PREPARATION OF ENVIRONMENT FRIENDLY CELLULOSE DERIVATIVES AND PAPER FROM RICE STRAW

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ABSTRACT

In an attempt to take advantage of agricultural waste such as rice straw, which causes an environmental problem, it was used as a cellulose source by treatment with ionic liquid, which can be recovered after the reaction , into cellulose derivatives such as methyl cellulose, carboxymethyl cellulose and hydrogel preparation of these derivatives. Derivatives and hydrogels were used as additives to the pulp during the paper preparation process with other additives. The experiments showed an improvement in the mechanical and optical properties of the resulting paper. The study showed that the water absorption rate in the paper was increased with the addition of both MC and CMC to reach 230 and 290%, respectively. On the other hand , addition of both MC and CMC-hydrogels produced absorbed paper with water uptake till 773 and 600%, respectively.

Key words: Rice straw, cellulose derivatives , hydrogel ,absorbed paper.

INTRODUCTION

Egypt produces around 4 million tons of rice straw / annually. Fields must be cleaned from straw to make way for the next crop. Soil incorporation and field burning have been the major practice for removing rice straw. Field burning damage the land by killing useful microorganisms in the soil and

incorporation in the soil is slower , more expensive and may promote rice diseases (Moniz *et al.,* 2014) . The smoke from the rice straw combustions is also a potential health hazard for humans because it could give rise to asthma and cancer (Sindhu *et al*.,2012).

Cellulosic compounds are the most important renewable natural resources on earth. Cellulose is the main component of plant cell walls, and the basic building block for many textiles and for paper . Cellulose is a hard crystalline material fibrous enough to use as paper, textiles, clothes, strings, sanitary goods, etc. (Endo *et al*., 2016) .Cellulose is insoluble in water and most common solvents. Bonding between the individual chains prevents it from being broken by mild chemicals or water, and makes it resistant to enzyme decomposition (Deguchi *et al*., 2006 & Encyclopædia Britannica, 2008) . Hydrogen bonds, which give cellulose stability, are broken down through pretreatment methods by chemical reactions that take place in hydroxyl groups and glucosidic linkage of cellulose molecule (Dauenhauer *et.al*., 2016 & Gericke *et al.,* 2011). Cellulose has the ability to functionalize chemically to provide cellulose derivatives, such as cellulose esters and ethers which have important applications in our daily life such as in textiles, pharmaceuticals, food, and packaging industries. It is directly linked to the paper industry . Cellulose derivatives are further used as coatings, laminations, optical films and absorbents (Röder *et al*., 2013 & Jimming *et al*., 2017) .

Ionic liquids (IL) possess not only a high chemical and thermal stability, nonflammability and a negligible vapor pressure, but also the recycling of these solvents is comparably easy. Recently, certain ILs have been applied as green solvents which would dissolve cellulose (Pinkert *et al.,* 2009 & Krishna and Jianwen 2015) and function as inert and homogeneous reaction media (Liu *et al*., 2009 & Lauri *et.al.*, 2016) . Zhang Wu , Zhang and He , (2005), found that the ionic liquids containing Cl^{-} have excellent capability to dissolve cellulose e.g.1-butyl-3-methylimidazolium chloride (BMIM)+CL- . Cellulose solutions with up to 25 wt% cellulose can be prepared using 1-butyl-3 methylimlidazolium chloride under microwave heating. Cellulose is precipitated easily using methanol, water or ethanol and the regenerated cellulose is rarely degraded and has polymerization degree and polydisperity that is close to the initial cellulose (Wang *et.al*., 2012 & Yank *et al*., 2014) .

In the present work, rice straw was used to be converted into cellulose derivatives (methyl cellulose & carboxymethyl cellulose) using ionic liquids as cellulose solvents and treating them to prepare hydrogel. Hydrogel was added to rice straw pulp in little ratio to produce absorbed paper which can be used in many different purposes.

MATERIALS AND METHODS

1- Materials:

In our work, agriculture residue (i.e., rice straw) was used as raw material source. It was obtained from Northern Egypt (Delta Region), washed with water, air dried and cut into small pieces (4-6 inches) , then conditioned in a polyethylene bag for 48 hours. After that, it was characterized for its

moisture, ash, lignin and hollo-cellulose according to TAPPI T412 om-06,TAPPI T211 om-85,TAPPI T222 om-88&TAPPI T257 om-85,respectively.

Also, 5% (w/w) sulfuric acid , 10% (w/w) Na OH , sodium chlorite , acetic acid , [BMIM]+CL-(1-butyl-3-methylimidazolium chloride) , Dimethylsulphate , isopropanol , KOH , Sodium monochloroacetate , aqueous methanol , aqueous ethanol , Absolute ethanol, potassium persulfate , N,N – methylene bisacrylamide and neutralized acrylic acid were used.

2-Extraction of cellulose:

Cellulose was isolated from rice straw by:

1-pulping process (Delignification): the material was treated firstly with 5% (w/w) sulfuric acid followed by 10% (w/w) Na OH then the produced pulp was washed till neutrality, air dried and characterized for their moisture , ash , lignin and hollocellulose.

2- Bleaching process: unbleached pulp was treated with sodium chlorite and adjust pH to 9 with acetic acid then air dried and characterized for their moisture content , ash , lignin and α -cellulose .

3-Preparation of Cellulose Derivatives:

3-1-Dissolution of cellulose by IL: Grinded fibrous cellulose was treated with IL in ratio of 10 times its weight at 80 °C for 2 hours under stirring to complete dissolution of cellulose .A clear, colorless,viscous solution was obtained.

3-2-Preparation of methylcellulose (MC) (methylation): Dimethylsulphate was added to the dissolved cellulose in the ratio (1:10) and increasing the reaction temperature to 22 °C with stirring 24 hours . The product was precipitated in 2-propanol ,then filtered and washed with is several times . Finally dried in vaccum over KOH at 60 °C and Characterized with FT-IR and SEM .

3-3-Preparation of carboxymethylcellulose (CMC): 2-propanol solution was added to cellulose dissolved in {Bmim }$^{+}$CL^{-} with vigorous stirring, followed by aqueous solution of NaOH dropwise with stirring . 0.48 g Sodium monochloroacetate was added, filtered and the product was suspended in aqueous methanol then neutralized with acetic acid .After that, the product was washed with aqueous ethanol, then with ethanol and finally dried under vacuum . The product was weighed , and characterized using FT-IR&SEM.

3-4-Preparation of hydrogel from cellulose derivatives: Methylcellulose was treated with neutralized acrylic acid in the presence of potassium persulfate as initiator and N,N –methylene bisacrylamide as crosslinker under N2 atmosphere , the product was washed with aqueous methanol and dried under vaccum , then the product tested for water absorption (Ibrahim *et al.* , 2015) . The same previous steps was applied with carboxymethylcellulose. Both MC and CMC hydrogels was characterized using FT-IR & SEM,absorbance test.

4-Paper sheet formation:

The paper sheet was formed according to the SCA standard method , SCN-C26:27,SCAN-C5:76 standard tests. The sheets of paper were prepared from bleached pulp only , bleached pulp loaded with MC or CMC in 5 % (w/w) of the rice straw pulp also sheets of paper were loaded with 0.1% MC-hydrogel or CMC-hydrogel.

5-Absorption test:

The samples (CMC, MC -hydrogel) were immersed in distilled water , and left till equilibrium swollen. The samples were separated from the unabsorbed water by filtration. The water absorbency was calculated as grams of water per grams of samples (g ,g) using the following equation;

$$A_{H_2O} = \frac{W_2 - W_1}{W_1} x100$$

Where W_1&W_2 are the weights of the dry sample and the water swelling sample (g) respectively, while A_{H_2O} is the amount of absorbed water

6-FT-IR analysis:

FT-IR spectroscopy was used to confirm fiber results from rice straw, cellulose derivatives , and hydrogel –cellulose derivatives using JASCO FT/IR 6100.

7-Scanning Electron Microscope(SEM):

SEM characterization of the rice straw, cellulose derivatives and hydrogel cellulose derivatives was performed using a JEOL JXA-840A electron microscope analyzer (JOEL USA INC, Peabody, MA).

RESULTS & DISCUSSION

1-Raw Material Analysis: Agriculture residue(i.e. rice straw) was characterized before converting it to the pulp as mentioned in the experimental part , the results are listed in **Table (1)** which show a high content of the ash and lignin.

Table (1): Characterization of Raw Material (Rs).

Experiment	%
Waxes& resins	1.9
Moisture	7.5
Ash	**15.3**
Lignin	**22.3**
Hollocellulose	61.5

2-Preparation of Pure Cellulose from Rice Straw:

Ionic liquid does not work in the presence of lignin ,so we must get rid of or minimize lignin. For this reason, delignification of cellulose process was carried out to obtain pure cellulose. Table (2) shows the results after bleaching process which reveal that the lignin content was minimized to reach 0.08% .

The FT-IR of the delignified RS pulp was studied to identify the characteristic groups. Fig. (1) shows that the common specific bonds of cellulose appeared at 3413-3300 cm^{-1} characteristic for the (-OH) groups , and 2912cm^{-1} for (-C-H) group. Band at 1431 cm^{-1} is assigned to the absorbance of C-O-H bending in plane at C_6 which arise by changing the environment at C_6, while the band at 1337cm^{-1} is assigned to the C-O-H bending at C_2 or C_3. The absorption bands between 1430 cm^{-1} and 894 cm^{-1} are sensitive to the amount of the crystalline versus amorphous structure in

the cellulose. The bands at 1431, 1372, 1322, 1162, 1033, 896 cm^{-1} which are typical for pure cellulose, can be observed in the FT-IR spectra. Bands at 1165 cm^{-1} and 897 cm^{-1} are assigned as C-O- C stretching at the β-(1-4) glucosidic linkage. On the other hand, SEM was performed to the resultant sample in which fibers of cellulose clearly appeared as a separated fibers (Fig. 2).

Table (2): Characterization of bleached rice straw

Experiment	%
Moisture content	5.3
Ash	3.1
Lignin	**0.08**
α-cellulose	91.3
DP	198

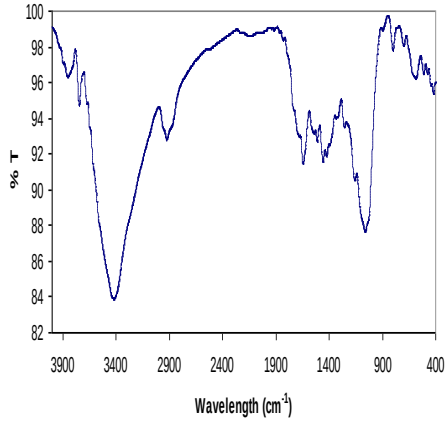
3-Dissolution of cellulose:

Cellulose solutions was prepared using 1-butyl-3-methylimidazolium-chloride [BMIM $]^+Cl^-$, where ionic liquid has Cl^- which is effective in breaking hydrogen bonding network that is present in cellulose, so cellulose can be dissolved. Both methylations and carboxylation processes were carried out in the presence of [BMIM $]^+Cl^-$.

4- Preparation of Cellulose Derivatives:

4-1- Preparation of Methylcellulose:

Methylcellulose was made from rice straw as mentioned in the experimental part . Figs. (3 & 4) illustrate the SEM and FTIR of MC-Rs .



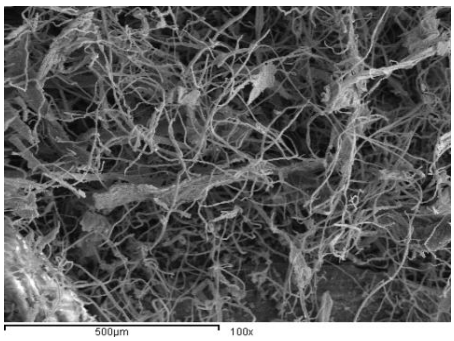


Fig. 1: FT-IR for rice straw-pulp **Fig. 2:** SEM for rice straw –pulp

Figure 3 shows the SEM for MC-Rs which illustrate that cellulose fibers in Fig.2 were changed from the individual fibers to compact and swollen fibers . This increases the absorbing properties of MC-RS, i.e. water and solvents. This property increases the use of MC in both the drug manufacture and food industry.

FT-IR spectrum was performed for MC-Rs . Fig. (4) illustrates that the absorption broad bands at 3426 cm^{-1} is characteristic to OH group, and sharp peak at 2928 cm^{-1} signed for C-H stretching. Peaks at 1692 $cm^{-1}$and 1645 cm^{-1} represent C-O-C carbonyl stretching from glucose of cellulose. Broad band at 1692 cm^{-1} is characterized to O-CH_3. Sharp peak at 1568 cm^{-1} that represents C-O-H bending at C_2 and C_3 indicate the presence of CH_3 group. Two peaks at 1456 and 1425 cm^{-1} are assigned for C-O-H bending in plane at C_6 ,where the appearance of very weak peaks indicate the change of crystalline regions to an amorphous regions. Peak at 1378 cm^{-1} is assigned as

C-O-C stretching at β(1-4) glucosidic linkage of cellulose. Two peaks at 1425 $cm^{-1}$and 1162 cm^{-1} are characterized for C-O-H at C_6, while sharp peak at 1079 cm^{-1} is characterized for C-O stretching asymmetric oxygen bridge. Sharp peaks at 889 cm^{-1} and 801cm^{-1} are characterized for ring stretching. The Sharp peak at 589 cm^{-1} is specific for cellulose. Also, the region from 1644 cm^{-1} – 801 cm^{-1} is specific for cellulose. Comparing Fig. 1 and Fig. 4, sharp peak at 3743 cm^{-1} in the Rs. pulp, Fig(1), was reduced to small peak at 3744 cm^{-1} and weak peak at 3730 cm^{-1} which may be referred to quaternary amine salt which bonded with Cl^- in the IL and present in the MC-Rs. Disappearance of sharp peak absorption band at 1828 cm^{-1} in Fig 1, which characterized C-O-H at C_2 and C_3 (sharp peak) and appearance of a weak broad bands at 1378 cm^{-1} and 1334 cm^{-1} in Fig (4) changed to a broad band at 1079 cm^{-1} which specified at C-O-stretching. Sharp peak at 1568 cm^{-1} is characterized to C=C or C=N may be from the IL. Appearance of very weak peaks at 1456 cm^{-1} and 1425 cm^{-1} are characterized for $–CH_3$ group. Appearance of two peaks at 889 cm^{-1} and 801 cm^{-1} are characterized for ring stretching. The DS (degree of substitution) equals 0.9.

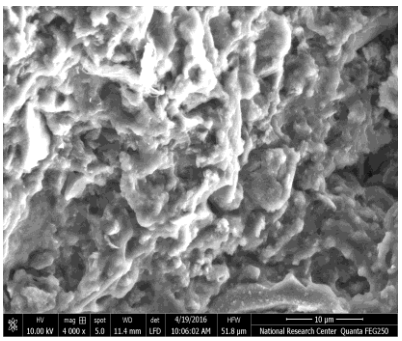


Fig. 3: SEM of MC-Rs

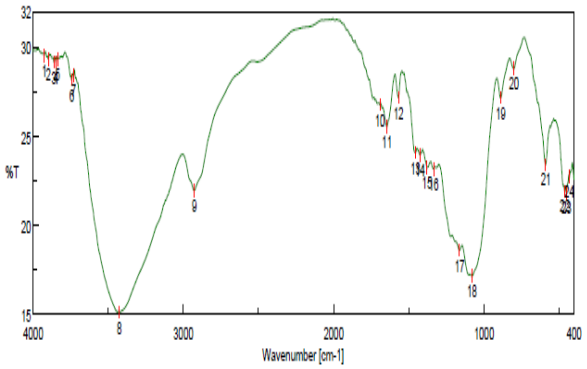


Fig. 4: FT-IR of MC-Rs

4.2- Preparation of Carboxymethylcellulose: Carboxymethylcellulose was made from Rice straw as mentioned in the experimental part. Fig. (5) illustrates SEM of CMC-Rs. SEM shows that the image of cellulose fibers was greatly different which transferred to a tube and gave the cellulose absorbing property to absorb water or any solvent and changed to a very viscous part used as thickner for a great variety of products .Its dissolving or swelling character depends on the DS value.

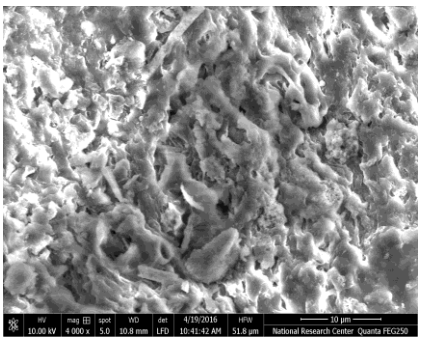


Fig. 5: SEM of CMC-Rs

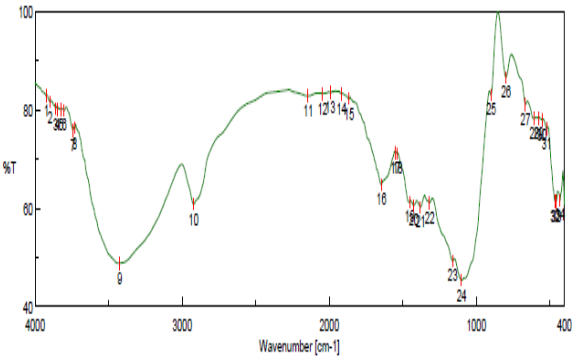


Fig. 6: FT-IR of CMC-Rs

Fig (6) illustrated FT-IR for CMC-Rs where sharp band for OH group of cellulose at 3436 cm^{-1} changed to a broad band at 3424 cm^{-1} in CMC-Rs chart, so as sharp peak at 2906 cm^{-1} shift to 2922 cm^{-1} broad band for –C-H stretch in CMC-Rs . Also band at 1644 cm^{-1} (sharp peak) change to broad band at the same wave length which is specific for cellulose, where peaks at 1544 cm^{-1}, 1510 cm^{-1} for C-OH bending in plane on C_6 appeared as a very weak peaks at 1549 cm^{-1}, and 1535 cm^{-1} in Rs. Peaks at 1453 cm^{-1} and 1426 cm^{-1} appears as a very weak peaks at the same region 1453 cm^{-1} and 1426 cm^{-1} in CMC-Rs which are specific for C-O-H bending in plane at C_6 . Peak at 1374 cm^{-1} assigned for C-O-H at C_2 and C_3 changed to a very weak peak at 1317 cm^{-1} in CMC –Rs and 1268 cm^{-1} (weak peak) in Rs chart which disappears in CMC-Rs. Weak band at 1161 cm^{-1} shifted to appear at 1159 cm^{-1} in CMC-Rs which is specific to C-O-C of glucosidic unit. Sharp and strong peak at 1028 cm^{-1} shifted to appear as strong peak at 1100 cm^{-1} for CMC-Rs, and the peak of C-O at 1100 cm^{-1} CMC-Rs especially for C-O stretching from asymmetric oxygen bridge. Small peak for C-O-C appears at 899 cm^{-1} in case of CMC –Rs. Two sharp peaks at 669 cm^{-1} and 606 cm^{-1} shifted to appear as sharp peak at 797 cm^{-1} is CMC-Rs. Carboxyl and methyl group are appeared at 1644 cm^{-1} and 1425 cm^{-1} for CMC-Rs . In general, the FT-IR shows the typical absorption of cellulose backbone as well as cellulose peaks at about 1644 cm^{-1} and 1424 cm^{-1} indicating the presence of CMC ether groups. The peak of OH group is clear at 3422 cm^{-1} so as the peak at 2922 cm^{-1} for C-H stretching and the peak of C-O at 1100 cm^{-1}, especially for the C-O stretching from the asymmetric oxygen bridge, where the DS of CMC-R is ~ 1.0.

4-3 Preparation of Hand made-Paper Sheet: The same pulp which resulted from pulping of rice straw through the two steps of pulping by acid (5%w/v) followed by 10 % (w/v) alkali (NaOH),and bleached with sodium chlorite,was used for the preparation of paper sheets . The weight of about 8 g were oven dried (OD) from the bleached pulp defibrated into the beater and converted into 5 sheets of paper. MC and CMC were loaded into the paper sheet as 5 % (w/w) of the sheet.

4-4-Addition of MC and CMC in Hand made Paper-sheet: methylcellulose was added at equal amount of starch and hydroxy ethyl cellulose in 20 ml water and mechanically stirred for 12 hours where a viscous solution was performed. This solution was added to the paper pulp during formation of the paper sheet (in paper making machine). The paper sheets were tested for both optical and mechanical properties and the results are scheduled on Tables (3) & (4).

Table (3) shows an improvement in the whiteness with the addition of MC and cooked starch so as the brightness, while opacity increases with the addition of MC, MC- cooked starch, and MC- cooked starch and hydroxy - ethyl cellulose.

Table (3): Optical properties of hand-made paper sheet

Sample	Bases wtg/m^2	Thickness mm	Whiteness	Brightness	Opacity	Percent of absorption
1	66.35	0.265	73.3	59.66	93.98	85.4
2	68.3	0.278	76.61	62.95	99.23	196
3	69.31	0.271	70.08	60.86	99.01	210
4	67.08	0.263	72.89	61.43	99.18	230

1- Blank without any addition 2- MC with cooked starch 3- MC with cooked starch and hydroxy ethyl celloulose 4- MC only

Table (4) illustrates that all the mechanical properties (Burst, Tensile, and Tear) were improved with the addition of: MC with cooked starch, MC with cooked starch and hydroxyl ethyl cellulose, and MC only, where a great improvement will occur with MC-cooked starch in tear resistance. The percent of water absorption was increased especially with the addition of: MC with cooked hydroxy ethyl cellulose and MC only.

Carboxymethylcellulose was added with equal amounts of starch and hydroxy ethyl cellulose in 20 ml water and mechanically stirred for 12 hours where a viscous solution was formed. This solution was added to the paper pulp during formation of the paper sheet (in paper making machine). The paper sheets were tested for both optical and mechanical properties and the results are listed in Tables (5) & (6).

Table (4): Mechanical properties of the hand-made paper sheet

Sample	Burst KPa	Burst Factor	Tensile Strength N/m	Breaking Length m	Tear Resistance	Tear Factor
1	7.4	7.84	1.74	1748	24	36.17
2	11.0	11.68	3.1	2186	54	69.80
3	25.0	24.01	5.6	3211	35	81.12
4	13.8	14.2	3.9	2715	51	76.0

1- Blank without any addition 2- MC with cooked starch 3- MC with cooked starch and hydroxy ethyl celloulose 4- MC only

Table (5) shows that the opacity was improved especially with the addition of CMC and cooked starch and CMC with cooked starch and hydroxy ethyl cellulose so as brightness of the sheet, while whiteness and brightness were improved with the addition of CMC with cooked starch and addition of CMC only.

Table (5): Optical properties of the paper sheets

sample	Bases wt-g/m2	Thickness mm	Whiteness	Brightness	Opacity	Percent of absorption
1	66.35	0.265	72.3	59.66	93.98	85.4
2	68.2	0.277	72.26	61.68	98.36	180
3	63.58	0.247	69.33	57.16	98.11	229
4	72.31	0.271	73.28	67.4	96.2	290

1- Blank without any addition 2- CMC with cooked starch 3- CMC with cooked starch and hydroxy ethyl celloulose 4- CMC only

On the other hand, Table (6) shows a great improvement in all mechanical properties by the addition of CMC with cooked starch and HEC but tear was improved only with the addition of CMC and addition of CMC with cooked starch. The percentage of water absorption was highly increased with CMC only and with CMC with cooked starch and hydroxy ethyl cellulose.

4-5-Modification of MC and CMC into MC-hydrogel and CMC – hydrogel: MC was modified to MC hydrogel through treatment with neutralized acrylic acid in the presence of potassium persulfate and crosslinker . Acrylic acid can connect with OH of cellulose units to give the polymer hydrogel. After gelation and formation of hydrogel; it was washed with water and ethanol-water then left to dry. The absorption test was carried out and the water absorbed was calculated.

After drying, the MC-hydrogel forms a membrane with tensile strength (4.8 KN/m) and tear factor (80), the membrane acquires the properties of elongation and elasticity which make it difficult to be cut, and when it is tested for its efficiency to absorb water, it gave a percentage of (400%) within

five minutes and by increasing the amount of water, the swelling of the membrane increases till it reaches (700%). Figs (7a,b&c) show the shape of the membrane with SEM in both dry and wet form (surface and cross section), where the presence of a large and more porous surface is shown.

Table (6): Mechanical properties of the paper sheets making

Sample	Burst kpa	Burst Factor	Tensile strength N/m	Breaking Length(m)	Tear resistance	Tear Factor
1	7.4	7.84	1.74	1748	24	36.17
2	9.0	9.28	1.8	1760	32	46.92
3	14.4	13.76	2.6	2355	24	32.61
4	10.0	9.72	1.7	1567	40	55.32

1- Blank without any addition 2- CMC with cooked starch 3- CMC with cooked starch and hydroxy ethyl celloulose 4- CMC only

Fig. (8) illustrates the FT-IR for the MC, in which the sharp band which was appeared at 3426 cm^{-1} in Fig. (4) for MC-Rs changed to a broad band and appeared in the range from 3689 cm^{-1}, 3651 cm^{-1}, 3621 cm^{-1} which represent OH, and also the sharp band at 2928 cm^{-1} was changed to very weak bands at 2979 cm^{-1}, 2875 cm^{-1} which characterize the CH stretching of C_6. The very weak band at 1378 cm^{-1} changed to a broad band at 1711 cm^{-1} which characterize C=O stretch. Sharp peak at 1645 cm^{-1} which is specific for cellulose, shifted to 1617 cm^{-1} in Fig. (8) for the MC-hydrogel. The sharp peak which is related to C=C at 1645 cm^{-1} disappeared and another sharp peak at 1617 cm^{-1} was appeared . Two peaks at 1465 cm^{-1} and 1429 cm^{-1} indicate the presence of CH_3, while the peak at 1345 cm^{-1} indicates the presence of C-O- at C_2 and C_3, where new sharp peak at 1201 was noticed

which is related to C-O stretch for acrylic acid. The disappearance of broad peak at 1079 cm^{-1} and appearance of small peak at 889 cm^{-1} which are typically (C-O-C at glucose unit) for pure cellulose, confirm entering of acrylic acid in these region.

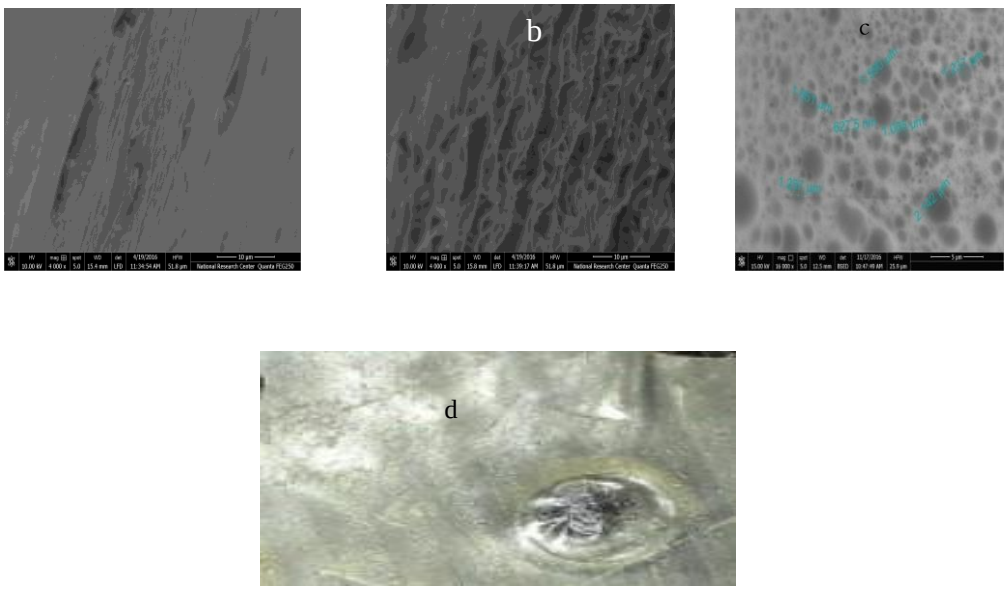


Fig (7):

a) The surface of the membrane of MC-Rs hydrogel
b) The cross section of membrane of MC-Rs hydrogel
c) The swelling membrane (400%) of MC-Rs hydrogel
d) Dry membrane of MC-Rs hydrogel

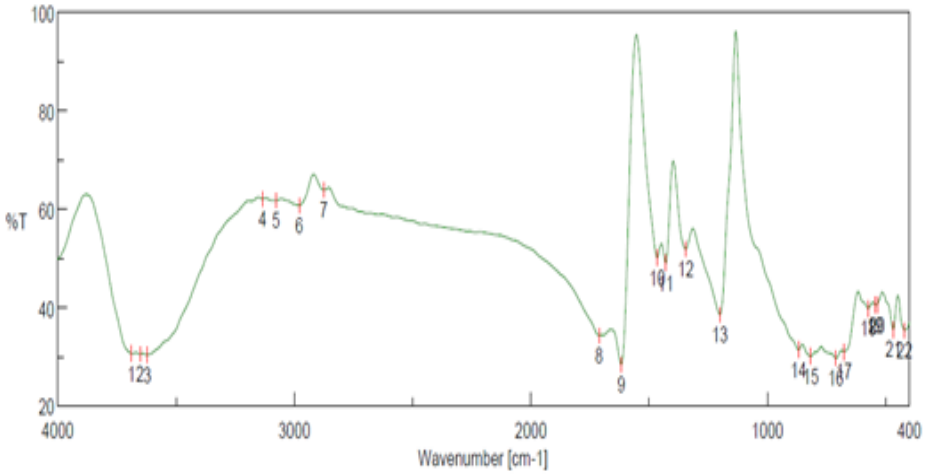


Fig (8): FT-IR of MC –Rs hydrogel

CMC was modified with neutralized acrylic acid as done in the previous MC experiment. The resultant product was characterized through FT-IR (Fig. 9), SEM (Fig. 10) and absorption test for water. The percent of absorption was 445%, and after drying it forms a membrane with tensile strength of (3.2 KN/m), tear factor (45), and it appears transparent as shown in Figure (10). By increasing the amount of water absorbed till (600%), the CMC hydrogel becomes viscous liquid which dries within (30 minutes) returning to its dry state.

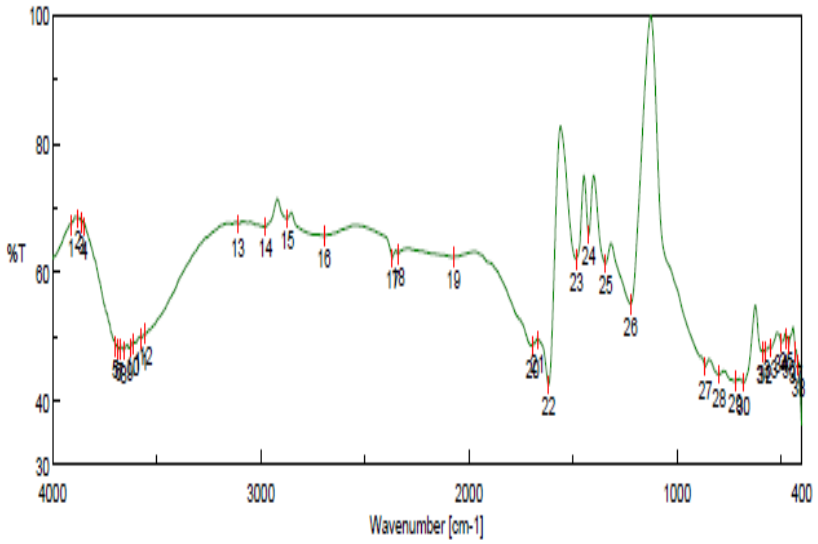


Fig. (9): FT-IR of CMC-Rs hydrogel

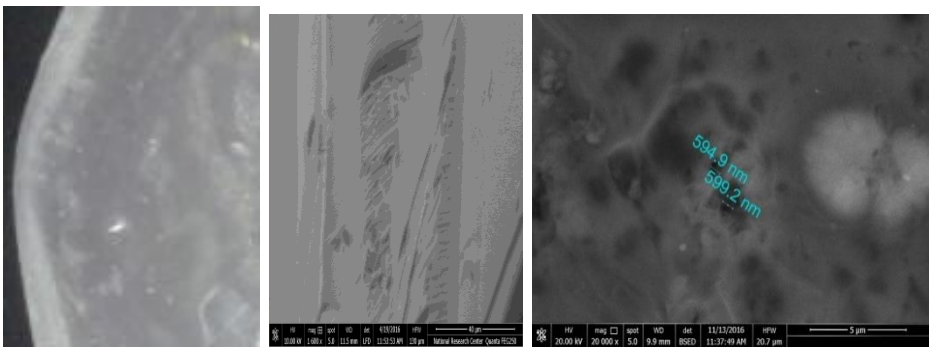


Fig.(10):

a) CMC- Rs dry membrane.
b) CMC-Rs at (445%) absorption.
c) CMC-Rs at (583%) absorption

The IR spectra (Fig.(9) indicates the typical absorption of the cellulose backbone , as well as , the presence of the carboxymethyl ether group at 1654, 1617 and 1613 cm^{-1} where additional peak at wave length of 2367 cm^{-1} may

be due to the existence of the contamination from impurities or combination band with water .Subsequently, bands around 1458 cm^{-1} and 1420 cm^{-1} are assigned to CH_2 scissoring. It is obvious that those in the broad absorption band of approximately above 3500 cm^{-1} is due to the stretching frequency of the hydroxyl group (OH).

Generally, broad band of OH group at 3424 cm^{-1} was changed to small broad bands at 3574 cm^{-1}, 3553 cm^{-1} and 3110 cm^{-1}. Sharp peak at 2922 cm^{-1}, assigned for CH stretching was changed to very weak band at 2976 cm^{-1} with the appearance of very weak band at 2872 cm^{-1} and 2696 cm^{-1} for aliphatic asymmetric and symmetric CH-stretching vibration .Broad band at 1644 cm^{-1}, especial for carboxyl group, was assigned to 1694 cm^{-1} as small peak and appeared also as small peak at 1670 cm^{-1} and sharp peak at 1617 cm^{-1} and all of them were assigned for carboxylic group. The very weak bands at 1453 cm-1and 1425 cm^{-1} were shifted to 1482 cm^{-1} and 1423 cm^{-1} where they are assigned for methyl group $–CH_3$ and appeared as sharp peaks. The very weak peaks at 1379 cm^{-1} and 1317 cm^{-1} for –C-O-H at C_2 and C_3 were appeared as broad and strong band at 1342 cm^{-1} for OH group which is assigned for the hydrogel group. New peak at 1222 cm^{-1} was assigned for C-O which is strong and sharp peak and it is specified for the hydrogel group. The disappearance of the region from 1159 cm^{-1} till 863 cm^{-1}, which is characterized C-O-H bending at C_6 and hydroxyl group, indicate the presence of the hydrogel group in the backbone of the cellulose.

4-7-Addition of MC-hydrogel and CMC–hydrogel to Hand-made Paper-sheets: Modified MC and CMC-hydrogels were added to (8g) of bleached rice straw pulp as 0.1% (w/w)during preparation of the paper sheet in the paper making sheet machine where they filled the pores between the fibre then the paper was dried and tested for absorbance of water. The hand-made sheets of modified MC-Hydrogel absorbed 455% water from its weight within 2 min and reached up to 773% after 6 min. While the addition of 0.1% CMC-Hydrogel is forming absorbed paper sheet that can absorb water up to 600% from its weight within 6 min. Both CMC-hydrogel and MC-hydrogel can be used as absorbed paper for different purposes.

CONCLUSION

In this work, we tried to make a combination of the renewable raw material of cellulose (e.g. rice straw) and the recyclable ionic liquid (1-butyl-3methylimidazolium chloride [(BMIM) Cl^-]) to give contribution to environmental protection and decrease economic cost. Rice straw was converted to MC of DS 0.9 and CMC of DS 1.0 where hydrogel were prepared from the resulting derivatives. Both MC and CMC, as well as, their hydrogels, were used as additives for paper making. Addition of both MC and CMC enhanced the paper properties, where it increases the mechanical and optical properties of the prepared paper. Moreover, the test of the water absorption of the resulted sheets indicated that the addition of both MC and CMC increased its value to reach 230 and 290%, respectively. On the other hand, addition of both MC-hydrogel and CMC-hydrogel produces absorbed paper with water uptake till 773 and 600%, respectively.

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تحضير الورق والمشتقات السليلوزية صديقة للبيئة من قش الارز

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المستخلص

فى محاولة للإستفادة من المخلفات الزراعية مثل قش الأرز والذى يسبب مشكلة بيئية، تم أستخدامه كمصدر سليلوزى مع السائل الأيونى، والذى يمكن استرجاعه بعد حدوث التفاعل، فى مشتقات سليلوزية مثل ميثيل السليلوز وكربوكسى ميثيل السليلوز ثم تحضير الهيدروجيل من المشتقات المحضرة،حيث تم إستخدام المشتقات والهيدروجيل كإضافات إلى عجينة الورق أثناء عملية تحضير الورق مع إضافات أخرى. وقد تم دراسة الخواص الميكانيكية والفيزيائية للورق الناتج بعد عمليات الإضافة٠ وقد أثبتت النتائج تحسن فى الخواص الميكانيكية والطبيعية للورق الناتج. كما تم دراسة عملية إمتصاص الماء للورق الناتج، حيث أثبتت الدراسة زيادة معدل امتصاص الماء فى الورق المحضر مما يعنى الحصول على ورق ذو درجة إمتصاص عاليه.