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Acrylic acid grafted cellulosic *Luffa cylindrical* fiber for the removal of dye and metal ions

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ABSTRACT

Acrylic acid grafted cellulosic *Luffa cylindrical* fiber was utilized for the removal of methylene blue and metal ions from the water system using batch process. The grafted sample used was found to demonstrate a maximum grafting efficiency of 90.8% under concentrations of 0.432×10^{-3} mol/L, temperature of 35 °C, time of 60 min and pH of 7.0 respectively. The remarkable improvement in thermal properties of the grafted sample was observed. The formation of new bands in FTIR spectra of grafted sample confirmed the grafting of acrylic acid onto the cellulosic fiber. The maximum adsorption capacity of dye onto adsorbent was observed to be 62.15 mg g^{-1} at 175 min. A maximum removal of 45.8% was observed for Mg^{2+} as compared to other metal ions. High values of correlation coefficient for methylene blue (0.995) and metal ions such as Mg^{2+} (0.996), Ni^{2+} (0.995), Zn^{2+} (0.996) confirmed the applicability of Langmuir isotherm that assumed a monolayer coverage and uniform activity distribution on the adsorbent surface.

1. Introduction

Biodegradable polymeric materials derived from renewable sources have been considered as the most potential adsorbent materials due to their easy availability and cost effectiveness. Recently the use of cellulosic fibers in various applications has received increased attention from environmental scientists. These materials offer advantages such as low specific gravity, suitable mechanical properties and recyclability. Moreover, they are obtained from renewable resources, have lower weights and cost less than synthetic fibers such as glass, carbon, etc. (Singha & Rana, 2010).

Luffa sponge mainly consists of cellulose, hemicelluloses and lignin; their weight (%) being of the order of 60, 30 and 10 respectively (Rowell, James, & Jeffrey, 2002). Cellulose structure consists of monomeric unit of a β-D-glucopyranose linked through 1,4-glucosidic linkage (Boynard & D'Almeida, 1999). Cellulose is renewable, cheap, and low in density, exhibits better processing flexibility and is a biodegradable material. Cellulose is a highly functionalized, linear stiff chain homopolymer, characterized by its hydrophilicity, chirality, biodegrability and broad chemical modifying capacity (Abd, Nada, Mohamed, & Hesham, 2007). However, due to the presence of hydrophilic hydroxyl groups on the surface of cellulosic fibers, their use is restricted under moist atmospheres and polar solvents (Pathania, Kumar, & Bhatt, 2009; Pathania, Rana, & Singh, 2009). Further these fibers are more prone to the attack of chemicals such as acids, bases and salts. Therefore these fibers need surface modifications in order to improve their properties before they can be used in various technical applications. The grafting of vinyl monomers onto cellulosic fiber using initiators have been investigated by different researchers for producing desired alteration in physicochemical properties (Clasen & Kulicke, 2001; Freddi et al., 1996; Pathania, Sharma, & Singh, 2013). The grafting onto natural cellulosic fiber by vinyl monomers have resulted in improved elasticity, water adsorption, ion exchange capability and heat resistance etc. (Pathania & Sharma, 2012a).

Pollution of the aquatic environment has been increasing mainly due to the non-degradable toxic compounds being discharged by the effluent emanating from the industries. Heavy metals and dyes are the most important constituents among the toxic compounds present in the effluent (Gupta, Carrott, Carrott, & Suhas, 2009; Gupta, Agarwal, & Saleh, 2011; Gupta, Gupta, Rastogi, Nayak, & Agarwal, 2011; Siddiqi & Pathania, 2002). Out of these pollutants, dyes are recognized easily due to their visibility to human eye. Thus due to the toxicity to human health, both metal ions and color removal from water system has drawn considerable attention in the last few years. Many methods such as chemical precipitation, ion exchange, electrodialysis, ultra filtration membrane separation, photodegradation, electrochemical oxidation etc.

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have been used for the removal of metal ions and dyes from water (Bhattacharyya & Sharma, 2005; Gupta & Ali, 2008; Gupta, Mittal, Kurup, & Mittal, 2006; Gupta, Mittal, Gajbe, & Mittal, 2006; Gupta, Mittal, Malviya, & Mittal, 2009; Pathania, Kumar, et al., 2009; Pathania, Rana, et al., 2009; Wang & Zhu, 2007). However due to the various disadvantages associated with conventional methods for treating dye and metal containing waste, the adsorption process has been adopted by many workers (Gupta, Pathania, & Sharma, 2012; Gupta & Rastogi, 2009; Gupta, Rastogi, & Nayak, 2010b; Pathania, Kumar, et al., 2009; Pathania, Rana, et al., 2009; Pathania & Sharma, 2012a,b). 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 and metal ions (Zhao, Zeng, Hu, Gao, & Zou, 2012a; Zhao et al., 2012b). In the view of above discussion and also because no work has been reported on the surface modification of *Luffa cylindrical* fibers through graft copolymerization using acrylic acid in presence of chromic acid, the present work is thus undertaken.

Grafted cellulosic fibers have been currently used as adsorbents for the removal of hazardous metal ions and dyes from aqueous solutions because of their good selectivity, favorable physicochemical stability, adjustable functionality, enhanced surface area and porosity, structural diversity. The polymer grafting fibers usually increases the density of adsorption sites and increases the sorption selectivity for the target metal and dyes. Different grafted cellulosic fibers have been reported in literature for the effective removal of metal ions and dyes from aqueous solutions (Gupta, Pathania, Agarwal, & Sharma, 2013; Pathania et al., 2013).

Thus present work has been attempted for the grafting of acrylic acid (AA) onto *Luffa cylindrical* natural cellulose fiber by using chromic acid. The effect of different parameters such as reaction time, monomer concentration, temperature and pH of reaction on the grafting yield was studied. The graft samples were characterized different instrumental techniques. The samples were subjected to the evaluation of their physicochemical properties. Moreover the utility of the grafted sample was explored for the removal of some metal ions and dye from water system.

2. Material and methods

2.1. Materials

Luffa cylindrica fibers were obtained from a dried fruit by immersing in fresh water at a temperature of 25–30 °C for about 4 days. The fibers were then taken out and individual fibers were rinsed with distilled water. The fibers were then made free from impurities such as waxes, oils, etc. by extraction with acetone in soxhlet extraction apparatus for 52 h. The fibers were then pretreated with 0.1 M sodium hydroxide for 60 min to increase the hydrophilicity. The fibers were washed with distilled water until all sodium hydroxide removed. After washing, *L. cylindrica* fibers were dried in oven at 50 °C for 12 h. Methylene blue were purchased from Sigma-Aldrich, India and used without further purification. Acrylic acid (AA) and chromic acid were received from CDH, India. Sodium hydroxide and hydrochloric acid were obtained from E. Merck, India, Ltd. 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). Dye absorbance was determined using double beam UV–vis spectrophotometer (Systeronics, model 2202). The other chemicals such as acetone, dimethyl formamide (DMF), CCl_4, etc. were of analytical reagent grade and used as received without further purification. The stock solution (1000 mg L^{-1}) of metal ions was prepared by dissolving fixed amount of metal nitrates in 1000 mL double distilled water. The solutions of desired concentrations were prepared by diluting the stock solution with double distilled water.

2.2. Preparation of adsorbent

The graft polymerization of acrylic acid onto *Luffa cylindrica* fibers was investigated at optimized reaction conditions such as monomer concentration, reaction time, reaction temperature and pH of reaction mixture to obtain the maximum grafting yield. The grafted sample was washed thoroughly with distilled water, extracted with methanol for 5 h in order to remove the homopolymer adhered to the surface. The grated sample was then dried in an oven at 50 °C. The grafting yield and grafting efficiency of the grafted samples were determined as follow:

$$\text{Grafting yield} = \frac{W_3 - W_1}{W_1} \times 100$$

$$\text{Grafting efficiency} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

where W_1 is the initial weight of the sample, W_2 is the final weight of the sample before the extraction of homopolymer and W_3 is the weight of the grafted sample after extraction.

2.3. Batch equilibrium experiment

In batch equilibrium method, 0.5 g of adsorbent was added to 100 mL of metal ion/dye solution and placed in a set of 250 mL glass stoppered Erlenmeyer flasks at different contact time. The mixture was agitated in a thermo shaker at a speed of 100 rpm for a given time at 30 °C. The suspensions were centrifuged at 2500 rpm for 5 min and filtered. The equilibrium concentration of metal ions and methylene blue in the supernatant liquor was analyzed by double beam UV–vis spectrophotometer at 662 nm with its initial concentration of 100 mg L^{-1} as discussed earlier (Gupta et al., 2013). The concentration of metal ions in the supernatant liquor was determined titrimetrically with its initial concentration of 300 mg L^{-1}. The amount of dye adsorbed per unit mass of adsorbent, q_e (mg g^{-1}) and percentage metal ion removal R was obtained using following equations (Gupta, Rastogi, & Nayak, 2010a):

$$q_e = (C_0 - C_e)\frac{V}{M} \quad (1)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of metal ions and dye in solutions (mg L^{-1}), V is the volume of the solution (L), and M is the mass of the adsorbent used (g).

2.4. Characterization

2.4.1. Thermal analysis

Thermogravimetric analysis of samples was carried out on Perkin Elmer thermal analyzer of Pyris Diamond make. Thermal analysis was carried out in presence of air at a heating rate of 10 °C/min.

2.4.2. Scanning electron microscopy (SEM)

Scanning electron micrographs of samples was recorded on Leo Electron Microscopy machine (435-VP). The samples were coated with Gold suspension before focusing the electron beam.

2.4.3. X-ray diffraction studies (XRD)

X-ray diffraction studies were performed on X-ray diffractometer (Brucker D8 Advance). XRD studies were carried out using Cu

Kα radiation, a Ni-filter and a scintillation counter as a detector at 40 kV and 40 mA on rotation from 5° to 50° at 2θ scale. Each sample was finely powdered into small particle size and homogeneously mixed before subjecting to X-ray radiation. The angle of scattering of diffracted beam was measured with respect to the incident beam of X-rays and relative intensity was obtained. Percent crystallinity and crystallinity index (C.I.) using following equations:

$$X_{c\%} = \left\{ \frac{I_c}{I_a + I_c} \right\} \times 100\%,$$

$$\text{C.I.} = \frac{I_C - I_A}{I_C}$$

where I_C is the intensity of crystalline phase, I_A is the intensity of amorphous phase, X_c is the percentage of crystallinity, C.I. is the crystallinity index.

2.4.4. Fourier transformer infrared spectroscopy (FTIR)

Fourier transformer infrared spectroscopy samples were performed using Perkin Elmer spectrometer (Spectrum 400, USA). The FTIR spectra of the samples were determined in the range 500–4000 cm^{-1} using KBr pellets.

2.5. Studies of physico-chemical properties

2.5.1. Swelling behavior in different solvents

The swelling studies were performed in water, dimethyl formamide (DMF) and *n*-butanol. In this a definite weight of samples was immersed in different solvent for 24 h. The samples were then taken out and excess of solvent removed. The final weight of the sample was determined as per method reported earlier (Pathania, Kalia, Sharma, & Reena Sharma, 2012).

2.5.2. Moisture absorption studies

Moisture absorbance behavior was investigated under humidity levels of 40%. A sample of known weight was placed in the humidity chamber maintained at a definite humidity level for 2 h. Each sample was placed in hot air oven at 60 °C for 12 h in order to make it moisture free. The sample was then taken out and final weight was recorded immediately. Percent moisture absorbance was determined as per method reported earlier (Pathania et al., 2012).

2.5.3. Chemical resistance studies

The chemical resistance of the grafted samples was studied as a function of percent weight loss. In this known amounts of samples were subjected to the effect of acids and bases of different strengths for definite time interval in order to evaluate their chemical resistance. The samples were weighed again to get the final weights. The percent weight loss was determined as per method reported earlier (Singha & Rana, 2012).

2.5.4. Water uptake study

The water uptake studies of samples were carried out using concept of capillary action. The wicks of different sample of same diameter were prepared and initial ink mark was drawn on 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.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. Fourier transform infrared spectroscopy

FTIR spectra of raw and grafted samples were shown in Fig. 1(a and b) in the wave number ranging from 500 to 4000 cm^{-1}. The absorption peak at 3349 cm^{-1} may be due to the presence of –OH group on the surface of adsorbent (Boufi & Alila, 2011). The peaks at 897 cm^{-1} and 1056 cm^{-1} may be due to β-glucosidic linkage and C–O stretching vibrations. In Fig. 1(b) new absorption band for grafted sample which appeared at 897 cm^{-1}, 1108 cm^{-1} and 1559 cm^{-1} may be due to the presence of –COOH group of acrylic acid. The appearance of new bands successfully confirmed the grafting chemical modification of *Luffa cylindrica* cellulosic fiber with acrylic acid.

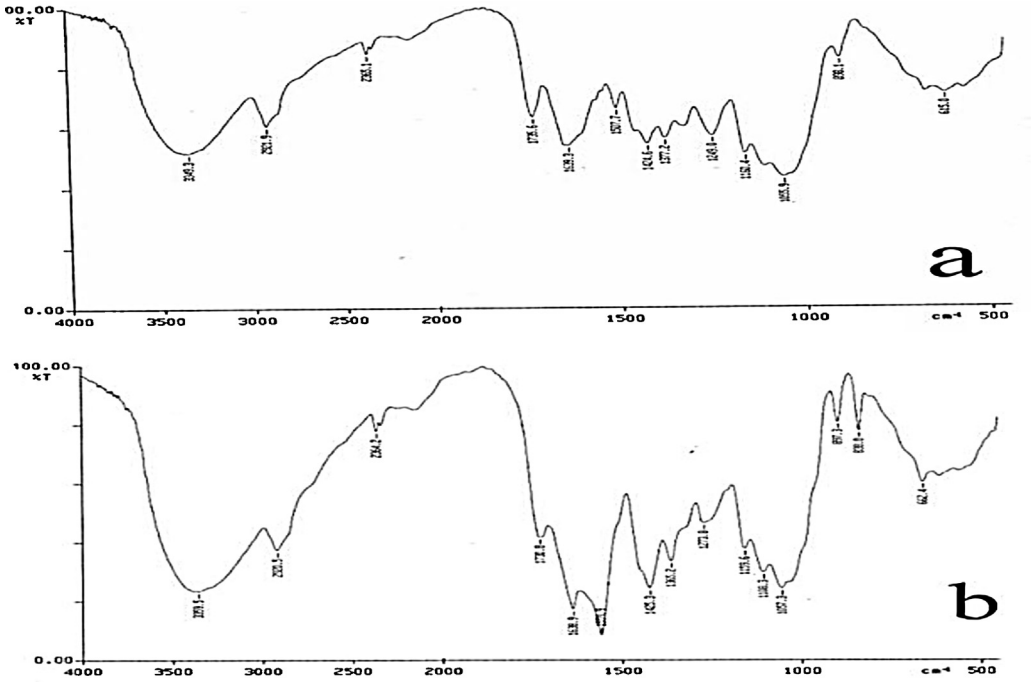

Fig. 1. FTIR spectra of (a) raw fiber and (b) grafted sample.

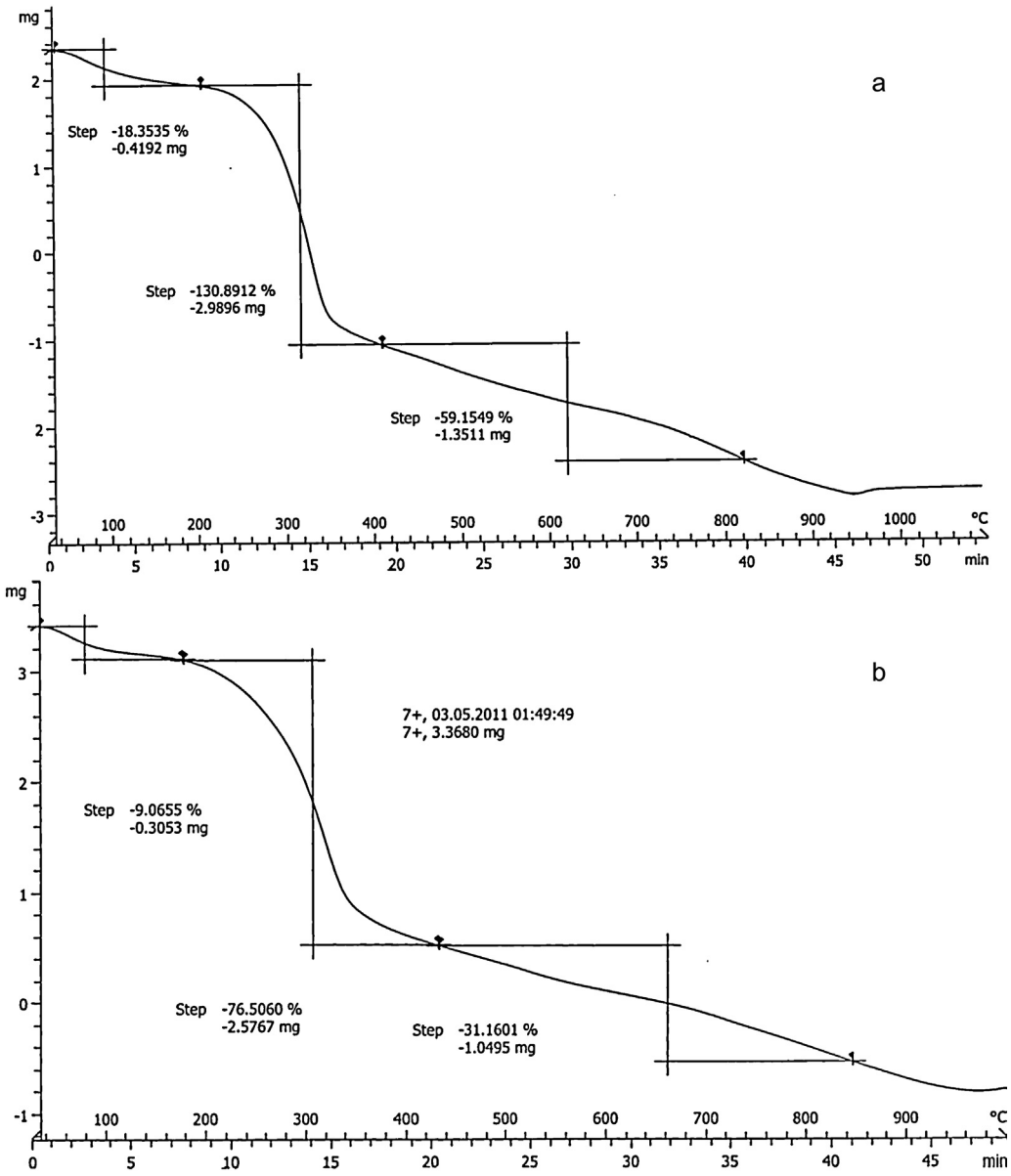

Fig. 2. TGA of spectra of (a) raw fiber and (b) grafted sample.

3.1.2. Scanning electron microscopy

Fig. 2(a and b) shows the SEM images of raw and grafted samples at different magnification. It has been found that considerable amount of acrylic acid was deposited onto fiber backbone upon grafting which brought about various morphological changes in the fiber (Fig. 2(b). Further the surface of fiber became rough after grafting of the acrylic acid (Pathania & Sharma, 2011).

3.1.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis determines the decompositions, dehydrations and oxidation of organic compounds (Kaith & Kalia, 2011). Thermogravimetric analysis curves of raw and grafted were shown in Fig. 3(a and b). The result revealed that at temperature ranging from 35 °C to 120 °C weight loss of only 9% was observed for grafted fiber as compared to that of raw fiber where only 18.3% weight loss was observed. This may be attributed due to the breakage of cellulose as well as the loss of adsorbed water (Pathania et al., 2012). The major weight loss of 76.5% was recorded for grated sample at temperature range of 130 °C to 300 °C as compared to raw fiber (130%). Therefore grafting polymerization has allowed the thermal stability to be regained.

3.1.4. X-ray diffraction

The XRD pattern of raw and grafted sample was shown in Fig. 4. The characteristics peaks of raw fiber were observed at 22.50 and 16.18 with relative intensities at 1072 and 506 respectively. The peaks of grafted sample were found at 22.30 and 16.80 with relative intensities of 651.8 and 404.1 respectively. This infers that grafting has resulted in the decrease in the peak intensity of grafted sample. It has been observed that the incorporation of acrylic acid to the backbone impaired the crystallinity of the fiber. Therefore, on grafting, percentage crystallinity decreases with reduction in stiffness and hardness. The lower value of crystallinity index (Table 1) in case of grafted sample indicated the poor order of cellulose crystals in the fiber.

Table 1
Optimization of various reaction parameters.

S. no.	Monomer (mol/L)	Solvent (mol/L)	Temperature (°C)	Time (min)	pH	Grafting yield (%)	Grafting efficiency (%)
1	0.144	100	20	60	1	2	50
2	0.432	100	35	60	3	6	60
3	0.432	100	35	60	7	40	90.9
4	0.432	100	60	90	7	28	77
5	0.432	100	60	100	9	6	60
6	0.432	100	100	150	7	12	60
7	0.576	100	35	60	7	16	66
8	0.721	100	60	100	7	20	71.4
9	0.865	100	100	150	7	36	85.71
10	0.576	100	100	100	7	24	75

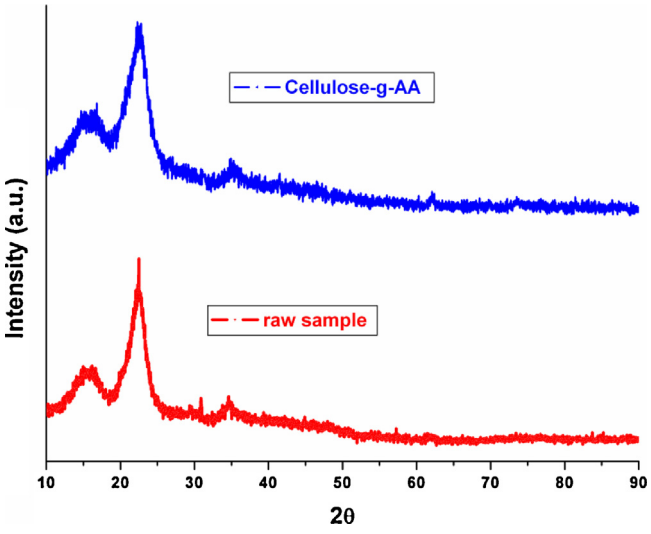

Fig. 3. X-ray diffraction pattern of raw fiber and grafted sample.

3.2. Optimization of reaction parameters

The optimization of different reaction parameters such as monomer concentration, pH, temperature and reaction time were carried out for the grafting of acrylic acid onto *Luffa cylindrica* fiber. The maximum graft yield of 40% was observed at monomer concentration (0.432×10^{-3} mol/L), reaction temperature (35 °C), time (60 min) and pH (7.0).

3.2.1. Effect of monomer concentration

It is evident from Fig. 5(a) that the grafting yield decreased with monomer concentration. This may be due to the dominance of homopolymer with increase in monomer concentration (Pathania et al., 2012). Moreover, due to homopolymerization the viscosity of the reaction medium increases which restrict the movement of the free radical toward active sites resulted in decrease in graft yield.

3.2.2. Effect of pH

The effect of pH onto grafting yield was shown in Fig. 5(b). It was revealed that grafting yield increased to 40% with increase in pH from 1 to 7. With further increase in pH beyond 7, the grafting yield was found to decrease. This may be due to the generation of $HO^{\bullet}$ radical in basic medium which combines with the back bone free radical and results in termination of the chain reaction.

3.2.3. Effect of temperature

The effect of reaction temperature on the grafting yield was studied in the temperature range of 35 °C–100 °C as shown in Fig. 5(c). The maximum grafting yield was observed at 35 °C, further increase in temperature leads to the decrease in graft yield. This may be due to occurrence of various hydrogen abstraction reactions and formation of homopolymer.

3.2.4. Effect of reaction time

The effect of reaction time on grafting yield was shown in Fig. 5(d). It was evident that the maximum grafting yield was obtained at 60 min. With further increase in reaction time a decrease in grafting yield was observed. This decrease in grafting yield may be due to formation of homopolymer along with some side reaction.

3.2.5. Swelling studies

The swelling behavior of raw fiber and grafted sample in different solvents were shown in Table 1. The swelling behavior of raw sample in different solvents followed the trend as water > *n*-butanol > DMF. It may be due to more affinity of water for –OH groups present in raw cellulosic fiber, thereby, facilitating its penetration deep into the fiber and resulting in high swelling. The swelling behavior in grafted sample shows the trend as DMF > water > *n*-butanol. This may be due to the blockage of

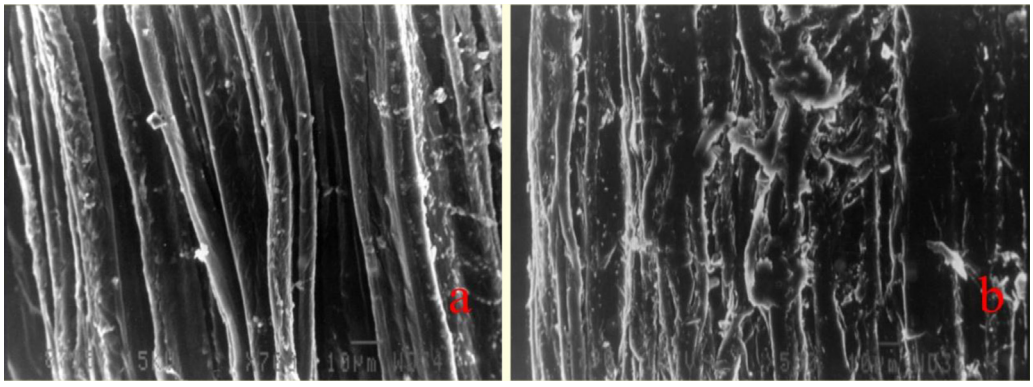

Fig. 4. SEM images of (a) raw fiber and (b) grafted sample.

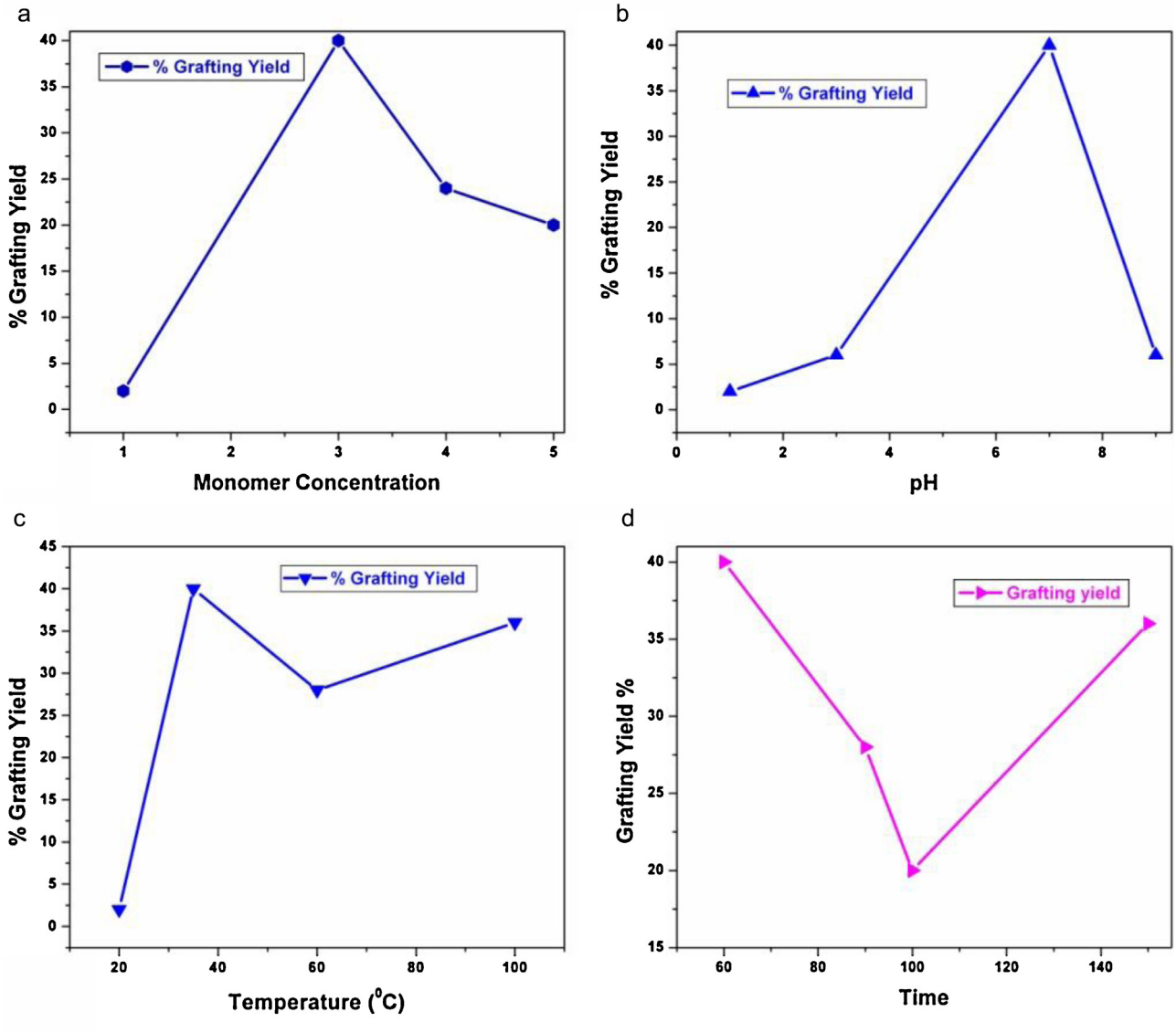

Fig. 5. Optimization of different reaction parameters for maximum graft yield: (a) monomer concentartion; (b) pH of reaction mixture; (c) reaction temperature; (d) reaction time.

Table 2
Percentage crystallinity and crystallinity index of raw and grafted sample.

Sample	2θ (°)	FWHM (°)	Intensity		Percent crystallinity	Crystallinity index (C.I.)	Crystallite size L (Å)
			I_C	I_A			
Raw fiber	22.5	2.68	1072	506	67.9	0.52	33.5
Grafted fiber	22.3	10.08	651.8	404.1	61.7	0.38	8.4

active sites on the raw fiber by acrylic acid which may cause the change in sorption behavior.

3.2.6. Water uptake study

It is revealed that the water uptake capacity of grafted sample was less as compared to that of raw fiber. This may be due to the incorporation of active sites as a result of graft co-polymerization.

3.2.7. Moisture absorbance studies

It has been observed that moisture absorbance was more for raw fiber than for grafted sample (Table 1). This may be due to the blockage of active sites on raw fiber responsible for maximum moisture absorbance by grafted acrylic acid.

3.2.8. Chemical resistance studies

It has been investigated that chemical resistance of grafted sample was more than that for raw fiber (Table 1). This was due to the deactivation of active sites on raw fiber backbone by polyacrylic

Table 3
Swelling behavior of raw fiber and grafted sample in different solvents.

Solvent	Percent swelling	
	Raw fiber (%)	Grafted sample (%)
Water	233.33	133.33
n-butanol	200	66
DMF	33.33	216.66

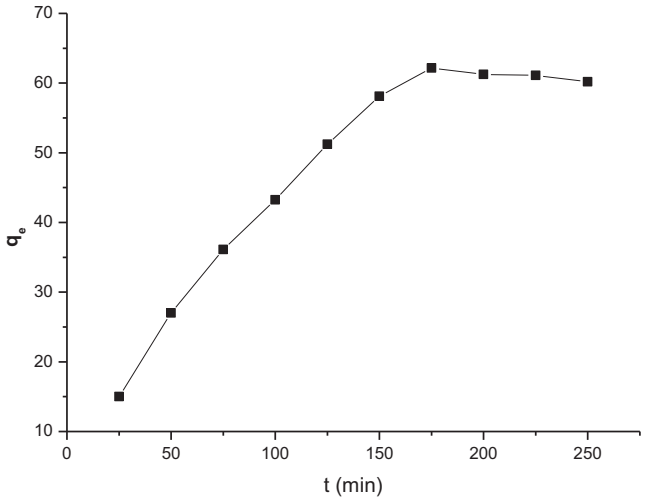

Fig. 6. Effect of time on the adsorption of methylene blue dye onto grafted sample.

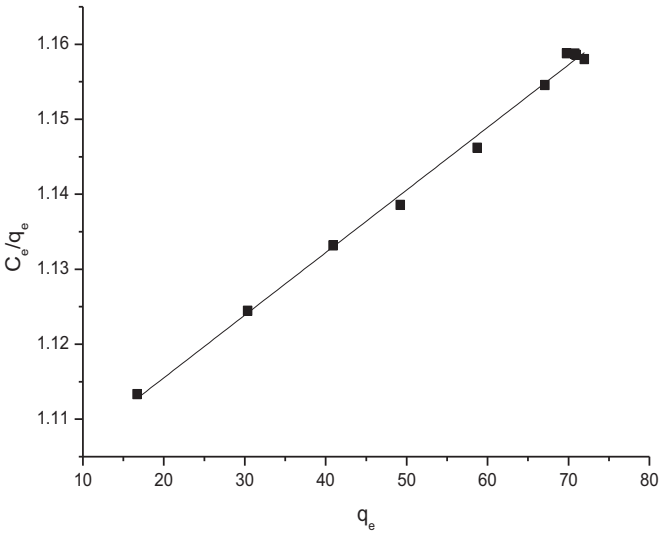

Fig. 7. Langmuir isotherm for the adsorption of methylene blue dye onto grafted sample.

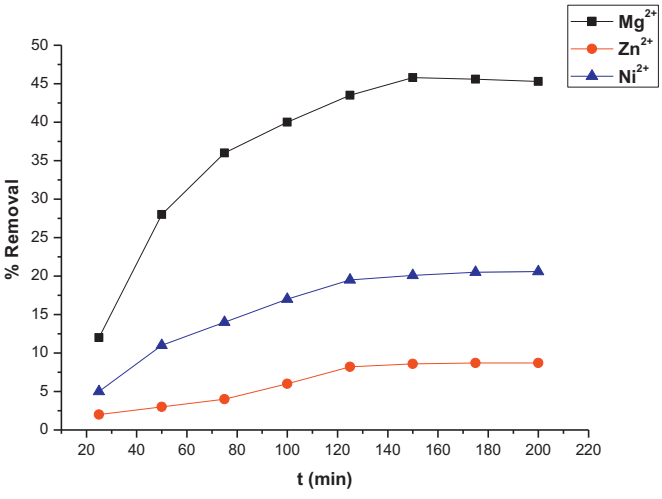

Fig. 8. Effect of time on the adsorption of different metal ions onto grafted sample.

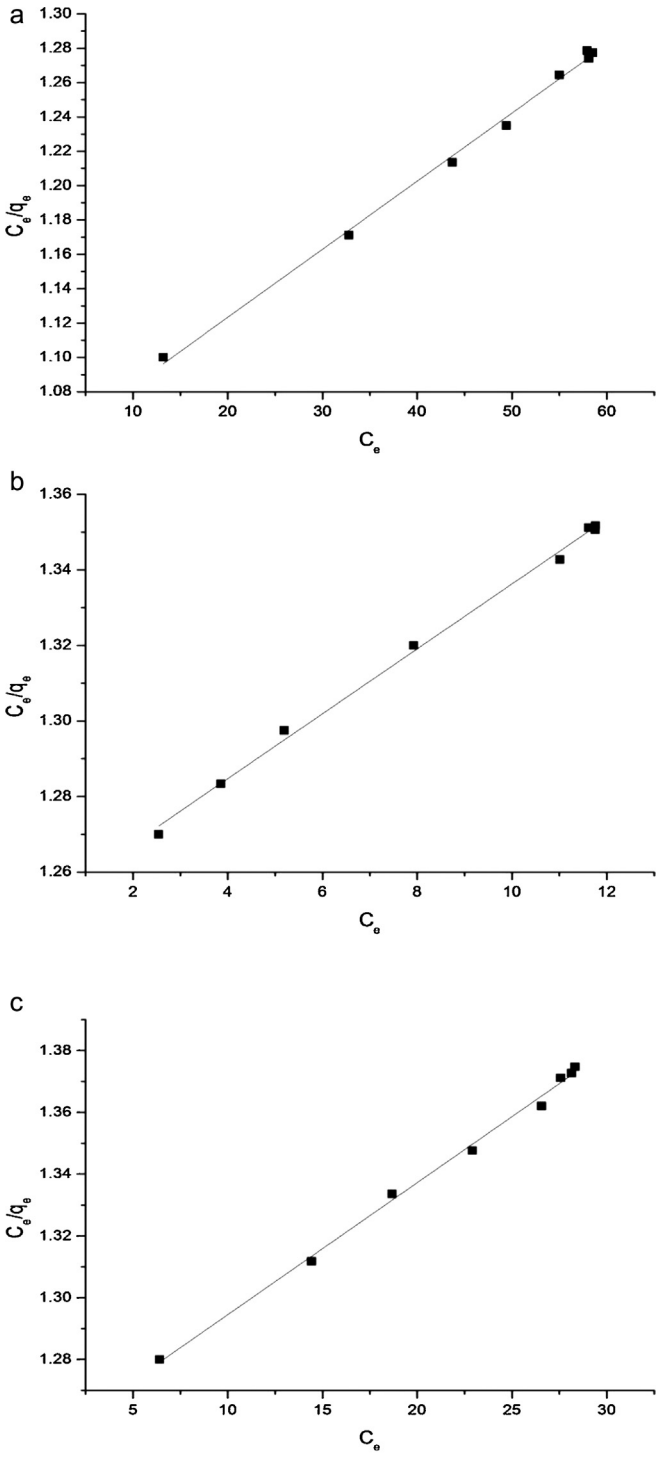

Fig. 9. Langmuir isotherm for the adsorption of (a) Mg(II); (b) Zn(II); (c) Ni(II) onto grafted sample.

acid chain. The grafted sample was found to be more stable in 1N NaOH as compared to 1N HCl (Tables 2–4).

3.2.9. Adsorption study

The effect of contact time on adsorption of methylene blue dye was investigated under optimized dose of adsorbent (0.5 g), dye concentration (200 mg L^{-1}), pH of solution (7) and temperature (25 °C). It was revealed that the adsorption gradually increased with time and attained equilibrium after 175 min (Fig. 6). The rapid intake initially was due to the availability of the more surface

Table 4
Moisture absorbance and chemical resistance studies of raw and grafted fiber.

Sample	% moisture absorbance	Chemical resistance % weight loss
Raw fiber	50	75
Grafted fiber	37.5	33.3

sites on the adsorbent for adsorption. It has been observed that the adsorption was also influenced by attractive Van der Waals forces and electrostatic attractions (Gupta et al., 2012). The Langmuir isotherm indicated that the maximum adsorption was due to a saturated monolayer on the adsorbent surface (Theivarasu & Mylsamy, 2010). The plot of C_e/q_e versus C_e (figure not shown) gives a straight line with a correlation coefficient of 0.995 which indicates that the adsorption of methylene blue onto the adsorbent fits the Langmuir isotherm practically well (Sarin & Pant, 2006).

The amount of metal ions removal versus time curve shows that rate of adsorption increases with time (Fig. 7). It has been revealed that maximum removal was observed for Mg^{2+} and attained the equilibrium after 150 min. The attractive forces between the metal ions and the adsorbent such as Van der Waals forces, electrostatic attractions and fast pore diffusion into the intraparticle matrix helped to attain equilibrium (Li, Lin, Zhang, & Yan, 2009). Langmuir isotherms for different metal ions (figure not shown) reveals a high value of correlation coefficient for different metal ions such as Mg^{2+} (0.996), Ni^{2+} (0.995), Zn^{2+} (0.996) and further confirmed the applicability of Langmuir isotherm (Figs. 8 and 9).

4. Conclusions

The grafting of acrylic acid onto natural *Luffa cylindrical* was confirmed by FTIR and SEM analysis studies. Thermal analysis showed the greater thermal stability of grafted sample as compared to raw fiber. X-ray diffraction results indicated the low values of percentage crystallinity and crystallinity index for grafted sample. Moreover the grafted sample was found to be an effective adsorbent for the removal of methylene dye and metal ions from aqueous solutions. The adsorption of dye onto the grafted adsorbent was found to gradually increase with increase in contact time and finally attained the equilibrium after 175 min. Among the metal ions tested, maximum removal was reported for Mg^{2+}. The adsorption data was satisfactorily explained by Langmuir isotherm for the adsorption of both dye and metal ions onto adsorbent.

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