environmental sciences proceedings

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Proceedings

Fractionation and Homogenization of Recuperated Pulp Fibers from Brazilian Paper and Pulp Industry†

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† Presented at 2nd International Electronic Conference on Forests – Sustainable Forests: Ecology, Management, Products and Trade.

Abstract: With a projected growth of the Brazilian pulp and paper industry of about 20% over the period 2020-2025, the innovations in waste management and reutilization of side-products originating from the pulp- and paper industry may mostly contribute to a sustainable development of forest-based products, e.g., by implementing the recuperation and innovative processing of side-stream products at a local level. In this study, we analyze the feasibility for the reuse of recovered cellulosic fibers collected from pulp and paper mill sludge by considering some practical issues and evaluation of the quality for different side-stream fractions originating from rejects, deinking sludge, primary sludge and secondary sludge. The situation for the Brazilian pulp and paper industry will be used as a model, for which the potential for recovery of fibers from waste waters will be evaluated from the analysis of available data. First, the water consumption and effluents from paper mills are reviewed together with an estimation of the fiber recovery potential from primary sludge and fine fiber rejects. Second, the specific characteristics and appearance of certain fiber fractions might imply constraints on their further processing properties. Therefore, we describe some insights in the fiber fractions that could provide highest potential for future valorization. Based on the degree of compositional homogeneity and concentration of cellulose fibers in several waste fractions, the processing of fibers from primary sludge and/or fine fiber rejects are estimated as the most economically feasible. The homogenization of the fiber fractions yield fibrillated cellulose materials with various morphologies depending on the selection of recuperated fractions. Through thorough characterization of the resulting fiber fraction, new application markets can be selected.

Keywords: Pulp and Paper, Residues, Sludge, Valorization, Cellulose, Nanocellulose

Citation: Samyn, P. Fractionation and Homogenization of Recuperated Pulp Fibers from Brazilian Paper and Pulp Industry . *Proceedings* **2021**, *68*, x; https://doi.org/10.3390/xxxxx

Published: date

1. Introduction

Concerns arise on the worldwide use of petroleum-based plastics because of their environmental impact and non-biodegradability. The problems in using synthetic polymers include persistence in the environment, shortage of landfill space, resource depletion and emissions during incineration. Innovative bio-based plastics would reduce our dependency on depleting fossil resources and are CO_2 neutral [1]. From the political, industrial and society points of view, there is an urgent need to develop materials from renewable feedstock and improving their efficiency [2]. The annual biomass production of lignocellulosic materials is about 1 trillion tons worldwide, making it an almost inexhaustive resource that is produced by photosynthesis without affecting feedstock. However, the consumption of raw materials is expected to increase with population growth and should be controlled in parallel with global challenges on environmental pollution, limited resources and energy supply. The Environmental Action Program (EAP) advises that resource limitations can be addressed by more efficient processes and utilization.

Therefore, the sustainability consumption of resources should consider the full exploitation of material fractions from various processing streams, including residual or side-stream products.

Especially the Kraft pulping process [3] is an environmentally demanding industry that needs huge amounts of water and generates up to 60 % side-products such as lignin, hemicelluloses and an important amount of cellulose fine fiber rejects. The by-products and extractives collect in the black liquor and in the water effluents where they remain as an under-valorized fraction. The Brazilian pulp and paper industry represents the second largest sector in the country and is ranked as the fourth worldwide producer of pulp with a total production of 11.4 million tons short fiber (eucalyptus), 1.8 million tons long fiber (pine) and 1.1 million tons specialty fibers [4]. The Brazilian pulp and paper industry is the second largest national economy with 220 companies spread over 450 municipalities in 17 states, and occupying 2.2 million hectares of forested area for industrial use. The total pulp export amounts US $ 5.0 billion (14.4% of Brazilian Trade Balance) with over 40 % going to Europe. The worldwide highest rotation and yield rate for hardwood pulp species such as eucalyptus (7 years, 44 m^3/ha.year) and softwood pulp species such as pine (15 years, 38 m^3/ha.year), make Brazil as the most important player in improving the sustainability of available resources [4]. Therefore, the country has become the world benchmark for the pulp industry with a projected production growth of 20% in 2020-2025 [5].

The efficient and sustainable use of resources in the pulp and paper industry can be enhanced by integrating side-products and fiber rejects into innovative bio-based materials before the materials are finally being disposed in bioenergy production at the end-of-lifetime [6, 7]. This study particularly considers the recuperation processes of residues from water effluents. The recuperated small fiber rejects are estimated to be at around 120000 tons/year and are not profitable for burning as they have a lower energetic value than the lignin fraction. A main hurdle in material use of the residual pulp fractions is their heterogeneous composition and incompatible chemical and physical nature of cellulose in combination with other biopolymers. Therefore, nanotechnological approaches may be applied for converting the residual fractions into homogeneous compounds that can be used as building-blocks for creating new materials with enhanced properties.

2. Materials and Methods

2.1. Fiber collection and characterization

As the respective waste streams from pulp and paper mills have very diverse origins, the composition of subsequently recovered fibers should be considered separately by including different waste streams. The primary and secondary sludges were received as never-dried samples from a Brazilian pulp mill (Klabin, Sao Paulo), which produces the kraft pulp from *E. globulus*. The primary sludge was obtained after mechanical treatment in the wastewater plant and is commonly handled as industrial waste. In the first step of wastewater treatment, the suspended solids are removed by a sedimentation process taking place in the first clarifier unit and the sediments are subsequently pressed into a primary sludge. The primary sludge was produced in the paper mill and consists of screening, filtration, flotation and sedimentation in order to collect the suspended solids in a dewatered sludge. The secondary sludge was obtained from the same mill after biological wastewater treatment and can be considered as municipal sewage waste. The latter process is often considered as an activated sludge treatment for the breakdown of organic matter by means of biodegradation. The third type of sludge originates from the processing water (white-water) collected from the furnish during formation of the papersheets. Depending on the mesh sizes of the screens, the fine rejects are fractionated in a coarse fraction (1.8 mm holes screen) and a fine fraction (0.17 to 0.2 mm holes screen).

The composition was determined in terms of ash content and $CaCO_3$ by means of combustion testing at 575°C and 950°C respectively (TAPPI 211), moisture content and organic versus inorganic content by means of theremogravimetric analysis (ADTM-E1131-03) and elementary analysis of the ash content by means of X-ray fluorescence analysis. Size distributions of the collected fibers were determined through a screening test with first-stage hole openings of 0.2 mm and subsequent screen sizes of 100 to 500 mesh. Tests were conducted on a sample of 500 ml disintegrated sludge slurry with 0.5 wt.-% solid content.

2.2 Fiber processing and characterization

The recovered fractions of cellulose fibers were further processed by homogenization in a microfluidizer (type EH-110, Microfluidics, Westwood, MA) at a consistency of 2 wt.-%. The sludge suspension was therefore first diluted in deionized water and mixed for 1 hour in a high shear mixer. The fibrillation was done with a simple set-up of interaction chambers in order to illustrate the feasibility and variations in morphology depending on the sludge types. The chamber sizes included a first run through a homogenization chamber (H210 Z-shaped with pressure of 500 bar), followed by 2 or 7 runs through a 200 μm interaction chamber (H30 Z-shaped with pressure of 1000 bar).

The fibrillated cellulose samples were characterized by optical microscopy (BX50, Olympus, Hamburg, Germany), scanning electron microscopy (TM3000, Hitachin Krefeld, Germany), and Raman spectroscopy (Raman Flex 400F, Perkin Elmer, Rodgau, Germany).

3. Results

3.1. Fiber characterization and fractionation

As a first source for fiber recovery, the primary sludge is evaluated. In general, the paper sludge contains high levels of dry solids because it is rich in fibers and therefore dewaters quite easily: the dry solid content of the residues generally varies between 40 to 70% depending on its origin. Through the subsequent recovery steps, it has been demonstrated that the sludge contains up to 70 % fiber fines, where a small content 5 to 20 % may be associated with insoluble lignin, 5 % of sand and 25 to 30 % of precipitated calcium carbonate [12]. An illustration of the primary sludge samples is shown in Figure 1a. The composition of primary sludge, secondary sludge and sludge from process water clarification generated during fiber recovery from white process water, is listed in Table 1. Especially primary sludge from the Kraft pulp production of Eucalyptus Globulus was evaluated in more detail, having 34.5% total ash, 4.8% total lignin and 60.4% total carbohydrates. The calcium carbonate content in the primary sludge is 27%. The latter calcium carbonate is responsible for the alkalinity of primary sludge (pH = 8.3).

As an alternative source for fiber recovery, the fine fiber rejects or short paper fibers from the whitewater were analysed, as characterized by the morphology shown in Figure 1b. Typically, the recovered SPF fractions have a fiber length below 0.2 mm. More precisely, the fraction of "fines" is determined as the fraction of the pulp suspension able to pass through a 76 μm aperture. The results of a sludge fractionation test indicate that percentage of fine fiber rejects (fibers shorter than 0.2 mm) amounts up to 63 % of the total recovered fiber fraction. A typical analysis for SPF indicates high amount of cellulosic fibers and moisture contents of above 50%. The components of SPF are short fibers, clay and some mineral fillers such as calcium carbonate up to 38%, with consequently pH = 8.1 to 9.3.

Based on the degree of compositional homogeneity and the concentration of cellulose fibers in several waste fractions, the recuperation of fibers from primary sludge and/or fine fiber rejects are estimated as the most economically feasible. Sludge from biological and/or chemical treatment generally contains lower amounts of fibers and are not further considered as an option.

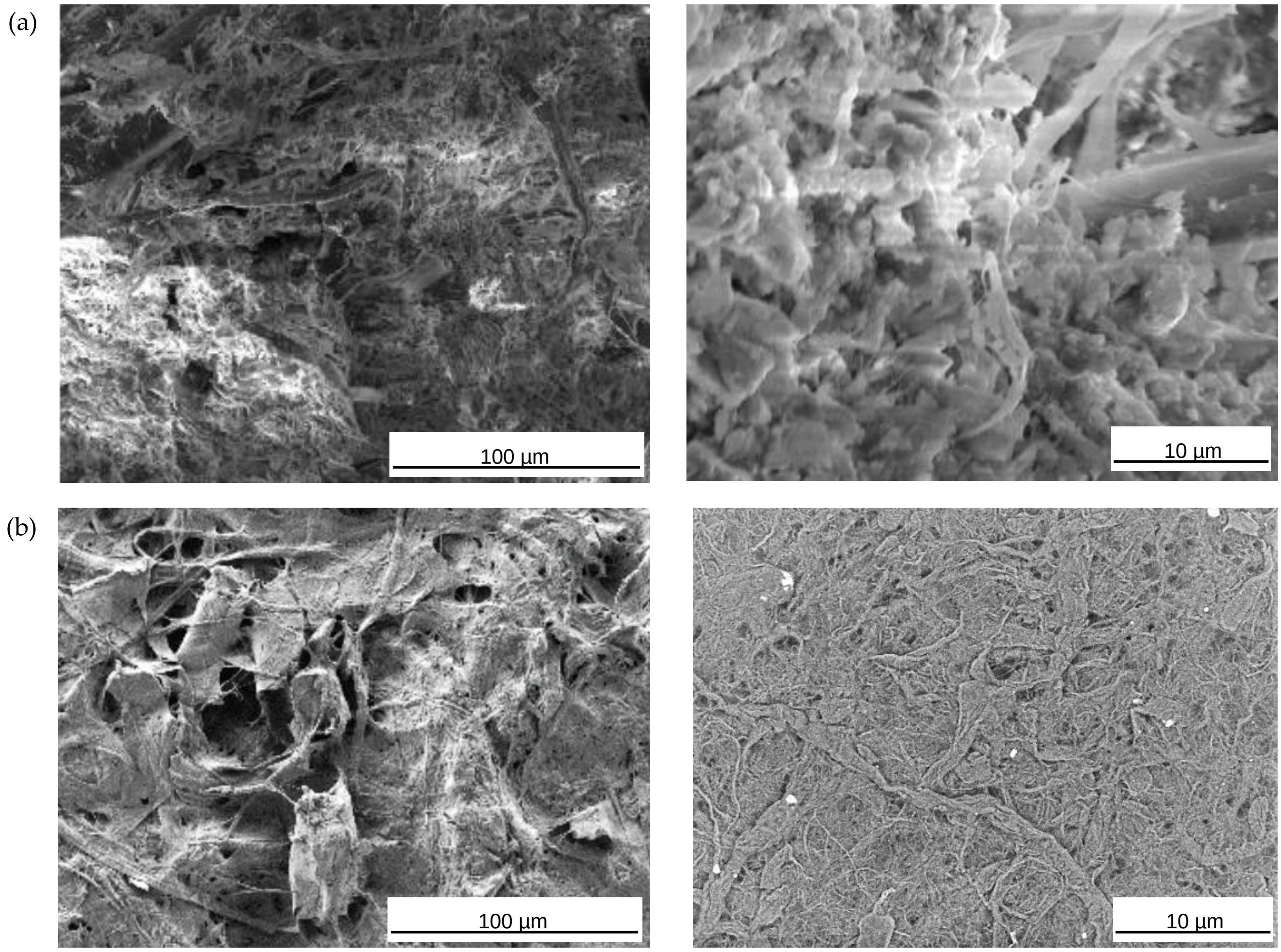

Figure 1. Morphological analysis of recovered sludge types from the pulp mill by means of scanning electron microscopy, (a) primary sludge, (b) sludge from white-water with fine fibers.

Table 1. Compositions of different sludge types recuperated from a paper mill

	Primary sludge	Secondary sludge	Sludge from white-water with fiber fines
Dry solid content [%]	48	32	59
Volatile solids [% DS]	33	48	76
Total Organic Carbon [%]	19	23	< 5
Pb [mg/kg DS]	41	22	50
Cd [mg/kg DS]	< 0.7	< 0.7	0.01
Cr [mg/kg DS]	24	17	9
Cu [mg/kg DS]	238	71	20
Ni [mg/kg DS]	6	8	9
Hg [mg/kg DS]	0.1	0.09	0.1
Zn [mg/kg DS]	141	135	34

3.2. Fiber homogenization

After dilution of the recovered sludge, the changes in fiber morphoplogy during fibrillation after different runs through the microfluidizer were followed. Depending on the number of passages through the high-pressure chambers, the morphology of the short paper fibers gradually changed with higher fibrillation at the surface (Figure 2). In parallel, the fiber morphologies become more homogeneous and larger fractions are broken. By varying the processing conditions, we are able to tune the morphology of the resulting fibers with diameters of 10 to 20 nm and micrometer length scale. In combination with mild chemical treatment and recyclable solvents, short cellulose fibers can be obtained with 100 to 300 nm length. The properties of the MFC mainly change if the diameter of the interaction chamber was decreased from 200 μm to 80 μm. During the homogenization of the fiber fractions in a high-pressure microfluidizer, the processing conditions for the fibers were further optimized. At first, the processable fiber concentration could be increased from originally 3 to 6 wt.-% solid cellulose fiber content in the suspension, without further influencing the final fiber morphology. This increase followed from the detailed rheological study before, where a relation between the shear rate and gelation point of the fiber network was first established for the given fiber grades and concentration. the processable fiber concentration could be increased from originally 3 to 6 wt.-% solid cellulose fiber content in the suspension which can be controlled by the pressure drop over the interaction chamber of the microfluidizer. At the end, the MFC was available in a homogeneous and stable aqueous dispersion with a maximum of 6 wt.-% fiber fraction and appropriate viscosity.

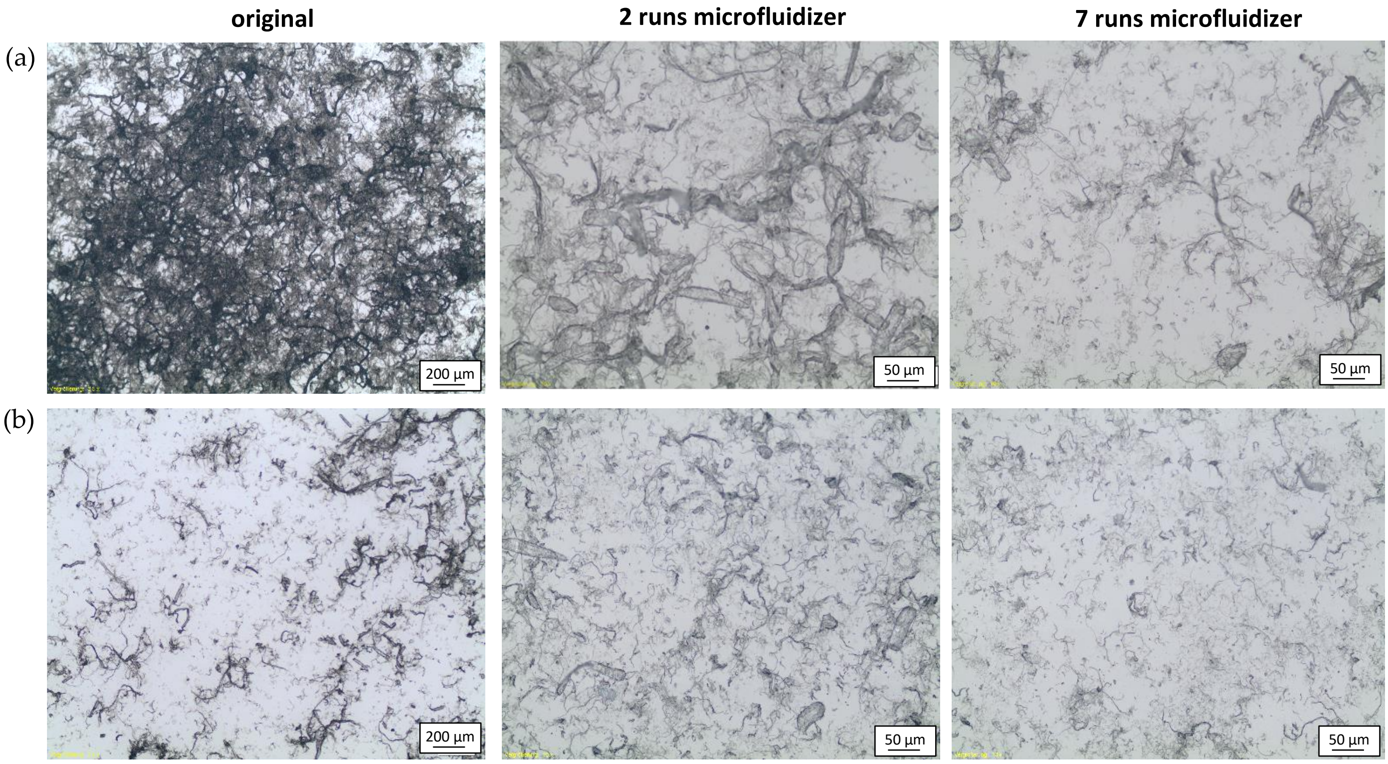

Figure 2. Homogenized fiber fraction produced from recovered sludge fibers in a EH-110 microfluidizer over different runs, (a) primary sludge, (b) sludge from processing whitewater with short paper fibers.

The quality of the final fraction microfibrillated cellulose (MFC) after 7 runs versus the original short paper fibers was evaluated by Raman microscopy (Figure 4). The Raman spectra at around 1100 – 1000 cm^{-1} illustrate the influences of the microfibrillation process: a higher intensity at 1150 cm^{-1} (C-O, C-C stretch); 1120 cm^{-1} (C-O-C symmetrical stretching); 1095 cm^{-1} (C-O-C asymmetrical stretching) for MFC demonstrates the improved structural properties after microfibrillation. Especially, the amorphous zones of the cellulose fibers are removed and/or re-oriented after processing resulting in a better organization of the cellulose structure with better perfection of the crystalline domains. These observations confirm the efficiency of homogenization in improving the quality of recovered fiber residues from the paper mill sludges.

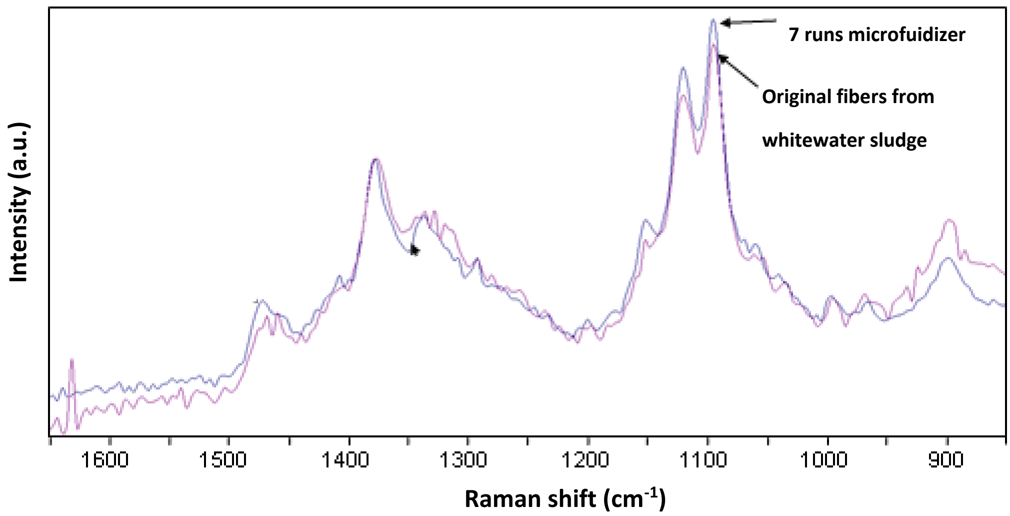

Figure 3. Raman spectroscopy of original fibers from whitewater sludge and after homogenization in EH-110 microfluidizer.

3. Conclusions

This study demonstrates the high potential for valorizing side-products from the pulp and paper industry in Brazil. The compositional analysis for the latter indicates best recovery potential for the primary sludge and short paper fibers from whitewater. However, the secondary sludge seemed not to provide economically feasible potential due to its composition. A homogenization process of the recuperated cellulose fibers from primary sludge and whitewater clearing by means of a high-pressure microfluidizer provides excellent processing conditions for forming homogeneous microfibrillated cellulose (MFC) with fiber diameters of 10 to 20 nm and micrometer length scale. The quality of the recuperated fibers is demonstrated by a higher crystalline quality compared to the original fibers in the sludge fractions. The favourable production of nanocellulose from sludges provides an attractive roadmap for the valorization of side-products from pulp and paper industries towards novel biomaterials and high-end applications.

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