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Research article

Development of Biodegradable, Cellulose-Based, Essential Oil and Chitosan Drug Delivery Systems for Cosmetic Mask Applications

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Abstract.

The goal of this research was the development of cellulose-based biodegradable drug delivery systems solutions for cosmetic mask applications. Cellulose-based materials derived from natural renewable sources provide a sustainable alternative to nonwoven cosmetic masks derived from nondegradable fossil-based raw materials. An experimental design was executed to assemble the 3D cellulose fibres matrix and the water in oil emulsion comprising the active molecules from *Mentha piperita* L. Two types of biopolymeric additives were used, one derived from a nano/micro fibrillated cellulose pulp and another one including chitosan. A 3D computational simulation study was performed to enhance porosity and strength properties. The results indicated that the cosmetic face mask optimized prototypes, made from a biodegradable 3D matrix of cellulose fibres and active molecules, are suitable for dermic use.

Keywords: biopolymers, dermic application, drug delivery systems (DDS), essential oil, *Mentha piperita*

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1. Introduction

Cellulose is a polymer, consisting of long chains of glucose anhydride, also known as anhydridoglucose (AGU), which has three hydroxyl groups. These groups give cellulose the ability to make hydrogen bonds, which allows for great stability and resistance [1,2].It is produced by the biosynthesis of plants, animals and bacteria in the Eubacteria domain, it leads to many variations of it [3]. Cellulose is properly structured, as it has crystalline and amorphous areas. Cellulose from plants requires processes to remove lignin and hemicelluloses, which can be tricky to solve experimentally [4]. Cellulose is a renewable source of bio-polymers, being produced by several species, such as plants,

animals and bacteria. Cellulose is the structural unit of plants, and is therefore one of the most abundant natural materials [4].

Chitosan is a polysaccharide, vastly abundant like cellulose, becoming an inexpensive resource. Chitosan is derived from organisms such as crustaceans and fungus, and since its common in nature it presents the benefits of being biodegradable, biocompatible and innocuous [5]. Essential oils are multifaceted as they are used in various industries, such as the cosmetic, pharmaceutical and food industries [6]. These are produced by plants and extracted from them, in which many extracts have been recognized as GRAS (Generally Recognized as Safe) [7]. These by-products have anti-inflammatory, antimicrobial and even antiviral properties [8]. Essential oils can be extracted from various parts of the plant such as flowers, fruits, seeds and leaves. Other extractions can be done in a variety of ways, such as solvent extraction and cold pressing [9]. The extraction product's consistency, quantity, and composition can differ depending on environment, soil composition, plant organ, age, and vegetative cycle stage [10]. To obtain the same composition of EOs, they must be harvested under the same conditions, i.e., from the same organ of the plant, which must be growing in the same soil, atmosphere, and season [11]. Each essential oil is a complex sample, composed by many volatile compounds, mostly terpenes [12]. Monoterpenes are present in all essential oils. They are made up of 10 carbon atoms that are derived from two isoprene units. Monoterpenes may have a straight-chain or a single ring backbone. Because of their smaller size, they respond easily to air and heat, and they degrade faster than their more complex molecules [7]. Due to the high volatility of essential oils, the dermal application in the form of masks has the advantage of storing the therapeutic molecules, prolonging their period of action [13]. The innovation of this project is the development of a cosmetic face mask prototype, made from an optimized 3D matrix, containing micro and nano cellulose fibres, obtained by a combination of mechanical and enzymatic processes, to achieve the desired porosity and strength [14-16]. The biopolymer chitosan is also being investigated as an additive, to promote the controlled release of peppermint active molecules [5].

2. Material and methods

Bleached and unbleached *Pinus pinaster* and Eucalyptus pulps from FibEnTech (University of Beira Interior) Research Laboratory were used.

In this study hardwood and softwood industrial Kraft pulps processes were disintegrated according to the ISO 5263/1. The fibres' morphological properties were

determined automatically by image analysis of a diluted suspension (20 mg/L and 30 mg/L 145 to hardwood and softwood samples, respectively) in a flow chamber in MorFi Fiber Analyzer (TECHPAP, Grenoble, France). After their characterization, the hardwood and soft wood pulps were mixed in different ratios.

The cellulose fibres were modified using enzymatic and mechanical treatments. The mechanical treatment was applied to the kraft pulp using a PFI mill at 500-7500 revolutions, under an intensity of 3,33 N/mm. Enzimatyc treatments were performed using an enzyme dosages of 10 g per ton of pulp, for 30 and 60 minutes. The assays were carried out at a consistency of 4%, pH 7, and 40ºC, with continuous mechanical agitation. To stop the reaction sodium hypochlorite was added to the pulp suspension. After these enzymatic treatments, the pulps were mixed in a ratio of 80:20. A more detailed description of this study can be found in the work of Morais et al. [13-15,18].

Different mixtures with additives were made to understand their influence. The micro/nanofibrillated cellulose (MFC/NFC) was incorporated in a never-dry (slush) bleached eucalyptus kraft pulp, according to loads of 1%, 5%, and 10%. A chistosan additive was also incorporated in the same fiber pulp slurry, at the same dosages. A more detailed description of this study can be found in the master thesis document of the author Moreira, J.

The tissue structures were produced in a batch laboratory sheet former according to an adaptation of ISO 5269/1. The adjustments consisted of the production of structures with a basis weight of 20 g/m^2 and of 60 g/m^2 and suppression of the pressing operation.

The prototype mask samples were conditioned at 22±1ºC, with a relative humidity of 50±2%, according to ISO 187. For all assays, the tissue properties for handsheets were measured in terms of structural and functional properties. The basis weight (ISO 12625-6) was obtained by the ratio between the average mass of each structure and the respective area (0,02138 m^2). The thickness (ISO 12625-3) was obtained using a Frank-PTI micrometer. The bulk (ISO 12625- 3) was obtained by the quotient between the structure thickness and the basis weight. A water in oil emulsion was prepared using a ratio of 1:4 (w/w) and 3700 rpm. The water phase is a peppermint infusion, and the oil phase is made using a carrier sunflower oil and the *Mentha piperita L*. essential oil. The emulsion was incorporated in the fibre mixture bulk, and the mask prototype was stored between 0ºC and 4ºC [18]. The fibres length, width, coarseness and fine content were characterized using an automated analyser. The essential oil was analysed using Gas Chromatography–Mass Spectrometry (GC-MS). The Gas Chromatography was performed using an Agilent technologies 7890A GC A.01.13 with Agilent Technologies

5975 inert XL MSD with Triple-Axis Detector. SEM images were performed using Hitachi S-2700 (Tokyo, Japan). The structures were cross-sectioned were covered with gold using a Sputter Quorum Q 15 OR ES (Laughton, East Sussex, UK) and analysed at different magnifications. FTIR-ATR was used to analyse the face mask prototypes without and with peppermint essential oil active molecules. The equipment used was a FTIR-ATR Thermo-Nicolet IS10.

The 3D fibrous matrix computational simulation was performed using Matlab®, according to a previously validated model [18,19]. The fibrous material simulation model was used to simulate the deposition of fibres and the assembly of the mask structure prototype.

3. Results and discussion

The assembly of the mask prototype and its structural hierarchy is presented in Figure 1. Cellulose microcrystalline and chitosan molecular structures are represented in Fig1.b) and c).

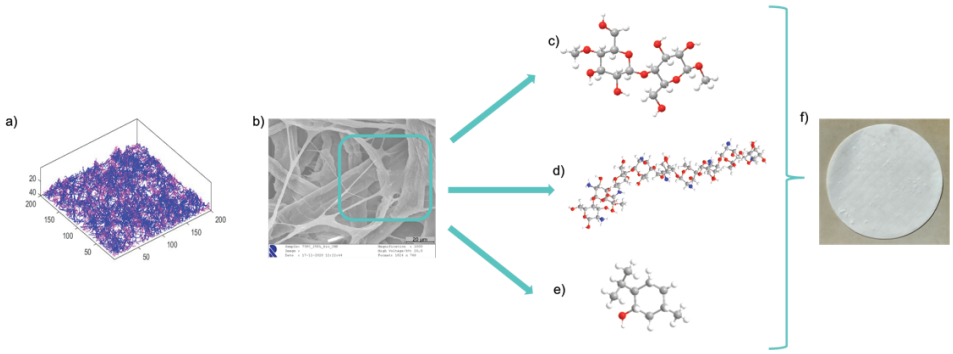


Figure 1: Visual representation of the mask prototype structural hierarchy. a) Structures obtained by Computational Simulation, representing fibres at the end of their deposition, b) SEM image of the fibrous matrix, c) cellulose, d) chitosan, e) menthol and f) laboratory made mask prototype. Molecules made using ChemDraw ® Professional 16.0 by Moreira, J. Model and computational Simulation by Curto, J.

The fibres morphology and biometry changes with the type of raw-material and the mechanical and enzymatic processes are presented in table 1 and table 2.

To identify the components of *Mentha piperita* essential oil, a Gas Chromatography–Mass Spectrometry (GC-MS) analysis was performed. The results (table 3 and fig.2) indicate that the major component is menthol (35.31%).

With this result, we can conclude that after nine months there's still some molecules of peppermint essential oil in the structure, due to the wavelength interval within 2700-3000 cm $^{-1}$.

Table 1: Biometry of different raw materials and mechanical and enzymatic operations.

	Hardwood Fibre	Softwood Fibre	Softwood Fibre + Enzymatic treatment	Softwood Fibre + Mechanical treatment (4000 rev. PFI)	Softwood Fibre + Enzymatic + Mechanical treatment (4000 rev. PFI)
Fibres (million/g)	21,269±0,010	4,742±0,538	5,542±0,265	6,714±0,058	6,704±0,067
Length weighted in length (mm)	0,793±0,003	1,858±0,047	1,889±0,052	1,693±0,026	1,745±0,009
Width (µm)	19,3±0,1	30,1±0,2	30,6±0,4	32,3±0,3	32,2±0,1
Coarseness (mg/100 m)	0,0692±0,0002	0,2052±0,0323	0,1692±0,0065	0,1581±0,0021	0,1509±0,0017
Fine elements (% in length)	36,8±0,2	24,4±21,3	37,9±1,7	42,7±2,2	37,8±1,5

Table 2: Characterization of different raw materials and mechanical and enzymatic operations

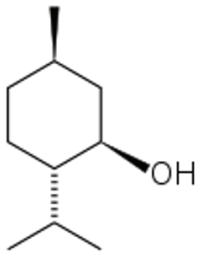
	Hardwood Fibre	Softwood Fibre	Softwood Fibre+ Enzymatic treatment	Softwood Fibre + Mechanical treatment(4000 rev. PFI)	Softwood Fibre+ Enzy-matic+Mechanical treatment(4000 rev. PFI)	Softwood Fibre +Microcrystalline cellulose+Chitosan
Porosity (%)	84,710±1,96	90,376±1,22	86,847±2,1	72,926±19,46	80,736±4,19	81,964±0,45
Tissue Thickness (µm)	135,378±43,46	138,854±0,18	146,462±0,031	91,710±38,195	93,919±32,00	230,800±7,085
Sheet Density (g/cm^3)	0,229±0,039	0,144±19,64	0,197±64,662	0,406±0,291	0,289±0,063	0,271±0,006
Bulk (cm^3/g)	4,432±0,58	7,066±1,15	5,181±0,72	2,945±0,921	3,593±0,64	3,698±0,091
Grammage (g/m^2)	31,845±13,24	20,080±4,06	30,583±19,15	36,220±24,19	28,815±17,48	62,404±0,56

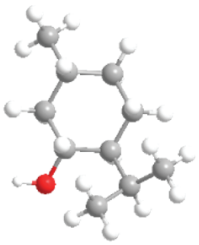
Table 3: a) Relative chemical composition (%) of *Mentha piperita L.* essential oil b) Menthol Molecular structure in 2D and 3D. Molecules made using ChemDraw ® Professional 16.0 by Moreira, J.

a)

Compound	**RI**	
β-pinene	978	1,0
Limonene	1030	2,0
1,8-Cineole	1032	5,5
Menthone	1151	20,8
Menthofuran	1164	7,3
Neomenthol	1167	3,2
Menthol	1177	35,3
Terpinen-4-ol	1177	1,3
Pulegone	1234	1,7
Menthyl acetate	1296	7,1
β-Caryophyllene	1420	2,9
Germacrene D	1481	2,0

b)





The results indicate that *Mentha piperita* active molecules are retained in the cellulose fibres porous structure.

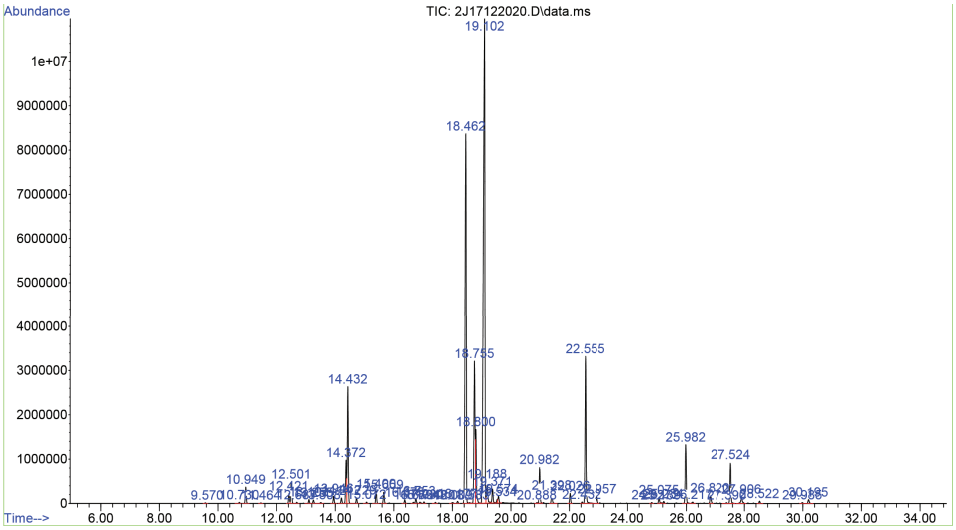


Figure 2: Chromatogram representing the relative chemical composition (%) of *Mentha piperita L.* essential oil

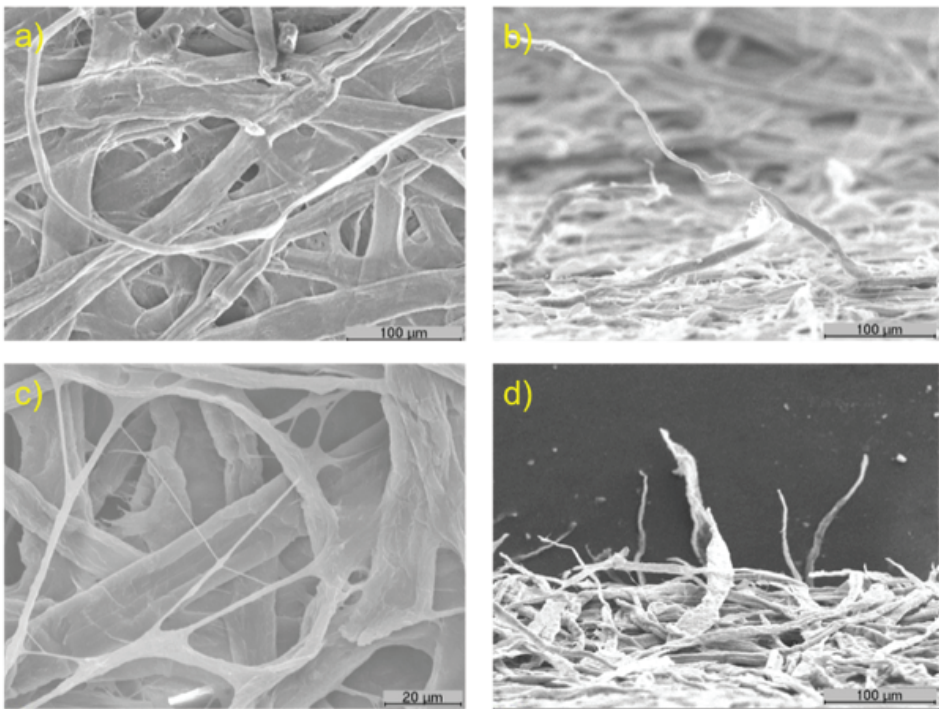


Figure 3: SEM image of the structures of cellulose that went through enzymatic and mechanical treatment, where it can be visualized (a) how the cellulose fibres deposit (magnification of x300), (b) fibrilization of the fibre (magnification of x300), (c) diversity of pore dimensions (magnification of x1000) and (d) fibre in a z axis (magnification of x300).

4. Conclusions

A 3D cellulose fibres matrix was used to make a biodegradable *Mentha piperita* Delivery System, suitable for dermic application. With the mechanic and enzymatic treatment is it possible to see many changes, including in porosity and bulk. With SEM images it was

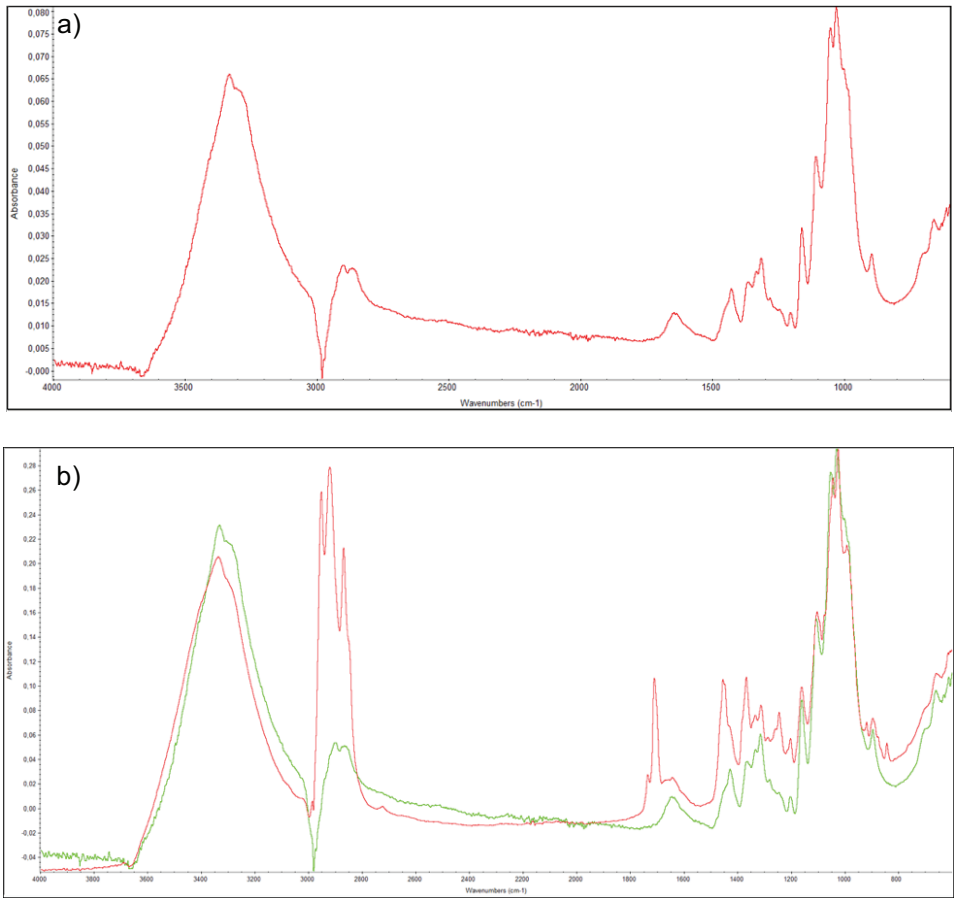


Figure 4: FTIR-ATR spectrum of fibrous matrix without essential oil **b)** FTIR-ATR spectrum of fibre refined containing *Mentha piperita L.* essential oil (red) compared with the fibrous matrix without essential oil (Green).

possible to visualize the pore diversity that is present in every structure and also the fibrilization of cellulose fibres that occur with mechanical and enzymatical treatment. FTIR-ATR results indicate that the peppermint essential oil is retained in the fibrous structure, as is possible to visualize the peak in the wavelength 2700-3000 cm $^{-1}$ that represent the OH groups, since the main component of the essential oil is menthol.

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