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Optimization of organosolv Pulping, Bleaching process and Physico-chemical Characteristic for Mango Seed paper

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Abstract

There is a growing concern over use of wood pulp for paper making which has led to increase the usage of low-cost non-wood pulp for papermaking. Mango seed hard cover is having great potential for cellulose. Hence the present research paper focused on Mango seed hard cover as a source of Pulp and Paper industries. Developed Paper from mango seed using Flat sieve and Hand sheet press mould methods was compared based on Porosity, Thickness, absorbency, Tensile strength, etc. Physic chemical characteristics of paper were deliberated by optimizing organosolv process followed by bleaching.

Keywords: Mango seed, pulp, Organosolv, Bleaching, etc..

Introduction

Mangifera indica (Mango) belongs Anacardiaceae family[1]. Mango is addicted for having high nutritional and medicinal value, due to its tastes and flavour. Mango adds value as by-products are used for animal fodder, and the timber is used for canoe building and making charcoal. Mango friut source are effective against many diseases viz- arthritis, tumours, infections etc[2].

The major constituents of wood fibers are lignin, cellulose, hemi-cellulose, extractives agricultural waste. These non-wood fibers are used in more than 50% of pulp production in India and china[3]. The economic advantage in many developing countries is the presence of non-wood resources, a growing domestic market for paper, reasonable labour costs, and absence of wood raw materials[4]. Nowadays, the highest ratio of non-wood to total papermaking pulp capacities are in the developing market economies of Asia, Africa and Latin America, as well as the centrally planned economies of Asia. Some of these regions have more non-wood plant pulping capacities than wood pulping capacities. Indeed, China has more than twice as much. Further, total non-wood plant pulping capacity worldwide is increasing faster than the wood pulping capacity. With this background special emphasis on pulp and paper from MSHC is in increasing demand for eco-friendly materials and the desire to reduce the cost of pulp, agricultural wastes have been developed for reduction of wood pulp in paper industries[5].

India is rapidly industrial and economical growing country resolves that demand supply gap for paper. Researchers have attended on pulp achieved from agricultural wastes as a replacement for the wood pulp to reduce deforestation. Mango seed act as renewable sources for pulp making due to presence natural products that are identical for wood pulp. Yet, researcher has been paid attention on pulp for paper industry developed from mango seed wastes. Hence, the attempt was made to investigate more on mango seed wastes for the extraction of pulp, processing it towards the paper making, and it's various applications.

Materials and Methods

Raw material preparation: Mango seeds from fruit were separated manually and sun dried for five weeks. After separation, the outer hard cover and inner kernel was separated and sun dried for two weeks. Hard cover was chopped and converted in to chips of an approximate size of 1 cm and oven dried at 50 ^oC to remove moisture.

Pulp making by organosolv method[6]: Fabrication from mango seed hard cover pulp was carried out by the chemical process. Initially, mango seed hard cover in cooking operation, a revolving (at 2 rpm) laboratory rotating digester with a capacity of 15 litres was used. 40% Ethanol–water liquor was used as cooking liquor, according to the general principles of Kleinert (1975)[7]. Catalyst (H_2SO_4) was added to the liquor to increase delignification. In this study, the pulp was treated at 95 ^oC for 60 min by 8% alkaline environment. Precipitated pulp which is cleaned from organosolv lignin was washed with water. The pH value of extracted pulp and black liquor, taken from the digester at the end of cooking, was measured.

After these operations, the pulp was filtered and uncooked material was separated. The pulp was then squeezed to 20-25% ratio of solid particle and placed into polyethylene bags and used for further process of paper making.

Optimization condition for manufacturing of pulp from mango seed hard cover: Optimization for manufacturing of pulp from mango seed hard cover was carried out to obtain maximum yield of pulp by using organosolv method. The following optimization studied by varying different conditions such as by varying percentage of Ethanol–water, percentage of catalyst (H_2SO_4), by varying time at constant temperature 95 ^oC and pressure at 25 kg cm-2 and by varying percentage of NaOH.

Table-1
Optimization for manufacturing of pulp from mango seed hard cover by varying following cooking conditions

% Ethanol-Water	% catalyst (H_2SO_4)	Time /min @ T- 95 ^oC and P- 25 kg cm^{-2}	%NaOH
10	0.1	20	2
20	0.2	30	4
30	0.3	40	6
40	0.4	50	8
50	0.5	60	10
-	0.6	70	12

Oxidation of Pulp /Bleaching of pulp: The Hydrogen Peroxide bleaching process was conducted at 10% pulp consistency with 2% H_2O_2 based on oven dried pulp in plastic bags placed in a water bath. 3% Na_2SiO_3 based on oven dried pulp was used as peroxide stabilizer. Before adding bleaching chemicals, the pulp was pre warmed. During the bleaching experiment the pulp was mixed every 15 minutes for uniformity in bleaching process.

Characterization of paper A) Using Flat sieve and B) Using Hand sheet press mold: Manufacture of paper sheets was carried out by above two methods. Characteristic of it was observed by following conditions.

GSM (Grammage per square meter): Grammage of a sheet of paper in g/m^2 is calculated by following formula,

Grammage= $\frac{W \times 100}{a \times b}$

Where: w+ weight of sheet in g , a= length of sheet in cm, b= width of sheet in cm

Thickness/ Caliper: Thickness is measured by using properly calibrated thickness measurement micrometer.

Density: Density of hand sheet is calculated by following calculations.

Density= $\frac{\text{Basis Weight}}{\text{Thickness}}$

Ash Content: Ash contain was determined as per the standard crucible method.
Ash, percent by weight = $100 * \frac{w-x}{W-x}$

Where: w= weight in g of the crucible and the ash, X= weight in g of the crucible, W+ weight in g of the crucible and the material

Moister content:
% Moisture content= $\frac{\text{Initial Weight}-\text{Final Weight}}{\text{Initial Weight}}$X100

Tensile strength: Tensile Strength is measured by standard TAPPI T 494 method.

Porosity: Porosity of paper is measure by Air resistance of paper (Gurley method) T 460.[8]

Filtration Speed: Filtration speed of the developed paper is measured as the time in second required passing 100ml of soft water at ambient temperature under gravity flow.

Water absorbency: Total weight of dry bowl and dry paper was measured with the help of digital balance and is to be considered as dry weight. The combined weight of the bowl and the wet paper will be called the wet weight.

The weight of the water absorbed by the paper = wet weight - dry weight

Water penetration test: Around six strips of paper are put in a glass container by 1 cm of its bottom deep in water. Water penetrated by sheet is then observed by average distance (cm) travelled by water in 1 min.

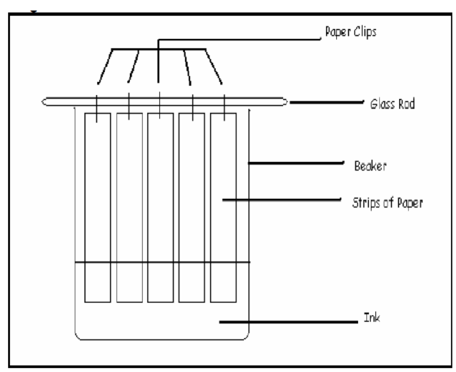

Figure-1
Water penetration test (Capillary rise)

Ink Absorption Test: 10 ml of 1% ink solution taken in beaker. Strip of MSHC sheet are fixed to paper clip onto the end of it. Slide the paperclip onto the glass rod, so that the paper hangs down. Glass rod is placed in the beaker so that the ends of the paper are in the ink with taking care that the strip of paper does not touch. When the ink reaches top of the strip then taken out it from the ink solution. Time and distance covered by ink is measured.

Results and Discussion

Optimization for manufacturing of Pulp from Mango seed hard cover by using Organosolv method by varying different conditions: Optimization for manufacturing of pulp from mango seed hard cover was carried out to obtain maximum yield of pulp by using organosolv method. The results for optimization study are expressed in following Tables and Figures.

Table-2
Optimization for manufacturing of pulp from Mango seed hard cover by varying Ethanol–water %

% Ethanol-water	% Yield	% catalyst (H_2SO_4)	% Yield	Time /min	% Yield	% NaOH	% Yield
10	25	0.1	46	20	16	2	19
20	32	0.2	51	30	32	4	33
30	47	**0.3**	**58**	40	49	6	46
40	**59**	0.4	53	50	56	**8**	**62**
50	61	0.5	47	**60**	**61**	10	65
		0.6	45	70	55	12	69

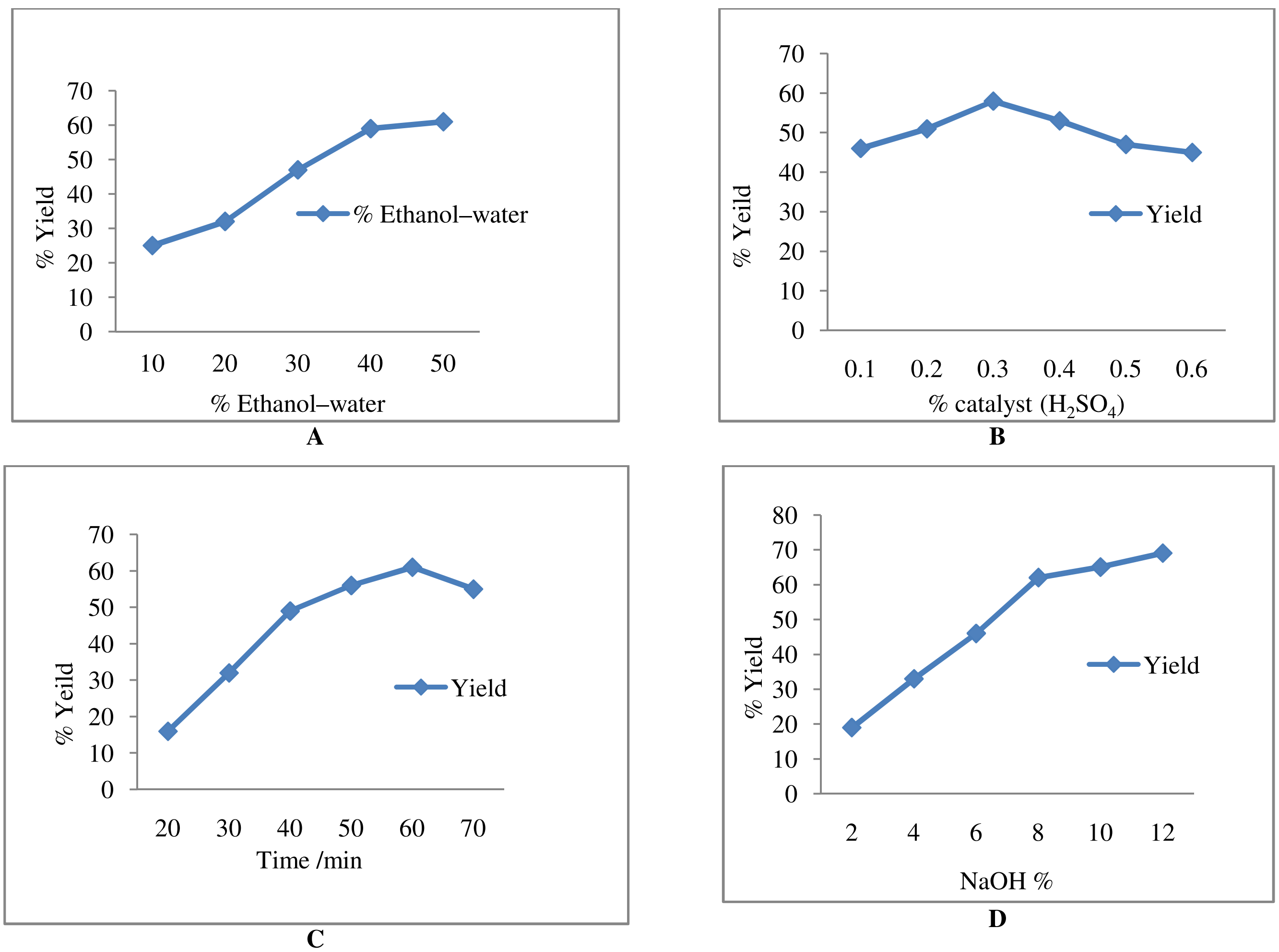

Figure-2
Optimization for manufacturing of pulp from Mango seed hard cover by varying
A. Ethanol–water %, B. catalyst H_2SO_4 %, C. time at constant temperature 95 ^oC D. pressure at 25 kg cm-2

Table-3
Optimization for manufacturing of pulp from Mango seed hard cover by varying Ethanol–water %

Method	Ethanol ratio	Pulping time	Pulping temp	Catalyst ratio	Maximum pressure	Black liquor	Liquor / chips
	(%)	(Min.)	^{o} C	(H_2SO_4) (%)	kg cm^{-2}	pH	% Ratio (w/w)
Reference method	40	60	95	1.1	25	9.3	1/8
Optimized method	40	60	95	0.3	25	9	1/8

As shown in Figure-2 Ethanol-water concentration it is observed that as the concentration of percentage Ethanol-water goes on increasing from 10 to 50% the pulp yield increases. Also till 40% concentration the increase in pulp formation is steep and the yield was observed only 2% rise when it moves from 40 to 50%. Maximum pulp formation was on observed at 40% Ethanol-water concentration which was selected for the further exercise.

According to Table-2 and Figure-2 indicates that the optimization for manufacturing of pulp from mango seed hard cover by varying catalyst percentage H_2SO_4. It is observed that percentage yield increases from 46 to 58% by increasing the concentration of catalyst from 0.1 to 0.6 respectively. There was sharp drop in the quality and quantity of the yield of pulp when further increase in concentration from 0.4 to 0.6 and the yield was 53% to 45% respectively. Hence 0.3 % H_2SO_4 selected for the study.

Optimization for manufacturing of pulp from mango seed hard cover was carried out by varying time at constant temperature 95 ^{o}C and pressure at 25 kg cm^{-2}. Obtained values are shown in Table-2. The reaction time increases from 20 minutes to 60 minutes, there is a gradual increase in the yield from 16 to 61% respectively. This shows that the pulp manufacturing is a time bound process. Change in percentage yield was fluctuate some time as per season study the value noted after certain time at 70 minutes there is decrease in the yield from 61 to 55%. Hence to observe perfect yield of pulp in the present study 60 min was selected.

Table-2 shows optimization for manufacturing of Pulp from Mango seed hard cover by varying percentage NaOH**.** Increases in percentage of alkali NaOH from 2 to 12% shown that linearity by increase in percentage yield from 19 to 69% respectively. Maximum pulp yield was observed at 8% NaOH alkali concentration having the yield was optimum with desired value 62% yield in pulp.

After optimizing the conditions of percentage yield of Pulp manufactured from Mango seed, the values where compared with reference method of Pulp making from cellulosic material. It was observed that the optimized values so obtained from Manufactured process was almost similar to conventional method of pulp making in terms of percentage Ethanol, Pulping time, and Catalyst ratio. Optimized cooking conditions applied for manufacturing of Pulp from Mango seed hard cover summarized in Table-3.

Optimizing the conditions was also confirmed with the analysis of physical characteristics of the manufactured pulp. It was observed that the pH of extracted pulp and black liquor is 10 and 12.2 respectively which is also seen in case of standard pulp making. Viscosity of the pulp prepared from MSHC was 16.8 centipoise, which is similar to the standard viscosity of cellulosic pulp having viscosity in the range of (15-21 centipoise). This manufactured raw pulp obtained from optimized process was further considered for pulp bleaching process.

Oxidation of Pulp /Bleaching of pulp: The Hydrogen Peroxide bleaching process was conducted at 10% pulp consistency with 2% H_2O_2 3% by using Na_2SiO_3 as peroxide stabilizer. During the bleaching experiment the pulp was mixed every 15 minutes, due to this uniformity in bleaching process seen. A fast decomposition of H_2O_2 was occurred due use of alkaline solutions at temperature 95 ^{o}C. The bleaching reaction is carried out in alkaline condition at high temperature as shown in below reaction.

$$H_2O_2 + NaOH \rightleftharpoons H_2O + Na^+ + HO_2^-$$

$$2\,HO_2^- \rightleftharpoons O_2 + 2\,OH^-$$

Reaction-1
Bleaching reaction

As a consequence, more reactive radicals such as hydroxyl radicals (HO-) and superoxide anions (O_2–) are produced, which are responsible for lignin degradation. This technique is used for bleaching and delignification purposes to improve the brightness of pulp as it reacts with colored carbonyl containing structures in the lignin. After bleaching process the white pulp that obtained is taken further for its characterization (Figure-3).

Characterization of Paper Prepared From Pulp Obtained from Mango Seed Hard Cover: Characterization of paper (Handsheet) prepared from pulp obtained from mango seed hard cover is showed that results as, GSM is an acronym standing for 'Grams per Square Meter'. Quite simply, it allows print buyers and print suppliers to know exactly about the quality of paper that is being ordered. The higher the GSM number, the heavier the paper. The GSM value of the paper made by using Flat sieve is ranging from 1400 – 1600 gr/m^2 and that of the paper made from Hand sheet press mold is 1000 gr/m^2. It is due to the external uniform pressure on the paper surface is applied on to the paper making as shown in Figure-4.

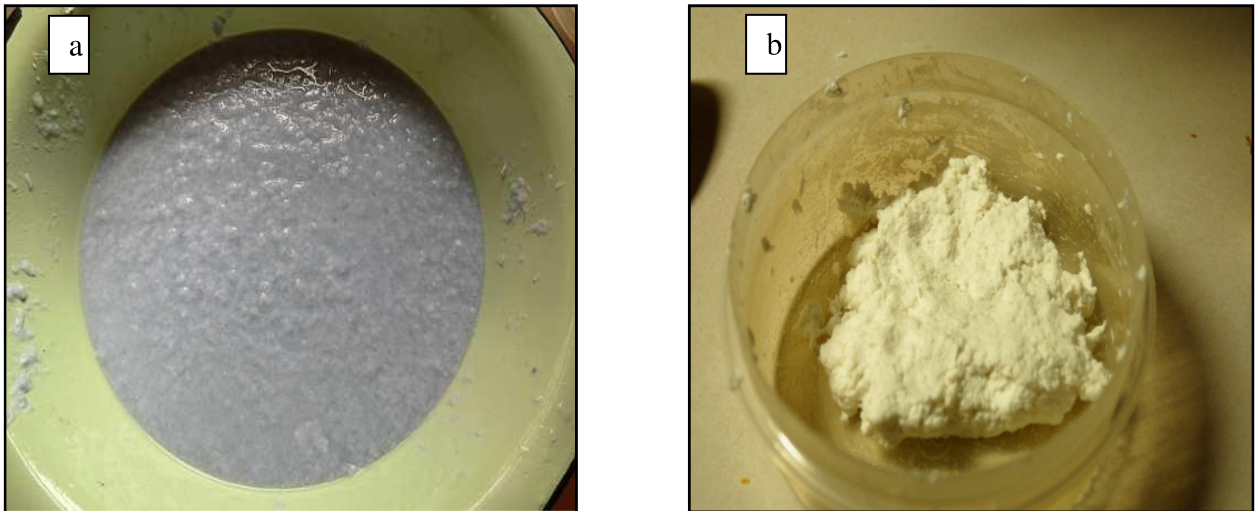

Figure-3
a. Grayish coloured raw pulp obtained from mango seed hard cover by Organosolv method, b.White coloured pulp from mango seed hard cover after Bleached reaction.

Figure-4
Manufacturing of paper using a. Flat Sieve method, b. Hand sheet mold press method

Paper density is its mass per unit volume. (ISO 534:2011, Paper and board) Determination of thickness, density and specific volume, indicates it is expressed in grams per cubic centimeter. The paper made by using Flat sieve is not exhibiting constant reading (3.6 - 4.1mm) of thickness and density 0.34-0.44 g/cm^3 due to its uneven of surface. The thickness of paper was measured by thickness measurement micrometer. Using Hand sheet press mold the obtained paper was observed constant reading (2.3mm) of thickness and density 0.48 g/cm^3. It is due to the external uniform pressure on the paper surface is applied on to the paper. Uniform caliper is good for good roll building and subsequent printing. Variations in caliper it affects several basic properties of paper including strength, optical and rolls quality etc. Thickness is important in filling cards, printing papers, condenser paper, saturating papers and many more.

Air Resistance Gurely Method is the resistance for the passage of air, offered by the paper structure, when a pressure difference exists between two sides of paper. It is measured as the time for a given volume of air to flow through a specimen under specified conditions. Air resistance is indirect indicator of degree of beating, compaction of fibers and type and amount of fillers. The Gurely Method is explained in TAPPI T 460 and TAPPI T 536 for low and high air resistance respectively.

The ash content was seen equal in both type of hand sheet paper that is 44 to 50%. The moisture content obtained for paper using Flat sieve was more 20 to 25% than paper of Hand sheet press mold i.e. about 2 to 4%. The knowledge of the moisture concentration of the paper pulp in the initial stages of manufacturing process would facilitate inclusion of feed-forward control techniques that could reduce deviations from the desired paper quality, thus reducing waste.

The samples for the machine direction tensile testing had a gauge length of 200 mm. The samples for the cross direction tensile testing had a gauge length of 100 mm. During the testing recorded, the rate of extension used was 20mm/min. "Elongation" is the maximum percentage of elongation of the sample before the sample ruptured. Form following Table-4 is conclude that the paper of Hand sheet press mold is showing good tensile strength values than paper of Flat sieve due to it obtained greater strength during its manufacturing process of as it gained external pressure on the paper surface.

Since paper is composed of a randomly felted layer of fiber, follows that the structure has a varying degree of porosity. Thus, the ability of fluids, both liquid and gaseous, to penetrate the structure of paper becomes a property that is both highly significant to the use of paper. Paper is a highly porous material and contains as much as 70% air.

Porosity is a highly critical factor in Printing Paper, Laminating Paper, Filter Paper, Cigarette Paper, Bag Paper, Anti-tarnish Paper and Label Paper. Porosity is the measurement of the total connecting air voids, both vertical and horizontal, that exists in a sheet. Porosity of sheet is an indication of absorptivity or the ability of the sheets to accept ink or water. Porosity it is one of important factor in a vacuum feeding operation on a printing press.

MD = Machine (longitudinal) direction. CD = Cross direction

Table-4
Results of tensile testing for paper manufactured by Flat sieve and Hand sheet press mold

Test	**Paper obtained from method**	
	Flat sieve	**Hand sheet press mold**
Tensile Strength (N) - MD	782.7	663.2
Elongation (%) MD	5.1	5.9
Tensile Strength (N) - CD	658.1	588.5
Elongation (%) MD	9.3	8.8

Filtration speed of the developed paper is measured as the time in second required passing 100ml of soft water at ambient temperature under gravity flow. This was seen 100 ml/120 sec and 100 ml/80 sec for paper made from Flat sieve and Hand sheet press mold respectively. Paper prepared from Flat sieves method required more time to pass 100 ml of water than the paper prepared with Hand sheet press mold. Water passing capacity in methods is because of its non uniformity and more thickness.

The water absorbing capacity is observed more for paper of Flat sieve which was 8 gm than for paper of Hand sheet press mold was 5 gm. This observation is due to its more thickness. The results are shown in following Table-5.

Table-5
Water absorbency test of MSHC sheet

Time (Seconds)	**Water absorbed by paper (gms)**
5	10
10	12
15	15
20	18
25	20
30	20

Water penetration property of paper is observed by average distance (cm) travelled by water in 1 min. Water penetrates more faster in paper of Hand sheet press mold (9cm) than paper of Flat sieve (5cm) it is due to uniform surface which improves the capillary rice characteristic of paper.

The water penetration property is tested to papers and boards which have been rendered water resistant or waterproof by internal sizing, by surface sizing, by coating, or by lamination using waterproof laminants or by any other method, and is not suitable for corrugated fibre board by may be applied to components of such board.

Figure-5
MSK hand sheet strips for water penetration test

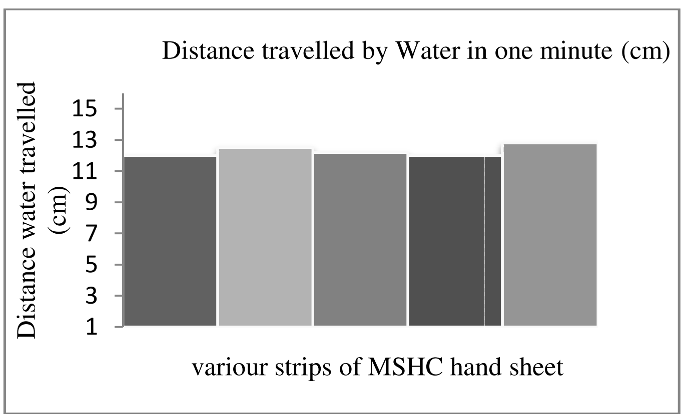

Figure-6
Water penetration test

The ink absorbing property of paper is mainly surface phenomena. A very hard, very smoothly glazed paper will scarcely absorb any ink. If we write on such a paper, the ink takes a long time to dry; and what makes the writing is simply a layer of the solid matter left by the ink. This layer lies on the outside of the paper, and can almost be scrapped away.

The ink absorbing capacity is seen more for paper of Flat sieve that is 10 cm/60 sec than for paper of Hand sheet press mold 10 cm/60 sec, it may be due to its more thickness. This test proves the affinity of dye or ink toward this paper which helps in further study of application of paper.

Figure-7
Ink absorbency test was carried out on paper prepared from using Flat Sieve method.

Table-6
Characterization of paper (Handsheet) prepared from pulp obtained from mango seed hard cover

Characteristics	**Physico- chemical characteristics**	
Hand sheet from MSHC pulp	**Using Flat sieve**	**Using Hand sheet press mold**
GSM (gr/m^2)	1400 - 1600	1000
Thickness (mm)	3.6 - 4.1	2.3
Density (g/cm^3)	0.34-0.44	0.48
Ash Content (%)	44 - 50	44 - 50
Moister content (%)	20 -25	2 -3
Porosity/ Gurley Air Resistance (sec)	5 -8 sec	4-6 sec
Filtration Speed	100 ml/120 sec	100 ml/80 sec
Water absorbency	8 gm	5 gm
Water penetration test	5 cm	9 cm
Ink Absorption Test (Capillary rise)	4 cm/60 sec	10 cm/60 sec

Conclusion

Paper pulp was successfully prepared in the laboratory by well-known Organosolv method from mango seed hard cover. Bleached pulp was further characterized to produce maximum yield (62%) at standard operating conditions. Paper was successfully prepared using this optimized pulp using Flat sieve and Hand sheet press mold techniques. It is also concluded that Hand sheet press mold technique is the modern techniques and the quality of paper is better due to its sacrificial uniformity. Characterization study of prepared paper was study on the basis of its various applications and it was so concluded that it can be used in industries such as filtration or printing press.

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