environmental sciences proceedings

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Proceeding Paper

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

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† Presented at the 2nd International Electronic Conference on Forests—Sustainable Forests: Ecology, Management, Products and Trade, 1–15 September 2021; Available Online: https://iecf2021.sciforum.net/.

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 utilization of side-products originating from the pulp and paper industry may mostly contribute to 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 wastewaters 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 into the fiber fractions that could provide the 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 is estimated as the most economically feasible. The homogenization of the fiber fractions yields 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

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Citation: Samyn, P. Fractionation and Homogenization of Recuperated Pulp Fibers from Brazilian Paper and Pulp Industry. *Environ. Sci. Proc.* **2022**, *13*, 6. https://doi.org/10.3390/IECF2021-10793

Academic Editor: Miha Humar

Published: 31 August 2021

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

The Kraft pulping process [3] is an especially environmentally demanding industry that needs significant 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 liquid 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 of short fiber (eucalyptus), 1.8 million tons of long fiber (pine), and 1.1 million tons of 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 occupies 2.2 million hectares of forested area for industrial use. The total pulp export amounts to USD 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 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 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 disposed of 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 120,000 tons/year and are not profitable for burning as they have a lower energetic value than the lignin fraction. The 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 consisted 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 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 (whitewater) collected from the furnish during the formation of the paper sheets. 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 thermogravimetric 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, USA) at a consistency of 2 wt.%. The sludge suspension was therefore first diluted in deionized water and mixed for 1 h 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 the first run through a homogenization chamber (H210 Z-shaped with a pressure of 500 bar), followed by 2 or 7 runs through a 200 µm interaction chamber (H30 Z-shaped with a 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 the first source for fiber recovery, the primary sludge was evaluated. In general, the paper sludge contained high levels of dry solids because it was rich in fibers and therefore dewatered quite easily: the dry solid content of the residues generally varied between 40 to 70% depending on its origin. Through the subsequent recovery steps, it was demonstrated that the sludge contained up to 70% fiber fines, where a small content of 5 to 20% may be associated with insoluble lignin, 5% of sand, and 25 to 30% of precipitated calcium carbonate. 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.

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

	Primary Sludge	Secondary Sludge	Sludge from Whitewater with Fiber Fines
Dry solids 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

Primary sludge from the Kraft pulp production of Eucalyptus Globulus was specifically 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 was 27%. The latter calcium carbonate was 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 analyzed, as characterized by the morphology shown in Figure 1b. Typically, the recovered SPF fractions had 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 indicated that the percentage of fine fiber rejects (fibers shorter than 0.2 mm) amounted to 63% of the total recovered fiber fraction. A typical analysis for SPF indicated a high amount of cellulosic fibers and

moisture content above 50%. The components of SPF were short fibers, clay, and some mineral fillers, such as calcium carbonate up to 38%, with a consequent 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 was estimated as the most economically feasible. Sludge from biological and/or chemical treatment generally contained lower amounts of fibers and was not further considered as an option.

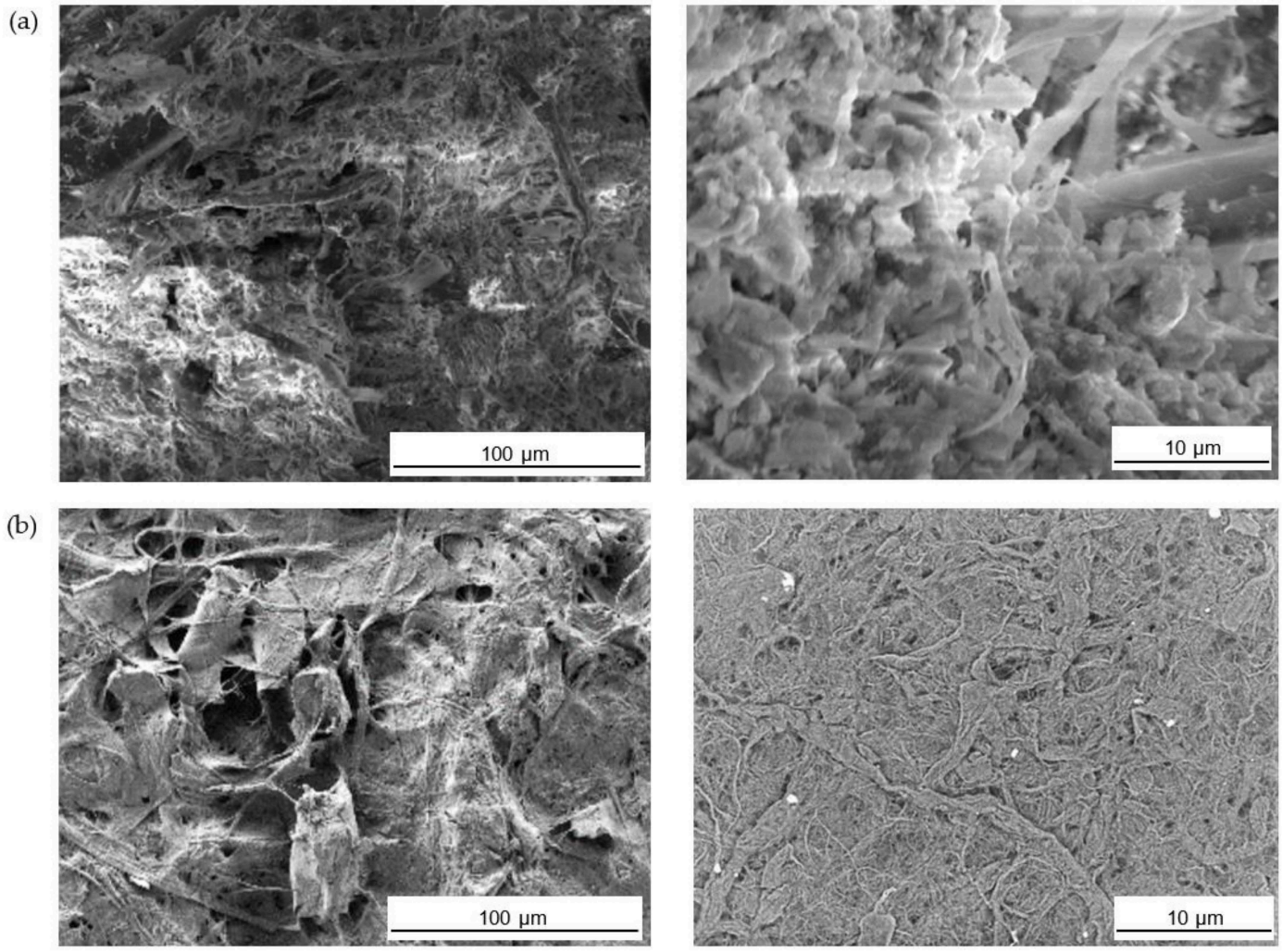


Figure 1. Morphological analysis of recovered sludge types from the pulp mill by means of scanning electron microscopy, (**a**) primary sludge, (**b**) sludge from whitewater with fine fibers.

3.2. Fiber Homogenization

After dilution of the recovered sludge, the changes in fiber morphology 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 became more homogeneous and larger fractions were broken. By varying the processing conditions, we were able to tune the morphology of the resulting fibers with diameters of 10 to 20 nm and a micrometer length scale. In combination with mild chemical treatment and recyclable solvents, short cellulose fibers could be obtained with 100 to 300 nm length. The properties of the MFC mainly changed 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 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 relationship 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 3 to 6 wt.% solid cellulose fiber content in the suspension which could 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.

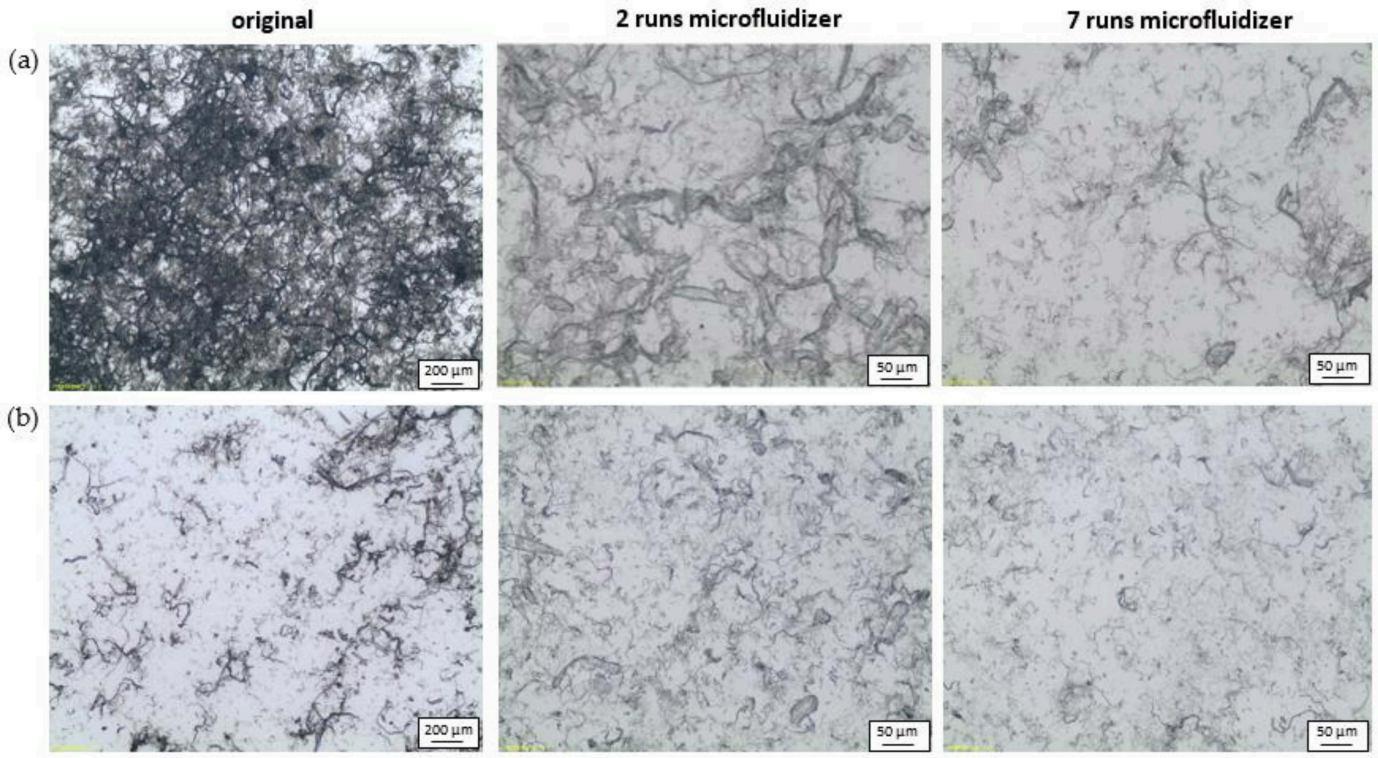


Figure 2. Homogenized fiber fraction produced from recovered sludge fibers in a EH-110 microfluidizer over different runs, (**a**) primary sludge, (**b**) sludge from processing whitewater with short paper fibers.

The quality of the final fraction micro fibrillated cellulose (MFC) after seven runs versus the original short paper fibers was evaluated by Raman microscopy (Figure 3). The Raman spectra at around 1100–1000 cm^{-1} illustrated the influences of the micro fibrillation 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 demonstrated the improved structural properties after micro fibrillation. Specifically, the amorphous zones of the cellulose fibers were 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 confirmed the efficiency of homogenization in improving the quality of recovered fiber residues from the paper mill sludges.

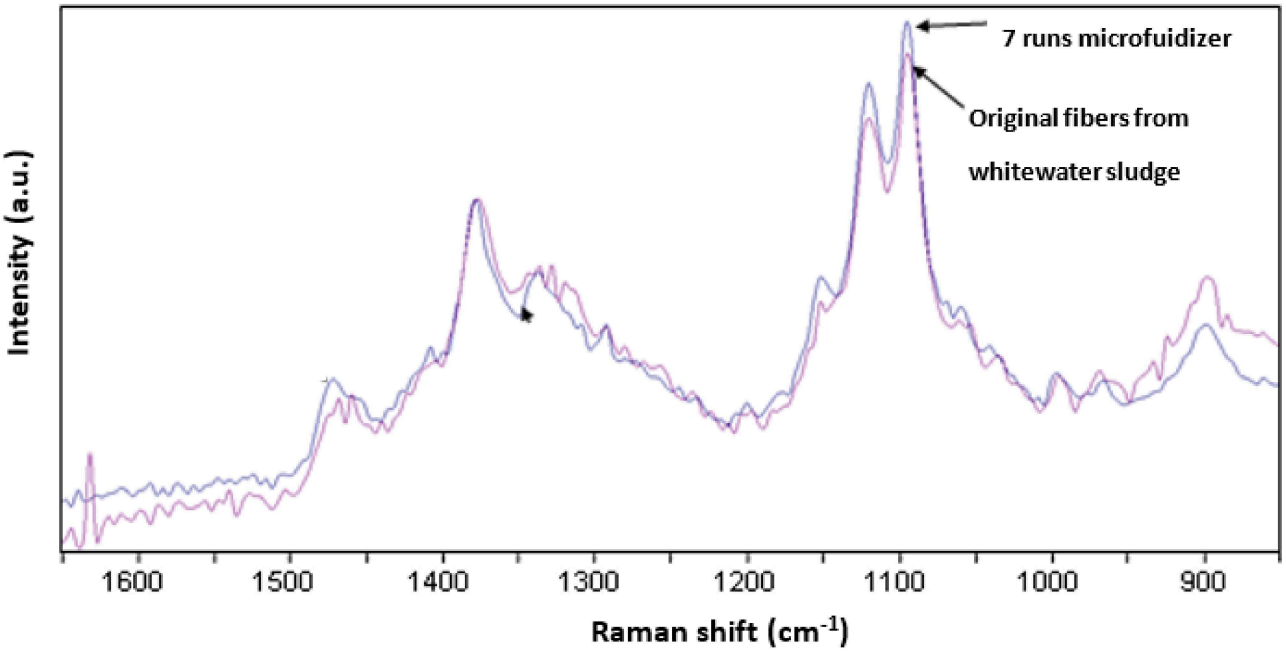


Figure 3. Raman spectroscopy of original fibers from whitewater sludge and after homogenization in EH-110 microfluidizer.

4. Conclusions

This study demonstrated the high potential for valorizing side-products from the pulp and paper industry in Brazil. The compositional analysis for the latter indicated the 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 provided excellent processing conditions for forming homogeneous micro fibrillated cellulose (MFC) with fiber diameters of 10 to 20 nm and a micrometer length scale. The quality of the recuperated fibers was demonstrated by a higher crystalline quality compared to the original fibers in the sludge fractions. The favorable 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.

Funding: This research was funded by Robert Bosch Foundation grant number "Foresnab".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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