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Use of Weeds and Agro-Based Raw Materials and their Blends for Handmade Paper Making

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ABSTRACT

This study was carried out with the objective of studying the feasibility of making handmade paper from non-wood lignocellulosic raw materials (such as *Lantana camara*, *Parthenium histerophorus* and *Eichhornia crassipes*) and agro wastes such as bagasse, rice straw and wheat straw. The non-wood raw materials used are all weeds, present as invasive, abundant biomass. The agro wastes, even after reutilization by respective industries, are abundantly available for paper industry. Each of these materials was pulped by conventional chemical methods using sodium hydroxide and sodium sulphide by the Kraft process. These pulps were innovatively blended with one another and with recycled paper and bamboo to obtain handmade paper having different attributes such as fibre strength, porosity and folding endurance. These attributes are important for determining the suitability of paper for different uses. From among the blends studied, it was found that the blend of rice straw and *Lantana camara*, yielded paper of superior quality. The results of the study indicate that the innovative raw materials used have the potential to replace the raw materials that are either expensive or taxing the environment. The whole process is environment-friendly since the process of bleaching has been strictly avoided.

The blends yielded handmade paper sheets of good strength and quality well suited for conversion to paper products. Use of natural dyes, fibre shreds, flower petals, grasses etc. to enhance the aesthetic value of paper was found to present no problem during processing.

Abbreviations used:

CSF: Canadian Standard Freeness
GSM: Gram per Square Metre
L: Litre
OD: Oven Dried
1N: 1 Normal Solution

Key words: Agro waste, Blends, *Eichhornia crassipes* Handmade paper, *Lantana camara*, *Parthenium histerophorus*, Weeds

INTRODUCTION

Whatever the source, paper is basically made up of cellulose, the most abundant organic compound on earth. In addition to cellulose, there are two more structural components of plants, namely, hemicellulose and lignin. Cellulose, hemicellulose and lignin are all large polymeric molecules. Cellulose is embedded deep in the structural polymeric web of lignin and hemicelluloses (Figure 1) and is not easily accessible to chemical reagents and microbial organisms. In order to make paper from wood, the structural matrix has to be disrupted to release cellulose fibres. This is achieved by pulping under harsh conditions of chemicals, high temperatures and pressures.

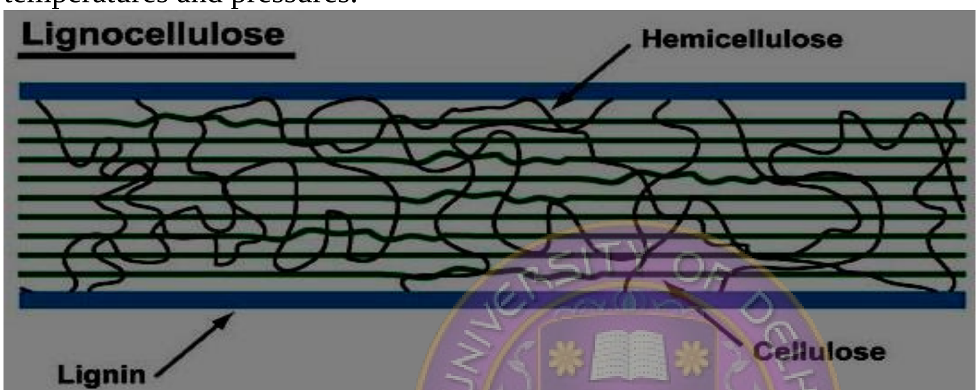

Fig 1: Cellulose embedded in the ligin and hemicellulose matrix

Although India has one of the lowest per capita consumption of paper (7 kg in 2007 projected to grow to 12 kg by 2020), the demand for paper is growing significantly and is projected to rise to 20 million tons by 2020 from current 13 million tons. India's growing literacy is expected to keep this demand buoyant (1, 2).

An important development in Indian paper industry over the years has been the classification of paper mills based on the fibre source. A look at the statistics presented in Table 1 makes it obvious that agro based and waste paper based paper making is growing. This may be attributed primarily to the enhanced environmental consciousness about deforestation. The world scenario, though, is still largely wood based.

Table I: Fibre source of Indian paper industry

Period	Wood	Agro based	Waste paper
1970s	84%	9%	7%
Present	31%	22%	47%

Use of weeds and agro wastes is being explored by many research groups around the globe for possible alternatives to forest based raw materials (3, 4). While choosing suitable materials, attention is paid to cellulose content and lignin content. A high cellulose and low lignin content is ideally suited for paper making. However, it has to be studied along with extractive content, abundance, and availability of the materials. For the present study *Lantana camara*, *Parthenium histerophorus and Eichhornia crassipes* were chosen as they are available in abundance locally. Our motivation has been to explore the possibility of using weeds and agro wastes either alone or in combination for handmade paper making. The objectives are tuned to turn simple, easily available raw materials into paper of good quality that can serve as material for articles of utility and aesthetics.

METHODOLOGY

Paper manufacturing involves identification, collection and processing of raw materials, rich in cellulose. A pictorial presentation of the process is depicted in Figure 2.

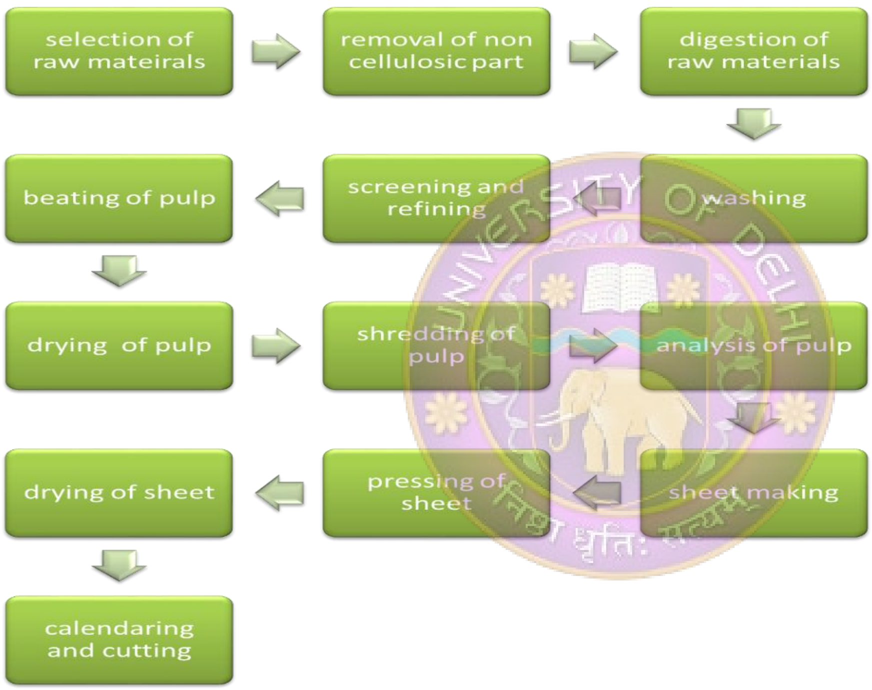

Figure 2: Methodology Flow Chart

Each of these steps is explained below:

1. SELECTION OF RAW MATERIALS

The raw material for all papers is cellulose fibre which comes from a wide range of natural materials. Cellulose is a structural polysaccharide incorporated in plant cell walls and has great strength and resistance to decomposition. Cellulose fibres cling to each other when soaked in water and continue to cling together in a mesh when dried.

A guiding principle for selection of raw materials for paper making is the proportion of cellulose and lignin in the source. A high cellulose and low lignin content in the raw material is ideal for paper making. However, along with these, the other important criteria for selection of raw materials are:

(a) Supplies should be plentiful and uninterrupted,

(b) The fibre should conform to certain size requirements,

(c) Pulp yield should be high,

(d) Fibre should not deteriorate and lose strength quickly during storage,

(e) Fibre isolation should be technically and economically feasible,

(f) Collection, transport and storage should be economical, and

(g) Competitive uses of the chosen material should be few.

Keeping in mind the requirement of high cellulose and low lignin content and also the above mentioned criteria, the following raw materials were selected for the study.

Weeds: *Lantana camara, Parthenium hysterophorus and Eichhornia crrasipes.*

Agro waste: Bagasse, rice straw and wheat straw.

Along with cellulose content and lignin content, the fibre dimensions such as length and thickness also play an important role in handmade paper making (4-6). The relevant data for the materials chosen for this study is presented in Table II.

Table II: Approximate Cellulose content, Lignin content and Fibre Length of raw materials.

Raw Materials	CELLULOSE %	HEMICELLULOSE %	LIGNIN %	AVERAGE FIBRE LENGTH (mm)
Rice Straw	45-55	25-33	18-23	1.4
Wheat Straw	33-35	28.9	23-25	1.4
Parthenium	48-54	32	4-6	-
Lantana camara	60-65	2.5	8-10	-
Bagasse	35-37	26.04	10-12	1.7

However, the quality and amount of cellulosic fibre varies depending on the source from which it is obtained. The quality of fibre is responsible for the quality of paper which is made from it. If the cellulose fibre is long it gives good quality paper. The fibre obtained from rice or wheat straw is short and has to be often mixed with other pulp to give a reasonable quality of paper, whereas the bagasse fibre is longer than rice and wheat straw and thus gives good quality paper. The average fibre length of these agro materials are given in Table II above.

2. REMOVAL OF NON-CELLULOSIC PART

This involves processes like debarking, chipping and depithing. One or more of these processes needs to be used depending on the raw material chosen. For instance, bagasse would have been reduced to suitable size at the sugar mill but the pith needs to be removed. In the case of rice and wheat straw the straw is cleaned to remove dust and then cut into smaller pieces. If wood is used, it needs to be chipped to a smaller size. The bark of a tree needs to be removed from the stem and its outer skin is also removed. It is then beaten with a hammer to obtain fibres. In case of water hyacinth, stems are used whereas roots and leaves are discarded. The stems are cut into small pieces and then left in sun for 4-5 days to reduce the water content before pulping.

3. DIGESTION OF RAW MATERIALS (PULPING)

Digestion is a process of removing lignin and other components of wood from cellulose fibre required for paper making. Lignin is an organic substance binding the cells, fibers and vessels which constitute wood. It is the second most abundant natural polymer in the world, surpassed only by cellulose. But it rapidly decomposes and discolors the paper if left in paper and thus needs to be removed. Digestion also separates fibers from each other by mechanical energy.

There are three types of basic pulping techniques

a. Mechanical pulping
b. Bio-pulping
c. Chemical pulping

Mechanical pulping basically involves separating the fibres using mechanical energy. For the production of mechanical pulp, wood is ground against a water lubricated rotating stone. The heat generated by grinding softens the lignin binding the fibres and the mechanized forces separate the fibres to form ground wood.

Bio-pulping involves the treatment of wood chips and other lignocellulosic materials with natural wood decay fungi prior to thermo-mechanical pulping. Mainly white rot fungi are used for this purpose. It is the most efficient and environment friendly process in pulping.

Chemical pulping requires the material to be chopped fine and then treated with sodium hydroxide and sodium sulphide under conditions of high temperature and pressure. This process is known as Kraft process and commonly referred to as ‘cooking’. Cooking removes lignin and extractives and separates the wood into cellulose fibres. The resulting slurry contains loose but intact fibres which maintain their strength. During the process, approximately half of the wood dissolves into what is called the black liquor. The cooked pulp is then washed and screened to achieve a more uniform quality. The black liquor is separated out from the pulp before bleaching process.

Except water hyacinth, all raw materials are pulped in chemical digesters using sodium hydroxide in two ratios1:4 and 1:8 depending on the material. Caustic soda dissolves away the unwanted material like lignin leaving only the useful papermaking fibres. Since water hyacinth sample had a low dry weight, it was pulped in a bomb digester which is the standard method for low dry weight materials.

4. WASHING OF PULP

After digestion, pulp was washed with water .Washing was done to remove lignin and alkali soluble impurities. Removal of lignin is necessary because any lignin remaining with the pulp eventually leads to undesirable yellowing of paper.

5. SCREENING AND REFINING

The pulp washed down was made uniform in a beater and agitated using agitator. Agitated pulp was screened to remove the uncooked material and residual waste. Screener with small pores continuously vibrates and passes uniform fibres through it. The uncooked fibres are rejected and only cooked fibres pass on. Refining is done to slice material into finer pulp.

6. BEATING OF PULP

At this point, the individual cellulose fibres are still fairly hollow and stiff, so they must be beaten down somewhat to help them stick to one another in the paper web. This is accomplished by "beating" the pulp in the refiners - vessels with a series of rotating serrated metal disks. At the end of the process, the fibres will be flattened and frayed, ready to bond together in a sheet of paper.

After beating, Canadian Standard Freeness (CSF) value for pulp of each raw material was obtained. It is the amount of water passed randomly through the paper pulp. CSF value gives us an idea whether more beating is required or not. It gives the idea of water holding capacity of the paper.

7. DRYING OF PULP

After screening of pulp, the residual waste and uncooked raw material was removed. The screened pulp was wrapped in a cloth and was put in the spin dryer. Spin dryer removes all of the water present in the pulp and gives the dry mass. Spin dryer works in the same way as a dryer in a washing machine only that the intensity of rotation is much higher. Dry pulp can be stored and used according to need.

8. SHREDDING OF PULP

Since drying takes out all water from the pulp, it leads to lump formation in the pulp mass. The mass is usually somewhat hard. As and when the dried pulp is required to be used, it is ground in the shredder. The lumps break to give a more uniform dry pulp mass.

9. ANALYSIS OF PULP

a. Calculation of GSM of paper

GSM refers to gram per square metre. It tells us about the quality of paper. 1% pulp solution in water was put in a fibre disintegrator. After disintegration, the pulp was mixed with water to make a stock solution that was continuously wobbled with pressure so as to make the pulp more uniform. From this stock solution 1 L of solution was taken and put in the ring maker machine. The ring maker machine consists of a cylindrical portion with a mesh present at the bottom. Due to gravitational force as water comes down, fibres get entangled with one another and give a circular sheet which is dried and GSM calculated for the sheet.

b. Calculation of kappa number (k)

Amount of residual lignin present in the pulp is denoted by kappa number (k).It is a measure of the degree of delignification. Lower values of kappa number are sought as they indicate that delignification has occurred to a desirable extent. The kappa number is the volume in millilitres of 0.1N potassium permanganate solution consumed by one gram of moisture free pulp under the conditions specified in literature method (7). A standard value of kappa number which is considered suitable for paper making is 16.

Procedure**:** A sheet of washed pulp was made. After drying, 1g of oven dried sample was shredded into small bits and soaked into 700mL distilled water at 25^0C.In about 3 hours the fibre completely dispersed in water. 100mL 0.1N $KMnO_4$ and 100 mL 0.1 N H_2SO_4 solution was added. 100 mL of distilled water was added (Total volume =1000mL). After 10min, 20mL of 1N KI solution was added. This solution was titrated with 0.2N sodium thiosulphate ($Na_2S_2O_3$) solution using starch as an indicator.

FORMULA TO CALCULATE KAPPA NUMBER, k

k= p x f/w ; p= (b-a) x N/0.1

Where,

k= Kappa number.

F= Correction factor for permanganate consumption as given in tables in reference (7)

p = Volume of permanganate consumed (mL)

w=Weight of moisture free pulp (grams)

b= Volume of $Na_2S_2O_3$ solution used for blank (mL)

a= Volume of $Na_2S_2O_3$ consumed by pulp

N=Normality of $Na_2S_2O_3$ solution

10. SHEET MAKING PROCESS

Thoroughly mixed pulp was put in a sink having greater dimensions than that of deckle. This ensures that vat is firmly held and dipped in water for upward and downward motion. At this stage, different dyes, fillers, chemical premixes can be added to enhance the quality of paper. In this study no chemicals were added to the pulp. Only natural colours were used. The pulp mixture is spread on a net, which enables the water present to settle down and form a paper sheet. These paper sheets are blotted on a cloth. Similarly other paper sheets are also mounted and eventually all the sheets are collected in a heap.

11. PRESSING

The stack of handmade paper is usually squeezed in a screw press operated by hand. Pressing reduces the bulkiness of the paper and the sheets become more compact. This improves the physical properties of the paper and facilitates drying.

12. DRYING OF SHEETS

The sheets are dried by hanging them in open areas of sunlight to remove the rest of the moisture. During cloudy days, drying may be done in an enclosed space with some form of additional heat and air flow.

13. CALENDERING AND CUTTING

The sheets are placed between metallic plates and passed through spring loaded rollers in a calendering machine. The paper becomes smooth and its gloss is enhanced. The sheets are neatly cut to the required size using a cutting machine.

FORMATION OF BLENDS

The blends were made by studying the individual properties of sheets made from the raw materials chosen for the study. Sheets which were found to be weaker in strength were mixed with 20% bamboo pulp. As the fibres of bamboo are longer, they provide great strength to sheets. Recycled paper pulp was also used for making blends. Blending was contained to within 20% as greater percentages did not lead to any significant improvement in quality of paper.

RESULTS AND DISCUSSION

The research results which include composition of the blends created, the specific pulping conditions used for different raw materials and the various attributes of the sheets made are presented in Tables III-V.

Table III: Composition of Blends

Blend Number	Composition
1.	Rice straw (80%), Bamboo (20)%
2.	Bagasse (70%), Bamboo (30%)
3.	*Eichhornia crassipes* (80%), Bamboo (20%)
4.	Wheat Straw (80%), Recycled Paper (20)%
5.	*Lantana camara* (80%), Recycled Paper (20%)
6.	*Parthenium hysterophorus (80%)*, Bamboo (20%)
7.	*Lantana camara (20%)*, Recycled Paper (20%), Wheat Straw (60%)

Table IV: Pulping conditions of Blends

Cooking conditions					
S.No.	Blends	NaOH %	Time, Hrs	Temperature ºC	Bath ratio
1.	Rice (80%), Bamboo (20%)	14	2	160	1:4
2.	Bagasse (70%), Bamboo (30%)	14	2	160	1:4
3.	*Eichhornia crassipes* (80%), Bamboo (20%)	14	2	160	1:4
4.	Wheat straw (80%), Recycled paper (20%)	8	2	160	1:8
5.	*Lantana camara* (80%), Recycled paper (20%)	8	2	160	1:8
6.	*Parthenium hysterophorus* (80%), Bamboo (20%)	14	2	160	1:4
7.	*Lantana camara* (20%), Recycled paper (20%), Wheat Straw (60%)	8	2	160	1:8

Table V: Sheet Attributes

Blend Number	Blends	Lustre	Strength	Remarks
1.	Rice (80%), Bamboo (20%)			excellent quality sheets
2.	Bagasse (70%), Bamboo (30%)			Suitable for card board boxes
3.	Water hyacinth (80%), Bamboo (20%)			Poor strength
4.	Wheat straw (80%), Recycled paper (20%)			High strength
5.	*Lantana* (80%), Recycled paper (20%)			Paper suitable for card board boxes
6.	*Parthenium* (80%), Bamboo (20%)			Average quality sheet
7.	*Lantana* (20%), Recycled paper (20%), Wheat straw (60%)			High quality sheet

The handmade sheets made out of agriculture waste were found to be good in strength. Paper made out of weeds was also good in strength except the one made from water hyacinth. The sheets made of bagasse can be used in making card board boxes.

In order to improve the strength and shine of the sheets, blends were prepared. Bamboo is one of the common fibre materials which are used for blending due to its long and strong fibres. Among all the blends of agro-waste, the sheet made from rice straw and bamboo exhibited maximum strength. Bamboo fibres provided extra strength to the small fibres of rice straw. The sheets made from water hyacinth were very soft and had low strength. Even after blending, the sheets did not exhibit the required strength. Blending of agro waste gave improvement in most of the properties of sheets. Blending with recycled paper pulp also further increased the strength of the sheets.

CONCLUSIONS

The shift observed in fibre source of present day paper industry in India, is clearly encouraging the use of agro based and non-wood raw materials. The non-wood lignocellulosic raw materials used in the study have a high cellulose content which is important for successful pulping. These materials also have modest lignin content which means that they require milder pulping conditions. The materials used are either weeds or surplus agro wastes. Their use in paper making is a step towards environment friendly method of waste utilization. Many of the blends created have shown very good attributes in terms of strength and lustre. Their suitable uses have also been suggested and indicated in Table V. There is a growing trend to link the eco friendliness of paper to three criteria namely, fibre source (wood or non- wood), chemical processing (fewer chemicals and lesser amounts) and ability to be recycled. All the blends created in the study fulfil these criteria, thus making it an environment friendly endeavour.

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