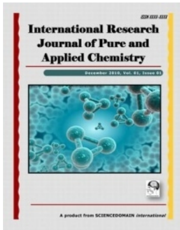

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Improvement of Paper Properties of Rice Straw Pulps by Microcrystalline Cellulose/Calcium Carbonate

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Rice straw is a locally available lignocellulosic material. In this study rice straw was pretreated by soaking it in water for 48 hours at room temperature. The pretreated straw was cooked in 5% NaOH at 100ºC and atmospheric pressure. The structure and mechanical properties of paper made from cooked pulp was investigated. Hydrogen peroxide as a bleaching agent was applied to the pulp to enhance its brightness level in a single stage process in the presence of sodium hydroxide and magnesium sulfate. Rice straw pulp, bleached using 2% hydrogen peroxide solution, was selected to prepare microcrystalline cellulose (MCC). The MCC was characterized by 45.5% crystallinity and nano in size vide XRD and TEM respectively. Microcrystalline cellulose and calcium carbonate were added to unbleached pulp as fillers. Air permeability of filled paper was improved in the presence of MCC more than in the presence of calcium carbonate alone. Optical properties and water permeability of filled pulp showed improvements in the presence of microcrystalline cellulose filler compared to unfilled pulp.

Keywords: Rice straw; microcrystalline cellulose; water permeability; air permeability.

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1. INTRODUCTION

Many cereal straws, particularly rice straw, have been used as raw materials for paper production. Non-wood raw materials account for 5-7% of the total pulp and paper production worldwide [1]. Jahan [2] studied the effect of hot-water and alkaline pre-extraction treatment of rice straw on soda-anthraquinone pulping. His results showed that rice straw with alkaline pre-extraction treatment had better pulp yield and strength properties compared with the pulp obtained by hot-water pre-extraction treatment. In another work, the potential of using bleached wheat straw pulp (BWSP) was explored to improve the tensile strength of the high-yield pulp (HYP) while preserving its high bulk property. The explanation was that micro fines from refined BWSP can act as binders to improve the HYP inter-fiber bonding, as a result, the HYP tensile strength can be improved by using a small amount of BWSP, while the HYP bulk is not significantly affected [3]. Bleaching of pulp with alkaline hydrogen peroxide resulted in conversion of conjugated chromophoric groups associated with lignin structure to carboxylic acids and other degradation products [4]. Previous studies also reported that the number of charged groups increases in peroxide bleaching and/or alkaline treatment of mechanical pulps due to alkaline hydrolysis of ester groups in the pulps [5]. Cellulose is a classical example of a renewable and biodegradable structural plant polymer which can be processed into whisker-like micro fibrils [6,7]. Recently, researchers reported the extraction of cellulose fibers from rice husk by alkaline and bleaching treatments, which were subsequently converted to nanocrystals using sulfuric acid (H_2SO_4) hydrolysis treatment [8]. Isolation of microcrystalline cellulose has been carried out from jute cellulose by using the same acid hydrolysis (H_2SO_4) approach [9] Microcrystalline cellulose could be produced from alpha cellulose obtained from wood pulp by hydrolysis with hydrochloric or sulphuric acid [10].

Microcrystalline cellulose (MCC) is widely used as a filler, strength enhancer and a binder [11]. Eriksen et al. [12] found significant tensile index increase at 4% addition of microcrystalline cellulose to thermo mechanical pulp (TMP) hand sheets independent of the production method. Mörseburg, Chinga-Carrasco added microfibrillated cellulose to clay loaded layered TMP sheets and found that the strength properties improved [13]. Optimizing a certain type of filler for a specific paper grade usually results in a compromise among the obtainable properties with this filler. In cases where one single pigment does not meet all the requirements, filler combinations are applied. There is a continuous trend towards fully or partially replacing specialty pigments by regular or modified regular fillers. Recently, rice straw is used for paper making or as a filler in wood plastic composites industry. In the present investigation, it is used for the production of micro crystalline cellulose by hydrolysis using hydrochloric acid. The aim of the present work is to produce high yield pulp from rice straw at low temperature and at atmospheric pressure. Improving the properties of paper made from this pulp was achieved by adding microcrystalline cellulose and calcium carbonate as fillers to the pulp.

2. EXPERIMENTALS

2.1 Pulping

Rice straw was used as a raw material in this research. It was cut into pieces of approximately 3 cm length. Rice straw was pretreated through soaking in water at room temperature for two days [2]. After the soaking water was decanted, the pretreated straw was cooked using 5% sodium hydroxide (obtained from El Nasr Pharmaceutical Chemicals

Co, Egypt, as an analytical grade) based on oven dry weight of the raw material. The condition of pulping was as follows:

Liquor ratio: 1:8, based on oven dry rice straw, pulping time: 2 hours, pulping temperature: 100ºC at atmospheric pressure. After the required time pulp was allowed to cool, filtered, and washed by water till neutrality. Pulp was dried to a constant weight at 105ºC in an oven to calculate the yield.

2.2 Bleaching

Aqueous solution of hydrogen peroxide (40% wt/v) as commercially available grade was used in bleaching process.

The conditions of bleaching were as follows: pulp concentration 10%, NaOH 2% on o.d. pulp, H_2O_2 charges were 1, 2, 4%, temperature 80ºC, treatment time 90 mins. and $MgSO_4 \cdot 7H_2O$ (0.6% on o.d. pulp) stabilizer was dosed into an alkaline medium (pH 9). All experiments on pulp bleaching were made in plastic bags placed in a thermostatic shaker water bath. After bleaching, the pulps were washed with water to attain neutrality and dried at room temperature. Magnesium sulfate was used in the peroxide stage in order to prevent radical degradation reactions of carbohydrates, since this salt is reported as being extremely efficient at reducing the rate of peroxide decomposition [14,15]. The optical properties of the unbleached control, bleached and unbleached filled pulp presented in brightness and opacity were measured using Hunterlab color difference meter D25-2. Calcium carbonate assay 99. 5% obtained from SRL. CO., Japan and the prepared MCC were added to unbleached rice straw pulp as fillers at 10% by weight based on o.d pulp before paper making by 1 hour.

2.3 Tests

Alpha cellulose of unbleached and bleached pulp was estimated using 17.5% sodium hydroxide solution, while T-211 method was used for ash estimation Hand-made paper sheets of 80g/m^2 were prepared using Tappi Standard Method 414. The sheets were tested for tensile strength according to German Standard method by means of a Karl Frank 468 tester (Weinheim–Berkenau) Water permeability, air permeability, bursting resistances were measured using BS 6906, ASTM D 737, and ASTM D 3786 (Tayousiki Japan methods) respectively.

2.4 Microcrystalline Cellulose Preparation and Characterization

2.5 g alpha cellulose of rice straw pulp (bleached using 2% H_2O_2) was added to 50 ml of 2.5 N hydrochloric acid (34%) This mixture was heated at 80ºC for 15 minutes. It was allowed to cool to 50ºC and centrifuged using magnetic stirrer for 10 minutes. The product was filtered and washed by water until it became free from acid, and then air dried followed by thermal treatment in the oven at 50ºC and weighed to calculate the yield. Microcrystalline cellulose was disintegrated by mortar. Crystallinity of MCC was obtained using a Brukur D8 Advance X-ray diffractometer (Germany). The size of MCC was elucidated by JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of the MCC particles were prepared by adding a small drop of the water suspension MCC onto a Lacey carbon film-coated copper grid then allowing them to dry in air.

3. DISCUSSION

3.1 Structural and Strength Properties of Rice Straw Pulp

The solid pulp yield from rice straw pretreated with water for 48 hours and pulped using 5% NaOH solution for 2 hour at atmospheric pressure was 74%. Water soaking pretreatment was adopted in this study as against the popular dilute acid pretreatment process to avoid the commonly encountered reactor corrosion problem. More so, pretreatment with water improved pulping efficiency of non-wood material and produced pulp containing 68.33% alpha-cellulose. This percent was suitable to prepare microcrystalline cellulose. The oxidative treatment of lignocellulosics by hydrogen peroxide in the presence of magnesium sulfate as a stabilizer in an alkaline medium was established. Table 1 indicates the effect of H_2O_2 charge on bleached rice straw pulp properties. Pulp obtained using 2% H_2O_2 had 72.7% alpha- cellulose content and 61.5% pulp yield. Yield of bleached pulp using 1 and 4% H_2O_2 was 67.85 and 62.9% respectively with corresponding alpha- cellulose content of 69.33% and 69.556% respectively at the same conditions. H_2O_2 charge had no effect on burst strength but tensile strength was improved by using 4% H_2O_2 in bleaching. Air permeability of paper sheets made from bleached pulp was greater than the unbleached one. This may be due to increasing porosity of bleached pulp as a result of partial loss in lignin content.

Table 1. Physical properties of unbleached and bleached rice straw pulp

Pulp	Air permeability, $Cm^3\backslash cm^2$.sec.	Burst, Kg\cm^2	Tensile strength, Kg/mm
Unbleached pulp	1.3	1.1	2.2
1%H_2O_2 bleached pulp	2.4	1.1	2.2
2% H_2O_2 bleached pulp	2.2	1	2.3
4% H_2O_2 bleached pulp	1.8	1.2	3

3.2 X-Ray Diffraction (Xrd) of Microcrystalline Cellulose

It is widely recognized that cellulose contains both crystalline and amorphous regions [16]. The X-ray diffraction (XRD) patterns of MCC obtained in this study were illustrated in Fig. 1. The crystallinity of MCC was 45.5%, with the remainder being the amorphous fraction. This indicates that the cellulose microfibrilles do not become single crystals.

3.3 Transmission Electron Microscopy of MCC

TEM of the MCC prepared from the rice straw's alpha- cellulose was illustrated in Fig. 2. The actual yield of MCC related to alpha cellulose content of rice straw pulp was 77.32%. MCC having nanoscale was obtained. The length of this micofibrill was 33 nm and its width was 2.5 nm which were in agreement with other studies [17].

3.4 Filler Effect on Paper Properties

The growing need to reduce production cost and increasing the opacity, brightness and surface smoothness has encouraged the use of fillers in papermaking. Filler usage improves optical properties, but reduces strength properties. Pre-mixing fillers with fines in a controlled fashion, prior to its addition to the pulp furnish, improves strength and optical properties of the sheet [18] Since calcium carbonate is binder-less and MCC was used as a binder and filler in many studies [19], the effect of these two substances on hand-made paper sheets properties was investigated. Table 2 illustrates this investigation. Binder-less character of $CaCO_3$ was shown from ash content of the unfilled pulp in comparison with the filled pulps (paper sheets). Regarding tensile strength of the paper sheets, there was a remarkable improvement attributed to the presence of all percents of calcium carbonate and MCC which was prepared in this study in nano scale. This is in agreement with Subramaniam et al. who found that increasing filler and microfines in chemical pulp handsheet improved internal bonding strength [20]. The microfibrill fines filled gaps between fibres in wet pressed sheets. The fibrillated MCC contains nanofibrils and has large specific surface area. The MCC readily adsorbs onto the fillers and fibres and improves packing and bonding during wet pressing.

Table 2. Physical and mechanical properties of unbleached filled pulp

Treated pulp	Air permeability, $Cm^3\backslash cm^2$.sec.	Burst, $Kg\backslash cm^2$	Tensile strength, Kg/mm	Ash%	Water permeability, litre/ sec.
Unbleached pulp(control)	1.3	1.1	2.1	14.4	1.4
10%calcium carbonate	1.3	1	4.8	15.1	0.6
5%calcium carbonate+5%MCC	1.5	1	4	14.7	0.6
2.5%calcium carbonate+7.5% MCC	1.5	1	3.8	14.5	0.8

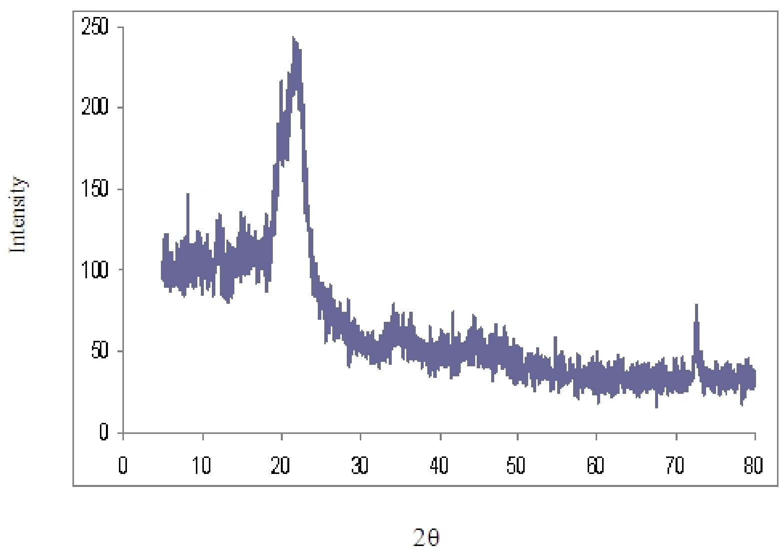

Fig. 1. XRD profiles of microcrystalline cellulose

Air permeability or air resistance of filled paper was improved to 1.5 cm^3/ cm^2.sec. in the presence of MCC as a filler, while the presence of calcium carbonate alone showed no improvement on this parameter when compared to the control pulp handsheet. Water permeability resistance of the paper sheets was improved in the presence of the two fillers; the water permeability decreased from 1.4 litre/sec (for control pulp handsheet) to 0.6 litre/sec on adding 2.5% MCC as a filler. Paper sheets filled by 7.5%MCC and 25% calcium carbonate blend have more water permeability than paper sheets filled with calcium carbonate alone. This is attributed to the hydrophilic nature of amorphous cellulose included in MCC. In addition, differences in particle size and particle morphology of the two fillers affect paper sheet properties [21,22].

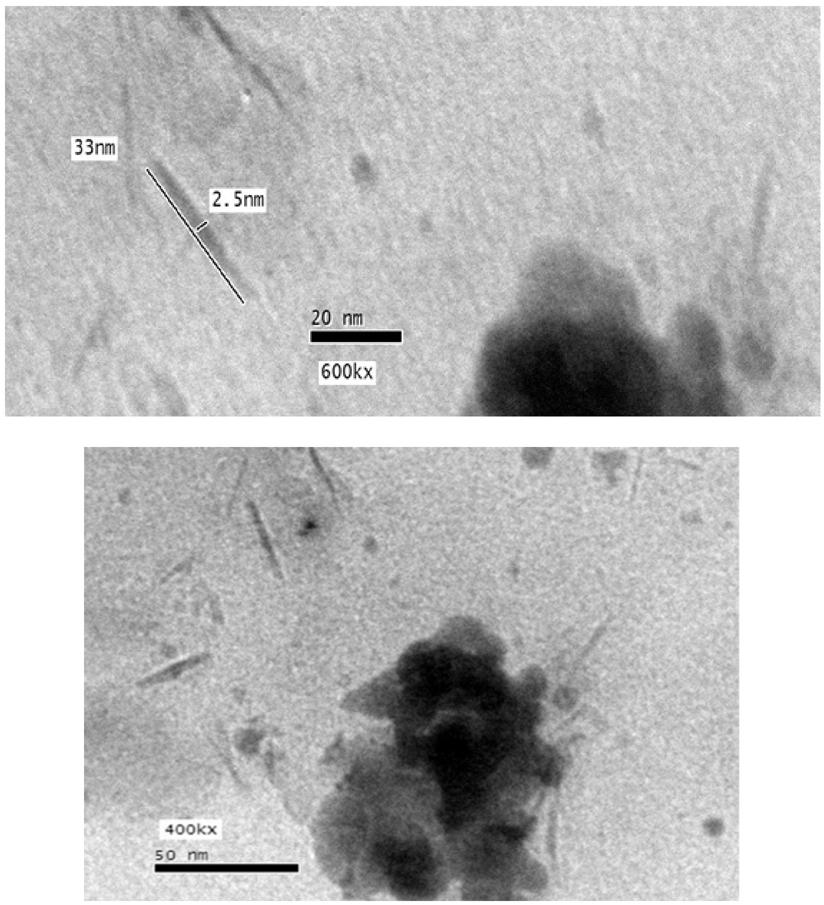

Fig. 2. TEM graphs of MCC from alpha- cellulose of bleached (2% hydrogen peroxide) rice straw pulp

3.5 Optical Properties of Unbleached, Bleached and Unbleached Filled Pulp

All chemicals used in bleaching rice straw are environmentally friendly substances because they contain hydrogen, oxygen, sodium and magnesium. NaOH is used to bring the pH up to 9 because H_2O_2 becomes active at this pH. Table 3 indicates higher brightness of bleached pulp compared to the unbleached pulp (control sample). Adding calcium carbonate alone or mixed with MCC filler to the unbleached pulp improves brightness of paper by a small percent, approximately 10.34%. Opacity is a measure of a material's ability to obstruct the passage of light. Sufficient opacity is important to prevent showing printed text or figures on the reverse side of a paper sheet. MCC and/ calcium carbonate are efficient in terms of opacity for unbleached paper because small internal voids do scatter light. It is clear from Table 3 that paper made from unbleached pulp filled by 10% calcium carbonate or 5%calcium carbonate+5% MCC or 2.5%calcium carbonate+7.5% MCC has higher opacity (99.3%, 99.5%, 99.1%) more than the unbleached sample (control, 77.7%).

Table 3. Optical properties of unbleached, bleached and unbleached filled pulp

Sample	Brightness, %	Opacity%
Unbleached pulp (control sample)	26.1	77.7
1%H_2O_2 bleached pulp	48.4	96.4
2% H_2O_2 bleached pulp	48.4	97.5
4% H_2O_2 bleached pulp	38.4	97.95
unbleached pulp +10%calcium carbonate	28.4	99.3
unbleached pulp +(5%calcium carbonate+5%MCC)	28.9	99.5
unbleached pulp +(2.5%calcium carbonate+7.5% MCC)	28.8	99.1

Enhancement in brightness and opacity of unbleached filled paper sheets reflects improved affinity of filler particles to fibers in the aqueous papermaking wet end system. When higher opacity is required, bleaching step can be neglected for economic reasons.

4. CONCLUSION

Rice straw is a locally available waste lignocellulosic non- wood material and can be converted into pulp at atmospheric pressure. This pulp can be employed in paper making industry and in preparing a valuable product like microcrystalline cellulose. Paper sheets filled by 7.5 % MCC and 2.5% calcium carbonate blend have higher water permeability than paper sheets filled with calcium carbonate alone. The effect of moisture on packaged products depends on the product. For some products, it is necessary to maintain the moisture content at a high level to prevent the product from drying out. For others the reverse may be the case, as by absorbing moisture the product may loose texture. Compared with the unfilled paper, MCC and calcium carbonate fillers gave slightly more increase in air permeability. Burst strength was not affected by fillers. Adding calcium carbonate alone or mixed with MCC filler to unbleached pulp improved brightness of paper by a small percent approximately; 10.34%. Calcium carbonate and MCC are efficient in terms of opacity for unbleached paper. Enhancement in brightness and opacity of filled paper sheets reflect improved affinity of filler particles to fibers in the aqueous papermaking wet end system. When higher opacity is required, bleaching step can be neglected for economic purposes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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