



Valorization of waste paper sludge as a sustainable source for packaging applications

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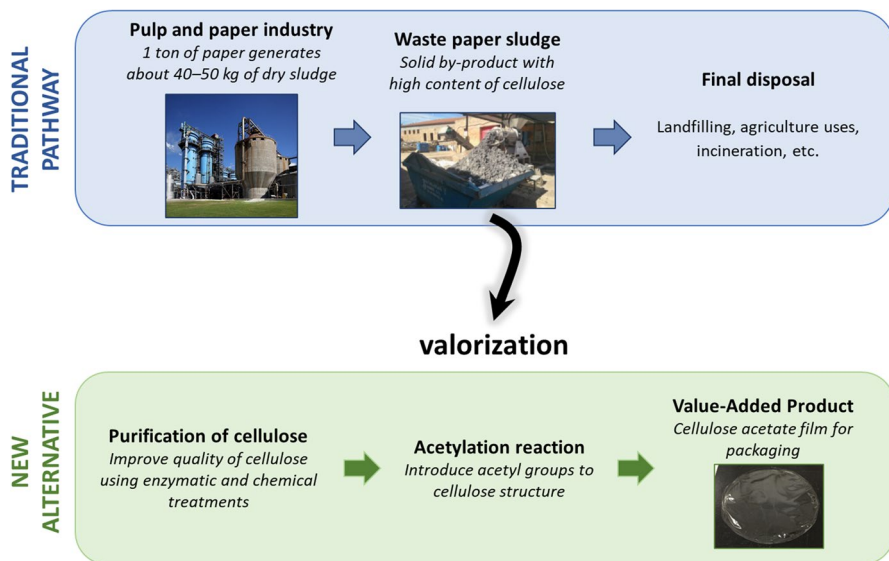
Abstract

Paper sludge consists mainly of wet short cellulose fibers that are lost during paper-making and of residual chemicals used in the manufacturing process that remain dissolved in the water. Each ton of paper generates about 40–50 kg of dry sludge, of which 70% is primary sludge. Paper production, which exceeded 400 million tons globally in 2020, generates vast volumes of solid waste. Primary sludge is usually fiber-rich and hence suitable to be recycled back into the papermaking process. However, if the sludge is to be disposed of in landfills, sustainable practices must be developed in order to recover the fibers as they are valuable source for manufacturing high value-added products. This study investigates the valorization of paper sludge discarded by a filter paper manufacturer, with the purpose of producing cellulose acetate films for food packaging. The process involves recovering cellulose fibers from the sludge, purifying them and through acetylation reaction produce cellulose acetate films. FTIR spectra confirmed successful acetylation of fibers and also that acetyl groups reduced the hydrophilicity of cellulose—the contact angle was increased to over 80° from 50° in native cellulose. The films exhibited very good water barrier properties at both 50% and 90% relative humidity (RH).

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Graphical abstract



Keywords Acetylation · Cellulose acetate · Films · Food packaging · Paper sludge · Valorization

Introduction

The paper industry generates vast volumes of waste paper sludge. In fact, the global production of paper was more than 400 million tons in 2020 [1] and each ton of paper generates about 40–50 kg of dry sludge. This solid by-product has to be collected and properly handled for appropriate disposal, and its final disposal is a problem for pulp and paper industry because it is costly and the environmental concerns related to management have gained increasing attention. The composition of sludge depends on the raw material, manufacturing process, chemicals and additives used, as well as on the nature of the end-product and the wastewater processing technologies employed [2]. Paper sludge includes three type of sources: (i) de-inking sludge produced from the de-inking process of recovered fiber; (ii) primary sludge which consists mainly of fibers, fines, and inorganic materials; and (iii) secondary sludge also called biological sludge, which is the residue from biological treatments of wastewater [3–5].

In the past, paper sludge was considered waste and largely disposed of by landfilling—a practice that persists. However, this disposal method is being increasingly discouraged or even banned due to the potentially significant environmental impacts on soil and water of the heavy metals it can contain. Landfills are required to comply with strict regulatory standards in order to avoid environmental problems arising

from soil and watershed contamination. Thus, in Europe, landfills must follow European Landfill Directive 1999/31/EC [6]. Sludge additionally contains a high proportion of moisture (30–80%) that makes it expensive to transport. Moreover, the transportation of sludge is costly due to its high moisture content that varies from 30 to 80%. Other sludge disposal or management practices include incineration to recover energy (biogas or bioethanol production), which accounts for 19% [6]; land application as an organic soil amendment or composting; and incorporation as an additive into cement, asphalt, wood or plastics [3, 7]. There are also some innovative uses of sludge including heat insulation materials, paper and wood adhesives, dried mixture for use as pesticides or fertilizers carriers in agriculture and building materials [6, 8–11].

The European framework directive on Waste 2008/98/EC, prioritizes recycling paper sludge over energy recovery or disposal in agricultural fields. Moreover, if landfilling is going to be reduced or even banned, current management practices will certainly prove not sufficient to manage the vast amounts generated each year [8, 12]. Therefore, in agreement with SDG 12, which pursues responsible consumption and production, then more sustainable practices such as valorizing sludge and recovering fibers will be needed [8]. Valorizing primary sludge, which is fiber-rich and accounts for 70% of all sludge generated in a paper mill, is an attractive choice to convert waste into a different, potentially useful material with a substantial impact on circular economy as it can reduce generation of solid sludge—and consumption of virgin raw materials as a result.

Interest in using cellulose to replace petroleum derivatives has increased substantially over the last decade, particularly as regards food packaging applications relying on so promising features as recyclability, biodegradability and availability [13–15]. However, bio-based packaging is not yet popular enough and most conventional food packaging is still made from fossil-based materials, including polyvinylchloride (PVC), polystyrene (PS), polyethylene (PE), polypropylene (PP) and Polyethylene terephthalate (PET). Synthetic polymers offer good strength and good barrier properties such as resistance to heat, moisture, oxygen, among others; however, they are not biodegradable, so their wide use has raised serious pollution problems worldwide [16]. Among all properties, protection against oxygen is a key factor. The appropriate packing atmosphere is needed to avoid color or taste deviations, oxidation of grease, formation of microorganisms or degradation of nutrients [17]. Meeting these requirements often entails using expensive multilayer co-extruded or laminated plastic films consisting of aluminum foil or oil-based barrier resins such as copolymers of ethylene vinyl alcohol (EVOH), aromatic polyamide (MXD6) and polyvinylidene chloride (PVDC) [18].

On the other hand, biobased packaging basically, uses biodegradable materials or biocompatible bionanomaterials, which provide sustainable alternatives to conventional choices; however, they fall short of gas, water and heat barrier properties, and also of mechanical strength [16]. Researchers can add environmentally friendly nanofillers like silica, starch, and cellulose into biodegradable polymers. These fillers have the potential to improve the mechanical strength, barrier properties, and thermal stability of packaging materials. Moreover, they can also offer additional features, including antimicrobial properties, oxygen scavenging

capabilities, and UV resistance, which can extend the shelf life of food products [19]. As reported by Credence Research, the market for biodegradable food packaging is likely to reach USD 7058.8 million by the end of 2023, with a compound annual growth rate (CAGR) of 11% over the period 2016–2023 [16]. Also, the price of pulp and paper varies considerably depending on purity and quality (~ \$0.1–0.6/lb.), but is still lower than that of commodity petroleum-based polymers (\$0.65–1.2/lb.), which makes lignocellulosic materials economically attractive [20]. In addition, cellulose polymer possesses other interesting properties such as biocompatibility, non-toxicity and good mechanical properties [21]. However, the hydrophilic character conferred by its hydroxyl groups, its porous structure and the resistance of cellulose to dissolve in typical solvents due to its well-structured hydrogen bond network and partially crystalline structure, somehow restrict its potential use. Nevertheless, cellulose applications can be extended by introducing new functional groups to reduce its hydrophilicity, disrupt its highly ordered regions, and open up pores and cavities to improve its accessibility and facilitate dissolution as a result.

Acetylation is a common chemical modification in which acetyl groups (CH_3CO^-) react with the surface hydroxyl groups ($-\text{OH}$) in cellulose, making its surface less hydrophilic. The acetylation process depends on the fiber accessibility and the susceptibility of $-\text{OH}$ groups in its crystalline and less crystalline domains of cellulose [22]. The more accessible fibers are, the easier it is for the reactants to diffuse into the interior of the network. The generic methods for acetylation are those in heterogeneous (in fiber dispersions) and homogeneous (in solution) phase. Cellulose acetate (CA) is commercially produced by reacting high quality cellulose fibers, namely, dissolving grade pulps, derived from cotton or wood (α -cellulose content of $>95\%$) with excess of acetic anhydride (typically 5–15 wt%), in acetic acid using sulfuric acid as a catalyst [23–25]. The extent of acetylation is measured as the so-called degree of substitution (DS), which is the average value of acetyl groups replacing the hydroxyl groups in the anhydroglucose units (AGU) of cellulose. Although CA can be produced with different range of DS, the most common level is a DS of 2.5 due to good solubility in common solvents, molecular weights, and melt properties. These interesting properties allow CA to be used in a variety of consumer products including cigarette filters, textiles and apparels, plastics, photographic films, membranes, and others [26]. In any case, the dominant application segment for the global cellulose acetate market is cigarette filters, which accounted for over 80% of the market share in the past few years, followed by textile and apparel.

Recently, cellulose acetate was reported to be a suitable material for fabricating objects with complex geometries by 3D Printing [27]. However, cellulose acetate fibers have certain drawbacks such as poor fiber strength, abrasion resistance and thermal retention [28]. Importantly, in terms of biodegradability, acetyl groups require the presence of esterases enzymes for initial biodegradation, whereas native cellulose can be directly biodegraded by cellulases. Moreover, cellulose acetate is photochemically degraded by UV wavelengths shorter than 280 nm, but has limited photodegradation in sunlight due to the lack of chromophores for absorbing UV light, although many consumer products have additives, such as titanium dioxide, that can significantly boost photodegradation [26]. The global cellulose acetate

market was USD 6.15 billion in 2020 and is expected to reach USD 10.25 billion by 2028.

This study focuses on the valorization of waste paper sludge, discarded by a filter paper manufacturer, by recovering fibers and reusing this source to produce cellulose acetate films by means of a casting technique. The films were compared with commercial cellulose acetate films and assessed in terms of hydrophobicity, barrier and optical properties, with a view to their potential use in food packaging applications. To enhance the efficacy of acetylation, the recovered fibers underwent initial conditioning and purification processes in order to increase cellulose content and reactivity.

Notably, our research not only addresses the critical challenges of waste paper sludge management but also explores sustainable alternatives for packaging materials. Unlike prevalent revalorization methods that often focus on agricultural use or incorporating the recovered mineral compounds into building materials, ceramics and cements, our work emphasizes the exploration of cellulose fiber recovery—an aspect typically receives less attention.

Materials and methods

Materials

The starting material for this work, paper sludge, was obtained from the separation of suspended solids from the recycling drainage water circuit of a filter paper mill in Spain. The recirculated water system uses physical decantation to separate fiber pulp from white water. The water is passed through mesh and sand filters before sedimentation and then stored in a large tank for filtering, after which the clarified water is returned to the stock chest. By its side, the fiber stream that is deposited in the bottom of the decanter is recovered with a suction pump and the sludge is thickened before dewatering in a screw press separator (FAN PSS) (Fig. 1a). The concentrated solids thus obtained are considered waste and disposed of after treatment, and the manufacturer kindly supplied the sludge for research purposes.

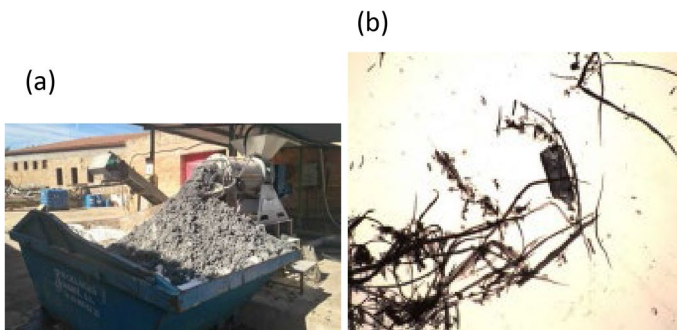


Fig. 1 a Waste paper sludge. b Optical microscope image of the waste paper sludge ($\times 20$)

Bleached virgin fibers consisting of 53% hardwood (USA and France), 38% softwood (Spain and Portugal) and 9% cotton linters (China) are the raw materials used to manufacture filter papers, and the waste sludge had same composition. An optical microscope image of the waste sludge is shown in Fig. 1, and its chemical characteristics are detailed in Table 1. The content in extractives was analyzed by Soxhlet extraction with acetone following TAPPI T204. Thus, an amount of about 2 g oven dried pulp was placed with 50 mL of acetone in a flask which fitted to an extractor. Then, acetone was allowed to boil (heating temperature 140°C) for 135 min. Finally, acetone was recovered and residual solvent in the pulp let to evaporate. The ash content (inorganic matter) was determined according to TAPPI standard T 211 om-02. Carbohydrate composition was determined using high performance liquid chromatography (HPLC). Samples were studied on a duplicate basis using a modified version of TAPPI 249 cm-09 test method (see “[Characterization of the raw sludge](#)” section).

A highly purified bleached fibers of cotton linter pulp, provided by Celsur (Spain), was also used as a reference sample and with comparison purposes.

The endoglucanase used was produced from *Cerrena unicolor* and supplied by Fungal Bioproducts® (Spain). The activity as U/g dry enzyme powder of the cellulase preparation was 1700 CMCase U/g and 680 U/g for the cellulase and xylanase activity on the cellulase, respectively. In both cases, the cellulase activity was determined by measuring the amount of reducing sugars released from carboxymethyl cellulose (CMC, Sigma-Aldrich) according to Somogyi–Nelson method.

All other chemicals were purchased from Sigma-Aldrich, were analytical grade and used without prior purification.

Washing of the sludge

Prior to valorization, the raw sludge was washed with 2% NaClO at 4% consistency for 2 h, and then filtered with a glass filter funnel and dried at room temperature.

Enzymatic hydrolysis and cold caustic treatment of the sludge

Recovered fiber was subjected to two different treatments, namely: (i) enzymatic hydrolysis with an endoglucanase, resulting in fibers that are denoted as E; (ii) cold caustic extraction before endoglucanase treatment, resulting in fibers that are denoted as CCE + E. The purpose of introducing an endoglucanase treatment was to

Table 1 Chemical characteristics of the raw sludge used as a raw material

	Ash	Extractives	Glucan	Xylan	ISO brightness	Fock reactivity
Raw waste sludge (WS)	6.47 ± 0.2	0.63 ± 0.01	86.8 ± 0.09	13.2 ± 0.09	73.83 ± 0.64	19.58 ± 3
Cotton linters	–	–	> 98	–	> 90%	~ 60

Results are expressed in %

boost cellulose reactivity, and that of cold caustic extraction to facilitate the dissolution of hemicellulose and increase the content in cellulose as a result.

The enzymatic treatment was performed in polyethylene bags that were placed in a laboratory water bath, at 10% solids (w/w) in 0.05 M sodium acetate buffer at pH 5.5 at 55 °C for 1 h and with 12 U/g oven dried pulp (odp) enzyme. The samples were periodically kneaded, and the reaction was stopped by washing the fibers with de-ionized water in a porous glass filter funnel of porosity grade 2. The cold caustic extraction was also conducted in a polyethylene bag. The treatment was performed at 10% (w/w) solids adjusted with 9% (w/v) NaOH at 25 °C for 1 h. Treated fibers were washed with de-ionized water to neutral filtrate pH [29].

Acetylation of cellulose

The resulting purified samples were submitted to homogeneous acetylation reaction. For this purpose, 2.5 g oven-dried pulp (odp) of respective purified sample was disintegrated and then filtered using a filter paper (Whatman 1) for water removal. After, 50 mL of acetic acid (99.7% w/w) was added to the sample, stirred 5 min and then filtered in a glass filter funnel. This step was done by duplicate. After filtration, 45 mL of acetic acid and 0.25 mL sulfuric acid (95% w/w) were dropped into the sample and stirred for 1 min. Then, 5.35 g Ac₂O/g dried fiber (\approx 12.5 mL Ac₂O) was added and continuously stirred for 30 min at room temperature. The reaction was quenched with the addition of 6.25 mL of distilled water and acetic acid at a ratio of 3:7 v/v, respectively. Finally, cellulose acetate (CA) was obtained by pouring the viscous reaction mixture into distilled water obtaining a continuous droplet and with constant stirring. With precipitation, cellulose acetate was regenerated. The obtained product was washed with distilled water until neutrality and subsequently dried using a freeze-drying [30].

Film production

Cellulose acetate (CA) obtained in the previous step was used to prepare transparent films by means of a casting method. Dried cellulose acetate was dissolved in acetone in order to obtain a concentration of 8 wt%. The solutions for film casting were firstly centrifuged at 6000 rpm for 10 min, then the supernatant was carefully transferred and centrifuged again at 2000 rpm for 5 min. The films were cast by pouring the transparent solution onto a glass plate, spread uniformly and dried in a vacuum desiccator for at least 2 h. All films were kept in the desiccator until use.

Characterization of the raw sludge

The starting material was characterized in terms of ISO brightness (ISO 2470:2009), viscosity (ISO 5351:2004), cellulose reactivity by Fock's method [31] and carbohydrate composition.

Carbohydrate composition of original recovered sludge and the resulted purified pulps were determined using high performance liquid chromatography (HPLC).

Samples were studied on a duplicate basis using a modified version of TAPPI 249 cm-09 test method. Hydrolysis was carried out in two steps: (i) A strong hydrolysis step with concentrated sulfuric acid. Approximately 50 mg of sample with known moisture content was treated with 5 mL of H₂SO₄ 72% and kept at 30 °C for 1 h with gentle stirring, (ii) A mild acid step at high temperature. Tube contents were put into 250 mL-flasks and diluted to 4% H₂SO₄. Flasks were put into an autoclave for 1 h at 103 kPa. Solution was then cooled and passed through a glass filter to remove insoluble lignin. Prior to HPLC analysis samples were filtered using a 0.45 μm pore size Whatman membrane. Chromatographic analysis was performed using a 1200 Agilent HPLC instrument furnished with a Biorad Aminex HPX-87H ion-exchange column. Concentrations were calculated by interpolation into calibration curves ran from standards of glucose, xylose, rhamnose and arabinose.

Determination of the degree of acetylation

Fourier transform infrared (FTIR) spectra for cellulose acetate films were analyzed in duplicate at room temperature using an ATR-FTIR spectrophotometer (Spectrum 100, PerkinElmer, USA). Each spectrum was recorded in the range of 400–4000 cm⁻¹ and 64 scans were run at a 1 cm⁻¹ resolution. According to Hurlbut [32], FTIR spectra were used to determine the degree of substitution (DS) of the films.

Firstly, the percentage of the acetyl group (% AG) of acetylated films is calculated from the ratio of peak absorbance of C=O bond stretching at 1750 cm⁻¹ and O–H bond at 3400 cm⁻¹ (R), following Eq. (1):

$$\% \text{ AG} = 43.69 \times (1 - e^{-0.974 \cdot R})^{2.153} \quad (1)$$

Secondly, the degree of substitution (DS) is obtained from the value of the percentage of acetyl groups (% AG) through Eq. (2).

$$\text{DS} = \frac{162 \times \% \text{ AG}}{43 \times 100 - ((43 - 1) \times \% \text{ AG})} \quad (2)$$

where 43 is the molar mass of the acetyl group, g mol⁻¹ and 162 is the molecular weight of the anhydroglucose unit.

Characterization of films

Barrier properties

Oxygen permeability (OP) was measured using MOCON OX-TRAN® Model 1/50 with an atmospheric oxygen concentration of 100% at 23 °C temperature and at two different RH conditions, 0 and 90%, in 24 h. The water vapor transmission rate (WVTR) of the films was measured according to ISO 2528 (2017) at 25 °C and at two relative humidity conditions, 50 and 90%. Each film sample was placed in a glass cup containing calcium chloride (CaCl₂) salt as a desiccant. Then, the set was sealed using hot glue

stick and parafilm in order to prevent water vapor penetration, and placed in a climatic chamber under controlled conditions. Samples were weighed at different intervals of 24 h for more than 80 h. The WVTR ($\text{g m}^{-2} \text{day}^{-1}$) was calculated using the following Eq. (3):

$$\text{WVTR} = \frac{m \times 24 \times 10^4}{S \times t} \quad (3)$$

where m is the increase in mass, in grams, of the assembly during the time t ; S is the area in the tested surface of the test piece in cm^2 , and t is the total duration, in hours, of the last two stable exposure periods. A minimum of 3 replicates were tested for each film sample, and the average values were represented.

Finally, the sample's WVP was calculated using Eq. (4), according to Babae et al. [33]:

$$\text{WVP} = \frac{\text{WVTR}}{P(R1 - R2)} \times x \quad (4)$$

where x represents the film thickness (μm), P indicates the water saturation vapor pressure at 25°C (3.17 kPa), $R1$ shows the relative humidity in the chamber (50% or 90% RH), and $R2$ refers the relative humidity in the cups (0% RH).

Hydrophobicity

Wettability of acetylated films was assessed in terms of static water contact angle (WCA). WCA measurements were performed using a Dataphysics OCA15EC contact angle goniophotometer using an image capture ratio of 25 frame/s. A $4 \mu\text{L}$ water drop was delivered to the sample surface, and at least five measurements were performed for each sample. Water absorption behavior was evaluated using the water drop test (WDT) (TAPPI T835) in which a drop of water is deposited on the surface of the film and then it is measured the time that it took to disappear the specular gloss of the drop of water.

Optical transparency

Film transparency was calculated as follows [34, 35]:

$$\text{Transparency (\%)} = \log \%T_{600}/x \quad (5)$$

where $\%T_{600}$ is the percentage of transmittance at 600 nm and x is the thickness of film (mm). The UV blocking capacity was determined by measuring the light transmittance at 280 nm.

Figure 2 depicts the experimental procedure followed in this work.

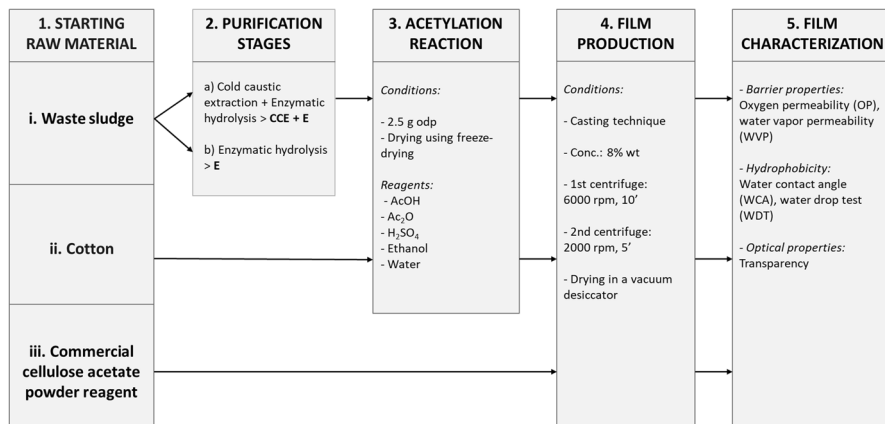


Fig. 2 Schematic illustration of the experimental plan

Results and discussion

Precursor fiber characterization

Cellulose acetylation process is based on the reaction of hydroxyl groups ($-OH$) of cellulose with acetic anhydride as activator and sulfuric acid as a catalyst, giving the introduction of acetyl functional groups. Therefore, in order to achieve good substitution, it is desired to have a high content of cellulose and good accessibility of hydroxyl groups by the reagents that are involved in the reaction. As known from the literature, hemicelluloses are undesirable impurities that affect the processability and the quality of final product, therefore relative low hemicelluloses (1 to 10%) are recommended [36, 37]. This potential problem was addressed here by subjecting raw waste sludge with 13% of xylan to different conditioning and purification treatments that included: (i) enzymatic hydrolysis and a (ii) sequential treatment using cold caustic extraction, followed by enzymatic hydrolysis. Cold caustic extraction allows to dissolve hemicelluloses selectively [37, 38], while endoglucanase randomly cleaves β -1,4-glycosidic bonds in polysaccharide chains. The enzyme preferentially degrades amorphous cellulose located on the fiber surface and in between microfibrils, thereby increasing exposed crystalline surfaces, and the swelling ability and reactivity of pulp [39, 40], which in turn allows pulp viscosity to be finely adjusted [39, 41–43].

Carbohydrate composition was determined by HPLC. As can be seen from Table 2, the most efficient treatment for removing hemicelluloses was achieved by cold caustic extraction, which reduced their content, to 9.9%, counted as xylan fraction, which means a 25% of hemicellulose removal with respect to the original sludge. The sequential treatment (CCE + E) failed to further extent hemicellulose removal relative to the alkaline treatment, leading to a final content of 9.6% xylan, which correspond to a total hemicellulose removal of 27%, with respect to original sludge. The endoglucanase treatment did not provide a significant

Table 2 Viscosity and carbohydrate composition results

	Raw waste sludge (WS)	Enzymatic hydrolysis (E)	Cold caustic extraction (CCE)	Cold caustic extraction + Enzymatic hydrolysis (CCE+E)	Cotton
Viscosity (mL/g)	620±25	273±12	314±1	256±23	694±38
Chain scission (CS)	–	1.6	1.2	1.8	–
Glucan (%)	86.8±0.09	88.3±2.52	90.1±0.03	90.4±0.01	98.8±0.1
Xylan (%)	13.2±0.09	11.7±2.52	9.9±0.03	9.6±0.01	1.2±0.1

reduction of hemicellulose since the final content was 11.7%, in comparison to 13.2% of original sludge. The result suggests that the enzyme was not involved in the extraction of hemicelluloses—rather, as reflected in the viscosity measurements, the reduction can be ascribed to considerable cellulose degradation. Significantly, samples obtained from the sequential treatment (i.e., cold caustic extraction treatment and the combined treatment) showed an acceptable glucose content, above 90%.

Based on viscosity values (Table 2), all purification treatments caused an important degradation of cellulose chain with respect to original sludge. Endoglucanase enzymes are known to randomly cleave β -1,4-glycosidic bonds in polysaccharide chains, so they are likely to degrade amorphous cellulose located on the fiber surface [39, 40]. As observed by other authors [44], the mechanism of action of endoglucanase substantially reduced the degree of polymerization and led to a viscosity loss of 56% (a final viscosity of 273 mL/g) as a result. On the other hand, cold caustic extraction selectively dissolved hemicelluloses [38, 45], but also caused some cellulose degradation. The effect brought by cold caustic extraction itself was significant, although smaller than the enzymatic hydrolysis, reaching a viscosity loss of 49%. Interestingly, the combination of cold caustic extraction and the endoglucanase treatment resulted in the greatest viscosity loss, nearly 59%. These results suggest that cold caustic extraction slightly enhanced the subsequent action of endoglucanase. Unfortunately, such low viscosity values may somehow limit the potential applications [39, 46].

Cellulose degradation can also be assessed by chain scission values (CS), as calculated from intrinsic viscosity results by using the equation $DP^{0.85} = 1.1 \eta$ of Evans and Wallis [47] (SCAN-CM 15:88). Bouchard et al. [48] define the number of scissions in the cellulose chain as that of chain cleavage steps per initial cellulose chain:

$$CS = \frac{DP_o - DP}{DP}$$

CS values greater than 1 reflect a major cutting effect, associated to cellulose degradation.

In a previous work, Quintana et al. [29] explored the use of endoglucanase to convert biobleached sulfite pulp to dissolving pulp. They examined the effects provided by a CCE treatment and a CCE + E. Although same treatment conditions were followed in both works, different effects were observed. Biobleached sulfite pulp had an initial hemicellulose content of 11.7% and a viscosity of 453 mL/g. The viscosity loss caused by endoglucanase was about 23.2%, with no appreciable contribution of CCE or CCE + E. As confirmed by CS data, the enzyme acted completely differently on waste sludge and biobleached fibers. Thus, waste sludge suffered a major cutting effect (CS = 1.6), that was not observed in the biobleached sulfite pulp (CS = 0.4). In conclusion, cellulose chain was preserved to a much greater extent than here, where cellulose degradation was about 56, 49 and 59% for E, CCE and CCE + E treatment, with respect to raw sludge. In terms of hemicellulose removal on biobleached sulfite pulp, CCE was responsible to

eliminate 42% of hemicellulose, while endoglucanase contributed to 37% and the sequential treatment 50%. Definitely, hemicellulose was more efficiently removed from biobleached sulfite pulp (down to a content below 6%) than it was from the waste sludge.

Cotton was used as reference sample since has high content of cellulose, measured as glucan (98.8%), and suitable viscosity values (694 mL/g).

The success of acetylation reaction was assessed by FTIR spectroscopy. As shown in Fig. 3, all spectra were similar, with only slight changes in intensity. The structural changes of acetylated fibers were confirmed by the presence of three new bands characteristic of the acetyl group vibration at about 1741, 1368 and 1220 cm^{-1} . The peaks located at 1741 cm^{-1} were attributed to the C=O stretching of carbonyl in the ester bonds. The peaks located at 1368 cm^{-1} were assigned to C–H symmetrical deformation in methyl group. The vibration peaks between 1259 and 1277 cm^{-1} corresponded to C–O stretching of the acetyl group. The absence of peaks in the 1840–1760 cm^{-1} region confirmed that there was no residual, unreacted acetic anhydride in the acetylated fibers [49–52]. The acetylating agent, acetic anhydride (AA) has no swelling power on crystalline cellulose and therefore acts as surface reactant in crystalline region [49]. The degree of substitution was calculated according to Eq. 1, and all acetate samples showed a high DS, around 2.9, confirming the obtention of cellulose triacetate.

The water contact angle (WCA) measurement is the common parameter used to evaluate the surface hydrophobicity of the films. It is defined as the angle at which the liquid/vapor interface meets the solid substrate when water is used as a testing fluid [53]. WCA is mainly affected by surface chemistry and roughness of material [54]. Assessing the absorption behavior of surfaces is interesting, particularly when food-packing materials are used in environments with high humidity [55]. Figure 4 shows the WCA values for various cellulose acetate films. Acetylated cellulose was expected to have higher water contact angle values than native cellulose because

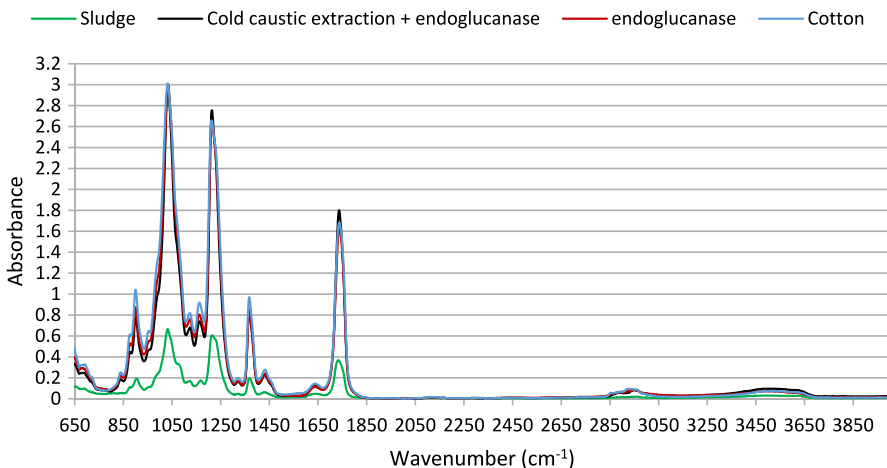


Fig. 3 FTIR spectra for acetylated samples

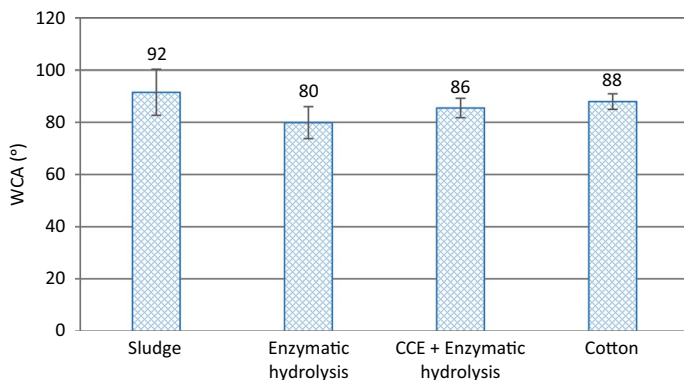


Fig. 4 Water Contact Angle (WCA) of cellulose acetate films of different samples

replacing surface hydroxyl groups with acetyl groups decreases the hydrophilicity of cellulose. As references, a paper from TCF eucalyptus pulp had a contact angle of 34° , without water resistance capacity since the absorption of water drop took less than one minute. Also, a bacterial cellulose (BC) film from *K. xylinus* had a WCA of 49° but took up to 69 min to absorb the drops [56]. On the other hand, acetylated films had $\text{WCA} > 80^\circ$ with only slight differences among samples, but similar acetylation profiles and same DS values. The highest contact angle was that for cotton, followed by that for the material resulting from combined treatment (CCE + E) and the enzymatic treatment alone (E). These results can be correlated with the glucan content of the samples, among which cotton presented the highest glucan content (98.8%)—the others had a glucan content around 90% and 88%, respectively. The presence of substantial amounts of hemicelluloses can prevent acetyl groups from distributing uniformly on the film surface and result in differences in WCA. The acetylated sludge had $\text{WCA} > 90^\circ$, a surprising result that is inconsistent with the previous explanations since the hemicellulose content of the sludge was higher than that of the purified samples (13% vs 9%). Therefore, WCA must also be affected by film appearance (unevenness or defects) and influenced by surface roughness [57]. Moreover, according to air permeability results (measured by the Bendtsen method, ISO 5636-3:2013), sludge sample showed the highest resistance to air (12 mL/min vs 42, 59 and 30 mL/min for Endoglucanase, CCE + Endoglucanase and cotton samples, respectively) giving as a result a more integrated and denser structure. These results are also in agreement with oxygen permeability property.

According to literature, materials with contact angle values higher than 90° are considered hydrophobic. The purified acetylated films exhibited values below 90° , but in terms of water absorption resistance, measured as the time that it took the specular gloss of a drop of water deposited on the surface of the film to disappear, was substantial. As shown in Table 3, the films took above 120 min to absorb water, which is clearly much longer than the time taken by native fiber-based materials.

As shown in Fig. 5, both films appeared highly transparent to the naked eye. Also, when the given films were analyzed using visible wavelength, the transmittance

Table 3 Water contact angle (WCA) and water drop test (WTD) measurements

Sample name	WCA [°]	Time to absorb water drop [min]	Transmittance at 280 nm [%]	Transmittance at 600 nm [%]	Thickness [mm]	Transparency (Log %T600)/x
Raw waste sludge (WS)	92 ± 3	> 60	–	92 ± 3	0.042	39.2
Enzymatic hydrolysis (E)	80 ± 6.1	> 120	68 ± 2.4	80 ± 6.1	0.051	21.8
Cold caustic extraction + Enzymatic hydrolysis (CCE+E)	86 ± 4.7	> 120	71 ± 0	86 ± 4.7	0.061	45.6
Cotton	88 ± 3.7	> 120	72 ± 1.4	88 ± 3.7	0.050	37.5

Optical transmittance at 600 nm for the acetylated films



Fig. 5 Visual appearance and qualitative transparency of acetylated samples

of all acetylated films at 600 nm was more than 50%, reaching values between 80 and 92%, so they exhibited good optical transparency. These results are in accordance with high transmittance of CA in the visible wavelength, as has been previously reported in the literature by Rowen [58] and Orelma [59]. In the UV range (250–400 nm), a band at 280 nm was found with a transmittance of around 70% indicating that films blocked UV light penetration to some extent (Table 3). This is an essential property for packaging films, because UV light can accelerate the oxidation of food, and make it prone to deterioration and nutrient losses as a result [60].

One of the greatest disadvantages of cellulose-based films is their high moisture sensitivity, which results in a high water vapor transmission rate (WVTR) [13, 14]. This is due to the amorphous structure of cellulose and the presence of surface hydroxyl with strong hydrophilic nature [53, 61]. However, introducing acetyl groups by homogeneous acetylation can be expected to improve water vapor barrier properties, mainly due to increase in hydrophobicity as evidenced by the increase in water contact angle. In fact, a study of Rodionova et al. [49] demonstrated that the WVTR of pure nanofibrillated cellulose (NFC) films was decreased from 234 to 167 g m⁻² day⁻¹ after 30 min of acetylation treatment, although at 3 h of acetylation the WVTR was increased. These findings are explained by two facts: the initial fall in WVTR may be caused by a decreased solubility of water in the amorphous parts of the microfibrillated cellulose (MFC) structure as more acetyl groups are incorporated; while the subsequent increase in WVTR may be caused by slightly more open network structure resulting from the replacement of hydroxyl groups by acetyl groups reducing the hydrogen bonding between the microfibrils and leading to an increased pore volume in the films [49]. Minelli et al. [62] observed that the use of carboxymethylated pretreated CNF produced a more uniform and less porous film than enzyme pretreated CNF and resulted in better water vapor barrier property below 80% RH.

Overall, the WVTR remained quite low (below 180 g/m² day) at low relative humidity (50%), but at severe humidity conditions (up to 90%), the water vapor transfer rate increased drastically, with an average extend of about 500% (Fig. 6). As relative humidity increases, the saturation of water binding sites increases, and cause high swelling of cellulose. As a result, cracks can be developed in the cellulose matrix and consequently increase the water vapor transfer rate in the films [63, 64]. The best WVTR values at both relative humidity levels (50% and 90%) were obtained with cellulose acetate fibers, and the worst with waste acetylated sample without any pre-treatment. The difference between the two amounted to 31% at 50% RH and 30% at 90% RH. Interestingly, the combined treatment (CCE + E) provided

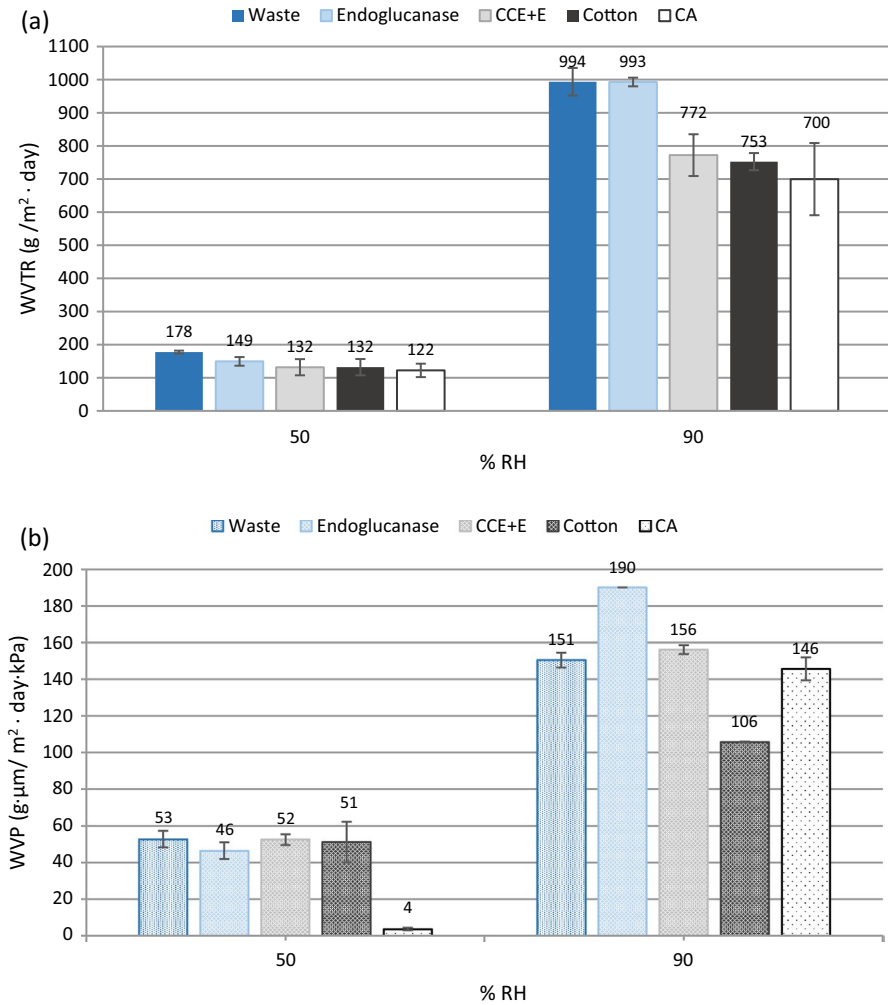


Fig. 6 **a** Water vapor transmission Rate (WVTR) and **b** water vapor permeability (WVP) at 50 and 90% relative humidity (RH) of cellulose acetate films of different samples

films with the same WVTR as cotton films at 50% RH, and a difference of only 2.6% at 90% RH, which is in agreement with the slightly differences in contact angle results.

Accurately comparing results between films of different nature entails considering their thickness and their vapor pressure at 25 °C. So, converting WVTR data to water vapor permeability (WVP) data led to values below 100 g µm/m² day kPa, which, according to Wang [65] correspond to films with a high water vapor barrier capacity (40–400 g µm/m² day kPa). Interestingly, no clear differences in WVP at 50 RH% between samples were found, with exception of CA, which exhibited a very high-water vapor barrier property (<40 g µm/m² day kPa). At 90% RH, water

vapor permeability was significantly reduced, but still fell in the grade of high barrier capacity. Waste, CCE+E and CA samples were similar in this respect, while cotton exhibited the best results and the waste sample the worst.

Since oxygen is one of the main cause of food spoilage by effect of lipid oxidation and microbial growth, it is essential for food packaging films to develop adequate oxygen barrier capability [66]. Currently, most commercial food packaging materials are made of polyethylene terephthalate (PET), which exhibits an oxygen transmission rate (OTR) of approximately $110 \text{ cm}^3/\text{m}^2\cdot\text{day}$ [55, 67]. According to ASTM F1927 standard, films possess a low oxygen barrier capacity if they have a transfer rate $>200 \text{ cm}^3/\text{m}^2 \text{ day atm}$, when tested with an oxygen partial pressure difference of 1 atm [65]. As shown in Fig. 7, the acetylated films did not exhibited good barrier to oxygen, and this poor response can be attributed to inadequately compact and dense structure, which let oxygen to diffuse [61]. Rodionova [49] found that the OTR of acetylated CMFs was bigger as the degree of substitution was higher. The

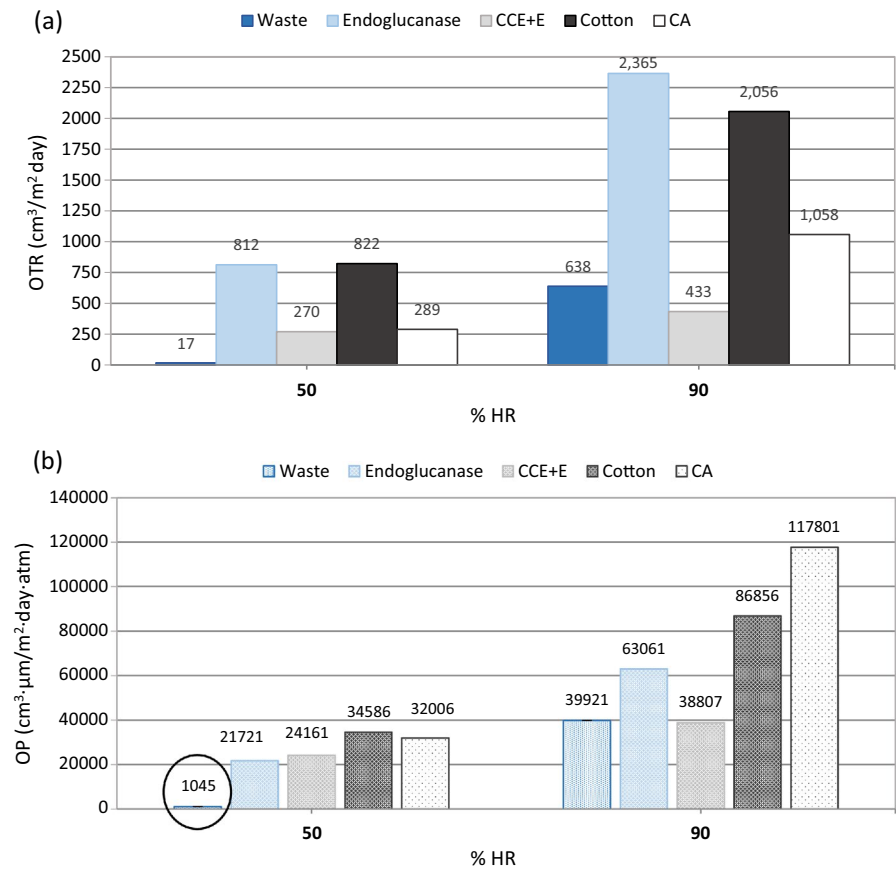


Fig. 7 a Oxygen transmission rate (OTR) and b Oxygen permeability (OP) at 50 and 90% Relative Humidity (RH) of cellulose acetate films of different samples

more hydrophobic nature of the modified cellulose decreases the cohesive energy density leading to increasing oxygen gas transmission [68]. Indeed, cellulose ester films have poorer oxygen barrier properties than other cellulose derivative films with more hydrophilic functional groups [69]. At 50% RH, which correspond to common atmospheric conditions, the acetylated waste sample showed interesting result, while CCE+E and commercial acetate samples showed minimally acceptable values but far from those of PET. From 50% RH to 90% RH, all samples exhibited increased oxygen transmission rate values, although CCE+E sample experienced the smallest variation (+60%) and its OTR value fell in the medium range of barrier capacity on the scale of Abdellatief [70].

Apparently, the previous definition fails unless film thickness is considered. Thus, Wang [65] suggested a classification of oxygen permeability (OP, $\text{cm}^3 \mu\text{m}/\text{m}^2 \text{ day atm}$) for packaging materials in five categories: poor (>40000), low ($4000\text{--}40000$), medium ($400\text{--}4000$), high ($40\text{--}400$) and very high (<40), without specifying a relative humidity conditions. Moreover, Hult et al. [71] define a material as “high oxygen barrier” if its oxygen permeability is less than $75 \text{ cm}^3 \mu\text{m}/\text{m}^2 \text{ day atm}$ at 25°C and 50% RH. Considering these classifications, all films were in the range of low barrier capacity with exception of waste acetylated sample at 50% RH. At 90% RH, the waste and CCE+E samples remained on low rating scale, but all others had a very poor oxygen barrier capacity. This limitation needs to be solved since adequate oxygen barrier properties are essential to preserve quality throughout the lifecycle of foods. Schmid et al. [17] developed a whey protein formulation coating with excellent oxygen barrier properties, almost comparable to those values offered by ethylene vinyl alcohol copolymers (EVOH). Other promising alternatives are bio-based laminates containing cellulose nanocrystals (CNCs), which provide outstanding gas barrier properties [18].

As shown in Table 4, other natural polymers such as starch and chitosan have a higher oxygen permeability than our samples. Polyethylene terephthalate (PET) is a

Table 4 Barrier properties of different polymers

Sample	Water vapor permeability (WVP) ($\text{g}/\text{m s Pa}$)	Oxygen permeability (OP) ($\text{cm}^3/\text{m s Pa}$)	References	Test conditions
Starch	3.87×10^{-10}	1.79×10^{-17}	[55, 72, 73]	–
Chitosan	$3.66\text{--}4.8 \times 10^{-11}$	1.3×10^{-14}	[65]	–
PET	3.3×10^{-12}	4.5×10^{-17}	[55, 72, 73]	23°C , 50% RH
Waste + acetylation	$6.1 \times 10^{-13}\text{--}1.74 \times 10^{-12}$	$1.2 \times 10^{-13}\text{--}4.6 \times 10^{-12}$		50% RH–90% RH
Endoglucanase + acetylation	$5.37 \times 10^{-13}\text{--}2.2 \times 10^{-12}$	$2.5 \times 10^{-12}\text{--}7.2 \times 10^{-12}$		50% RH–90% RH
CCE+E+acetylation	$6.07 \times 10^{-13}\text{--}1.8 \times 10^{-12}$	$2.8 \times 10^{-12}\text{--}4.4 \times 10^{-12}$		50% RH–90% RH
Cotton + acetylation	$5.9 \times 10^{-13}\text{--}1.22 \times 10^{-12}$	$4 \times 10^{-12}\text{--}9.9 \times 10^{-12}$		50% RH–90% RH
Commercial cellulose acetate	$4.1 \times 10^{-14}\text{--}1.69 \times 10^{-12}$	$3.6 \times 10^{-12}\text{--}1.3 \times 10^{-11}$		50% RH–90% RH

commercially available conventional petroleum-based food packaging material with ultrahigh barrier properties in the same order of magnitude as starch. However, in terms of water permeability, our samples exhibited the best results attributed to the presence of acetyl groups in the cellulose structure [55, 60, 67, 72, 73].

As shown in Fig. 8, the relationship between OP and WVP provided information about the index barrier properties. At 50% RH, under similar WVP results (in the range from 43 to 53 units), waste sample exhibited the best oxygen permeability, followed by Endoglucanase-treated sample (E). At similar OP levels, two groups were found, where endoglucanase and CA samples exhibited the best WVP results for each group. At 90% RH, the CCE+E and waste samples showed the best results in both properties, WVP and OP.

Conclusions

In this study, the sludge obtained from the treatment of effluents within the paper industry was evaluated with the aim of recovering cellulose fibers and utilized them as a source to produce acetate films for food packaging applications. To achieve high content of cellulose and improve the processability of acetylation reaction, the original sludge was firstly submitted to two different purification treatments. One treatment involved enzymatic hydrolysis with endoglucanase in order to improve the accessibility of cellulose, while the other one employed cold caustic extraction followed by endoglucanase treatment to remove residual hemicelluloses and improve cellulose accessibility. For comparative purposes, cotton fibers with high cellulose content (>90%) were used as a reference.

Then, fibers were modified through homogenous acetylation with the purpose to introduce acetyl groups and reduce the hydrophilic nature of cellulose. The successful achievement of the acetylation reaction was confirmed by FTIR spectra analysis and water contact angle measurements for all samples. In terms of barrier properties,

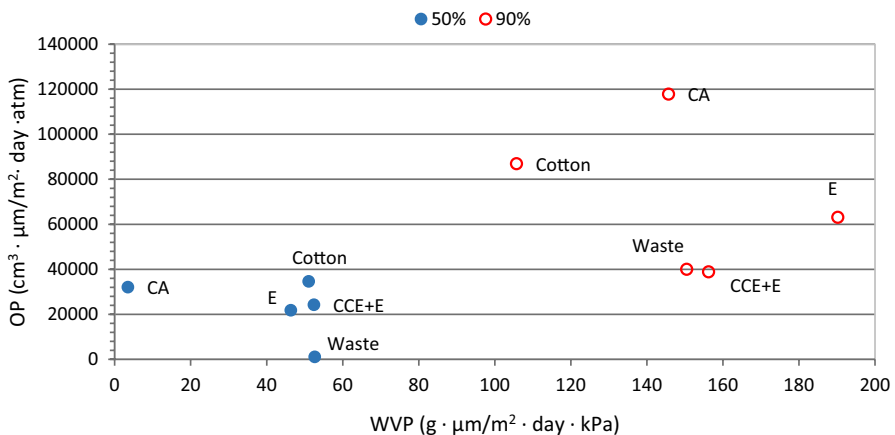


Fig. 8 Relationship between OP and WVP. Graphic was created with excel

the substitution of hydroxyl groups for acetyl groups increased the hydrophobic nature of cellulose, resulting in reduced water vapor transmission rates and providing results in the range of high vapor barrier capacity. However, the incorporation of acetyl groups decreased the cohesive energy density, leading to poor oxygen barrier capacity. Among all the studied samples, the original waste and sequential treated sample, CCE+E, exhibited the best properties, especially at 90% RH. Although the oxygen permeability should be improved to meet the desired level for food protection against spoilage and contamination, the valorization of rejected sludge for producing modified cellulose acetate films contributes to the circular economy and reduces the consumption of virgin feedstock.

Author contribution EQ: Design of the work, acquisition and analysis of data, interpretation of data, writing the main manuscript, editing. MBR and CV: Critical revision of the manuscript, validation of the final version.

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Data availability Data of the manuscript are available from the corresponding author on request.

Declarations

Conflict of interests The authors declare no competing interests.

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