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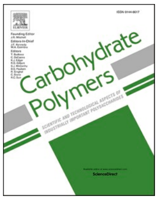

Recycling of TEMPO-mediated oxidation medium and its effect on nanocellulose properties

Hongyu Xu, Jose Luis Sanchez-Salvador, Angeles Blanco, Ana Balea, Carlos Negro *

Department of Chemical Engineering and Materials, Complutense University of Madrid, Avda. Complutense s/n, 28040 Madrid, Spain

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ABSTRACT

The potential of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)-mediated oxidation (TMO) to produce cellulose nanofibrils (CNFs) is hindered using costly and environmentally harmful catalysts, limiting its large-scale implementation. To promote sustainability, the TMO medium should be reused but there is a lack of knowledge on this process. The novelty of this research is the identification of the key parameters that affect the recirculation of the TMO medium, and their impact on the quality of the oxidized pulps and CNF products. Contrary to previous hypothesis, results show that the accumulation of salts is not a key parameter; instead, the pulp consistency during oxidation plays a vital role since concentrations higher than 10 g/L led to better CNF quality. Thus, reusing 75 % of the reaction medium, when high pulp consistency is used, does not alter the CNF properties. By reusing the reaction medium up to six times, the catalyst dose is dramatically reduced by >90 % for TEMPO and 80 % for NaBr, compared to the conventional process (0.1 mmol of TEMPO/g and 1 mmol of NaBr/g without medium reuse). Additionally, the high consistency oxidation enables a reduction of >80 % in the reaction time and effluent, and thus a threefold increase in CNF production.

1. Introduction

According to ISO/TS 20477:2017 standard, cellulose nanofibrils (CNFs) are defined as nano-sized fibers with a width diameter range of approximately 3 nm to 100 nm and typically up to 100 μm in length (ISO, 2017). This size reduction is achieved through mechanical methods such as high-pressure homogenization, microfluidization, or grinding, which physically break down the cellulose fibers into smaller dimensions (Abdul Khalil et al., 2014; Besbes et al., 2011). The unique properties of CNFs, such as their high mechanical strength, sorption capacity, high surface area, light weight and functionalization possibilities (Pennells et al., 2019), have led to significant progress in their production and application since the first production of CNFs by Turbak et al. (1983). However, the industrial application of CNFs is still facing several challenges related to their production due to high production costs, scalability issues, and environmental impact. Many CNF production methods are energy-intensive and use harsh chemicals, which can result in high carbon emissions and waste generation. Therefore, there is a need to develop more cost-effective, sustainable, and scalable production methods to produce CNFs in large quantities without compromising their quality.

As mechanical treatments are high energy consuming, chemical and/or enzymatic pre-treatments are used to facilitate the cellulose defibrillation (Li et al., 2022; Nagarajan et al., 2021; Nechyporchuk et al., 2016). In case of chemical pre-treatments, they can introduce surface ionic groups through carboxymethylation, oxidation, cationization and sulfonation reactions (Abu Bakar et al., 2022; Akira Isogai et al., 2018; Liimatainen et al., 2014; Wang et al., 2023). This promotes interfibrillar repulsion which facilitates the isolation of CNFs with higher fibrillation and smaller size distribution of diameters, which ultimately determines the CNF quality and, therefore, their final use and application (Sanchez-Salvador et al., 2020). Different chemicals can be used with this aim. Recent research has demonstrated the isolation of nanocellulose using oxalic acid and a hydrothermal treatment in an autoclave or steam sterilizer at high pressure (Abu Bakar et al., 2022; Wang et al., 2023). Another option to obtain highly fibrillated nanocellulose is the quaternization, using N-(2-3-epoxypropyl) trimethylammonium chloride (Aulin et al., 2010) or periodate oxidation and quaternization with (2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride (Liimatainen et al., 2014). However, among all chemical pretreatments, TEMPO-mediated oxidation (TMO) is still considered as one of the most efficient and selective chemical pretreatments (Nechyporchuk et al., 2016; Saito &

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* Corresponding author.
E-mail address: cnegro@ucm.es (C. Negro).

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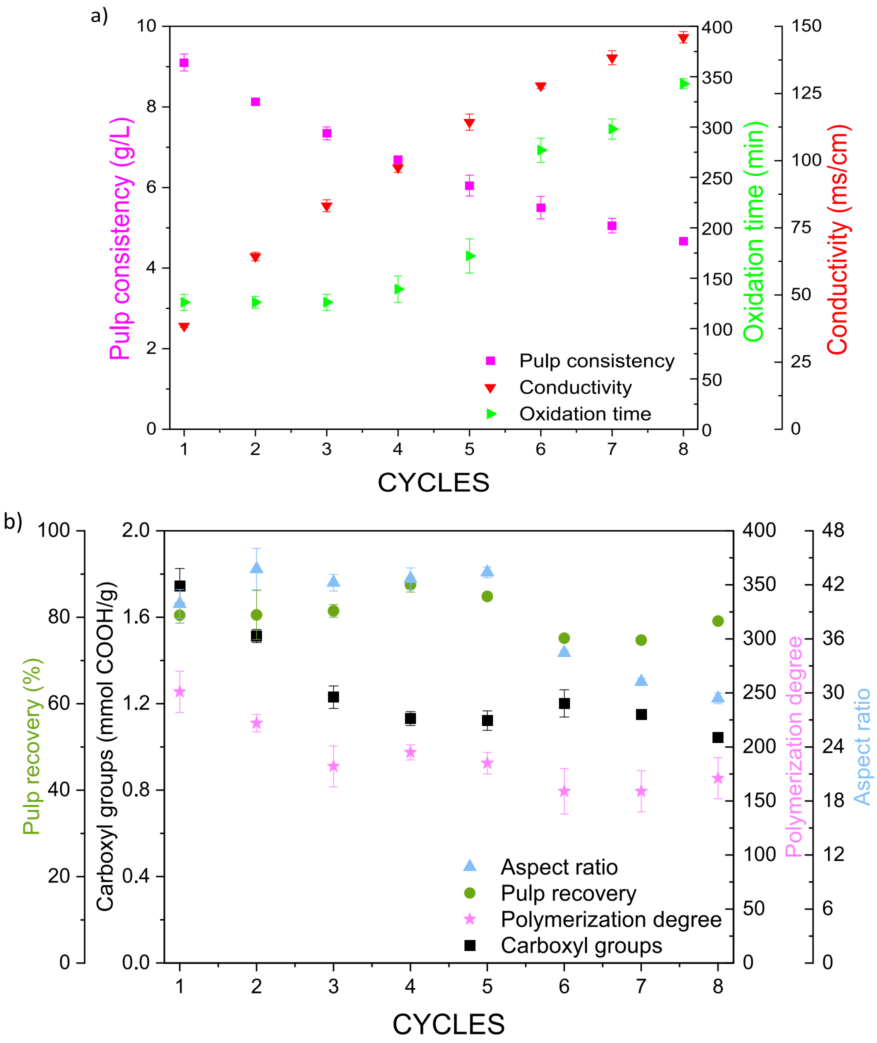

Fig. 1. Reuse of the TEMPO-mediated oxidation medium under conventional conditions: a) Parameters studied for monitoring the reaction; b) Oxidized pulp characterization (5 mmol NaClO/g; 0.1 mmol of TEMPO/g and 1 mmol of NaBr/g).

Isogai, 2006; Tarrés et al., 2016). This pretreatment involves the use of 2,2,6,6, tetramethyl-1-piperidinyloxy (TEMPO) as catalyst, sodium bromide (NaBr) as co-catalyst and sodium hypochlorite (NaClO) as oxidant. The mechanism consists of oxidizing the C6 hydroxyl groups of cellulose to aldehyde groups and subsequently to carboxyl groups at pH 10–11 and ambient temperature (Saito & Isogai, 2004). The introduction of carboxylic groups through TMO promotes electrostatic repulsion at the surface of the fibrils which makes the subsequent mechanical processes more efficient (A. Isogai et al., 2011). Nevertheless, the cost and the environmental impact of the process have limited its implementation at large scale (Balea et al., 2017).

In previous works, Xu et al. (2022) proposed a more sustainable TMO process for producing highly fibrillated CNFs. This approach was based on the optimization of reaction time and catalyst dosages which reduced the required amount of catalysts up to 75 % of TEMPO and 50 % of NaBr in comparison with the conventional conditions proposed by Saito et al. (2007). Although the catalyst concentration in the effluent was lower the flow was still very high. Therefore the next approach to improve the sustainability of TMO process is to reuse the reaction medium. Mao et al. (2010) reused five times the reaction medium at the end of the oxidation by filtering the pulp suspension and adding only NaClO in each reaction cycle. However, their results showed that the number of carboxyl groups decreased as well as the reaction rate, which required increasing the reaction time up to ≈15 %/cycle. Later on, Sanchez-Salvador, Campano, et al. (2021) have shown that the negative effect on product quality could be minimized by adding 25 % of fresh catalysts in each cycle. Recently, Chen et al. (2022) developed a method for integrating direct reuse and extraction recovery of TEMPO by distillation. In this method, 50–80 % of filtrated medium was directly reused, and 20–50 % of fresh catalysts were added to maintain the same initial reaction concentrations. The remaining TEMPO in the filtrated medium was recovered by extraction with ethyl acetate and then distilled and reused for the reaction. This process is more complicated energy intensive. The state of the art shows that although there is some progress in the improvement of the TMO process, there are still a lack of knowledge on the identification of the key parameters that affects the properties of CNFs during the medium reuse process.

Therefore, the aim of this research is to assess which main parameters influence the recirculation of TMO medium in multiple oxidation cycles and the quality of the oxidized pulp (OP) and the CNF produced. The reuse of the TMO medium has been studied at two different sets of conditions: conventional conditions according to Saito et al. (2007) and the optimized conditions proposed by Xu et al. (2022). TMO conditions (time, pulp consistency, pulp recovery and conductivity), oxidized cellulose properties (carboxyl groups, aspect ratio (AR) and polymerization degree (DPv)), and final properties of CNFs (transmittance and cationic demand (CD)) have been considered for the study of each cycle. This research is focused on developing a knowledge-based process considering circular economy concepts to facilitate the production and use of CNFs at large scale which represent a significant progress with respect to

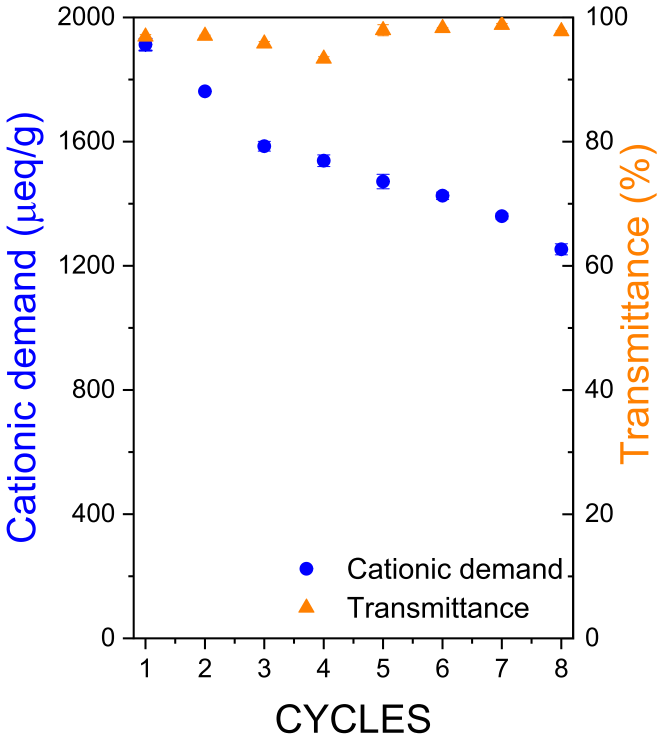

Fig. 2. Characterization of cellulose nanofibrils with the number of cycles of TEMPO-mediated oxidation under conventional conditions (5 mmol NaClO/g; 0.1 mmol of TEMPO/g and 1 mmol of NaBr/g).

the state of the art.

2. Materials and methods

2.1. Materials

Eucalyptus globulus ECF bleached kraft pulp (Torraspapel, S.A., Zaragoza, Spain) was used as cellulose source for the preparation of the CNFs. The raw material has a composition of 74 % of cellulose, 17 % of hemicellulose, 5.7 % of soluble lignin and 1.3 % of Klason lignin on a dry weight basis (Sanchez-Salvador, Campano, Balea, Tarres, et al., 2022).

For TMO pretreatment, TEMPO reagent was purchased from Sigma-Aldrich (St. Louis, MO, USA), whereas NaBr and 12 % (w/v) NaClO solution (previously titrated to determine the actual concentration) were purchased from Panreac AppliChem (Barcelona, Spain). Other reagents used for monitoring the reaction and for the OP and CNF characterization were NaOH, HCl, $Na_2S_2O_3$, KI and bis(ethylenediamine)copper(II) hydroxide solution, also supplied by Panreac AppliChem. Besides, 0.1 % (w/w) poly-L-lysine solution was purchased from Electron Microscopy Sciences (Hatfield, PA, USA).

2.2. TEMPO-mediated oxidation reaction

First, dry cellulose pulps were soaked in water for 24 h. Then, samples were disintegrated for 30,000 revolutions at 2 % (w/w) consistency in a pulp disintegrator (Mavis Engineering Ltd., London, UK). After that, the final concentration was adjusted at 1 % (w/w) using deionized water. On the other hand, different doses of TEMPO and NaBr were dissolved and added into the 5-L reactor together with the pulp. Temperature was maintained at 25 °C, using a cooling jacket, and the sample was agitated at 400 rpm. The reaction starts with the addition of NaClO to oxidize the fibers. The pH was adjusted in the range 10–10.5 with the addition of 2 M NaOH. Then, OP was filtrated and washed using 3 L of deionized water in all cases a neutral pH was achieved. The OPs obtained at ~7 % consistency was stored at 4 °C for characterization purposes, as well as homogenized to produce the CNFs.

2.2.1. Reuse of the TEMPO-mediated oxidation medium

In this study, the reaction medium was reused for eight successive cycles, with the same proportion of reagents in each cycle. The first cycle followed the standard protocol described previously. The entire recovered reaction medium was used in the next cycle, as TEMPO and NaBr were still present in the liquor. The amount of cellulose and NaClO used in the next cycles were recalculated to maintain the same proportion as in the first cycle.

The method to determine the NaClO content in the medium was a redox titration multi-step method (Lewin & Avrahami, 1955). 25 mL of sample from the reactor was added in an Erlenmeyer flask together with 15 mL of deionized water, 20 mL of 2 M HCl and 10 % (w/w) KI solution. The mixture was titrated with 0.13 M $Na_2S_2O_3$, adding 2 mL of 0.2 M starch solution as colour indicator, until the sample becomes transparent. The NaClO content is calculated as one-half of the titrated thiosulfate content.

2.3. Characterization of the oxidized pulps

To determine the consistency of OPs, samples are dried using a laboratory stove at a temperature of 70 °C until a constant weight is achieved. The amount of salts produced during the TMO reaction is quantified by incineration at 525 °C in accordance with the ISO 1762:2019 standard. Then, dry pulp content of OPs is determined by subtracting the salt content from the solid since the ash content of the raw material was insignificant, below 0.2 %.

Carboxyl groups of OPs are calculated using conductometric titration. 0.15 g of dry pulp are mixed with 5 mL of 0.01 M NaCl and deionized water until a final volume of around 60 mL. 0.1 M HCl is used to adjust the pH around 2.6–2.8. After each addition of 0.2 mL of 0.05 M NaOH, the conductivity is recorded until it increased at a constant rate. The carboxyl groups are calculated by Eq. (1) through the volume of NaOH spent in the weak acids corresponding to the intermediate part of the curve.

$$\text{Carboxyl groups}\left(\frac{\text{mmol COOH}}{\text{g dry pulp}}\right)=\frac{(V_e\,(\text{mL})-V_i\,(\text{mL}))\cdot\text{NaOH molarity}\,(\text{M})}{\text{dry pulp}\,(\text{g})} \tag{1}$$

Where, V_i and V_e are the volume of NaOH in the initial and end points in which the conductivity is constant.

Polymerization degree (DPv) is calculated from the intrinsic viscosity of the OPs, which is determined in accordance with the ISO 5351:2010 standard using bis(ethylenediamine)copper(II) hydroxide solution (CED) as a solvent. The calculation is based on Mark-Houwink-Sakurada equation, as described by Henriksson et al. (2008). Although, the interaction between the strong alkali conditions of the CED solution and the presence of some C6 aldehyde groups, acting as intermediates in the formation of C6 carboxyl groups, can trigger β-elimination of adjacent glycoside bonds at the C6-aldehyde units and provide a slight reduction of DPv compared to the real value (Shinoda et al., 2012), this effect is considered neglected due to the fast conversion of aldehyde groups to carboxyl groups.

Aspect ratio (AR), the ratio of OP fibers length to its diameter, is determined using the simplified gel point ($\varnothing_g$) methodology based on sedimentation of the OPs at different concentrations in graduated cylinders following Eq. (2) (Sanchez-Salvador, Monte, et al., 2021; Signori-Iamin et al., 2022).

$$\text{Aspect Ratio, AR} = 5.98 \bullet \sqrt{\frac{1000}{\text{Gel point}, \varnothing_g\left(\frac{\text{kg}}{\text{m}^3}\right)}} \tag{2}$$

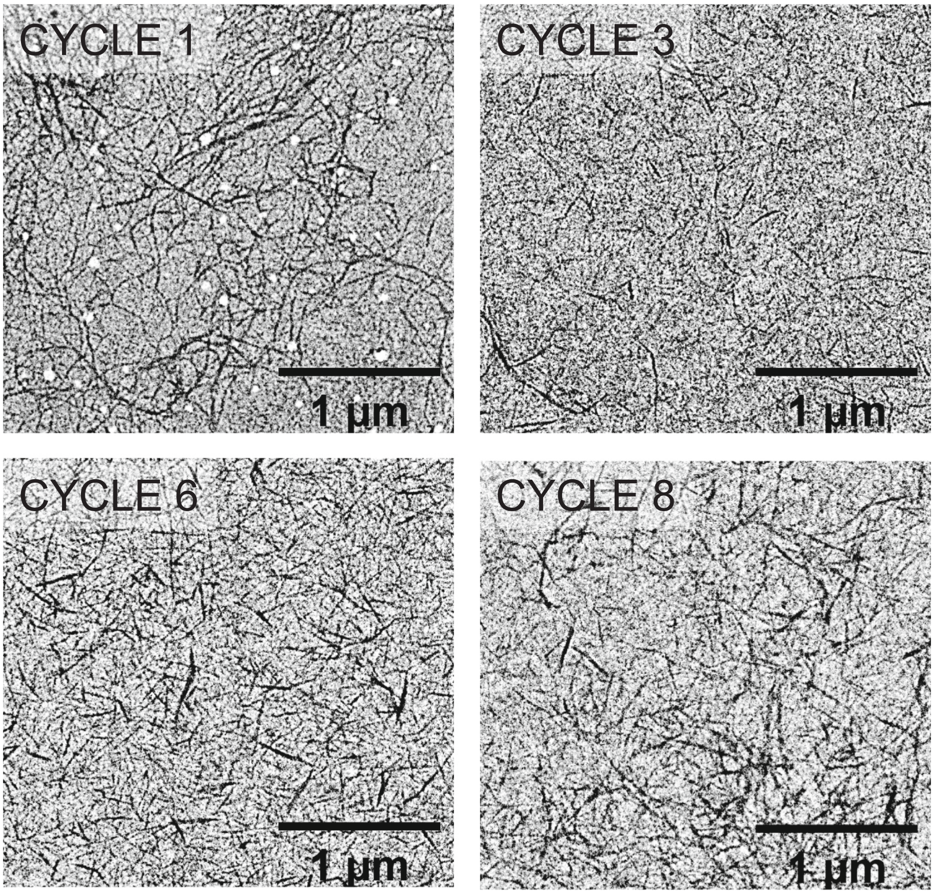

Fig. 3. TEM images of cellulose nanofibrils obtained reusing the TEMPO-mediated oxidation reaction medium and under conventional conditions (5 mmol NaClO/g; 0.1 mmol of TEMPO/g and 1 mmol of NaBr/g).

2.4. Cellulose nanofibrils production and characterization

CNFs are produced using a high-pressure laboratory homogenizer PANDA PLUS 2000 (GEA Niro Soavy, Parma, Italy). First, consistency of OPs is adjusted to 1 % (w/w) and then, samples are homogenized at 600 bar using a sequence of 4 passes. The resulting CNFs are stored at 4 °C with some drops of glutaraldehyde as bactericide to ensure better conservation.

Characterization of CNFs is described in detailed below. Transmittance measurements are performed at 600 nm using 0.1 % (w/w) CNF suspensions and a Cary 50 Conc UV–visible spectrophotometer (Varian Australia PTI LTD, Victoria, Australia). Cationic demand (CD) is measured by an inverse colloidal titration using a charge analyzing system (CAS) detector (AFG Analytic GmbH, Leipzig, Germany). Specifically, an excess of 0.001 N polydiallyldimethylammonium chloride (polyDADMAC) is added to 25 mL of 0.1 % (w/w) CNF suspension and then stirred for 24 h. The polyDADMAC that does not react with the sample is titrated with 0.001 N sodium polyethensulphonate (PesNa). Finally, Transmission Electron Microscopy (TEM) of CNFs is carried out with a JEM 1400 microscope (JEOL, Tokyo, Japan) in the National Centre of Electronic Microscopy (Madrid, Spain), following the procedure outlined by (Campano et al., 2020).

3. Results and discussion

3.1. Reusing of TEMPO-mediated oxidation medium under conventional conditions

The conventional conditions reported by Saito et al. (2007) were used in this experiment. Specifically, 30 g of dry pulp, 5/0.1/1 (NaClO/TEMPO/NaBr) mmol/g were mixed in the reactor. The final concentration of the pulp was adjusted to 1 % (w/w). The reaction was considered complete when the ratio of NaOH added per gram of pulp to the oxidation time was <0.005, and all the sodium hypochlorite was consumed while maintaining the pH. Once the TMO reaction was completed, the medium was separated from the OPs by filtration, obtaining a volume slightly lower than the initial, and reused for the subsequent cycle. Depending on the amount of recovery reaction medium, a new pulp was added with the concentration adjusted to maintain the ratio catalysts (TEMPO and NaBr) to pulp. Regarding the OPs, they were retained in the mesh and washed with 3 L of deionized water and stored at 4 °C until characterized. Although a small portion of TEMPO and NaBr remained with the OPs after TMO reaction, these both chemicals were effectively removed during the washing procedure.

Fig. 1a and b show the parameters studied for monitoring the TMO, namely pulp consistency, conductivity, and oxidation time in each cycle and the characterization of the OP, respectively.

Initially, the oxidation time required to deplete all the NaClO remained constant in the first 5 cycles around 120–150 min, and the pulp recovery is around 85 wt%. However, in the last three cycles, the time needed for oxidation increases up to 350 min, and the pulp recovery decreases slightly to 75 wt%. On the other hand, carboxyl groups of OPs decrease from 1.7 mmol COOH/g to 1.1 mmol COOH/g (cycle 4) and thereafter, the number of carboxyl groups is maintained. A possible reason of this change could be the accumulation of salts in the TMO reaction medium, resulting in the production of NaCl as by-product (Sanchez-Salvador, Campano, et al., 2021). This is supported by the increase in conductivity observed in the reaction medium from 38 ms/cm to 146 ms/cm. This hypothesis is in agreement with Jiang et al. (2000) who reported that an increase in salt concentration has a

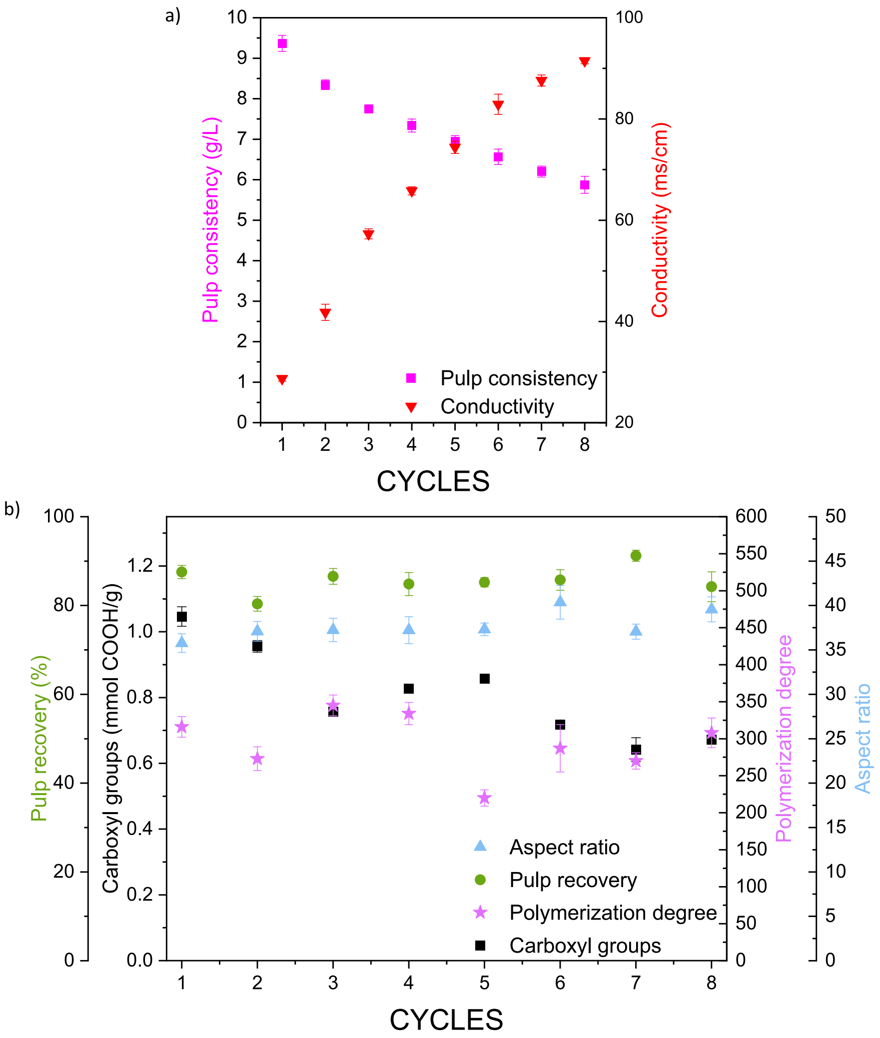

Fig. 4. Reuse of the TEMPO-mediated oxidation medium under optimized conditions (2.5 mmol NaClO/g; 0.025 mmol of TEMPO/g and 0.5 mmol of NaBr/g): a) Parameters studied for monitoring the reaction; b) oxidized pulp characterization.

negative impact on the oxidation rate due to the effect of ionic strength on the local concentration of oxidant species around the cellulose chains.

On the other hand, some TEMPO and NaBr are lost with the OP obtaining less amount of medium after filtration. Therefore, to maintain the ratio of catalyst to pulp in each cycle is necessary to decrease the pulp consistency in the reaction, from 9 g of pulp/L (first cycle) to 4.6 g of pulp/L (eighth cycle). This may lead to a reduction in the efficiency of the TMO reaction, as there is lower concentration of catalyst in the reaction medium.

Regarding to the DPv, there is a decrease from 250 to 160 monomers of anhydroglucose along the reaction cycles. The production of the hydroxyl radicals in the combination of TEMPO, NaBr and NaClO at basic pH brings a significant depolymerization of cellulose, which can result in the rupture of cellulose chains, leading to a remarkable decrease in pulp viscosity (Shibata & Isogai, 2003). In cycles 1–5, the AR is maintained at 42 and then, slightly decreases to 30 due to the reduction of OP length with the oxidation time as shown in DPv. These results are according to Sanchez-Salvador, Monte, et al. (2021) research which shows that longer oxidation times not produce a higher amount of carboxyl groups but the remaining NaClO is used to break the polymeric chains.

The characterization of the CNFs produced through homogenization with 4 passes at 600 bar, is shown in Fig. 2. The results show a decrease in CD from 1900 to 1250 μeq/g due to the reduction in the anionic surface charge of the fibers with each cycle. Meanwhile, the transmittance values remained high, ranging from 93 to 100 % because the transmittance is related with the proportion of nanofibrils in the sample, which would indicate that the oxidation process was still effective despite the reduction of carboxyl groups. Therefore, it is unnecessary to achieve high values of carboxyl groups, 1.1 mmol of COOH/g is enough to obtain highly fibrillated nanocelluloses as the fibers are electrostatically repelled and further oxidation is not required. As observed in TEM images of CNFs at different cycles of TMO (Fig. 3), the diameter range of the CNFs produced was between 10 nm and 40 nm for all the cycles although the carboxyl groups decrease. Nonetheless, in cycles 6 and 8, the CNFs appeared to be shorter compared to earlier cycles, which could be attributed to both the depolymerization of fiber chains and longer oxidation time, as demonstrated in Fig. 1.

3.2. Reusing the TEMPO-mediated oxidation medium under optimized conditions of catalysts and oxidant

Fig. 4a shows the parameters examined for the reuse of the reaction medium using the optimized conditions described by Xu et al. (2022). These conditions include 2.5/0.025/0.5 mmol/g, with each TMO oxidation cycle lasting 50 min instead of waiting for the NaClO to be fully consumed.

Compared to the conventional conditions (5 mmol NaClO/g; 0.1 mmol of TEMPO/g and 1 mmol of NaBr/g), the decrease in pulp consistency is slower when using the optimized conditions, with a value of

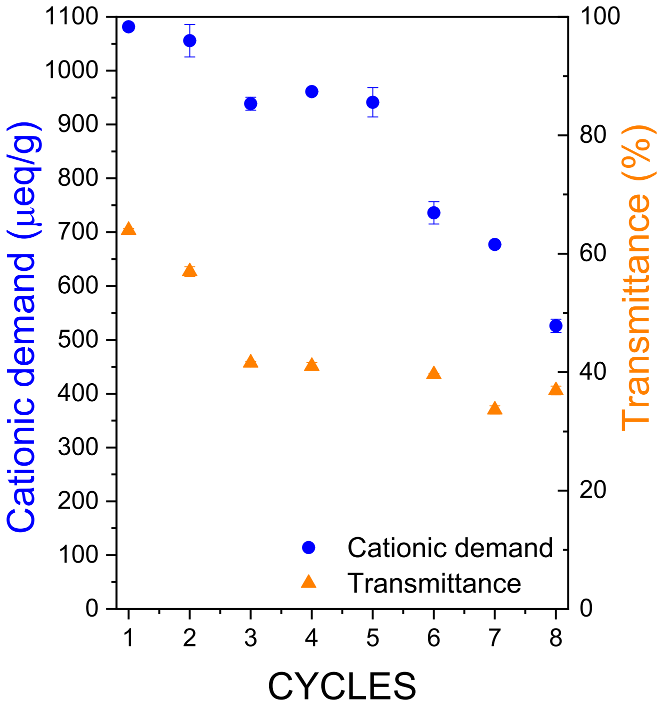

Fig. 5. Characterization of cellulose nanofibrils with the number of cycles of TEMPO-mediated oxidation under optimized conditions (2.5 mmol NaClO/g; 0.025 mmol of TEMPO/g and 0.5 mmol of NaBr/g).

5.9 g/L after 8 cycles instead of 4.6 g/L. This difference can be attributed to the use of a lower NaClO concentration (2.5 mmol/g per cycle) and shorter oxidation time (50 min per cycle). Under conventional conditions with a longer oxidation time (up to 5.7 h) and higher NaClO concentration (5 mmol/g), there is a higher wear away of the catalysts, resulting in a shorter lifespan and decreased efficiency. In contrast, the reduction of the oxidation time to 50 min in the optimized conditions leads to a lower accumulation of salts, resulting in a 38 % reduction in salt build-up after 8 cycles.

These improvements in the process have led to enhanced properties of the OP, such as the pulp recovery which increase and remains almost constant at 90 wt% in all cycles with a lower cellulose fraction dissolved in the medium. This is due to the fixed oxidation time, which leads to less intensive oxidation and fewer side reactions, thus reducing salt build-up. As a result, there is a sustained high pulp recovery observed throughout the cycles. Fig. 4b also confirms the lower dissolution of the pulp in the medium, as evidenced by a lower depolymerization of the fibrils compared with the conventional conditions with an average value of 294 ± 40 monomers in the cycles studied. Additionally, AR is maintained throughout the cycles, with an average value of 38 ± 2. Although the diameter of the OPs decreases, the length of the fibers decreases in a similar proportion, which contributes to maintain the AR in the cellulose network.

On the other hand, the amount of carboxyl groups is lower than with the Saito conditions due to use of a milder TMO. The carboxyl groups decrease progressively from 1.05 mmol COOH/g to 0.7 mmol COOH/g in cycle 1 and 8, respectively. However, this reduction of carboxyl groups does not necessarily imply a lower degree of fibrillation in the final CNFs (Fig. 4b). Previous studies have shown that even a lower amount of carboxyl groups could be sufficient for effective

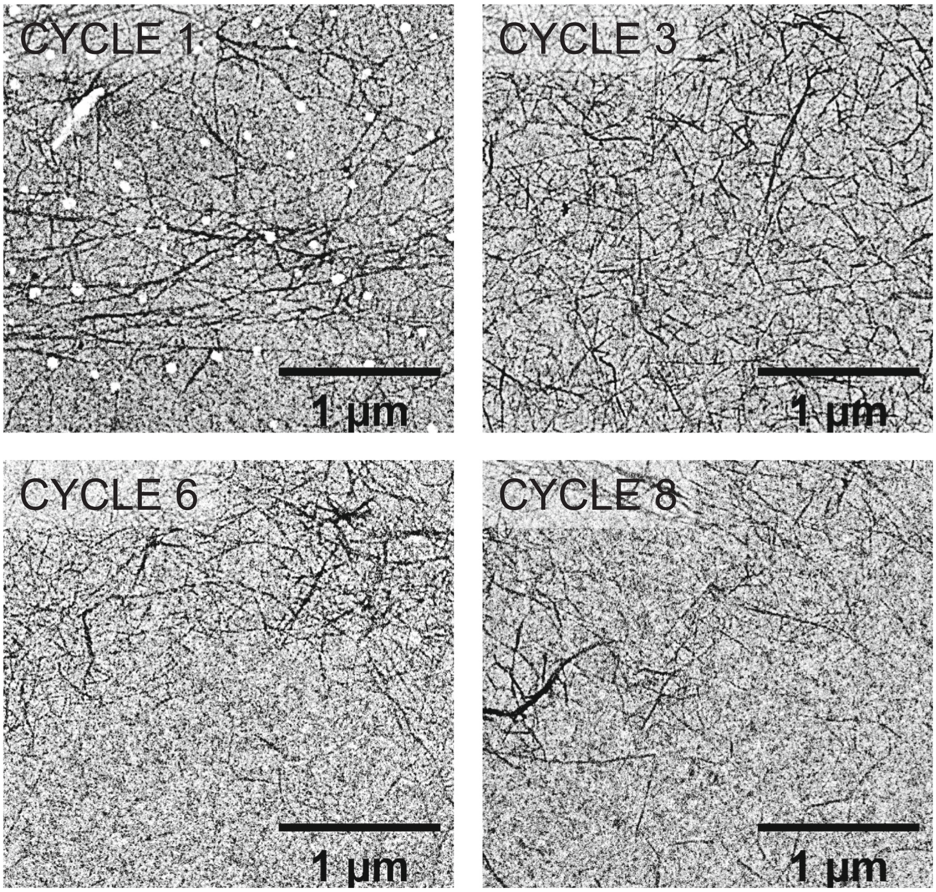

Fig. 6. TEM images of cellulose nanofibrils at different cycles of TEMPO-mediated oxidation under optimized conditions (2.5 mmol NaClO/g; 0.025 mmol of TEMPO/g and 0.5 mmol of NaBr/g).

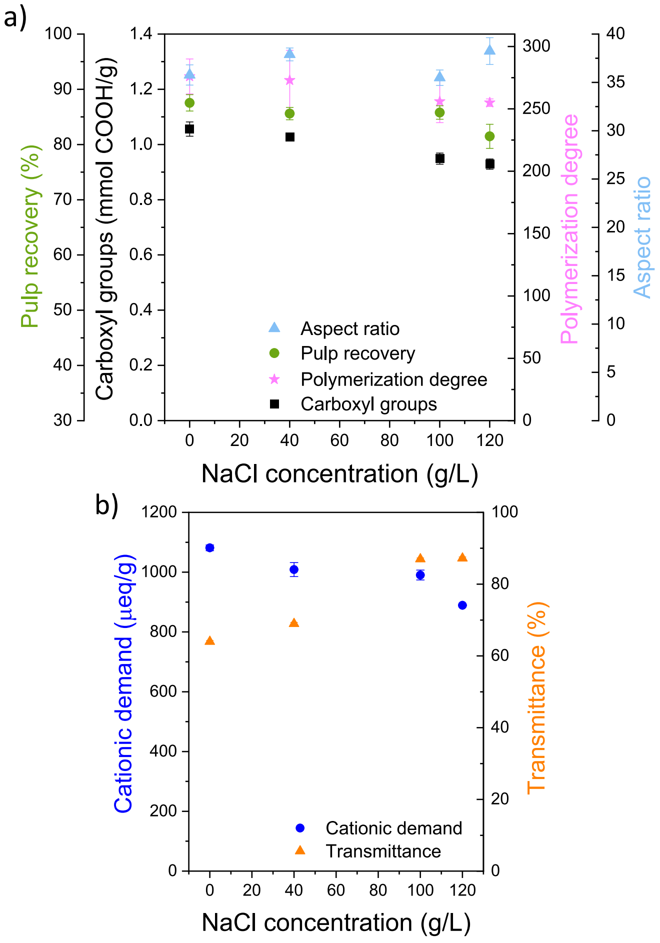

Fig. 7. Effect of NaCl concentration on the TEMPO-mediated oxidation: a) Oxidized pulp characterization, b) cellulose nanofibril characterization.

homogenization process (Besbes et al., 2011).

Fig. 5 shows the evolution of CD and transmittance throughout different cycles. CD shows the same tendency as carboxyl groups decreasing from 1100 (cycle 1) to 550 μeq/g (cycle 8). This decrease is likely due to the reduced number of carboxyl groups, which are a critical factor in determining the anionic charge of CNFs. The transmittance also decreases from 60 % to 40 %, as the oxidation efficiency decreases with the reusing of the reaction medium. The values of transmittance are lower than Fig. 2 because the TMO conditions used in this experiment were optimized to use a lower concentration of catalysts that decrease the reaction rate of TMO. Moreover, the decrease of transmittance can be attributed to the lower accumulation of salts that adversely affect the properties of OPs to obtain CNFs. This aspect will be further investigated and discussed in Section 3.3.

As can be observed in the TEM images (Fig. 6), the CNFs become more heterogenous and slightly wider with the reuse of the reaction medium. In the last cycles, some fibers could reach up to 60 nm, but the range of diameters still remains in the nanoscale.

The reason for the reduced performance of OP and CNF properties after multiple reusing cycles could be attributed to the accumulation of salts in the reaction medium, to the dilution of the pulp or to the accumulation of cellulose degradation products since all may affect the TMO efficiency. Therefore, in the next part of this research the amount of NaCl and the pulp consistency were independently modified during TMO reaction without reusing the reaction medium.

3.3. Effect of salts on TEMPO-mediated oxidation

To study the effect of NaCl on the oxidation of pulps, different concentration of salt, from 0 g/L to 120 g/L, were added into the reactor under the optimized TMO conditions (2.5/0.025/0.5 mmol/g).

Results are shown in Fig. 7. The amount of carboxyl groups decreases slightly, but not significantly, from 1.05 mmol COOH/g to 0.93 mmol COOH/g indicating that the concentration of NaCl in the reaction is not the primary factor influencing the decrease in carboxyl groups observed with the reusing of the reaction medium. Moreover, the DPv, AR and pulp recovery remain almost constant throughout all these experiments, suggesting that the accumulation of salts in the medium does not significantly impact the properties of the OPs.

On the other hand, as expected the CD exhibits a slightly decrease from 1090 μeq/g to 900 μeq/g with the addition of NaCl, due to the slightly decrease in carboxyl groups and to the neutralization effect of a higher ionic strength. However, the transmittance of CNFs shows a remarkable increase from 63 % to 87 % when the amount of NaCl increased from 0 to 120 g/L. This effect is due to the presence of the counterion Na^+ that has an important impact on CNF networking swelling increasing the amount of water between the CNFs. The counterion effect in the network swelling was examined by Maloney (2015), indicating that Na^+ form gives the highest swelling of various counterions ($Na^+ > H^+ > Ca^{2+}$) due to the high solubility of sodium salts. TEM images of the CNFs obtained at different salt concentrations are presented in Fig. 8, indicating that the dispersions are mostly composed of individual fibrils with diameters ranging from 10 to 45 nm and lengths between 0.5 and 2 μm determined by using image J program.

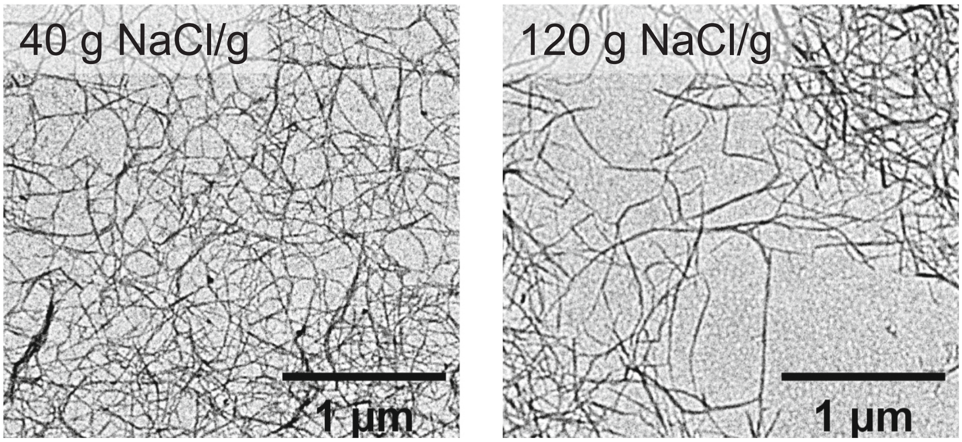

Fig. 8. TEM images of cellulose nanofibrils at different NaCl concentration.

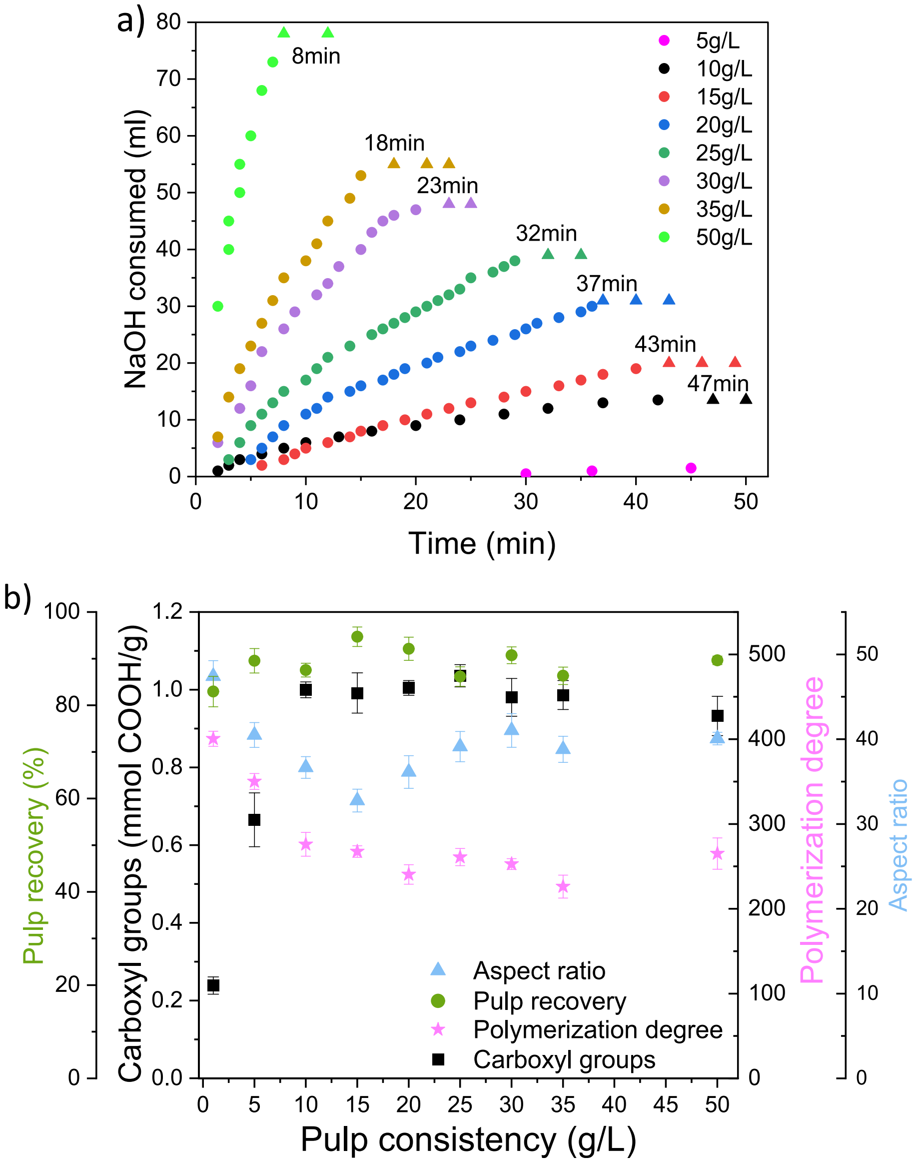

Fig. 9. Effect of pulp consistency on the TEMPO-mediated oxidation: a) NaOH consumed, b) oxidized pulp characterization.

3.4. *Effect of pulp consistency on TEMPO-mediated oxidation*

The reaction conditions used to study the effect of pulp consistency were 2.5/0.025/0.5 mmol/g and a reaction time of 50 min. Then, different concentrations of pulp, ranging from 1 to 50 g of pulp per litter, were added to the reactor, while maintaining the catalyst-to-pulp ratio. The oxidant, NaClO, was gradually added to maintain the pH at 10.5. Once all the oxidant was added, NaOH was used to neutralize the carboxyl groups formed during oxidation and keep the reaction medium at pH 10.5. No further consumption of NaOH was observed after pH stabilization, indicating reagent depletion.

Fig. 9a displays an interesting trend in the consumption of NaOH during the reaction. The increase in NaOH consumption indicates an increase in the reaction rate, which can produce carboxyl groups or even side reactions. The pulp consistency has a significant impact on the oxidant consumption rate; at 20 g/L pulp consistency, the addition of NaOH was stopped at 37 min, while at 50 g/L, it was stopped at 8 min. The triangular icons of Fig. 9a show the stabilization zone between the last addition of NaOH and the end of the reaction when the pH is maintained. The consumption of NaOH at 1 g/L pulp consistency was not included in Fig. 9a because the addition of NaClO was slower than in the other cases, resulting in oxidant remaining in the reactor after 50 min. In the case of 5 g/L pulp consistency, only 1.5 mL of NaOH was consumed to maintain the pH at 10.5 during the 50 min of oxidation. After the TMO, the amount of NaClO was determined to evaluate the unreacted NaClO. The results showed that after 50 min the reaction at 1 g/L and 5 g/L of pulp consistency were not finished. At this stage only 0.68 mmol of NaClO/g and 1.20 mmol of NaClO/g have reacted, respectively.

Fig. 9b shows the OP properties produced using different pulp concentration during the TMO reaction. The carboxyl groups of OPs remain nearly constant, around 1 mmol COOH/g, when the consistency of pulp exceeds 10 g/L. However, when the pulp consistency is 1 or 5 g/L, the carboxylic groups of OPs decrease to 0.24 and 0.67 mmol COOH/g, respectively. These results explain the observed decrease in carboxyl groups when reusing the reaction medium, as shown in Fig. 1b and 4b.

The DPv values of the samples with 1 and 5 g/L of pulp are 400 ± 9 and 350 ± 9, respectively, which indicate that the depolymerization of these fibrils is much lower than in other cases with a similar depolymerization and an average value of 256 ± 11. This is attributed to the lower oxidation of the cellulose and the lower concentration of catalysts in the reaction medium. When compared with the data presented in

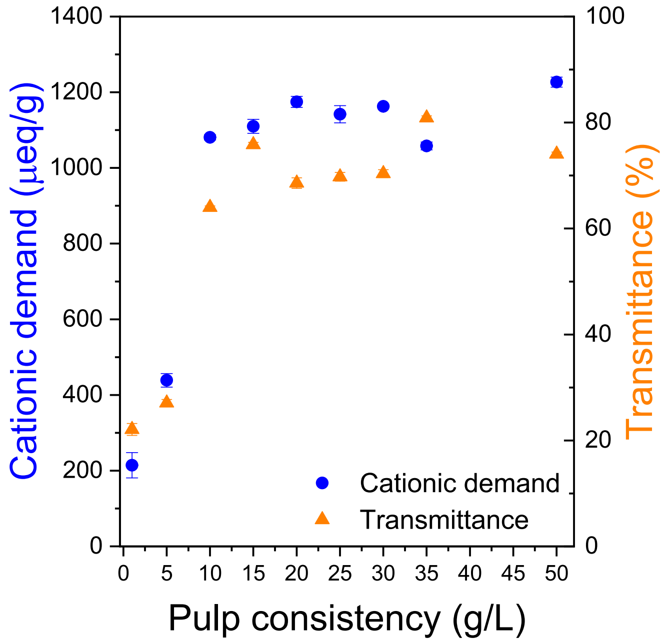

Fig. 10. Characterization of cellulose nanofibrils with different pulp consistency.

Fig. 4b of the Section 3.2, the DPv values are similar, indicating that low pulp concentration during the reaction reduces the oxidation efficiency. Furthermore, the AR of the samples follows a similar trend as the DPv, with the highest value observed for 1 g/L of pulp. This is attributed to the longer fiber chains resulting from the lower degree of oxidation in this case. Then, as the pulp concentration increases, the value of AR decreases because the fiber chains are fragmented into shorter lengths. The minimum AR value of 33 ± 1 is observed at 15 g/L of pulp consistency, and then it increases until is maintained above 40 ± 2 due to the decrease in fiber diameter while maintaining the same length of the polymeric chain. Finally, the pulp recovery remains relatively high, between 80 and 90 wt%, attributed to both a slight degradation of cellulose and hemicellulose, as well as the nearly complete degradation of Klason lignin.

The results shown in Fig. 10 indicate that a pulp consistency higher than 10 g/L during the TMO reaction leads values of transmittance and CD that remain practically constant around 72 ± 5 % and 1130 ± 58 μeq/g, respectively. These results are in line with the analysis of the OPs, where lower carboxyl group content in samples with 1 g/L and 5 g/L pulp consistency resulted in lower CD values. Moreover, when 1 g/L pulp consistency was used, CNFs were not obtained (diameter > 10 μm) even after the same number of homogenization passes as in the other experiments, as evidenced by TEM images (Fig. 11). Further analysis of TEM images revealed that the diameter distribution varied between 20 and 100 nm with 5 g/L pulp consistency, while it remained similar around 15–50 nm in the other cases.

3.5. *Reusing the TEMPO-mediated oxidation medium with higher pulp consistency*

As pulp consistency was identify as a key parameter, the recirculation of the reaction medium was carried out at a higher initial pulp consistency using 2.5/0.025/0.5 mmol/g. A pulp consistency of 30 g/L was finally chosen because higher values require a higher reactor stirring rate, resulting in higher energy consumption. Additionally, a higher pulp concentration would cause dead space in the reactor with a part of the cellulose not properly stirred.

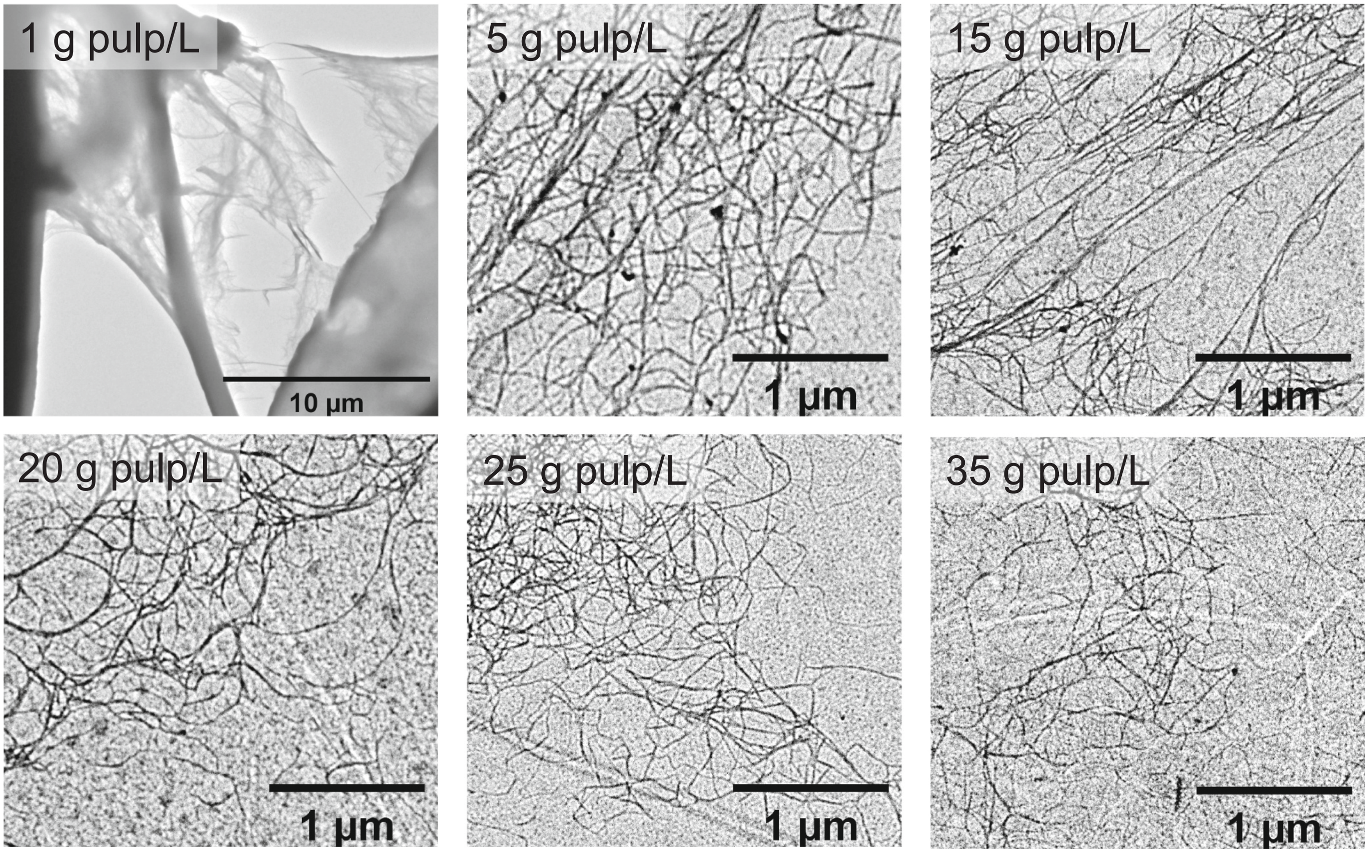

Fig. 11. TEM images of cellulose nanofibrils at different pulp consistency.

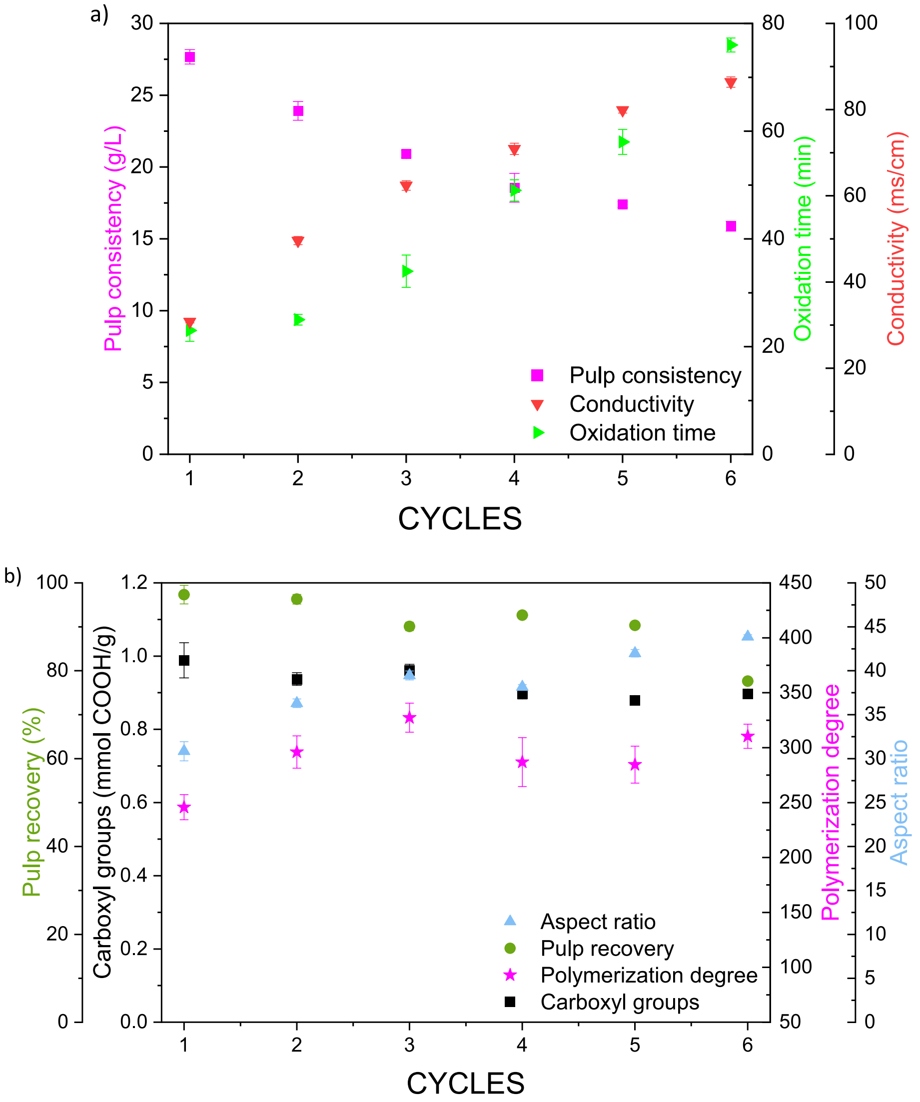

Fig. 12. Reuse of the TEMPO-mediated oxidation medium with higher pulp consistency: a) Parameters studied for monitoring the reaction; b) Oxidized pulp characterization.

The reaction was deemed complete when there was no further change in pH, and a titration was conducted to ensure all oxidant was consumed at the end of the reaction. Fig. 12a and b show the TMO monitoring parameters and OPs characterization. Although cycle 1 was not precisely at a pulp consistency of 30 g/L due to the addition of NaClO and NaOH, which dilutes the medium, subsequent cycles were maintained at same catalysts-pulp ratio. The oxidation time of TMO to consume all the oxidant increases from 23 min in cycle 1 to 76 min in the final cycle, mainly due to the dilution of the pulp from 27.7 to 15.9 g of pulp/L. Moreover, pulp recovery decreased from 97 wt% to 78 wt%, and the conductivity increased with the cycles because of the formation of salt as by-product. The carboxyl groups of OPs showed a slight decrease from 0.99 mmol COOH/g to 0.90 mmol COOH/g, which was not very noticeable due to the higher pulp consistency (> 15 g/L). DPv and AR increased gradually with the cycles from 246 ± 11 to 360 ± 18 and 31 ± 1 to 43.9 ± 0.3, respectively.

As shown in Fig. 13a, CD and transmittance remained stable, averaging 988 ± 76 μeq/g and 72 ± 5 %, respectively. Although the OPs obtained show a slight difference in their properties with the cycle, the CNFs produced present similar qualities as observed with CD and transmittance. As indicated in the TEM images (Fig. 13b), the diameter of the CNFs ranged from 10 to 40 nm in all cycles.

3.6. *Reusing the TEMPO-mediated oxidation medium adding fresh catalysts*

To minimize the negative effects of reusing the TMO medium, the addition of fresh catalyst was studied. The reaction conditions used for these experiments were 2.5/0.025/0.5 mmol/g and a reaction time of 23 min. Once the OPs were washed and stored, 75 % of the initial volume was recovered and used in the next cycle. As TEMPO and NaBr are lost with the OP, it is necessary to add fresh catalysts (25 % of initial volume) in each cycle to maintain the pulp consistency at 30 g/L and keep the catalyst-pulp ratio.

Fig. 14 shows the OP properties obtained in each cycle. The proportion of carboxyl groups in the OPs is almost invariable, close to 0.90 mmol COOH/g. Moreover, the values of pulp recovery and aspect ratio are remained stable around 93 wt% and 37 ± 2, respectively. In case of DPv, the number of monomers of anhydroglucose is between the range of 180 and 220 without significant differences. As shown in Fig. 15a, CNFs produced through different cycles present similar properties. The values of CD and transmittance are similar for 6 cycles, averaging 1033 ± 58 μeq/g and 82 ± 4 %, respectively. CNFs achieved are homogenous and highly fibrillated with the average diameter of 20 nm as shown in TEM images (Fig. 15b).

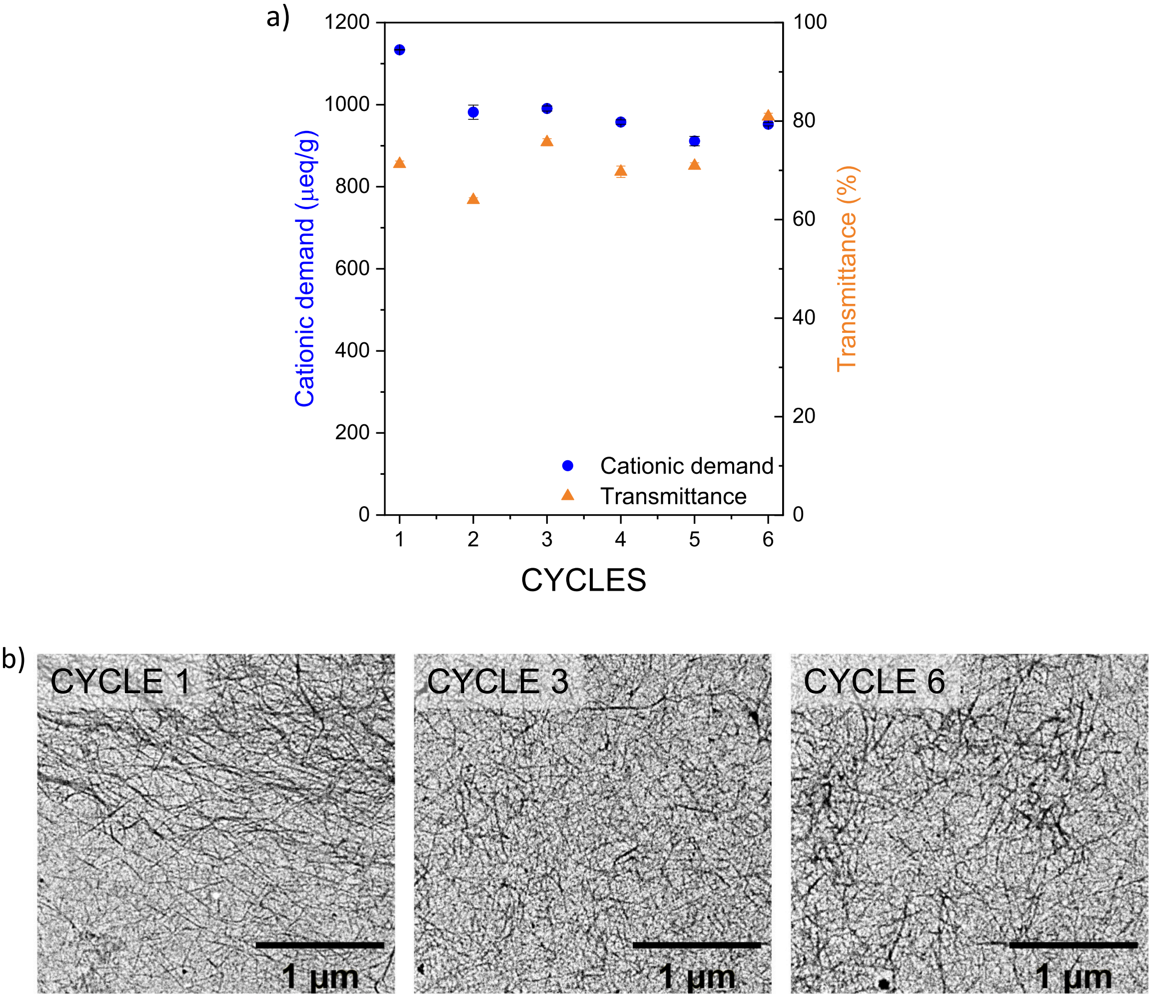

Fig. 13. Characterization of cellulose nanofibrils with the number of cycles of TEMPO-mediated oxidation with higher pulp consistency: a) Cationic demand and transmittance; b) TEM images.

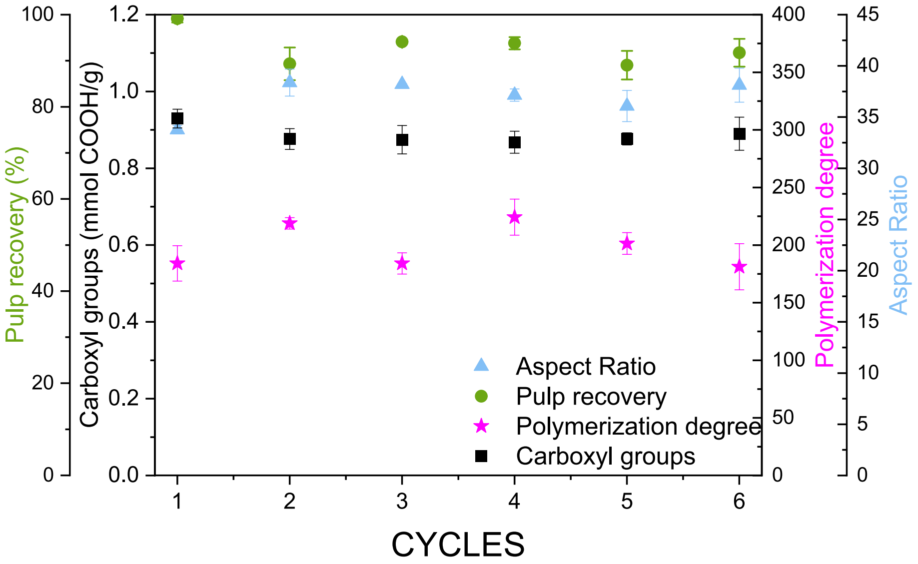

Fig. 14. Reuse of the TEMPO-mediated oxidation medium by adding fresh catalysts: Oxidized pulp characterization.

Compared to previous results obtained with Sanchez-Salvador, Monte, et al. (2021), that reuse the 75 % of reaction medium with TMO conditions (5/0.1/1 mmol/g) at 10 g of pulp/L and a reaction time of 50 min, our optimized conditions not only allow us to further reduced the doses of TEMPO and NaBr (75 % and 50 % respectively) but also to triplicate the production of OPs and reduce the reaction time to 23 min.

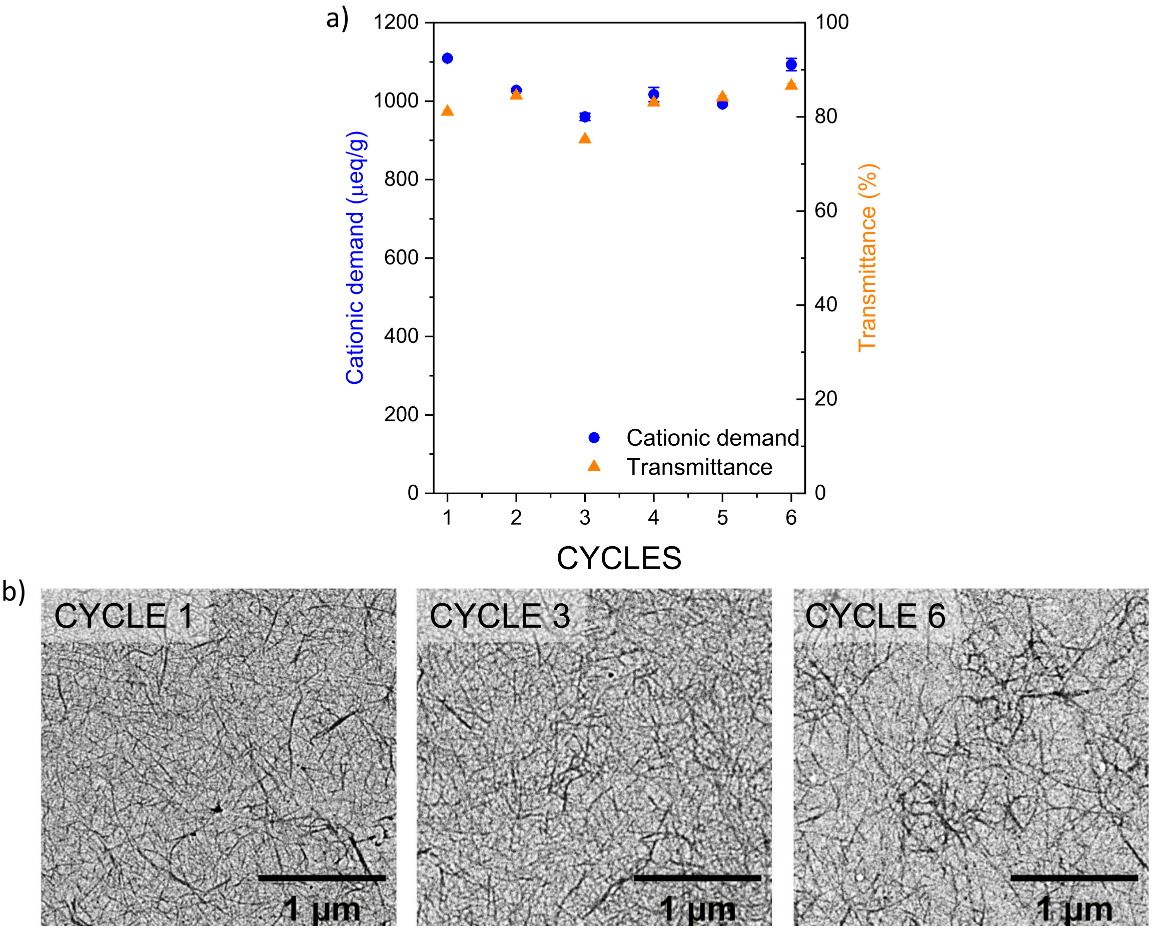

Fig. 15. Characterization of cellulose nanofibrils with the number of cycles of TEMPO-mediated oxidation by adding fresh catalysts: a) Cationic demand and transmittance; b) TEM images.

Compared to the conventional conditions of Saito, it is possible to save the doses of TEMPO and NaBr in a 91 % and 81 %, respectively. Besides, the oxidation time is reduced by >80 % and the effluent volume by 88 %.

4. Conclusions

A better understanding of the key parameters that influence the TMO reaction allows to highly improve the sustainability of the CNF production process.

Results demonstrate the feasibility of achieving a threefold increase in CNF production while simultaneously reusing the reaction medium and maintaining the high-fibrillation degree of the CNFs. The new oxidation conditions lead to substantial savings of 91 % in TEMPO and 81 % of NaBr compared to the conventional process conditions. Moreover, the oxidation time is reduced to just 23 min and the volume of effluents in an 88 %.

It is demonstrated that the accumulation of salts resulting from side-reactions in the reaction medium has minimal effects on the properties of the oxidized pulp, while it led to an increase of up to 20 % in the transmittance of the CNFs due to the network swelling. On the other hand, pulp consistency in the reaction is the key parameter that influences the TMO reaction. By maintaining a pulp concentration of over 10 g/L, it is possible to preserve carboxyl groups and achieve shorter reaction times, resulting in improved efficiency. On the other hand, it is unnecessary to achieve high values of carboxyl groups, 0.9–1 mmol of COOH/g is enough to obtain highly fibrillated nanocelluloses as the fibers are electrostatically repelled and further oxidation is not required.

In summary, this study provides new valuable insights into the parameters that affect the TMO process and the recirculation of the TMO medium and their impact on the quality of the final nanocellulose product. The identification of these key parameters as well as the optimal reaction conditions is essential to enable the implementation of this sustainable process at an industrial scale to unlock the future potential for engineered sustainable materials.

CRediT authorship contribution statement

Hongyu Xu: Investigation, Resources, Methodology, Visualization, Writing – Original Draft; **Jose Luis Sanchez-Salvador**: Validation, Methodology, Formal analysis, Writing – Review & Editing; **Angeles Blanco:** Conceptualization, Project administration and Writing – Review & Editing; **Ana Balea:** Supervision, Formal analysis, Writing – Review & Editing; **Carlos Negro:** Supervision, Conceptualization, Funding acquisition and Writing – Review & Editing.

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.

Data availability

Data will be made available on request.

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