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RESEARCH ARTICLE

Graft copolymerization of acrylamide onto wheat and rice straw cellulose using benzoyl peroxide as an initiator

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Abstract

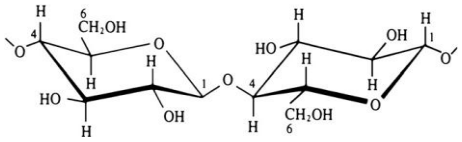
Cellulose dissolving pulps were prepared from wheat and rice straw followed by bleaching using hydrogen peroxide. The produced pulps where characterized by identifying alpha cellulose, crystallinity, ash contents. Graft copolymerization of acrylamide monomer onto cellulose using benzoyl peroxide as initiator was performed. The conditions of grafting such as monomer concentration, initiator ratio, grafting time and grafting temperature were evaluated. The structure of grafted fibers was investigated using FTIR and elemental analysis. The results have indicated that the optimum conditions for cellulose grafting were performed using a ratio of 1:4 between cellulose and monomer and 1: 0.3 between cellulose and initiator in 3 hours at 70°C.

INTRODUCTION

As known, agriculture produces significant amounts of wastes, which contain high quantities of organic matter. The agricultural wastes produced in a particular Period of the year pose potential pollution problems. Therefore, an efficient utilization Of such agricultural wastes is of great importance not only for minimizing the environmental impact, but also for obtaining a higher profit. Agricultural residue materials such as sugarcane bagasse and straws are abundant, inexpensive, and readily available as natural resources for chemicals and paper production [1-2]. There is an increasing interest in the utilization of agricultural residues as a cheap and environmentally save material for preparation of ion exchangers for removal of heavy metal ions and colorants from waste or industrial water [3-4].

Several agricultural products and byproducts are natural sources of cellulose. Among them, wheat straw, rice straw, cotton rice husk, sugarcane bagasse, palm kernel husk, peanut skin, pinus bark, corncobs, cane stick, jute stem, etc., have been tested as efficient adsorbent for heavy metal ions, especially adsorbent for divalent metal cations [5]. These byproducts are accessible in huge amount and they consist of cellulose, hemicelluloses, lignin, and some protein, lipids, wax, etc. [5,6]. Cellulose is regarded as the most abundant and renewable biopolymer in nature. It is one of the promising raw materials also for the modern industry, available in terms of cost for the preparation of various functional materials.

Cellulose is a carbohydrate homopolymer consisting of β -D-glucopyranose units joined together by β -1,4-glycosidic linkages(Fig. 1) [5,7].



✸ **To Soul of Dr. Abd El-Shafey I. Ahmed, Sep. 2105**

Fig. 1. Cellobiose unit: two β-D-glucopyranose unitsjoinedtogetherby β-1,4-glycosidic linkage

Cellulose is frequently modified in the preparation of a wide range of new materials that have proved to be very useful in several and diverse fields of application. The presence of three reactive hydroxyl groups on each glucan unit of cellulose makes it relatively easy to modify. One method of modifying cellulose that has been studied extensively is graft copolymerization [8]. By grafting of a monomer on the Cellulose back bone, some of drawbacks of Cellulose can be eliminated. Cellulose graft copolymers are very attractive because their products can readily be made to posses any number of the required properties [9-10]. Great numbers of grafting methods have been developed, but the free radical methods of generating radicals on the cellulose backbone before grafting have received the greatest attention [8, 11]. The use of benzoyl peroxide as an initiator to generate free radicals which initiate grafting reactions of cellulose with monomer or co-monomer has reported, [12-15].
The aim of this study was to optimize the graft copolymerization conditions of acrylamide onto cellulose. The effect of reaction parameters on the percentage of grafting was studied and evaluated. The use of Fourier transforms infrared spectroscopy (FTIR) to follow the structure and the functional group of the cellulose was also investigated.

2. Experimental

2.1. Materials

Straw of wheat and rice have been taken from sharkia, Egypt farms. It was first dried in sunlight to remove the moisture from the straw and then cut into small pieces (2– 3 cm), conc sulphuric acid, sodium hydroxide , hydrogen peroxide(30%) , Acetone were obtained from Republic Trading chemicals, pharmaceuticals and medical supplies , Acrylamide, benzoyl peroxide (BPO) were obtained from Burgoyne Urbidges, India.

2.2. Prehydrolysis

straw of wheat and rice were prehydrolyzed o reduce hemicelluloses. The straws were prehydrolyzed by sulfuric acid (3% related to the oven dry weight) at boiling 100°C and the liquor ratio was 1: 10 for six hours, under reflux. After the prehydrolysis the straw of wheat and rice were filtered and washes with distilled water until neutrality and dried till constant weight.

2.3 Pulping

In our study the chemical Pulping performed by alkaline process, pulping carried out using sodium hydroxide only (one stage pulping). Prehydrolyzed material (1 g, based on dry weight) was pulped using sodium hydroxide (1 N, 3.50 ml) and the liquor ratio was 1: 10 for 6 h at 100°C. The resulting pulps were filtered and washed with distilled water, then acidify with 0.05 % hydrochloric acid (HCL) till neutrality and in air.

2.4. Bleaching

The prepared fibers were bleached using alkaline hydrogen peroxide in water consistency of 20%. The fibers was kept in solution contains 2% H_2O_2 3% NaOH, 1% $MgSO_4$, (based on dry sample). In water bath for 1 h at 70°C with shaking and then the sample was washed with distilled water, filtered, acidify with 0.05 % hydrochloric acid (HCL) till neutrality, the procedure was repeated another time at the same condition, then dry in air till constant weight.

2.5. Grafting

Graft copolymerization of acrylamide onto Wheat and rice fibers was performed with benzoyl peroxide (BPO) as an initiator under vacuum. In a polymerization flask (100 mL), A known weight (1 g) of cellulose fabric was dissolved in 20 mL of distilled water and 4 mL of acetone in the polymerization flask and then the required amounts of initiator and monomer were added. The reaction flask was then closed and transferred to a thermostat maintained at desired temperature. After the required reaction time (grafting time), the reaction flask was removed from the thermostat, the sample was filtered, washed with distilled water, and then dried till constant weight at 60 °C (W1). This dried sample was extracted with distilled water in a soxhlet device for 48 hours to dissolve the formed homopolymer. After extraction, the sample was washed with distilled water and then air-dried at 60°C (W2).

3. Results and discussions

The specification of the raw material used in this work (straw of wheat and rice) are listed in table (1)

Table (1); Chemical analysis of the bleached and unbleached wheat and rice pulps

Pulp	**Yield%**	**α-cellulose%**	crystallinity **%**	**Ash%**
Unbleached (Wheat)	45.8	84.37	-	1.80
Bleached (Wheat)	45.3	90.62	87.4	0.16
Unbleached (Rice)	44.3	81.25	-	0.55
Bleached (Rice)	43.5.1	88	87.7	0.2

3.1 Factors affecting grafting efficiency G.E% of acrylamide onto wheat cellulose and rice cellulose.

The grafting efficiency of acrylamide onto cellulose was studied by changing monomer / cellulose ratio, initiator concentration /cellulose, reaction time, and reaction temperature. These factors were studied to optimize the conditions of grafting process.

Polymerization % (p %) = [(w1 – w)/w] x 100(1)

Graft % (G %) = [(w2 – w)/w] x 100

Graft efficiency % (GE %)= [(w2 – w)/weight of monomer] x 100

WRV = water retention value

Na binding capacity (m.eqwt/gm) = sodium binding capacity

3.1.1 Effect of monomer concentration:

Table (2): Effect of variation of monomer concentration on grafting parameters

sample	Monomer g / g cellulose	G%	G.E%	WRVgm/gm	Na binding capacity m.eqwt/gm
Wheat (A)	1: 2	57	29	1.10	853
	1: 2.5	72	31	3.33	1067
	1: 3	84	34	5.1	1223
	1: 3.5	153	42	6.3	1300
	1: 4	185	45	8.5	1426
Rice (B)	1: 2	15	7.5	2.54	714
	1: 2.5	30	13	4.06	912
	1: 3	40	14	4.28	1136
	1: 3.5	55	14	5.00	1222
	1: 4	60	15	5.66	1309

Reaction condition: pulp (1.0g), temperature (70°C), Reaction time(3hrs), BPO (O.2 g)

Table 2 and figures **(2a)**, **(2b**) shows the grafting effect of monomer ratio of acrylamide onto cellulose. It is clear that by increasing of ratio of monomer to cellulose increased the grafting G % and grafting efficiency GE %. Increasing the ratio of monomer to cellulose more than 3:1 causes a slightly increase in graft efficiency because increase the homopolymer formation due to the increase in the viscosity of grafting solution, which decreases the penetration rate of monomer solution through the cellulose chains, causing an increase of homo- polymer formation [16]. Water retention value and sodium binding capacity was increased as well with increasing the grafting.

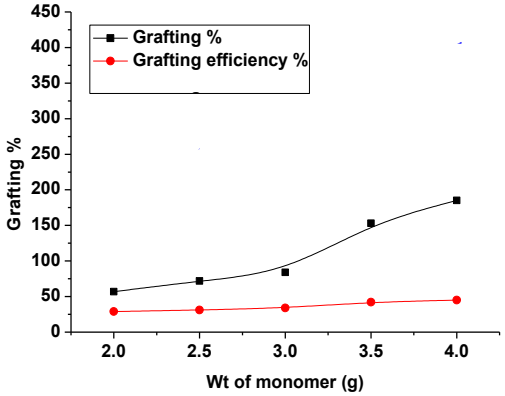


Figure 2 (a): wheat (A) Pulp (1 0.g), Temp(70°C), time (3 0.hrs), BPO (0.2 g)

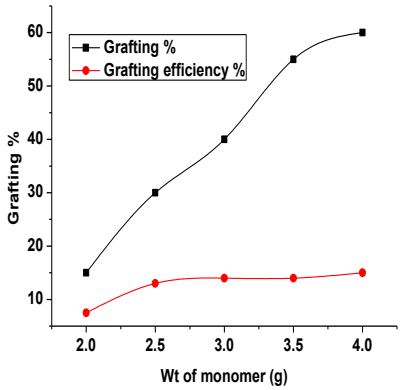


Figure 2 (b): rice (B) Pulp (1 0.g), Temp(70°C), time (3 0.hrs), BPO (0.2 g)

3.1.1 Effect of initiator (BPO) concentration:

Table (3): Effect of variation of initiator BPO concentration. on the grafting parameters.

sample	Initiator g / cellulose	G%	G.E%	WRVgm/gm	Na binding capacity m.eqwt/gm
Wheat (A)	0.10	0	0.3	3.64	823
	0.15	82	27.3	*3.92*	956
	0.20	84	34	4.2	1223
	0.25	153	42	4.35	1287
	0.3	185	45	5.1	1411
Rice (B)	0.1	18.5	45	1.66	908
	0.15	20	8.3	2.33	1012
	0.20	32	12	4.28	1136
	0.25	40	14	5.10	1187
	0.3	90	30	5.14	1257

Reaction condition: pulp (1.0g), monomer (3 .0g) , temperature(70 °C), Reaction time (3hrs)

The effect of initiator concentration on the grafting process is shown in **table 3** and Figures. **(3a), (3b**), Results show an initial increase in grafting process with an initial increase in the initiator concentration. It is clear from the **table (3)** and Figures. **(3a), (3b)** that increasing BPO concentration up to 0.3 gr give significant development in grafting parameters G % and G.E%. This increase resulted due to the formation of a great number of grafting sites on the cellulose backbone. At higher initiator concentrations, the number of grafting sites reaches a maximum value. Hence the molecular weights of the grafted chains are little affected by further increase in the BPO concentration [17]. It can be noted that the graft and graft efficiency were higher with wheat fibers more than rice fibers.

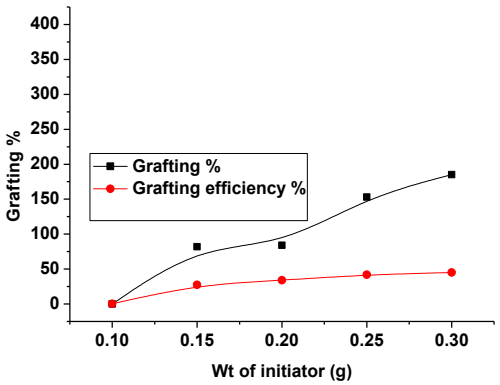


Figure 3 (a) :wheat(A) Pulp (1.0 g), monomer (3.0 g), temp(70˚C), time (3.0 hrs)

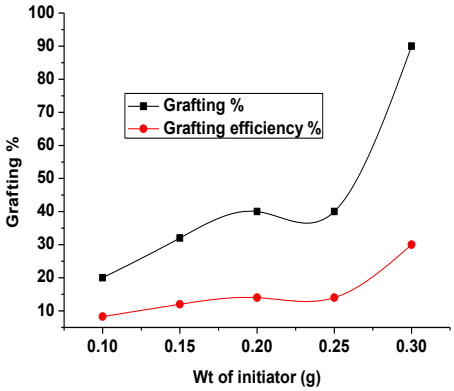


Figure 3(b): rice (B) Pulp (1.0 g), monomer (3.0 g), temp(70˚C), time (3.0 hrs)

3.1.3 Effect of reaction time:

Table (4): Effect of variation of reaction time on the grafting parameters.

sample	Time(hrs)	G%	G.E%	WRVgm/gm	Na binding capacity m.eqwt/gm
Wheat (A)	1	10	2.73	2.0	711
	1.5	10	3.31	3.25	834
	2	30	11	4.0	915
	2.5	66	23	4.71	1087
	3	84	34	5.1	1223
Rice (B)	1	10	2.73	2.26	724
	1.5	13	3.31	2.54	847
	2	30	11	3.55	967
	2.5	45	14	4.23	1017
	3	40	14	5.14	1136

Reaction condition: Pulp= 1g, monomer = 3 g, temperature = 70˚C, BPO = 0.2 g

As shown in **table 4** and figures **4.a, 4.b**, the effect of reaction time on different grafting parameters. It can be seen that the polymerization was happened after two hours, no grafting occurs in the first hour, the grafting G % , grafting efficiency GE % and the polymerization percentage increased with increase in reaction time on sample A, In sample B the results shows slightly decrease in grafting G % and the grafting efficiency GE % after 2.5 hours than sample A . This agrees with the earlier observation with free radical initiated polymerization.

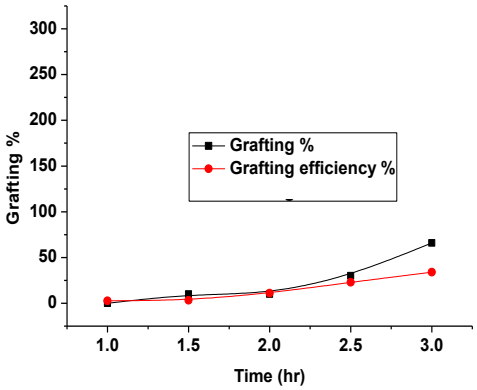


Figure 4 (a) :wheat(A) Pulp (1.0 g), monomer =(3.0g), BPO(0.2 g), temp(70˚C)

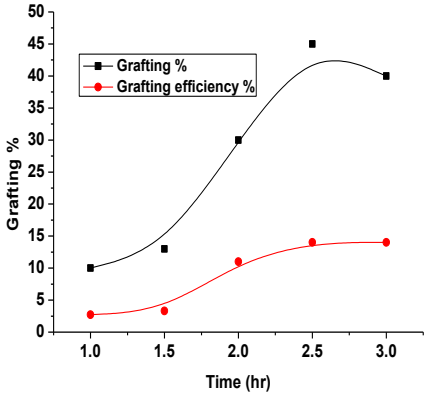


Figure 4(b): rice (B) Pulp (1.0 g) monomer = 3.0g, BPO(0.2 g), temp(70˚C)

3.1.4 Effect of reaction temperature:

Table (5) Effect of variation of temperature on the grafting parameters.

sample	Temperature ˚C	G%	G.E%	WRVgm/gm	Na binding Capacity m.eqwt/gm
Wheat (A)	40	0	0	2.2	700
	50	91	3.31	3.12	814
	60	170	38	4.88	1189
	70	84	34	5.1	1223
	80	60	18.75`	5.86	1318
Rice (B)	40	0	0	1.51	724
	50	5	2.85	2.75	787
	60	50	21	3.10	1093
	70	40	14	4.46	1136
	80	35	11`	5.14	1225

Reaction condition: pulp (1.0g), monomer (3.0 g), reaction time(3 hrs), BPO (0.2 g)

Table 5 and Figures **5a, 5b** shows the effect of reaction temperature on different grafting parameters. Graft copolymerization of acrylamide onto cellulose was carried out from 40 to 70 ˚C, The table shows that the grafting %, grafting efficiency % increased with increase in reaction temperature from 40 ˚C to 60 ˚C, it could be due to better decomposition of the redox system giving more free radical, increase of monomer molecules and higher rate of initiation of the graft chain [18]. The results show the grafting %, grafting efficiency % decreased with an increase in the reaction temp (above 60 ˚C), it could be attributed to the increase in the rate of radical termination and formation of homopolymer chains. this increase in graft after particular temperature is considered to be a detrimental effect.

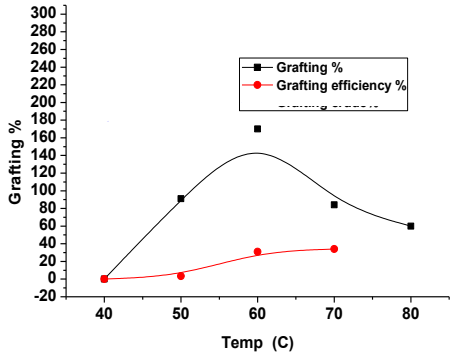


Figure 5(a) : wheat (A) Pulp (1.0 g,) Monomer(3. 0g), BPO (0.2 g), time (3.0 hrs)

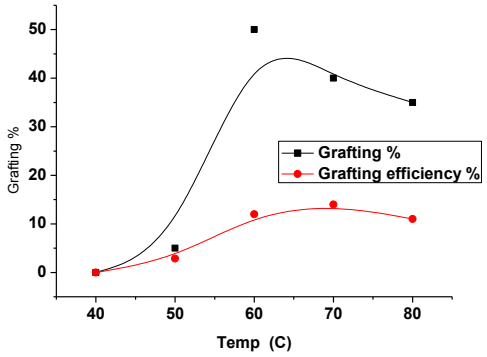


Figure5 (b): rice (B) Pulp (1.0 g) monomer (3.0g) , BPO (0.2 g), time (3.0 hrs)

FT-IR Spectroscopy

Infrared spectra of .grafted cellulose and ungrafted cellulose shown in Figures(7 to 10) for wheat samples and (11 to 14) for rice samples , As shown in figure it can be observed the characteristic absorption bands around 3420, 1650 and 2930 $^{cm-1}$. Compared with the ungrafted cellulose (bands a in all cases), a sharp peak appeared in grafted cellulose at 1650 cm^{-1}, corresponding to the stretching of the carbonyl (C=O) of the amide group in acrylamide. The ratio of the band intensity at 1650 cm^{-1} to the band intensity at 1215 cm^{-1} increased by grafting due to incorporation of $CONH_2$ groups on the fibre. Both IR spectra of the ungrafted and the grafted cellulose exhibited broad adsorption band at 3420 cm-1 due to hydroxyl group stretching vibrations from the cellulose structure, the ratio of this band intensity to band intensity of OH group was higher value in grafting than in case without grafting. Grafting increased the relative absorbance of CH vibration of CH_2 at 2930 cm^{-1}.

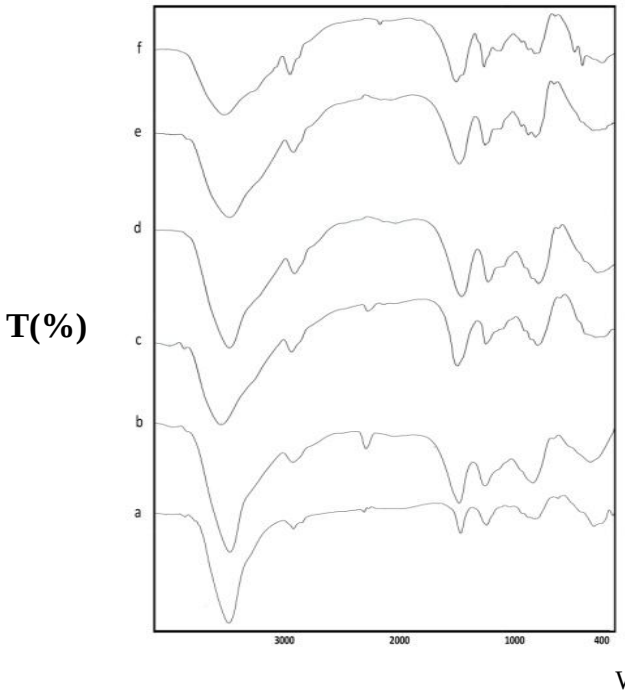


Fig. 7: I. R Spectra of wheat (A) at different concentration of monomer. a- ungrafted cellulose **b** – 1: 2 **c** – 1 : 2. 5 **d** – 1 : 3 **e** – 1 : 3.5 **f**– 1 : 4

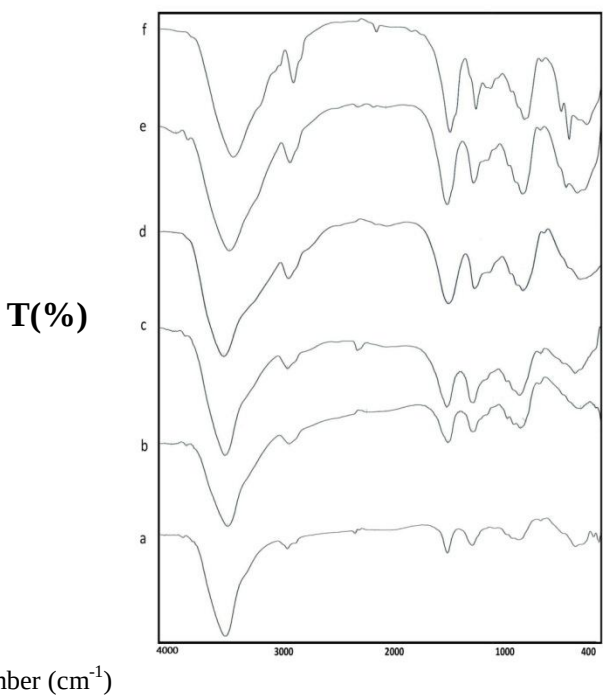


Fig. 8: I.R Spectra of wheat (A) at different concentration of initiator. **a**- ungrafted cellulose, **b** – 1: 0 :1, **c** – 1 : 0.15 **d** – 1 : 0.2 **e** – 1 : 0.25, **f**– 1 : 0.3

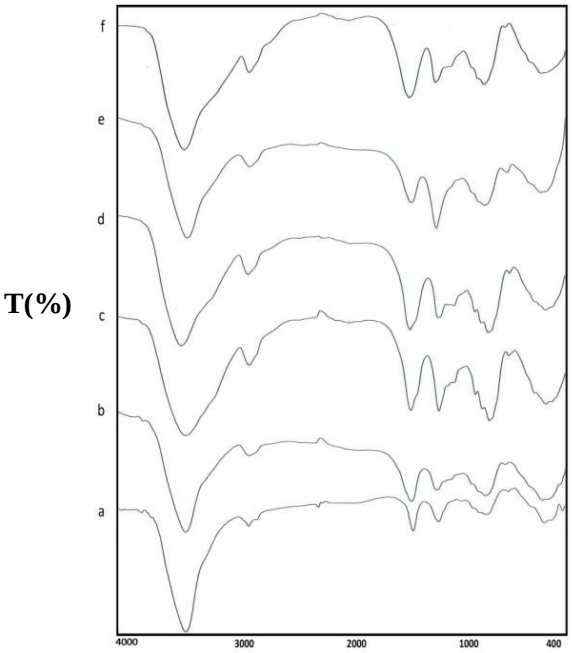


Fig. 9: I.R Spectra of wheat (A) at different reaction time
a- ungrafted cellulose **b** – 1.0 hr **c** – 1.5 hr
d – 2.0 hr **e** – 2.5 hr **f**– 3.0 hr

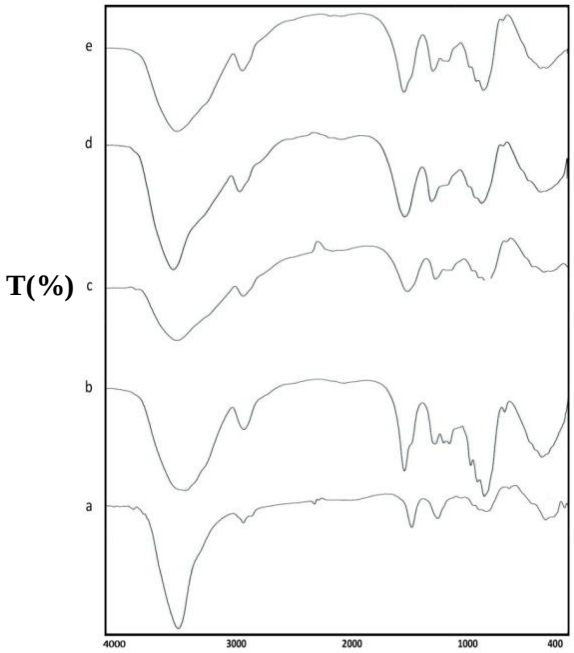


Fig. 10: I.R Spectra of sample A (wheat) at different reaction temperature. a- ungrafted cellulose
b – 50˚C **c** – 60 ˚C **d** – 70 ˚C **e** – 80 ˚C

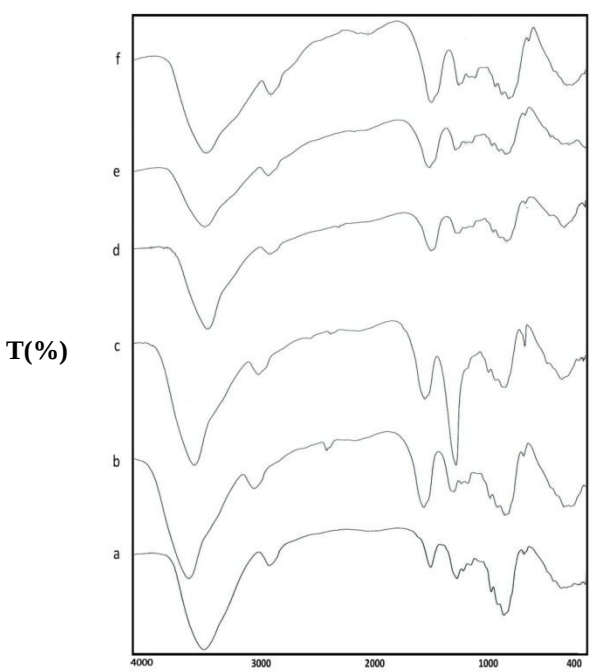


Fig. 11: I.R Spectra of rice (B) at different concentration of monomer. **a**- ungrafted cellulose, **b** – 1: 2
c – 1 : 2.5 **d** – 1 : 3 **e** – 1 : 3.5 **f**– 1 : 4

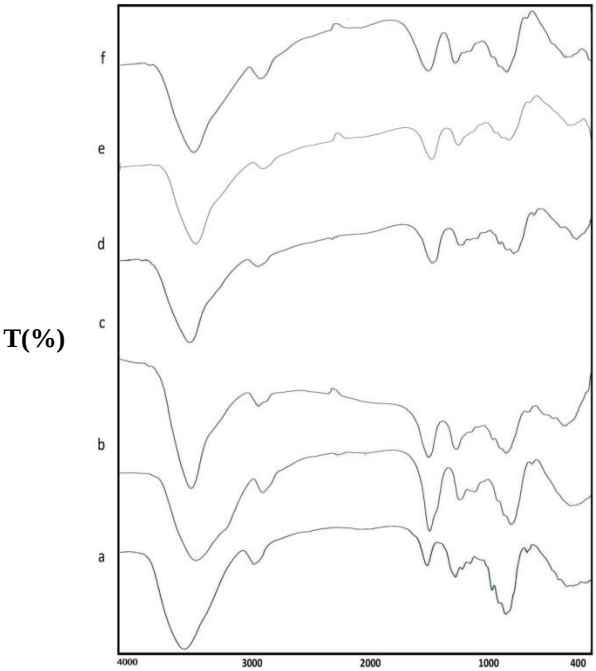
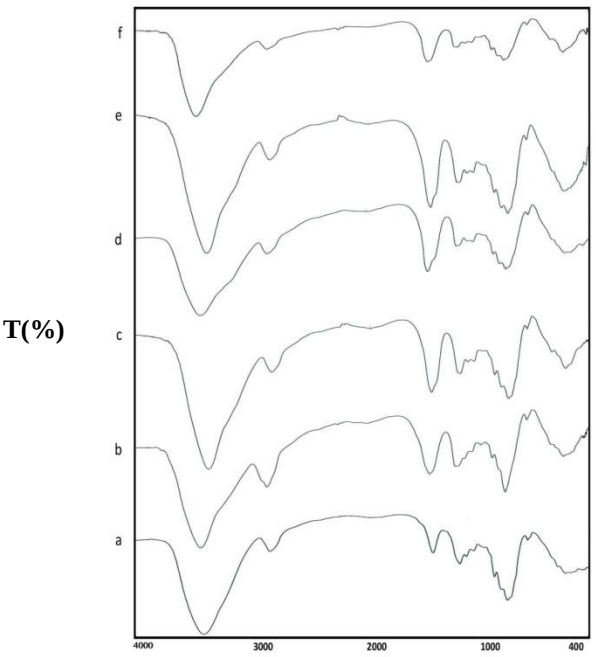
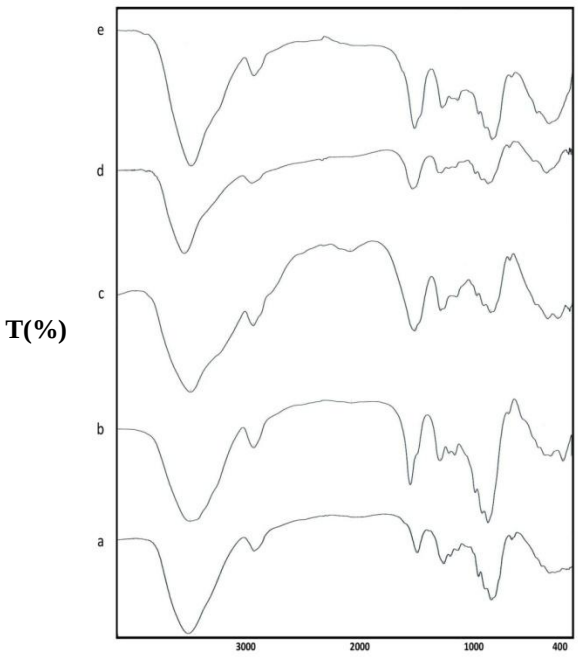


Fig. 12: I.R Spectra of rice (B) at different concentration of initiator. **a**- ungrafted cellulose, **b** – 1: 0.1
c – 1 : 0.15 **d** – 1 : 0.2 **e** – 1 : 0.25 **f**– 1: 0.3





Wavenumber (cm^{-1})

Fig. 13: I.R Spectra of rice (B) at different reaction time. **a**- ungrafted cellulose **b** – 1.0 hr **c** – 1 :5 hr **d** – 2.0 hr **e**- 2.5 hr **f**- 3.0 hr

Fig. 14: I.R Spectra of rice (B) at different reaction temperature. **a**- ungrafted cellulose **b** – 50 ˚C **c** – 60 ˚C **d** – 70 ˚C **e** - 80 ˚C

Conclusion

1- Wheat and rice straws were prehydrolyzed by using acid hydrolysis and thin the pulping was performed by with sodium hydroxide (one stage pulping).

2- Cellulosic pulps were subjected to one-step bleaching by using alkaline hydrogen peroxide.

3- Graft copolymerization of acrylamide onto wheat and rice fibers was carried out by using benzoyl peroxide as an initiator system.

4- Bleached wheat and rice fibers were graft-copolymerization at four varying conditions e.g. concentrations of monomer, initiator, reaction time, and reaction temperature. During graft- copolymerization keeping all other variables constant.

5- The optimum conditions of graft copolymerization of acrylamide onto wheat and rice fibers were liquor ratio 1:24, ratio of cellulose to monomer pulp 1:4, ratio of cellulose to initiator 1: 0.3, reaction time 3 hours and reaction temperature was 70 ˚C.

8- the water retention value and the sodium binding capacity had a positive relationship with increasing the gravity and the grafting (G%) efficiency (GE%).

6- Copolymers were characterized by FTIR and elemental analysis.

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