

MIT Open Access Articles

Hydrophobic cellulose ester as a sustainable material for simple and efficient water purification processes from fatty oils contamination

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

Citation: Lavagna, Luca et al. "Hydrophobic cellulose ester as a sustainable material for simple and efficient water purification processes from fatty oils contamination." *Wood Science and Technology* 53, 1 (October 2018): 249-261 © 2018 Springer-Verlag GmbH Germany, part of Springer Nature

As Published: <https://doi.org/10.1007/s00226-018-1060-8>

Publisher: Springer Science and Business Media LLC

Persistent URL: <https://hdl.handle.net/1721.1/128903>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of Use: Article is made available in accordance with the publisher's policy and may be subject to US copyright law. Please refer to the publisher's site for terms of use.



Hydrophobic cellulose ester as a sustainable material for simple and efficient water purification processes from fatty oils contamination

Luca Lavagna¹, Roberto Nisticò^{1,*}, Simone Musso^{1,2}, Matteo Pavese¹

¹ Polytechnic of Torino, Department of Applied Science and Technology DISAT, C.so Duca degli Abruzzi 24, 10129 Torino, Italy.

² Massachusetts Institute of Technology, 77 Massachusetts Ave, 02139, Cambridge, MA, USA

* Corresponding author: E-mail: roberto.nistico@polito.it

Abstract

In this study, cellulose fibers were chemically functionalized under mild conditions by introducing palmitate groups in order to produce a hydrophobic cellulose-based ester. The effectiveness and the degree of functionalization were evaluated by FTIR spectroscopy and thermo-gravimetric analysis (TGA), whereas the structural integrity was confirmed by XRD measurements. The prepared materials were tested in water remediation processes from fatty oils mixtures from both animal (cod liver oil) and vegetable (sunflower oil) sources. Experimental kinetic measurements, rationalized by means of the most common models, show that the best performances were reached by the sunflower oil, hence proving the promising application of such green materials as a sustainable alternative tool for oil-water remediation processes.

1. Introduction

According to the literature (Dave and Ghaly 2011; Nisticò et al. 2017; Nisticò 2017; Nisticò et al. 2018; Magnacca et al. 2018; Teas et al. 2001), the most diffuse and easily applicable cleanup technique for water remediation is based on physical adsorption, even if magnetically guided advanced oxidation processes (AOPs) are also emerging as a promising green solution alternative for the complete removal of organic contaminants (Bianco Prevot et al. 2017; Franzoso et al. 2017; Klamerth et al. 2010). The most widely used conventional adsorbents are polymer foams (mainly, polypropylene and polyurethane) as well as porous carbons (Dave and Ghaly 2011; Teas et al. 2001). However, in those years, in accordance with the guiding principles of the green chemistry and the circular economy, more eco-friendly alternative bio-based materials for water remediation processes have been properly designed (Ahmad et al. 2018; Huang et al. 2018; Mohanty et al. 2018; Yadav et al. 2018).

Quite recently, there has been a growing interest in the use of renewable bio-based materials, such as cellulose, as sources for the production of novel functionalized materials with enhanced specific properties in alternative to fossil resources-derived chemicals (Palmeros Parada et al. 2017). Cellulose is the most abundant biopolymer on earth since it is the principal structural component of plants and vegetables. Cellulose is a linear semi-crystalline polysaccharide, whose chains are formed by D-glucose units linked by β -1,4-glycosidic bonds (Coseri 2017, Lavagna et al. 2018). Since cellulose can easily be functionalized by reactions involving the three hydroxyl groups of the D-glucose unit, this biopolymer can be successfully used in a wide range of applications in several fields, mostly for the production of bio-based (nano)materials and (nano)composites and/or blends (Ardanuy et al. 2015; Khalil et al. 2012; Khalil et al. 2016; Trache et al. 2016). In particular, cellulose contains two types of hydroxyl groups: primary hydroxyl group at C-6 and secondary hydroxyl groups at C-3 and C-4 (Hokkanen et al. 2016). According to the literature, many complex chemical reactions are used to properly modify the structure of cellulose to induce particular properties. The main ones used are based on “click” chemistry processes which guarantee high and rapid yields at mild conditions (Krouit et al. 2008; Zou et al. 2018). Some of the simplest “click”

chemistry-mediated functionalizations are the following: cycloaddition (such as the copper catalyzed alkyne-azide cycloaddition CuAAC, metal-free [3+2]-cycloaddition, and Diels–Alder reaction, which is a [4+2]-cycloaddition), thiol-Michael and thiol-ene reactions, oxime-click reaction, and olefin cross-metathesis (Meng and Edgar 2016). Beside these, conventional approaches are also simple pathways of interest (e.g., esterification and etherification reactions) (Hokkanen et al. 2016).

During the last decades, the ongoing research for novel low-cost and sustainable absorbing materials for water purification has shown that cellulose-based adsorbents are indeed promising candidates due to the different functionalities that can be introduced (see Hokkanen et al. 2016; Hubbe et al. 2013 and references therein). Focusing on the removal of hydrophobic contaminants from water, the introduction of fatty substituent (with chain length greater than C6) in the cellulose to form hydrophobic esters is a significant and promising route to enhance the affinity of cellulose-based materials toward hydrophobic adsorbates (Willberg-Keyriläinen et al. 2016). An alternative solution could be the direct use of wood powder rich in several hydrophobic components derived from the lignin fraction and/or others fatty acids residues (Mahvi 2008). Despite this, the use of pure standard materials (namely, cellulose) guarantees several advantages, such as lowering any possible undesired side phenomena as well as facilitating the reaction selectivity (Rinne et al. 2005). In their recent study, Banerjee et al. (2006) reported the functionalization of sawdust by means of fatty acids for the removal of crude oil from contaminated seawater, evidencing different responses depending on the fatty acids chemical structure.

Thus, the aim of this study was the functionalization of natural cellulose by introducing C16 pending groups via a simple and versatile esterification of cellulose with palmitoyl chloride performed at mild conditions. In particular, the choice of palmitic acids (C16) as pending group is based on the chemical composition of the most common oils and fats (see Oil Palm Knowledge Base). With this functionalization, it is possible to modulate the wettability of the starting biopolymer to obtain a hydrophobic bio-based material that can successfully be used for the removal of hydrophobic fatty oil-derived contaminants from aqueous medium.

2. Materials and methods

2.1 Reagents and chemicals

For the production of hydrophobic cellulose ester, cellulose powder (CAS 9004-34-6, Carlo Erba reagents) and palmitoyl chloride (CAS 112-67-4, purity 98%, Merck) were used. The pristine cellulose powder showed a particle size distribution comprised in the 25-100 μm range (estimated by dispersing the pristine cellulose in acetone and by analyzing the suspension by means of an optical microscope) and a crystallinity degree of ca. 84% (estimated through XRD analysis). Two hydrophobic fatty contaminants were selected as model fatty oils mixtures for this study: i) cod liver oil mixture (abbreviated as CL in this paper) from animal source (by A.F.O.M. Medical S.p.A., cod caught in Westfjord Bergen, Norway) purchased from an herbalist shop located in Torino (Italy), and ii) commercial sunflower oil mixture (abbreviated as SF in this paper) from vegetable source (by Pam Panorama S.p.A., Venice, Italy) purchased from a supermarket of the Pam group located in Torino (Italy). All aqueous solutions were prepared using ultrapure water Millipore Milli-QTM. All chemicals were used without further purification. For the physicochemical and adsorption tests (*vide infra*), both bare cellulose and hydrophobic cellulose ester were kept in the dark in closed plastic vials maintained at room temperature.

2.2 Preparation of the hydrophobic cellulose ester

The hydrophobic functionalization of cellulose was performed by soaking ca. 5 g of biopolymer in a neat palmitoyl chloride solution (50 mL) for 10 minutes under magnetic stirring. This way, palmitoyl chloride reacted with the hydroxyl functional groups of cellulose to generate cellulose palmitate ester and hydrochloric acid as by-products. To terminate the esterification reaction, deionized water was added to the reacting medium. Additionally, water molecules also reacted with

the excess of palmitoyl chloride, thus creating a very low amount of palmitic acid. Last, the desired product was recovered by centrifugation and washed several times. The final material was dried in a furnace at 40 °C for 1 day.

2.3 Characterization methods

FTIR spectra were recorded in transmission mode in a Bruker Tensor 27 Fourier Transform Infrared spectrometer equipped with Globar source, DTGS detector and working with 128 scans at 4 cm⁻¹ of resolution in the 4000-500 cm⁻¹ range. FTIR analysis was carried out on KBr pellets. X-ray diffraction patterns were obtained using the X-ray diffractometer PW3040/60 X'Pert PRO MPD from PANalytical in a Bragg-Brentano geometry, with Cu K α anode source at 40 kV and 40 mA. Thermogravimetric analysis was conducted by means of a TGA instrument Mettler Toledo 1600. The analysis was performed in air atmosphere in order to quantify the amount of new groups introduced by the functionalization treatment of cellulose. Samples were heated from 25 °C to 800 °C with a constant heating ramp of 10 °C min⁻¹. The air was supplied with a constant flow rate of 50 mL min⁻¹.

2.4 Adsorption kinetic experiments

Qualitative adsorption experiments to assess oil absorption were performed following a procedure already reported in the literature (Chu and Pan 2012), by using as fatty oils both a cod liver oil mixture (CL) and a commercial sunflower oil mixture (SF) from animal and vegetable origin, respectively. These two fatty oil mixtures were individually poured drop-by-drop (2 mL) on the surface of water. Then, the hydrophobic cellulose ester was placed on the surface of the oil-water mixtures. Fatty oils were adsorbed by the hydrophobic cellulose within a few seconds.

The quantitative sorption capacity of the hydrophobic cellulose ester was evaluated via gravimetric analysis by weighting the cellulose sample before and after the direct contact with either SF or CL oils at different contact times (from 0 up to 60 minutes), expressing the sorption amount as mg of fatty oil adsorbed over the amount of hydrophobic cellulose before adsorption (mg g⁻¹). Three adsorption experiments were performed for each oil, and average values were reported. Additionally, in order to evaluate the selectivity toward the hydrophobic oils, quantitative sorption tests were also performed on water (W), giving almost negligible sorption.

3. Results and discussion

3.1 Physico-chemical characterization of hydrophobic cellulose ester

Figure 1 reports the FT-IR spectra of cellulose before and after the chemical functionalization with palmitate groups. According to the literature, the main IR signals of cellulose are the following: I) a broad band at ca. 3300 cm⁻¹ due to the stretching mode of O-H and C-OH functionalities; II) a signal at ca. 2600 cm⁻¹ due to aliphatic C-H stretching mode; III) a peak at ca. 1640 cm⁻¹ attributable to the OH bending mode of adsorbed water; IV) a signal comprised in the 1450-1300 cm⁻¹ range due to CH₂ stretching mode (i.e., 1430 cm⁻¹); V) the C-H symmetric bending vibrations from methoxy group at 1371 cm⁻¹; VI) the in-plane O-H bending mode at 1318 cm⁻¹; VII) a signal at ca. 1160 cm⁻¹ due to the C-O stretching mode; VIII) a broad absorption at ca. 1170 and 1082 cm⁻¹ attributed to C-O-C stretching of the pyranose ring skeletal mode typical of polysaccharide structures (Chen et al. 2014; Nelson and O'Connor 1964; Morán et al. 2008; Nisticò et al. 2015; Tang et al. 2014). For the sake of clearness, it is important to notice that the signals at ca. 3300 cm⁻¹ and at ca. 1640 cm⁻¹ can also be associated with the presence of water molecules adsorbed to KBr. The effectiveness of palmitate functionalization was demonstrated by the formation of two strong peaks at 2854 and 2923 cm⁻¹ due to the C-H stretching mode of CH₃ and CH₂ groups of the palmitate alkyl chains, and the sharp peak at ca. 1740 cm⁻¹ attributable to the C=O stretching mode of palmitate esters group with cellulose (see the highlighted peaks in **Figure 1**).

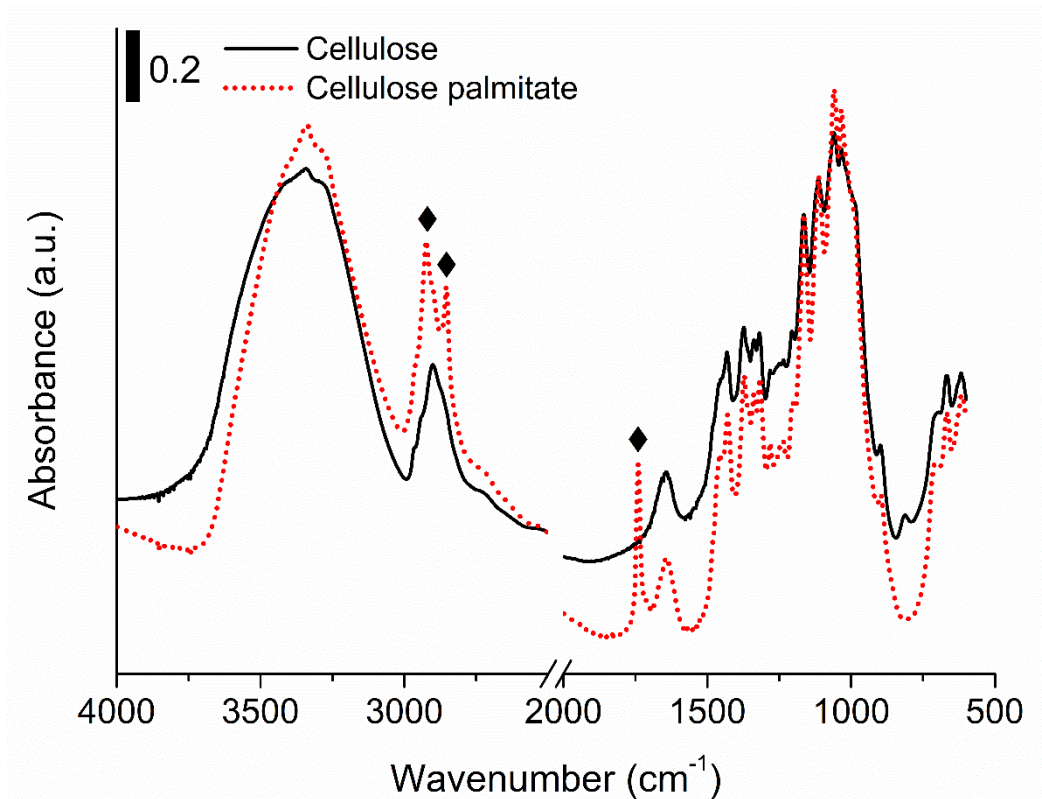


Figure 1: Absorbance FTIR spectra of both pristine cellulose (black solid curve) and after esterification with palmitate group (dotted curve). The signals indicating the effectiveness of the esterification are highlighted (black diamonds).

In order to evaluate whether the functionalization had some effects on the crystalline organization, XRD patterns of cellulose before and after functionalization were collected (**Figure 2**). According to the literature (Djahedi et al. 2015), crystalline cellulose exists in several polymorphs, and the structure of native cellulose (type I) is a combination two crystal structures (i.e., both α and β forms, where the latter is the main constituent in higher plants). In detail, pristine cellulose (before functionalization) showed three main reflection planes: a broad peak at around $\text{ca. } 2\theta = 14.9^\circ$, which is an overlap of two reflection planes (110) and ($1\bar{1}0$), a signal located at $\text{ca. } 22.6^\circ$ (200), corresponding to the distance between hydrogen-bonded sheets, and a weak reflection at $\text{ca. } 34.5^\circ$ (004), due to the ordering along the fiber direction (Boissou et al. 2014; Du et al. 2018; Zugenmaier 2008). All these signals are attributable to the crystalline pattern of type I_β cellulose. As well-demonstrated by the curves in Figure 2, the esterification process did not alter the crystalline structure of cellulose.

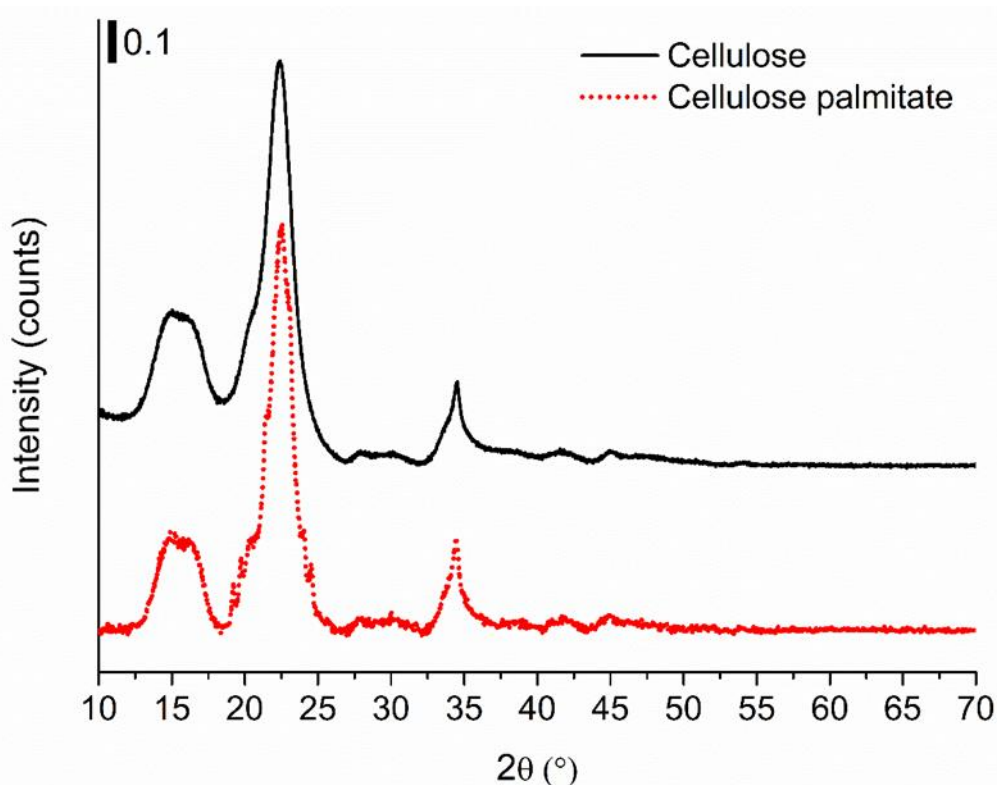


Figure 2: XRD pattern of both pristine cellulose (top, black solid curve) and after esterification with palmitate group (bottom, dotted curve).

The degree of functionalization was quantified by performing thermo-gravimetric analyses (TGA) of cellulose before and after esterification (Figure 3). As reported in the literature, the thermal degradation of pristine cellulose consists of two weight losses: the first one (ca. 5 wt.%), at around 100 °C, which is due to the elimination of physically adsorbed water molecules on the polymeric fibers surface, whereas the main one in the range 250–350 °C is due to the crystalline phase degradation of cellulose (Sonia and Priya Dasan 2013). Above 380 °C, the residual decomposition products showed a slow degradation profile, leaving at 800 °C a residue of ca. 17 wt.%. The introduction of palmitate groups caused the formation of a specific weight loss in the ca. 140-200 °C range due to decomposition of the alkyl chains grafted at the surface of the cellulose fibers. On the basis of this analysis, it is possible to estimate the quantity of palmitate being ca. 10 wt.%.

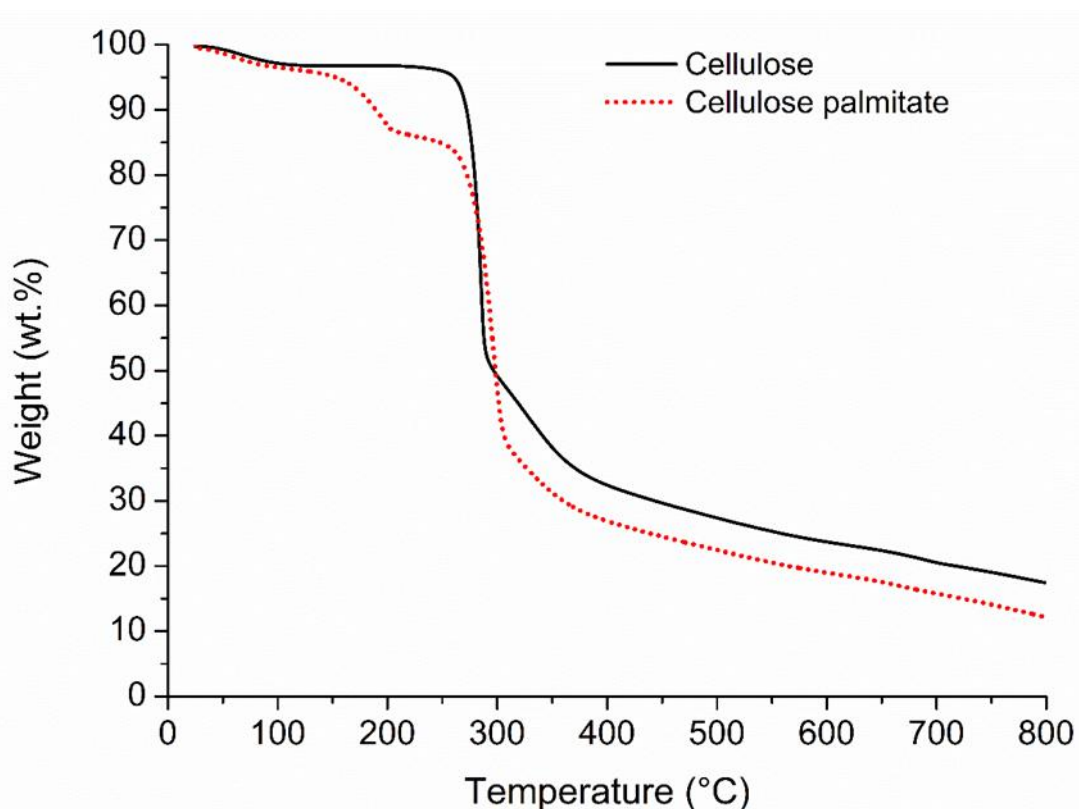


Figure 3: TGA profiles of both pristine cellulose (black solid curve) and after esterification with palmitate group (dotted curve).

3.2 Adsorption experiments on oil-contaminated water.

In order to evaluate the selective sorption capacity of hydrophobic cellulose esters, qualitative contact experiments were performed dropping on an aqueous medium a small amount of two mixtures of fatty oils: namely, cod liver oil (CL) and commercial sunflower oil (SF). Figure 4 reports the ability of functionalized hydrophobic cellulose to adsorb CL from contaminated water. For the sake of clearness, it is better to ascertain that the functionalized hydrophobic cellulose was not wet by water (*vide infra*), whereas the powdery sample was able to attract and sorb the fatty oils when put in direct contact with the drops of hydrophobic contaminants. Once the hydrophobic cellulose was removed from the aqueous environment, no oil residues remained in the aqueous medium, which was clean and colorless. In Figure 4, only the qualitative visual performance of the modified cellulose with CL is reported because it is colored (yellow) whereas SF is colorless. However, analogous behavior was also obtained in the case of SF contamination.

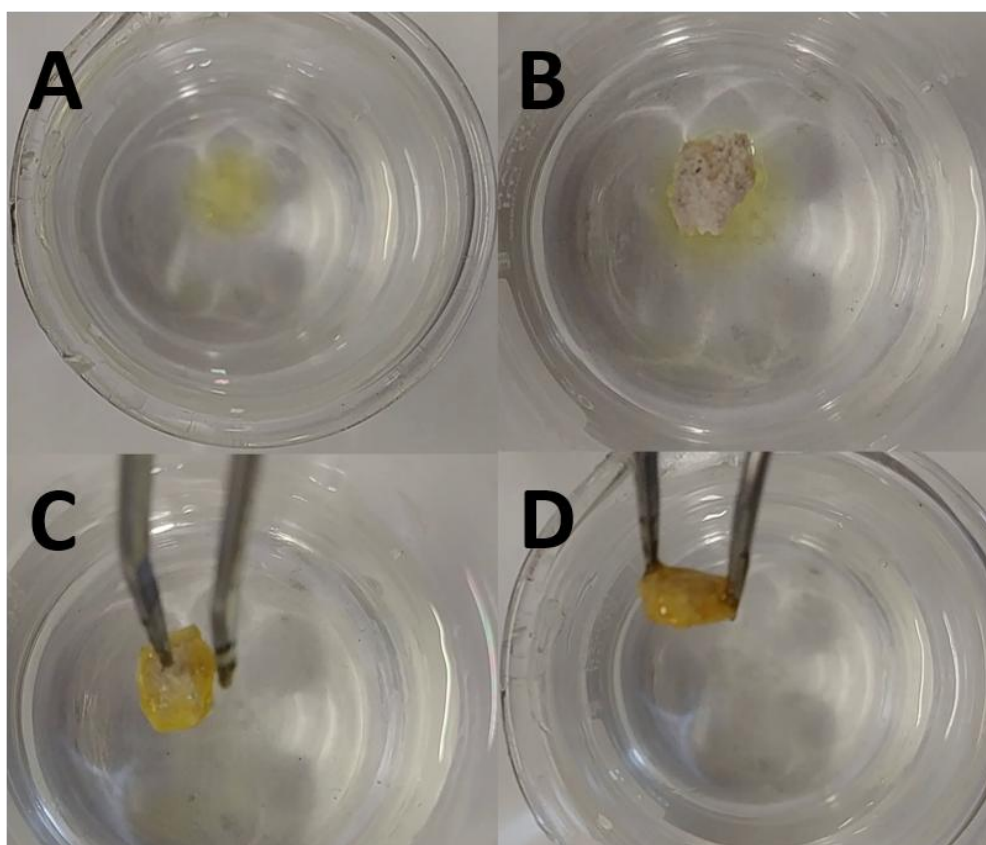


Figure 4: Qualitative removal of CL fatty oil from water surface by hydrophobic cellulose ester. CL was selected since it is yellow colored, thus it guarantees a clear observation. Panel A) Drop of CL in aqueous environment; Panel B) Addition of hydrophobic cellulose ester; Panel C) Sorption of CL by hydrophobic cellulose ester; Panel D) Removal of the hydrophobic cellulose ester at the end of the sorption experiment: CL is completely removed and the water is clean and colorless.

In order to quantitatively measure the sorption capacity of hydrophobic cellulose ester, specific kinetic contact experiments were performed on both CL and SF mixtures by measuring the sorption capacity via gravimetric analysis. Figure 5 reports the kinetic of sorption of hydrophobic cellulose toward both target oil mixtures (i.e., CL and SF). Additionally, in order to highlight the selectivity of the hydrophobic cellulose ester, quantitative sorption experiments were also carried out on water (i.e., W). As expected, the functionalized cellulose showed almost no water (W) adsorption, whereas excellent selective adsorption was found for both oils derived from animal (CL) and vegetable (SF) sources. Experimental data reveal that the oil-absorption capacity of functionalized cellulose after 60 minutes of contact was higher for SF (ca. 2100 mg g⁻¹) than for CL (ca. 1440 mg g⁻¹). The selective response between the two different oil mixtures is probably related to the composition of the two fatty oils mixtures, following the ancient principle “*like dissolves like*”. In fact, the content in C16-C18 fatty acids in SF is of ca. 99% (i.e., C16: 6%, and C18: 98%), whereas the C16-C18 content in CL is of ca. 66% (i.e., C16: 23%, and C18: 43%), thus significantly lower. Additionally, a further content of shorter (C14: 4%) and longer (namely, C20: 14%, C22: 14%, and C24: 1%) chains compounds that makes it hardly compatible with palmitate-cellulose. Results obtained are in line with the specific state-of-art literature. Interestingly, Ibrahim et al. (2009) tested chemically modified barley straw (an agricultural biowaste) for the remediation of wastewater from emulsified oils obtaining the maximum adsorption capacity of ca. 615 mg g⁻¹ for canola oil and ca. 585 mg g⁻¹ for standard mineral oil. The expansion and hydrophobization of clays (mostly vermiculite), instead, at basic pH favored the removal of ca. 10-50 mg g⁻¹ of different oil-based substrates (Mysore et al. 2005; Rajakovic et al. 2007), chitosan flakes and powders gave sorption capacity toward palm oil mills effluent of ca. 2000-3000 mg g⁻¹ (Ahmad et al. 2005), whereas

chemically modified rice husk favored the removal of machine oils from water reaching the significant value of ca. 20-25 g g⁻¹ (Sun et al. 2003). Quite recently, Ngaini et al. (2018) demonstrated that by incorporating fatty acid derivatives on cellulosic systems, it is possible to obtain hydrophobic sorbent with very high oil sorption capacity (ca. 5.0-6.0 g g⁻¹).

In order to rationalize the sorption mechanism of the hydrophobic cellulose ester here investigated, experimental sorption kinetic results were modeled using the pseudo-second-order (1) and the intra-particle diffusion (2) models:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (1)$$

$$q_t = k_p t^{0.5} + C \quad (2)$$

where q_t and q_e represent the sorbed amount of fatty acids at the time t and at the equilibrium (both expressed in mg g⁻¹), whereas k and k_p are the kinetic rate constants (Xu et al. 2018; Zhang et al. 2015). As reported in Figure 6A, the sorption mechanism for both fatty oils is well described by the pseudo-second-order modeling due to the high-linear trend and value of correlation coefficient ($R^2 \geq 0.9998$). Additionally, Figure 6B reported the intra-particle diffusion model. According to the literature (Xu et al. 2018), the non-linear curve confirmed a first initial sharp increase (also known as the instantaneous adsorption stage), more evident in the case of SF, attributable to the easily accessible sites at the surface of the hydrophobic cellulose ester. Once the cellulose was saturated (for SF after 1 minute, for CL after 5 min), fatty oils started to diffuse within the internal sites of the modified substrate with a progressive reduction in the diffusion rate (rate controlled stage) until reaching the equilibrium after ca. 10 minutes (Xu et al. 2018).

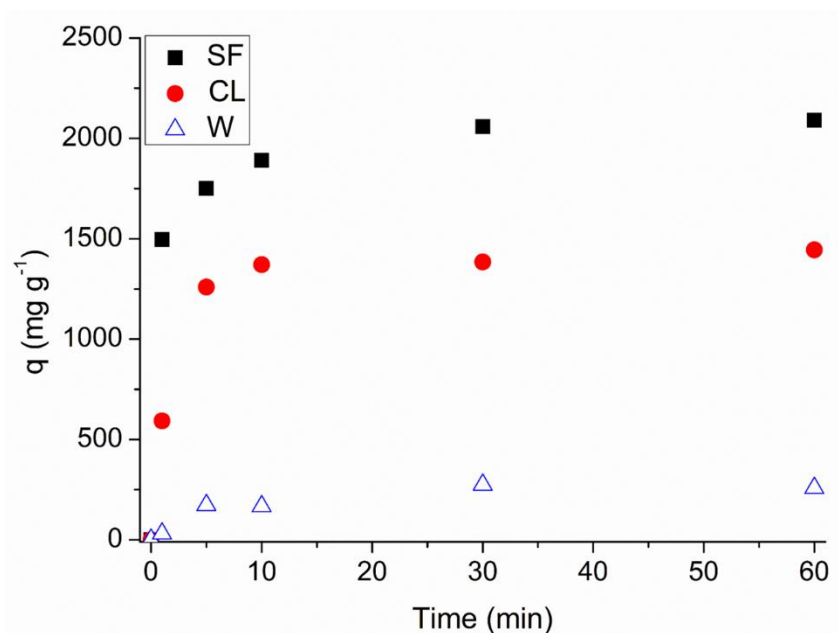


Figure 5: Experimental sorption kinetics of hydrophobic cellulose ester toward: SF (black squares), CL (circles), and W (white triangles).

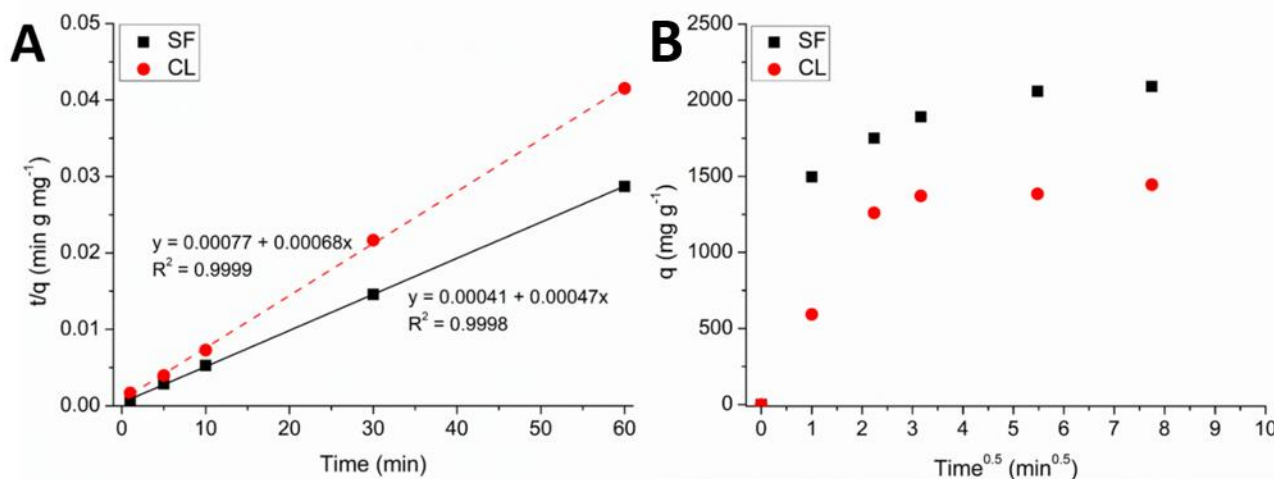


Figure 6: Modeling of the sorption kinetics of hydrophobic cellulose ester toward either SF (black squares) or CL (circles). Panel a) Pseudo-second-order sorption model; Panel b) Intra-particle diffusion kinetic model.

To testify the effectiveness of the hydrophobization treatment, sorption experiments were also performed on pristine cellulose. Figure 7 clearly shows that the oil absorption capacity of pristine cellulose after 60 minutes of contact time is remarkably lower (being ca. 50 mg g⁻¹ for SF and ca. 122 mg g⁻¹ for CL) compared to the hydrophobic cellulose ester data. On the contrary, pristine cellulose tends to preferentially interact with hydrophilic substrates since the water sorption is significantly higher (ca. 1500 mg g⁻¹) compared to the hydrophobic cellulose ester. This experimental test unequivocally demonstrates the selectivity of the hydrophobization process, driving the sorption process toward hydrophobic substrates rather than the hydrophilic ones.

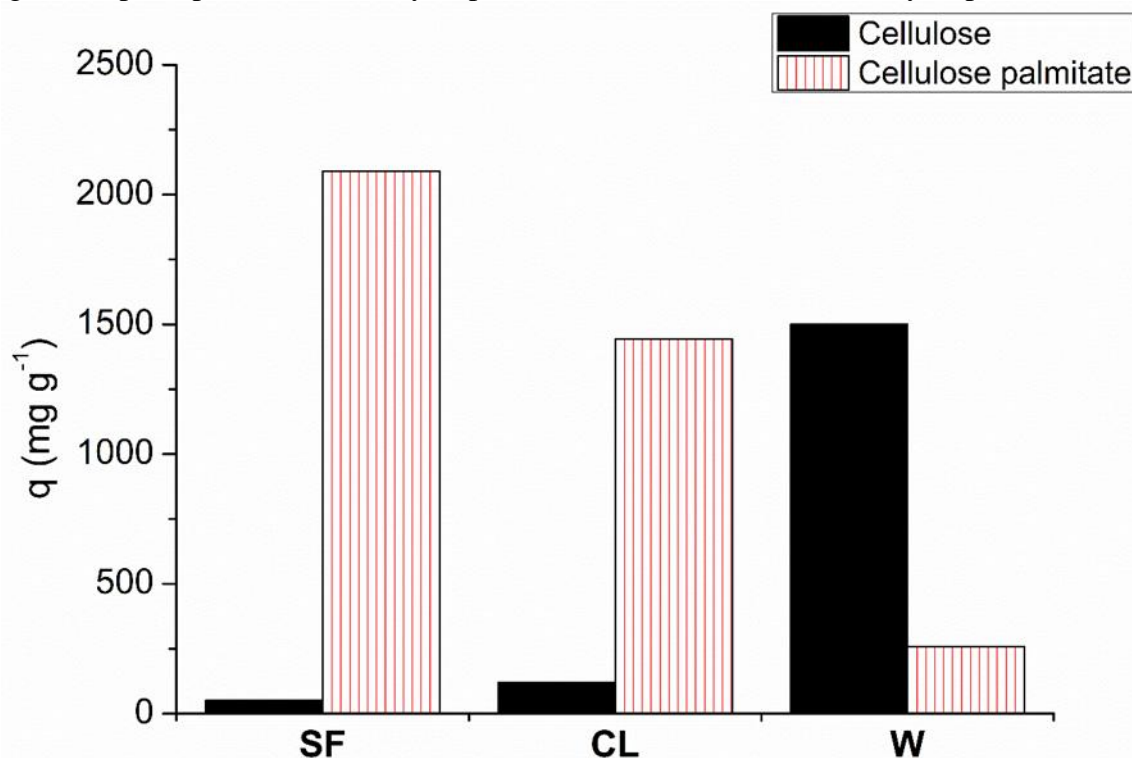


Figure 7: Experimental sorption of both pristine cellulose (black) and hydrophobic cellulose ester (striped) after 60 minutes of contact time toward SF, CL and W.

4. Conclusion

Cellulose, one of the most abundant (and low-cost) biopolymers on earth, was used as starting material for the production of hydrophobic cellulose by the esterification reaction with palmitate groups carried out under mild condition. The hydrophobic cellulose ester was physico-chemically characterized in order to evaluate the effectiveness and the degree of functionalization as well as the possible structural modifications induced by this process. The material obtained showed highly hydrophobic properties and was tested for the removal of fatty oils contaminants from aqueous environment. In this study, two different fatty oils mixtures were investigated as target pollutants: namely, cod liver oil (from animal source) and sunflower oil (from vegetable source). Interestingly the functionalized cellulose showed a greater selectivity and absorption kinetics for SF oil rather than for CL one, and chemisorption seems to be the main mechanism during exposure. Further studies are necessary in order to understand the performances of this cellulose-based material, however quantitative preliminary analyses revealed a significant removal capacity, encouraging the use of these materials as sustainable alternatives with respect to the more traditional (in)organic sorbing substrates.

5. Acknowledgements

Polytechnic of Torino is gratefully acknowledged for funding project Starting Grant RTD (project number: 54_RSG17NIR01).

6. Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

References

- Ahmad AL, Sumathi S, Hameed BH (2005) Adsorption of residue oil from palm oil mill effluent using powder and flake chitosan: equilibrium and kinetic studies. *Water Res* 29: 2483-2494. doi: 10.1016/j.watres.2005.03.035
- Ahmad Z, Gao B, Mosa A, et al (2018) Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass. *J Clean Prod* 180:437–449. doi: 10.1016/j.jclepro.2018.01.133
- Ardanuy M, Claramunt J, Toledo Filho RD (2015) Cellulosic fiber reinforced cement-based composites: A review of recent research. *Constr Build Mater* 79:115–128. doi: 10.1016/j.conbuildmat.2015.01.035
- Banerjee S, Joshi MV, Jayaram RV (2006) Treatment of oil spill by sorption technique using fatty acid grafted sawdust. *Chemosphere* 64:1026-1031. doi: 10.1016/j.chemosphere.2006.01.065.
- Bianco Prevot A, Bains F, Fabbri D, et al (2017) Urban biowaste-derived sensitizing materials for caffeine photodegradation. *Environ Sci Pollut Res* 24:12599–12607. doi: 10.1007/s11356-016-7763-1
- Boissou F, Muhlbauer A, De Oliveira Vigier K, et al. (2014) Transition of cellulose crystalline structure in biodegradable mixtures of renewably-sourced levulinate alkyl ammonium ionic liquids, γ -valerolactone and water. *Green Chem* 16:2643-2471. doi: 10.1039/c3gc42396d

- Chen C, Luo J, Qin W, Tong Z (2014) Elemental analysis, chemical composition, cellulose crystallinity, and FT-IR spectra of *Toona sinensis* wood. *Monatsh Chem* 145:175-185. doi: 10.1007/s00706-013-1077-5
- Chu Y, Pan Q (2012) Three-Dimensionally Macroporous Fe/C Nanocomposites As Highly Selective Oil-Absorption Materials. *ACS Appl Mater Interfaces* 4:2420–2425. doi: 10.1021/am3000825
- Coseri S (2017) Cellulose: To depolymerize... or not to? *Biotechnol Adv* 35:251–266. doi: 10.1016/j.biotechadv.2017.01.002
- Dave D, Ghaly AE (2011) Remediation technologies for marine oil spills: A critical review and comparative analysis. *Am J Environ Sci* 7:423
- Djahedi C, Berglund LA, Wohler J (2015) Molecular deformation mechanisms in cellulose allomorphs and the role of hydrogen bonds. *Carbohydr Polym* 130:175-182. doi: 10.1016/j.carbpol.2015.04.073
- Du L, Zhong T, Wolcott MP et al. (2018) Dispersing and stabilizing cellulose nanoparticles in acrylic resin dispersions with unreduced transparency and changed rheological property. *Cellulose*, in press. doi: 10.1007/s10570-018-1739-x
- Franzoso F, Nisticò R, Cesano F, et al. (2017) Biowaste-derived substances as a tool for obtaining magnet-sensitive materials for environmental applications in wastewater treatments. *Chem Eng J* 310:307-316. doi: 10.1016/j.cej.2016.10.120.
- Hokkanen S, Bhatnagar A, Sillanpää M (2016) A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Res* 91:156–173. doi: 10.1016/j.watres.2016.01.008
- Huang J, Kankanamge NR, Chow C, Welsh DT, Li T, Teasdale PR (2018) Removing ammonium from water and wastewater using cost-effective adsorbents: A review. *J Environ Sci* 63:174–197. doi: 10.1016/j.jes.2017.09.009
- Hubbe MA, Rojas OJ, Fingas M, Gupta BS (2013) Cellulosic substrates for removal of pollutants from aqueous systems: A review. 3. spilled oil and emulsified organic liquids. *BioResources* 8:3038–3097
- Ibrahim S, Ang HM, Wang S (2009) Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw. *Bioresour Technol* 100:5744-5749. doi: 10.1016/j.biortech.2009.06.070
- Khalil HPSA, Bhat AH, Yusra AFI (2012) Green composites from sustainable cellulose nanofibrils: A review. *Carbohydr Polym* 87:963–979. doi: 10.1016/j.carbpol.2011.08.078
- Khalil HPSA., Saurabh CK, Adnan AS, et al (2016) A review on chitosan-cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their applications. *Carbohydr Polym* 150:216–226. doi: 10.1016/j.carbpol.2016.05.028
- Klamerth N, Malato S, Maldonado MI, Agüera A, Fernandez-Alba AR (2010) Application of photo-fenton as a tertiary treatment of emerging contaminants in municipal wastewater. *Environ Sci Technol* 44:1792–1798

- Krouit M, Bras J, Belgacem MN (2008) Cellulose surface grafting with polycaprolactone by heterogeneous click-chemistry. *Eur Polym J* 44:4074–4081. doi: 10.1016/j.eurpolymj.2008.09.016
- Lavagna L, Nisticò R, Chiappone A, Pavese M (2018) Facile photo-induced growth of polymeric nanostructures onto cellulose: The poly(ethylene glycol) methacrylate (PEGMA)@cellulose case study. *Mater. Lett.* 227:202–204. doi: 10.1016/j.matlet.2018.05.074.
- Magnacca G, Guerretta F, Vizintin A, et al (2018) Preparation, characterization and environmental/electrochemical energy storage testing of low-cost biochar from natural chitin obtained via pyrolysis at mild conditions. *Appl Surf Sci* 427:883–893. doi: 10.1016/j.apsusc.2017.07.277
- Mahvi AH (2008) Application of agricultural fibers in pollution removal from aqueous solution. *Int J Environ Sci Tech* 5:275–285. doi: 10.1007/BF03326022.
- Meng X, Edgar KJ (2016) “Click” reactions in polysaccharide modification. *Prog Polym Sci* 53:52–85. doi: 10.1016/j.progpolymsci.2015.07.006
- Mysore D, Viraraghavan T, Jin YC (2005) Treatment of oily waters using vermiculite. *Water Res* 39:2643–2653. doi: 10.1016/j.watres.2005.04.034
- Mohanty SK, Valenca R, Berger AW, et al (2018) Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment. *Sci Total Environ* 625:1644–1658. doi: 10.1016/j.scitotenv.2018.01.037
- Morán JI, Alvarez VA, Cyras VP, Vazquez A (2008) Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose* 15:149–159. doi: 10.1007/s10570-007-9145-9
- Nelson ML, O’Connor RT (1964) Relation of certain infrared bands to cellulose crystallinity and crystal latticed type. Part I. Spectra of lattice types I, II, III and of amorphous cellulose. *J Appl Polym Sci* 8:1311–1324. doi: 10.1002/app.1964.070080322
- Ngaini Z, Noh F, Wahi R (2018) Facile sorbent from esterified cellulosic sago waste for engine oil removal in marine environment. *Int J Environ Sci Technol* 15: 341–348. doi: 10.1007/s13762-017-1389-9
- Nisticò R, Barrasso M, Carrillo Le Roux GA, et al. (2015) Biopolymers from Composted Biowaste as Stabilizers for the Synthesis of Spherical and Homogeneously Sized Silver Nanoparticles for Textile Applications on Natural Fibers. *ChemPhysChem* 16:3902–3909. doi: 10.1002/cphc.201500721
- Nisticò R, Franzoso F, Cesano F, et al (2017) Chitosan-Derived Iron Oxide Systems for Magnetically Guided and Efficient Water Purification Processes from Polycyclic Aromatic Hydrocarbons. *ACS Sustain Chem Eng* 5:793–801. doi: 10.1021/acssuschemeng.6b02126
- Nisticò R (2017) Magnetic materials and water treatments for a sustainable future. *Res Chem Intermed* 43:6911–6949. doi: 10.1007/s11164-017-3029-x
- Nisticò R, Celi LR, Bianco Prevot A, et al (2018) Sustainable magnet-responsive nanomaterials for the removal of arsenic from contaminated water. *J Hazard Mater* 342:260–269. doi: 10.1016/j.jhazmat.2017.08.034

- Oil Palm Knowledge Base. <https://oilpalmblog.wordpress.com/2014/01/25/1-composition-of-palm-oil/> (accessed on August 27th, 2018).
- Palmeros Parada M, Osseweijer P, Posada Duque JA (2017) Sustainable biorefineries, an analysis of practices for incorporating sustainability in biorefinery design. *Ind Crops Prod* 106:105–123. doi: 10.1016/j.indcrop.2016.08.052
- Rajakovic V, Aleksic G, Radetic M, Rajakovic L (2007) Efficiency of oil removal from real wastewater with different sorbent materials. *J Hazardous Mater* 143:494-499. doi: 10.1016/j.jhazmat.2006.09.060
- Rinne KT, Boettger T, Loader NJ, et al (2005) On the purification of α -cellulose from resinous wood for stable isotope (H, C and O) analysis. *Chem Geol* 222:75-82. doi: 10.1016/j.chemgeo.2005.06.010.
- Sonia A, Priya Dasan K (2013) Chemical, morphology and thermal evaluation of cellulose microfibrils obtained from *Hibiscus sabdariffa*. *Carbohydr Polym* 92:668–674. doi: 10.1016/j.carbpol.2012.09.015
- Sun XF, Sun RC, Sun JX (2003) A convenient acetylation of sugarcane bagasse using NBS as a catalyst for the preparation of oil sorption-active materials. *J Mater Sci* 38:3915-3923. doi: 10.1023/A:1026189911651
- Tang Y, Yang S, Zhang N, Zhang J (2014) Preparation and characterization of nanocrystalline cellulose via low-intensity ultrasonic-assisted sulfuric acid hydrolysis. *Cellulose* 21:335–346. doi: 10.1007/s10570-013-0158-2
- Teas C, Kalligeros S, Zanicos F, Stournas S, Lois E, Anastopoulos G (2001) Investigation of the effectiveness of absorbent materials in oil spills clean up. *Desalination* 140:259–264
- Trache D, Hussin MH, Hui Chuin CT, et al (2016) Microcrystalline cellulose: Isolation, characterization and bio-composites application—A review. *Int J Biol Macromol* 93:789–804. doi: 10.1016/j.ijbiomac.2016.09.056
- Willberg-Keyriläinen P, Talja R, Asikainen S, Harlin A, Ropponen J (2016) The effect of cellulose molar mass on the properties of palmitate esters. *Carbohydr Polym* 151:988–995. doi: 10.1016/j.carbpol.2016.06.048
- Xu X, Lin L, Papelis C, Xu P (2018) Sorption of Arsenic from Desalination Concentrate onto Drinking Water Treatment Solids: Operating Conditions and Kinetics. *Water* 10:96. doi: 10.3390/w10020096
- Yadav KK, Gupta N, Kumar V, Khan SA, Kumar A (2018) A review of emerging adsorbents and current demand for defluoridation of water: Bright future in water sustainability. *Environ Int* 111:80–108. doi: 10.1016/j.envint.2017.11.014
- Zhang Q, Du Q, Jiao T, et al (2015) Accelerated Sorption Diffusion for Cu(II) Retention by Anchorage of Nano-zirconium Dioxide onto Highly charged Polystyrene Material. *Sci Rep* 5:10646. doi: 10.1038/srep10646

Zou Y, Zhang L, Yang L, et al (2018) “Click” chemistry in polymeric scaffolds: Bioactive materials for tissue engineering. *J Controlled Release* 273:160–179. doi: 10.1016/j.jconrel.2018.01.023

Zugenmaier P (2008) *Crystalline cellulose and cellulose derivatives characterization and structures*. Springer, Berlin; New York.