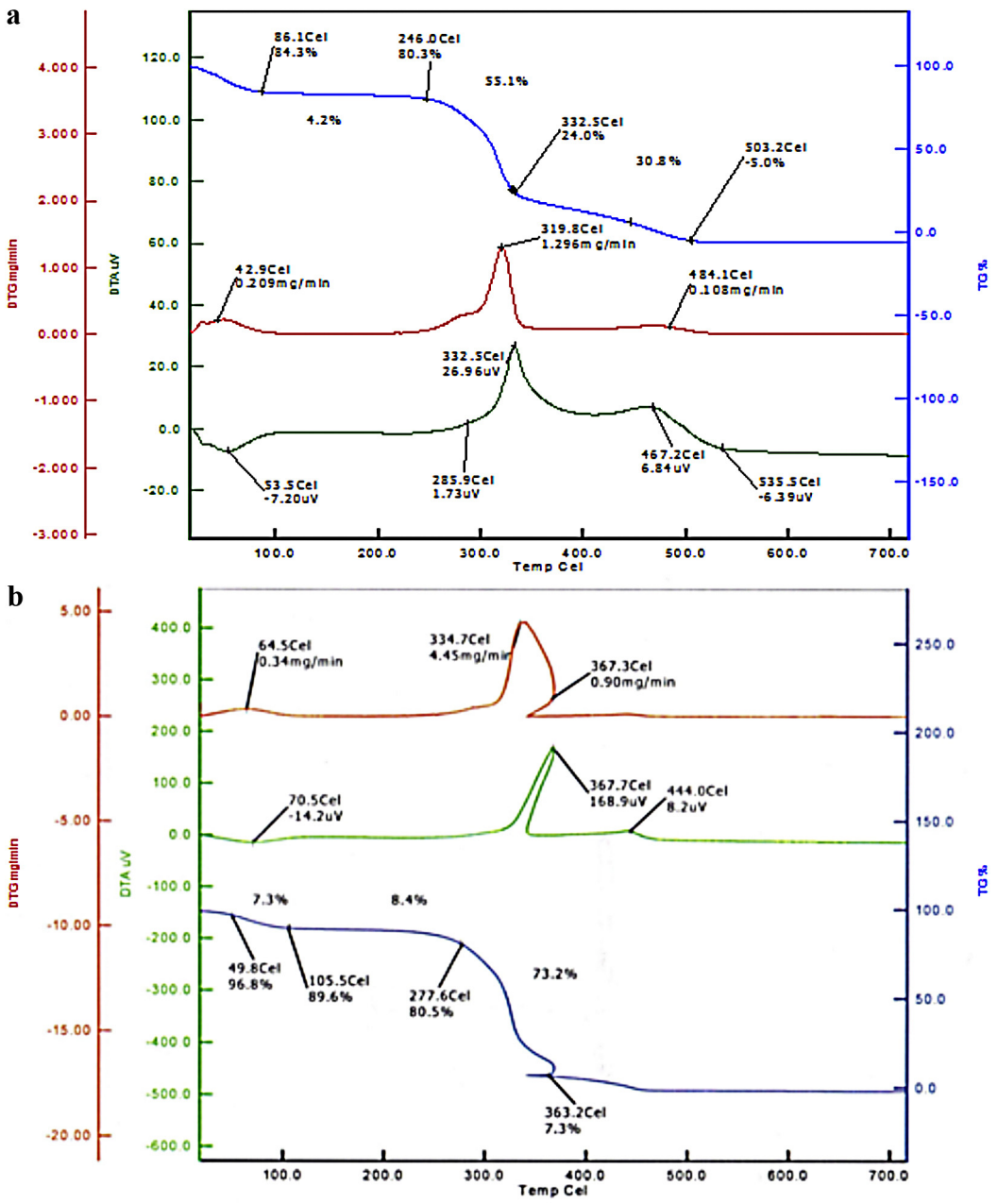


Fig. 2. TGA spectra of (a) LcF and (b) Lc-g-poly(MA/AAm).

due to attachment of polymer chains to the surface (Kalia et al., 2010; Pathania & Sharma, 2011).

3.4. Physico–chemical behaviors of Lc-g-poly(MA/AAm)

3.4.1. Swelling behavior in different solvents

The swelling behavior of *LcF and Lc-g-poly(MA/AAm)* in different solvents (water, DMF and benzene) was shown in Fig. 4(a) and (b). The *LcF* shows maximum swelling in water and the order of percentage swelling as: water > DMF > benzene. This was due to more affinity of water for free hydroxyl groups in raw cellulosic fibers (Taylor, Fanta, Doane, & Russell, 1978). The *Lc-g-poly(MA/AAm)* copolymer show more swelling in benzene than water and follows the trend as: benzene > DMF > water. This was due to blocking of active sites of *Luffa cylindrica* cellulosic fiber by grafting.

3.4.2. Moisture absorbance studies

The moisture absorbance studies on *LcF* and *Lc-g-poly(MA/AAm)* were carried out under different humidity levels. The percentage of moisture absorbance (M_{abs}) of the samples was shown in

Table 2
Percentage crystallinity and crystallization index of LcF and Lc-g-poly(MA/AAm).

Sample	2θ (°)		Intensity		%X_c	C.I.
	Crystalline peak	Amorphous peak	I_c	I_A		
LcF	22.35	15.48	779	442	63.80	0.43
Lc-g-poly(MA/AAm)	24.23	16.40	546	352	60.80	0.35

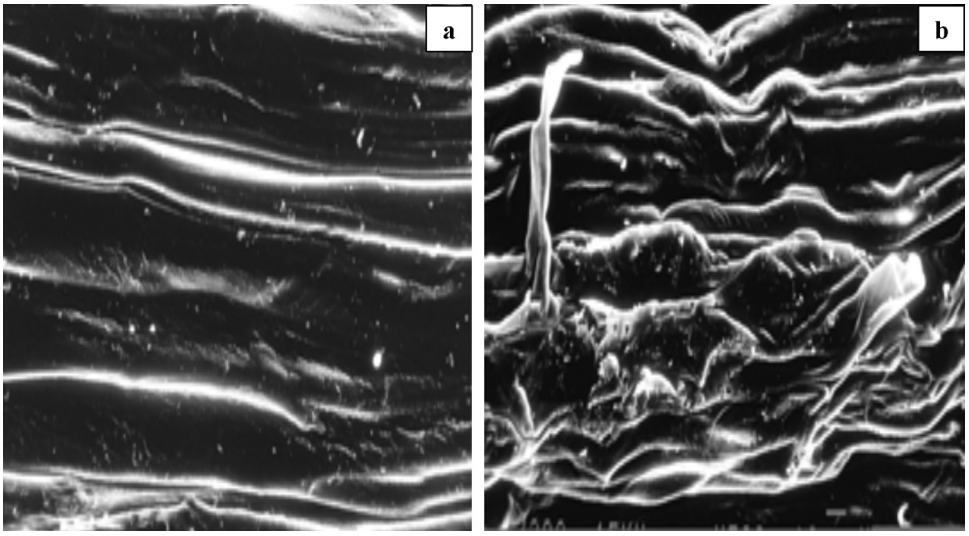


Fig. 3. SEM image of (a) LcF and (b) Lc-g-poly(MA/AAm).

Table 3
Moisture absorbance, water uptake and chemical studies of LcF and Lc-g-poly(MA/AAm).

Sample	Initial weight of sample (g)	Final weight of sample (g)	$\%M_{abs}$
(a) Moisture absorbance			
LcF	0.5	0.74	48
Lc-g-poly(MA/AAm)	0.5	0.67	34

Water uptake Sample	Length of fiber wick (cm)	Water uptake (cm)
(b) Water uptake		
LcF	5.0	3.6
Lc-g-poly(MA/AAm)	5.0	2.5

Sample	Percentage wt. loss in HNO_3	Percentage wt. loss in NaOH
(c) Chemical resistance		
LcF	89.2%	74%
Lc-g-poly(MA/AAm)	67%	48%

Table 3(a). It was observed that the *LcF* have high $\%M_{abs}$ (48%) due to presence of hydrophilic hydroxyl group than the $\%M_{abs}$ (34%) for *Lc-g-poly(MA/AAm)*. It was due to the blockage of active sites by graft copolymerization which led to decrease in hydrophilic character (Sanghavi & Srivastava, 2013; Singha & Rana, 2010).

3.4.3. Water uptake studies

The water uptake capacity of *LcF* and *Lc-g-poly(MA/AAm)* was studied using the concept of capillary action. Table 3(b) shows that low water uptake capacity of *Lc-g-poly(MA/AAm)* was due to blocking of active hydrophilic sites of the fiber by graft copolymerization thus decreasing hydrophilicity (Kalia et al., 2010).

3.4.4. Chemical resistance studies

The chemical resistance of *LcF* and *Lc-g-poly(MA/AAm)* was determined in 1 N NaOH and 1 N HNO_3. It has been observed that *Lc-g-poly(MA/AAm)* was chemically more resistant than *LcF* (Table 3(c)). This was due to deactivation of active sites by graft copolymerization onto cellulosic chains of the fiber (Pathania et al., 2009; Sanghavi & Srivastava, 2011).

3.4.5. Dye adsorption studies

The *Lc-g-poly(MA/AAm)* has been used for removal of congo red dye from water system. The results of dye adsorption onto grafted sample were shown in Fig. 4(c). It has been observed that dye adsorption capacity increased with the increase in concentration of dye. The adsorption of dye onto *Lc-g-poly(MA/AAm)* may be due to the grafting of carboxylic, amide, hydroxyl and ester groups of binary monomers onto cellulosic chains of *Luffa cylindrica* fibers.

3.4.6. Adsorption isotherms

The adsorption data obtained from experiments provides estimation of maximum adsorption capacity of the adsorbent and effectiveness of adsorbate–adsorbent system. The adsorption capacity and other parameters were evaluated using Langmuir and Freundlich, isotherm models.

The model expressions and their linearized forms are given in Table 4. Linear curve fitting procedure was used to fit the experimental data to the models and to the determination of the model parameters. The values of the isotherms parameters are given in Table 4. The Langmuir isotherm confirmed the monolayer adsorption onto a surface containing a finite number of adsorption sites via uniform strategies of adsorption with no transmigration of the adsorbate taking place along the plane of the surface (Gupta, Pathania, Agarwal, & Sharma, 2012). Fig. 4(d) shows a Langmuir isotherm from which isotherm constants, q_m (monolayer adsorption capacity of the adsorbent, mg/g), and K_L (Langmuir adsorption constant (L/mg), related with the free energy of adsorption) were calculated. It has been observed that the maximum adsorption capacity (q_m) was found to be 17.39 mg/g. A high value of coefficient of regression, R^2 (0.995) indicated the applicability of Langmuir isotherm. The K_L value determined was further used to calculate the dimensionless separation factor (R_L), which is given as:

$$R_L = \frac{1}{1 + K_L C_e} \tag{8}$$

where C_e is the equilibrium dye concentration. The magnitude of R_L value gives an idea about the nature of adsorption equilibrium. The $R_L < 1$ (0.427) indicated spontaneous adsorption of dye from aqueous solution (Pathania & Sharma, 2012a,b).

The Freundlich isotherm has been commonly used to describe adsorption characteristics for heterogeneous surface (Pathania, Sharma, & Singh, 2013). Fig. 4(e) shows a Freundlich isotherm from which isotherm constants K_F and n were calculated. The value of $n > 1$ observed from Freundlich isotherm indicated favorable and

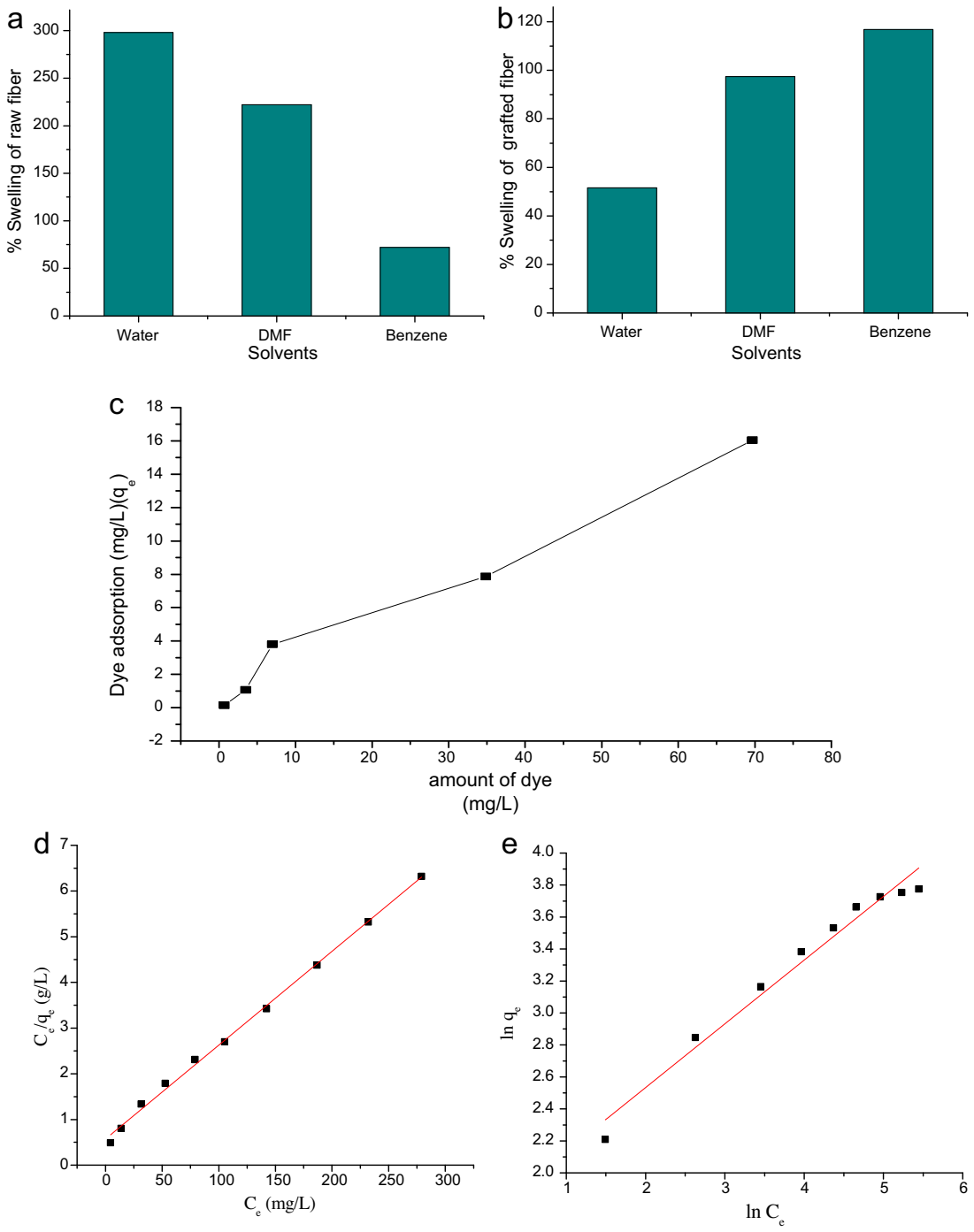


Fig. 4. Percentage swelling onto (a) LcF, (b) Lc-g-poly(MA/AAm) in different solvent. (c) Effect of concentration on dye adsorption onto Lc-g-poly(MA/AAm). (d) Langmuir isotherm. (e) Freundlich isotherm for dye adsorption onto Lc-g-poly(MA/AAm).

Table 4
Expressions for isotherm models, linearized forms, isotherms constants and correlation coefficients for the adsorption of CR dye onto Lc-g-poly(MA/AAm).

Isotherm	Expression	Linearized form	Parameters	Isotherm constants			
Langmuir	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e}$	K_L, q_m	q_m (mg/g)	K_L (L/mg)	R_L	R^2
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	K_F, n	17.39	0.021	0.427	0.995
				n	K_F (mg/g)	–	R^2
				2.63	4.49		0.918

heterogeneous adsorption. The isotherm constants and coefficient of regression R^2 have been given in Table 4.

A comparison of the coefficient of regression (R^2) for the isotherms (Table 4) indicated that the equilibrium data was best fitted in the Langmuir isotherm.

3.4.7. Adsorption thermodynamics

In order to study the thermodynamics of adsorption of congo red dye onto grafted fibers, three basic thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) of sorption were calculated using following equations:

$$\ln K_D = -\frac{\Delta G^0}{RT} \quad (9)$$

$$K_D = \frac{C_0 - C_e}{C_e} \quad (10)$$

$$\Delta G^0 = -2.303RT \log K_D \quad (11)$$

The other thermodynamic parameters such as change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were determined using the following equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

where R is universal gas constant (8.314 kJ/mol K), C_0 and C_e is the initial and equilibrium concentration (mg/L). ΔS^0 and ΔH^0 are obtained from the slope and intercept of the Vant Hoff's plot of $\ln K_D$ versus $1/T$. The positive value of ΔH^0 (21.27 kJ/mol) indicated that dye adsorption was physical and endothermic reaction. An adsorption process is generally considered as physical if $\Delta H^0 < 25$ kJ/mol and as chemical when $\Delta H^0 > 40$ kJ/mol (Gupta, Pathania, Agarwal, & Sharma, 2012; Gupta, Pathania, Agarwal, & Singh, 2012; Mittal, Mittal, Malviya, & Gupta, 2009; Mittal, Mittal, Malviya, & Gupta, 2010; Mittal, Mittal, Malviya, Kaur, & Gupta, 2010; Jain, Gupta, & Bhatnagar, 2003). The negative values of ΔG^0 (−139.52 kJ/mol) indicated spontaneous adsorption. Further, the positive value of entropy change, ΔS^0 (64.71 J/mol K) reflected the increased randomness at the solid–solution interface during the fixation of the adsorbate on the active sites of the adsorbent. This may be due to the fact that before the adsorption process starts, the adsorbate ions in solution are heavily solvated and the system is more ordered and the order is lost when the dye species are adsorbed on the surface due to the release of solvated water molecules (Gupta, Pathania, Agarwal, & Sharma, 2013). Moreover, adsorbed solvent (water) molecules which are displaced by the dye species, gain more translation entropy.

4. Conclusions

Graft copolymerization under the influence microwave radiations is one of the best methods for modifying the properties of natural fibers. *Luffa cylindrica* fiber has been successfully grafted without initiator by binary vinyl monomers MA/AAm and MA/AA under microwave radiations. The raw and grafted fiber were characterized by different techniques such as FTIR, XRD, TGA and SEM. FTIR results showed the formation of new bonds on the grafted sample. TGA spectra show thermal stability, XRD spectra revealed the decrease in the crystallinity after grafting and SEM images confirmed the improved surface morphology. Thus, it is concluded that grafted *Luffa cylindrica* fiber shows improved thermal, structural, chemical, and morphological properties so it can be used as an adsorbent for water purification, reinforcing material in polymer composites and for other industrial applications.

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