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Utilization of sarkanda for making pulp and paper using elemental chlorine free and total chlorine free bleaching processes

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ABSTRACT

A lignocellulosic non-wood material sarkanda available in abundance as waste, was evaluated for chemical constituents, pulping behavior, morphological properties, bleaching behavior and paper handsheet strength properties. Present study reveals that sarkanda contains cellulose 36.2 ± 0.5 %, hemicelluloses 35.2 ± 0.41 %, lignin 21.2 ± 0.22 % and ash 8.2 ± 0.3 %. Soda-anthraquinone pulping of sarkanda using 15 % active alkali resulted in unbleached pulp with 14.7 kappa number, 16.0 cP viscosity and 54.6 % pulp yield. With use of elemental chlorine free bleaching sequence, $OD_0E_{OP}D$, final bleached pulp achieved 85.7 % ISO brightness, whereas, using total chlorine free bleaching sequence, $OZ_{EOP}P_OP_O$, the brightness obtained was 81.9 % ISO. Elemental chlorine free bleached sarkanda pulp had tensile index of 39.4 N m/g, burst index of 3.4 kN/g and tear index of 5.7 mN m^2/g. The study exhibits that sarkanda has potential to be utilized for papermaking. Such approach of using non-wood raw material with elemental chlorine free bleaching and total chlorine free bleaching sequences for papermaking can be a valuable approach for reducing pollutants generation, utilization of waste biomass and fulfillment of fibrous raw material requirement for paper industry.

1. Introduction

Paper industry is presently facing difficulties in the availability of wood based raw materials due to increase in production capacity and environmental awareness (Liu et al., 2018). Stringent laws are being posed by the law making agencies of developing and developed countries for protecting the environmental resources. Therefore, mills are using more and more non-wood based raw materials like wheat straw, sugarcane bagasse and bamboo. The Indian paper industry contributes to about 4 % of the worldwide production of paper, paper board and newsprint. In India, per capita paper consumption is about 13 kg/ year and expected to reach to 17 kg/ year by the year 2025 (http://ipma.co.in/overview), which consequently will increase the demand of paper. Therefore, there is big scope for expansion of pulp and paper industry in India. Due to this rapid increase in production of paper with scarcity of fibrous raw materials, India will need to find out alternative raw materials for production of paper. Inadequate raw material availability is a major constraint for the Indian pulp and paper industry.

Wheat straw and sugarcane bagasse are the major agro residues used in agro based paper industries but their accessibility is also limited due to their other end uses and non availability throughout the year. Besides, these agricultural residues and other non-wood plants offer a very attractive opportunity to be utilized as resource for fiber (Samson et al., 2005). Worldwide non-wood raw materials account for 5–7 % of the total pulp and paper production (Ward et al., 2008). Various weeds like sarkanda which require negligible efforts to grow may be considered as potential raw materials for pulp and paper industry and also be beneficial for rural people. The chemical and morphological properties of some non-wood plants indicate that they can be successfully utilized for papermaking in place of wood based resources (Dutta et al., 2004). Many non-wood plants and their residues like rice straw, wheat straw, sugarcane bagasse, rapeseed straw, palm oil empty fruit bunches, kenaf, jute, hemp, banana stem, and sarkanda have been explored for their potential for pulp and papermaking (Ghosh, 2006; Jimenez et al., 2008; Rodriguez et al., 2010; Mousavi et al., 2013; Sharma et al., 2015; Tripathi et al., 2017; Kaur et al., 2018). Danielewicz and Surma-Slusarska (2019) revealed that miscanthus pulp has good properties, comparable with hardwood birch pulp and could replace that for packaging papers. Wheat straw and sugarcane bagasse are the most studied agro residues for pulp and papermaking (Jimenez et al., 2000; Garg and Singh, 2004a).

Sarkanda has the great potential for commercial utilization in paper industry. It is also known as Kana or *Saccharum munja roxb* and is available in India, Pakistan and Afghanistan (Rahar et al., 2011). In India it is primarily found in Bihar, Uttar Pradesh, Punjab, West Bengal and Odisha (Subrahmanyam et al., 2004). It grows as vertical grass in

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clumps with height up to 6 m. It grows rapidly with its enormous growth potential of about 180 t/ ha/ year and the fresh weight forms an abundant source of biomass by involving little input (Vasudevan et al., 1984). Subrahmanyam et al. (2004) reported that sarkanda pulp fibers are narrow, long, straight and having thick walls. They also reported that the fiber length ranges between 0.2 to 3.5 mm, width varies from 7 to 40 μm and the pulp also consists of vessel parenchyma and epidermal cells. Small or medium agro based paper mills may utilize this type of raw material. Due to the seasonal availability of sarkanda, mills can use this raw material along with other agro residues for uninterrupted supply of raw material. Pulp and paper industry has another big problem that it discharges highly polluted wastewater (Lindholm-Lehto et al., 2015). Wastewater from paper industry consists of high amount of biological oxygen demand, chemical oxygen demand (COD), colour, lignin derivatives and chlorinated compounds (Ashrafi et al., 2015). Chlorinated compounds like adsorbable organic halides (AOX) are the main culprit for environment. They are resistant to biodegradation, carcinogenic and have biomagnification property giving threats to aquatic life as well as human being. AOX are the reaction products of lignin and chlorine based bleaching chemicals formed during the pulp bleaching process. Based on previous studies, it can be concluded that it is a better option to prevent the pollution at its source rather than dealing with pollution after it has occurred. To reduce the AOX content in wastewater by pulp bleaching process modifications, many studies were carried out by different researchers (Tripathi et al., 2019b; Kaur et al., 2019a).

AOX content from pulp bleaching process can be reduced using ECF and TCF bleaching processes (Kaur et al., 2018). Studies are available on reduction of AOX content through ECF and TCF bleaching process for hardwood pulp bleaching (Tripathi et al., 2019b; Miri et al., 2015). But for non wood pulps only few research studies are available. More studies should be carried out for ECF and TCF bleaching of non wood pulps to examine its effects on pulp and effluent characteristics.

Very scanty literature is available on ECF and TCF bleaching of sarkanda pulp. It was found that hardwood and softwood pulps having more lignin content (about 20–25 kappa number) were used for bleaching (Hart et al., 2011); whereas sarkanda can easily be delignified to about 15 kappa number (low lignin content). Due to the low kappa number of sarkanda pulp, lesser bleaching chemicals will be required which will consequently generate lower toxic pollutants. The objective of this study was to evaluate potential of sarkanda raw material for papermaking using bleaching processes which generate less toxic pollutants. This paper illustrates different papermaking properties of sarkanda pulp like morphological properties, bleaching behavior, strength properties and analysis of bleaching filtrate for pollutants load.

2. Materials and methods

The experimental work is explained in Fig. 1.

2.1. Preparation of raw material

Sarkanda (*Saccharum munja roxb*) was collected from an agro based mill situated in northern part of India. The material was air dried to approximately 85 % dryness to prevent decay.

Chopping: Prior to pulping experiments, sarkanda was cut into 2 – 3 cm length so that it can be processed easily in further pulping study. Cutting of raw material also improves the penetration of cooking liquor due to more surface area and facilitates uniform pulping.

Wet cleaning: After chopping of sarkanda the material was stirred in water for washing/ cleaning to remove dust and non fibrous materials. After that the material was air dried to approximately 85 % dryness. After air drying the raw material was stored in bags to avoid moisture gain and to keep the raw material uniform throughout the study. Moisture content of air dried sarkanda raw material was analyzed as per Tappi T 210 cm-03 for carrying out experiments on oven dry weight basis. Bulk density of sarkanda raw material was analyzed as per Tappi UM 23.

2.2. Chemical analysis

For chemical analysis, sample was prepared according to Tappi T 257 cm-02. Thoroughly air dried sample grinded in Wiley mill and passed through 40 mesh screen as accept was collected for further analysis. After moisture determination of prepared raw material, proximate chemical analysis was carried out. Prepared material was characterized for hot water and one percent sodium hydroxide solubility, acetone extractives, lignin, ash content, hemicelluloses, and cellulose using standard methods. Hot water and one percent sodium hydroxide solubility were characterized as per Tappi T 207 cm-08 and T 212 om-07, respectively. The content of cellulose was analyzed using method described by Updegraff (1969). In this method cellulose in test specimen was hydrolyzed to form glucose which again converted to hydroxymethyl furfural and gave green color when reacted with anthrone. Intensity of color was measured at 630 nm against a reagent blank using UV–vis spectrophotometer. Ash content was determined by Tappi T 211 om-12. Acetone extractive content was determined as per Tappi T 204 cm-17. Hemicelluloses were analyzed as per Deschatelets and Errest (1986) which is based on formation of furfural under acidic conditions and furfural reacts with p-bromoanilline acetate to form pink color. Intensity of color was measured at 540 nm against a reagent blank using UV–vis spectrophotometer. Lignin content was determined as per Tappi T 222 om-11. For lignin estimation carbohydrates present in sample were hydrolyzed using sulphuric acid and insoluble lignin remained was gravimetrically measured after filtration. All the analysis was carried out in duplicate and some analysis in triplicate sets.

2.3. Soda pulping

On the basis of previous studies, soda anthraquinone (AQ) pulping was carried out in batch process for production of pulp. The soda- AQ pulping method is reported to be the most suitable for pulping of agricultural residues. AQ accelerates the reactions during pulping for lignin removal (Omer et al., 2019). The alkali dose applied on raw material (oven dry weight basis) and cooking time were optimized to get the pulp of approximately 15 kappa number. Based on previous studies 15 Kappa number pulp is within the categories of easily and moderately bleachable pulp (Danielewicz and Slusarska, 2006).

Cooking of chopped sarkanda was done in autoclave digesters having capacity of 2.5 L, rotating in electrically heated poly ethylene glycol bath at 166 °C using 1:4 bath ratio (solid to liquor ratio). Initially the temperature of glycol bath was raised to about 150 °C. Bombs containing desired amount of alkali (13 %, 14 %, 15 %, 16 % and 17 %), anthraquinone (0.05 %), water (to get bath ratio of 1:4) and raw material (150 g oven dried equivalent) were placed in rotating ring of the autoclave digesters and temperature of glycol bath raised to 166 °C in 5 min and maintained for 15 min and 25 min. At the end of pulping process pulps were washed and screened in the Somerville screen having 0.15 mm slots to remove the uncooked mass and finally the pulp was shredded for homogenization. Black liquor generated from soda-AQ pulping process was analyzed for pH, residual active alkali (RAA) and total solids as per standard methods. The most favorable conditions for soda-AQ pulping were selected on the basis of kappa number and viscosity of pulp. Unbleached pulp of kappa number 14.7 was selected for further bleaching studies.

2.4. Analysis of pulp properties

Accepted pulps from screen were analyzed for kappa no., brightness, viscosity according to standard test methods. Kappa number of unbleached pulp was analyzed as per Tappi T 236 om-06. The kappa number is the consumption of 0.1 N potassium permanganate solution

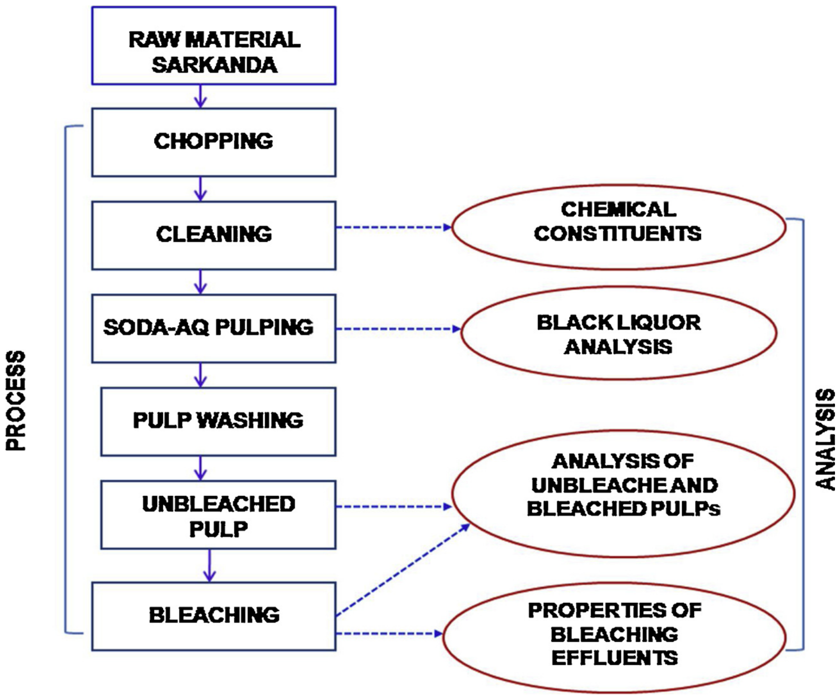

Fig. 1. The graphical presentation of experimental work.

by one gram of moisture-free pulp under the specified conditions. Viscosity of pulp was determined as per Tappi T 230 om-08 using 0.5 M cupriethylenediamine solution. The viscosity test gives indication of degradation of cellulose resulting from the pulping / bleaching process. Brightness, a numerical value of diffuse reflectance with respect to blue light of wavelength 457 nm was analyzed as per Tappi T 525 om-06.

Screened pulp yield was determined gravimetrically, after determination of moisture content as per Tappi T 412 om-06 in unbleached pulp. Refining of unbleached and bleached pulps was carried out using PFI mill as per Tappi T 248 sp-08. Mild refining of unbleached and bleached pulps was done using 500 PFI revolutions to increase ºSR level to 32–33 from initial ºSR level of 27-28. Drainability of pulps was measured as per ISO 5267 in terms of Schopper-Riegler (°SR). The handsheets of 60 g/m^2 were prepared as per Tappi T 205 sp-06 for measurement of paper properties. The handsheets were used for analyzing the physical properties. Morphological properties like average fibre length, width, coarseness and fibre length distribution of pulp were analyzed using L&W fibre tester as per Tappi T 271 om-07. Light microscopic images were analysed by light microscope (model Axio Scope) manufactured by Carl Zeiss, Germany.

2.5. Analysis of black liquor

Black liquor generated from soda- AQ pulping was analyzed for pH by electrometric method, IS 3025 (part II). Black liquor also analyzed for RAA and total solids as per Tappi T 625 cm-14 and Tappi T 650 om-15, respectively.

2.6. Bleaching of sarkanda pulp

The pulp with kappa number 14.7 was bleached with ECF bleaching sequence $ODE_{OP}D$ and TCF bleaching sequence $OZ_{EOP}P_OP_O$. Where, O - Oxygen bleaching; D - chlorine dioxide; E_{OP} - extraction stage using sodium hydroxide, oxygen and hydrogen peroxide; Z_{EOP} - Ozone bleaching followed by extraction stage; P_O- Hydrogen peroxide with oxygen at high temperature and pressure. The bleaching conditions employed on sarkanda pulp to obtain final pulp of about 85 % ISO brightness are given in the Table 1. Bleaching conditions were used as

Table 1
Experimental conditions[#] for different stages of bleaching.

Parameters	$OD_0E_{OP}D$				$OZE_{OP}P_OP_O$			
	O	D_0	E_{OP}	D	O	Z^*E_{OP}	P_O	P_O
Consistency (%)	10							
Temperature (°C)	95	55	80	75	95	50	100	100
Time (min)	30	45	120	180	30	3	90	90
End pH	10.8	2.5	10.7	3.5	10.8	2.2	10.2	10.3
Oxygen pressure (kg/cm^2)	3.5	–	3.0	–	3.5	–	3.0	3.0
NaOH (%)	1.5	–	1.2	–	1.5		2.0	2.0
Hydrogen peroxide (%)	–	–	0.6	–	–	0.6	2.0	1.5
Chlorine dioxide (%)	–	0.95	–	0.4	–	–	–	–
Ozone (kg/t)	–	–	–	–	–	5.0	–	–

[#]Experimental conditions based on Tripathi et al. (2019a; and 2019b).
*Z stage without washing followed by extraction stage E_{OP} at 70 °C for 30 min.

per earlier reported bleaching studies by Tripathi et al., (2019a; and 2019b).

Oxygen bleaching was carried out in air heated rotary digester having digital programmable temperature control system with a temperature recording probe in individual bombs and a system for inserting controlled volume of oxygen. Chlorine dioxide was procured from a nearby paper mill and bleaching was carried out in polythene bags at desired temperature in water baths. Extraction stage was carried out in air heated rotary digester. Ozone bleaching was carried out in ozone reactor having intermediate mixing arrangement. After each stage of bleaching, pulps were filtered and filtrates (bleaching effluent) were collected for analysis and all the pulps were washed in the same manner.

2.7. Scanning electron microscopic analysis

Scanning Electron Microscopic (SEM) analysis of pulp was carried out to see the effect of bleaching chemicals on pulp fibers. Unbleached pulp, ECF and TCF bleached pulps were studied by SEM model number JEOL JSM 6510 L V at 2500 resolutions. For the analysis pulp samples were prepared as reported by Kaur et al. (2019b); taken in size of

1 × 1 cm and before analysis samples coated with gold film of thickness 5 nm. In present study, the micrographs at 2500× magnification were used to compare the differences.

2.8. Physical properties of pulp

Laboratory handsheets of refined pulps were prepared using British handsheet former as per Tappi T 205 sp-06. Physical properties like tensile, tear, burst indices and folding endurance were analyzed as per Tappi T 220 sp-01.

2.9. Effluent analysis

The bleaching filtrates were collected from each stage of bleaching. The composite effluent samples were prepared by adding bleaching filtrates in their respective volumetric proportions. Effluent samples were analyzed as per Indian standard (IS) and American public health association (APHA) test methods. COD was analyzed in effluent by open reflux method, IS: 3025 (part 58) in which organic matter is oxidized by strong oxidizing reagent, potassium dichromate. After digestion, unused potassium dichromate was titrated with ferrous ammonium sulfate. Effluent was analyzed for color as per method APHA 2120 C, in which color unit was analyzed by measuring the chloroplatinate ion produced by 1.0 mg platinum/L. AOX of samples was analyzed by the AOX analyzer as per test method ISO: 9562. Initially, organic halides present in effluent samples were adsorbed on activated carbon and ignited under oxygen stream. Further AOX content in sample was determined using microcoulometry. Total dissolved solids (TDS) of effluent samples were analyzed as per test method IS:3025 (Part16).

3. Results and discussions

3.1. Chemical constituents of sarkanda

Chemical composition of raw-material gives an idea about its suitability for papermaking. Table 2 exhibits the chemical constituents of sarkanda and values are compared with other agro residue raw materials which are being utilized for papermaking. Sarkanda has 10.1 % hot water solubility which is slightly lower than rice straw (Kaur et al., 2018), hot water solubility extracts carbohydrates such as starch, sugar. One percent sodium hydroxide solubility of sarkanda was 33.1 %, sodium hydroxide solubility extracts low-molecular-weight carbohydrates primarily hemicellulose and degraded cellulose present in material. Sarkanda contains 36.2 % cellulose which is comparable with wheat straw and less than sugarcane bagasse whereas higher than rice straw. Raw materials having cellulose more than 34 % are reported to be suitable for pulp and papermaking (Syed et al., 2016). Cellulose is the principle component in any raw material influencing the pulp yield, consequently affecting the economy of paper production and its structure is responsible for resistance to chemical attack (Philip, 1992). Alpha cellulose content in raw material is directly proportional to unbleached and bleached pulp yields (Wood, 1981). Hemicelluloses content was the highest in sarkanda compared to wheat straw, bagasse and rice straw. The ash content in sarkanda was lower than the rice straw but higher than bagasse whereas wheat straw contained comparable ash content. Despite having high ash, wheat straw has been successfully utilized commercially for papermaking (Tripathi et al., 2018a). Minerals important for the growth of plant like Ca, Mg, N, P, S and K are contributed as ash in chemical analysis. Wood and non-wood raw material contains the same elements but concentration is low in wood plant compared to non-wood.

Present study reveals that the sarkanda raw material has less extractives content as compared to earlier studies reported for other non-woods like rice straw (Kaur et al., 2018), wheat straw (Tripathi et al., 2013, 2018a), bagasse (Tripathi et al., 2013) and khar grass (Sinha, 2015). Results of chemical constituents of sarkanda obtained in this study are comparable with the earlier reported values (Subrahmanyam et al., 2004). The chemical constituents of sarkanda raw material are similar to that of other agro-residues and therefore it has substantial potential for production of quality pulp.

3.2. Soda-AQ pulping of sarkanda

Before pulping experiments bulk density of sarkanda was determined as it is important parameter for pulp making. Bulk density for agro residues varies from 80 to 100 kg/m^3 (Shojaeiarani et al., 2019), in present study bulk density of sarkanda was 71. 0 kg/ m^3. Bulk density affects the handling and storage problem (Shojaeiarani et al., 2019). It also impacts the pulp yield and consequently pulp production.

Table 3 displays the black liquor and pulp properties at different active alkali and cooking time. The screened pulp yield was decreased from 58.5 %–54.4 % with the increase in alkali dose from 13.0 %–18.0 %, respectively. With the increment in cooking time from 15 min to 25 min the screened pulp yield was further reduced by 1.7 %–2.1 %. The similar trends were also reported by Bhardwaj et al. (2005) and Kaur et al. (2018) for pulping of rice straw. Increased concentration of alkali accelerates the degradation of polysaccharides along with lignin which may be responsible for reduced pulp yield.

Increase in alkali dose and cooking time reduced the kappa number at the same time reduction in pulp viscosity and screened pulp yield. It indicates that delignification rate increased with active alkali dose and cooking time. With increase in active alkali dose, black liquor pH, residual alkali and total solids were increased. Whereas, with the increased cooking time at same active alkali dose, the RAA was reduced. The unbleached pulp of 14.7 kappa number obtained with 15 % active alkali and 25 min cooking time was characterized for physical, morphological properties and used for further bleaching studies. Earlier studies also reported that pulp of about 15 kappa number found to be suitable for bleaching (Danielewicz and Slusarska, 2006; Kaur et al., 2018).

Table 2
Chemical analysis of sarkanda raw material in comparison to other non wood raw materials.

Parameters	Sarkanda (Present study)	Sarkanda (Subrahmanyam et al., 2004)	Wheat straw (Tripathi et al., 2013, 2018a)	Bagasse (Tripathi et al., 2013; Leponiemi, 2008)	Rice straw (Kaur et al., 2018)
Hot water solubility (%)	10.1	11.2	–	–	10.5
1% NaOH solubility (%)	33.6	37.3	–	–	–
Extractives (%)	2.3 ± 0.13*	–	3.2#	2.7#	2.43 ± 0.36*
ΨCellulose (%)	36.2 ± 0.5	39.9	36.6–47.8	32-47.2	33.3 ± 0.47
ΨHemicellulose (%)	35.2 ± 0.41	30.5	23.6-28.1	24.7-27.0	27.3 ± 0.36
Lignin (%)	21.2 ± 0.22	21.2	16.4-19.9	19.2-24.0	13.0 ± 0.07
Ash (%)	8.3 ± 0.3	8.2	5.2-7.1	1.5-2.6	12.6 ± 0.11

* Acetone extractives, #Ethanol-benzene extractives.
Ψ Cellulose and hemicelluloses were determined as per the methods described by Updegraff (1969) and Deschatelets (1986).

Table 3
Effect of active alkali dose and cooking time during pulping on black liquor and pulp properties.

Active alkali as NaOH (%)	Cooking time (min)	Black liquor properties			Pulp properties			
		pH	RAA as NaOH (g/L)	Total solids, w/w (%)	Kappa number	Brightness (% ISO)	Viscosity (cP)	Yield (%)
13	15	11.2	3.3	13.3	22.4	24.0	20.4	58.5
	25	11.0	1.4	13.9	18.7	25.9	18.5	56.6
14	15	11.4	3.7	13.7	19.9	25.5	19.0	57.5
	25	11.3	2.1	14.5	16.6	26.9	17.1	55.6
15	15	11.5	4.3	14.2	17.8	26.2	17.4	56.5
	25	11.4	3.0	15.1	14.7	28.3	16.0	54.6
16	15	11.7	4.9	14.8	16.3	27.2	16.7	55.4
	25	11.6	3.9	15.7	13.5	28.9	14.7	53.7
17	15	11.8	5.8	15.6	15.4	27.8	16.2	54.8
	25	11.7	4.7	16.3	12.8	29.2	13.8	53.0
18	15	12.0	6.6	16.1	15.0	28.0	15.9	54.4
	25	11.9	5.3	16.9	12.3	29.9	13.3	52.3

3.3. Morphological properties of pulp

The fiber morphological properties have the important role to find out suitability of any raw materials for paper production. On the basis of morphological characteristics of sarkanda (Table 4) it can be concluded that sarkanda has similar properties as other agro residues pulps. Sarkanda pulp has average fiber length of 0.939 mm which is comparable with bagasse and higher than wheat straw and rice straw pulps, while fiber width is comparable to wheat straw and less than bagasse. The fiber length has a significant impact on mechanical properties of paper (Kamoga et al., 2016). In comparison to shorter fiber longer fiber can create stronger network. Longer fiber length gives the advantage of higher tearing resistance of paper (Dwivedi et al., 2010; Monje et al., 2010) while longer fibers are likely to give a more open and less uniform sheet structure which may affect strength properties. Light microscopic images (Fig. 2) show that sarkanda pulp contains fibers, epidermal cells, vessels and parenchyma cells.

3.4. Physical properties of unbleached pulp

Physical properties of any pulp depend mainly on fiber morphology, fiber-fiber bonding, pulp refining, wet pressing and formation. Table 5 exhibits the physical properties of sarkanda unbleached pulp and values were also compared with earlier reported studies of other agro residue pulps. Sarkanda unbleached pulp has good strength properties in comparison to unbleached pulps of wheat straw and rice straw. Sarkanda pulp also has higher tear index but lower tensile index in comparison to bagasse pulp.

3.5. Optical properties of pulps after ECF and TCF bleaching

Optical properties of ECF and TCF bleached pulps are given in Table 6. Sarkanda pulp bleached with ECF bleaching sequence $DE_{OP}D$ has higher brightness of 85.7 % ISO as compared to brightness of rice straw (82.2 % ISO) and wheat straw (84.5 % ISO) pulps but lower than the bagasse (89.3 % ISO) pulp. Ghosh, 2006 also reported 85.0 % ISO brightness for wheat straw pulp bleached with DE_PD sequence. TCF bleached sarkanda pulp has lower brightness and whiteness values compared to ECF bleached pulp. ECF bleached sarkanda pulp has higher viscosity of 10.5 cP compared to TCF bleached pulp viscosity of 7.5 cP. It showed that ECF bleaching sequence protected the carbohydrate structure from deformations and degradation in comparison to TCF bleaching sequence.

3.6. Surface morphological properties of pulps by scanning electron microscopy

Surface morphology of unbleached pulp (a), ECF bleached pulp (b) and TCF bleached pulp (c) were illustrated in Fig. 3. The surface of unbleached pulp fiber seems very smooth and less fibrillated. After bleaching of pulp the fibers became rougher. ECF bleached pulp (b) showed rough surface and more fibrillated as compared to unbleached pulp. This indicated that fibers get damaged during the bleaching process. TCF bleached pulp showed rougher surface as compared to unbleached and ECF bleached pulp. This indicated that TCF bleaching process is more detrimental to the pulp fibers as compared to ECF bleaching process. SEM analysis of ECF bleached pulp reported by Kaur et al., 2019b showed that ECF bleaching process removes the lignin selectively and degrades the carbohydrate structure less in comparison to chlorine based sequences.

3.7. Physical properties of bleached pulp

It was found that tensile, burst and tear strength of paper from different pulps were decreased with multi-stage bleaching operations. Table 7 exhibits the physical properties of ECF and TCF bleached

Table 4
Morphological properties of sarkanda unbleached pulp and comparison with other non wood unbleached pulps.

Parameters	Sarkanda pulp	Wheat straw (Tripathi et al., 2013 and 2019)	Bagasse (Subrahmanyam et al., 2004; Tripathi et al., 2013)	Rice straw (Kiaei, 2014)
Average fiber length (mm)	0.939	0.818	0.85-1.52	0.843
Mean width (µm)	16.1	17.5	21.8-22.8	10.3
Coarseness (µg/m)	85.0	71.8	129.4	–
3.0–4.5 mm length (%)	2.5	–	–	–
1.5 – 3 mm length (%)	15.3	–	–	–
0.5-1.5 mm length (%)	48.3	–	–	–
0.2-0.5 mm length (%)	33.9	–	–	–
Kink index	1.304	–	–	–
Fines (Length- Length) (%)	2.7	–	–	–
Number of fibers per gram	107970	–	–	–

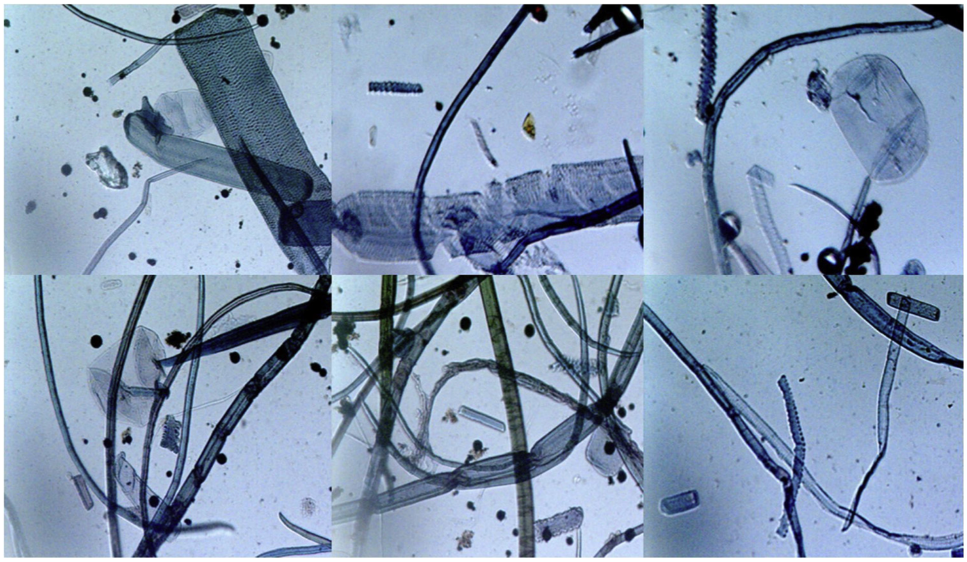

Fig. 2. Microscopic images of sarkanda unbleached and unrefined pulp fibers.

Table 5
Physical strength properties of unbleached sarkanda pulp and comparison with other non wood unbleached pulps.

Parameters	Sarkanda pulp (Present study)	Wheat straw (Kaur et al., 2019a)	Bagasse (Garg and Singh, 2004b)	Rice straw (Kaur et al., 2018)
Drainability (°SR)	32.0	29.0	37.0	34.0
Tensile index (N m/g)	50.9 ± 1.2	44.1 ± 1.1	60.7	42.2 ± 1.3
Burst index (kN/g)	4.30 ± 0.06	3.51 ± 0.07	3.65	2.46 ± 0.08
Tear index (mN m^2/g)	6.00 ± 0.09	5.91 ± 0.09	3.93	–
Double fold (no.)	78 ± 4	18	11	11

Table 6
Optical properties of bleached sarkanda pulp and comparison with other non wood bleached pulps.

Parameters	Sarkanda (Present study)		Wheat straw (Tripathi et al., 2019a)	Bagasse (Tripathi et al., 2013)	Rice straw (Kaur et al., 2018)
Bleaching sequence	$ODE_{OP}D$	$OZE_{OP}P_OP_O$	$ODE_{OP}D$	$DE_{OP}D$	$DE_{OP}D$
Brightness (% ISO)	85.7	81.9	84.5	89.3	82.2
CIE Whiteness	77.7	73.7	79.4	83.3	74.1
ASTM Yellowness	4.58	4.90	–	–	6.01

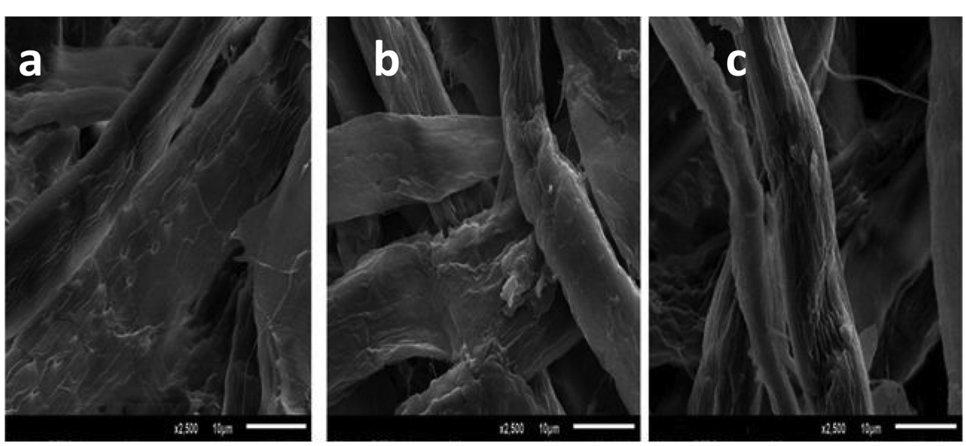

Fig. 3. SEM images of sarkanda pulps (x2500): (a) Unbleached pulp; (b) ECF bleached pulp; (c) TCF bleached pulp.

sarkanda pulps and values compared with strength properties of other non-wood pulps. TCF bleached sarkanda pulp has lower strength properties in comparison to ECF bleached pulp. Results were in agreement with viscosity trend of pulps; ECF bleached pulp has higher values in comparison to TCF bleached pulps. Results were also supported by SEM analysis, which showed that TCF bleached pulp illustrated damaged surface in comparison to ECF bleached pulp. ECF bleached sarkanda pulp has higher tensile and burst indices compared

Table 7
Physical properties of bleached sarkanda pulp and comparison with other non wood bleached pulps.

Parameters	Sarkanda (Present study)		Wheat straw (Tripathi et al., 2018b)	Bagasse (Tripathi et al., 2013)	Rice straw (Kaur et al., 2018)
Bleaching sequence	$ODE_{OP}D$	$ZE_{OP}P_OP_O$	$ODE_{OP}D$	$ODE_{OP}D$	$DE_{OP}D$
Drainability (°SR)	32.5	33.0	38.5	19.0	46.0
Basis weight (g/m^2)	60.4	60.6	–	60.5	–
Bulk (cc/g)	1.35	1.31	–	1.29	–
Tensile index (N m/g)	49.4 ± 1.7	34.2 ± 1.8	51.9	43.6	46.9 ± 1.8
Burst index (kN/g)	4.00 ± 0.10	2.80 ± 0.20	4.90	3.13	3.34 ± 0.50
Tear index (mN m^2/g)	5.7 ± 0.10	5.5 ± 0.15	6.7	6.06	5.42 ± 0.10
Double fold	222	188	62	51	76

Table 8
Effect of bleaching sequences on effluent characteristics.

Parameters	Sarkanda (Present study)		Wheat straw (Tripathi et al., 2018b)	Bagasse (Sudarshan et al., 2018)	Rice straw (Kaur et al., 2018)
Bleaching sequence	$ODE_{OP}D$	$ZE_{OP}P_OP_O$	$ODE_{OP}D$	$DE_{OP}D$	$DE_{OP}D$
COD (mg/L)	745 ± 10	2022	1120	1976	1422
Color (PCU)	522 ± 3.5	677	406	810	648
AOX (mg/L)	21.0 ± 0.2	0.11	11.0	–	35.5
TDS (mg/L)	2100	3312	2550	–	3120

to earlier reported values for bagasse and rice straw pulps but lower than wheat straw pulp. Sarkanda pulp has tear index of 5.7 mN m^2/g, higher than rice straw pulp whereas lower than bagasse and wheat straw pulps. Sarkanda has the highest double fold value as compared to that of other non-wood pulps.

3.8. Properties of bleaching effluents

Properties of bleaching effluents from ECF and TCF bleaching sequences were given in Table 8. Combined effluent generated during ECF bleaching of sarkanda pulp has 745 mg/l COD, 522 PCU colour and 21.0 mg/l AOX. The COD of the effluent generated in ECF bleaching of sarkanda pulp was lower in comparison to those reported values for wheat straw and rice straw pulps. This may be due to more fines and parenchyma cells present in wheat straw and rice straw pulps. Other effluent properties like color, AOX and TDS were comparable with reported values for other non-wood materials.

TCF bleaching sequence effluent has higher COD, color and TDS values in comparison to those with ECF bleaching sequence. This may be a result of the degradation of carbohydrates during bleaching with ozone and peroxide stages of TCF bleaching sequence. Tripathi et al. (2018b) also reported that more depolymerization of carbohydrates occurred in ozone stage of bleaching in presence of metal ions. This substantial degradation of carbohydrates in these bleaching stages increases the pollutant load in effluent. But effluent generated in TCF bleaching sequence can be recycled in chemical recovery system due to the absence of chloride compounds which may make it zero discharge bleaching process.

4. Conclusions

Sarkanda could be a promising raw material for pulp and paper production. Chemical constituents of sarkanda showed that it has potential to be used for papermaking. Increase in active alkali charge and cooking time negatively impacted the yield and pulp viscosity. Active alkali charge of 15 % and 25 min cooking time was found optimum to produce bleachable pulp of 14.7 kappa number and viscosity 16.0 cP. Sarkanda pulp has better morphological and physical properties in comparison to wheat straw and rice straw. Bleached pulp attained good optical properties as compared to other agro residue pulps except bagasse. It can be concluded that good quality writing and printing paper can be produced from sarkanda. In addition, pulp can be bleached more than 85 % ISO brightness using modern bleaching sequence. The conversion of sarkanda to pulp and paper will be beneficial to farmers, paper industry and waste management authorities. Use of sarkanda as papermaking raw material will cater to the need of the mills looking for alternative raw material.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Nirmal Sharma: Conceptualization, Methodology, Software, Writing - original draft. **Sandeep Kumar Tripathi:** Conceptualization, Supervision, Visualization, Investigation. **Nishi Kant Bhardwaj:** Conceptualization, Supervision, Writing - review & editing, Project administration.

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