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Bacterial Cellulose Membrane with Functional Properties

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2) Ribeiro, L. S.; Pinto, T.; Monteiro, A.; Soares, O. S. G. P.; Pereira, C.; Freire, C. and Pereira, M. F. R. Silica Nanoparticles Functionalized with a Thermochromic dye for Textile Applications. **Journal of Materials Science**, v. 14, p. 5085-5092, 2013.

3) Monteiro, A.; Jarrais, B.; Rocha, I. M.; Pereira, C.; Pereira, M.F.R. and Freire, C. Efficient immobilization of montmorillonite onto cotton textiles through their functionalization with organosilanes. **Applied Clay Science**, v. 101, p. 304-314, 2014.

4) Pinto, T.; Costa, P.; Sousa, M. C.; Sousa, C. A. D.; Monteiro, A.; Pereira, C.; Soares, O. S. G. P.; Silva, C. S. M.; Pereira, M. F. R.; Coelho, P. J. and Freire, C. Naphthopyran-based silica nanoparticles as new high performance photo responsive materials, **ACS Applied Materials & Interfaces**, v. 8, p. 7221-7231, 2016.

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- Patents

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“Have the courage to follow your heart and intuition. They somehow know what you truly want to become.”

Steve Jobs

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ABSTRACT

This work reports the development of economic and environmentally friendly Bacterial Cellulose Membrane (BCM) with functional properties.

The spherical mesoporous silica nanoparticles with average particle size around 51 ± 4 nm, obtained by sol-gel method and spherical silica nanoparticles with heterogeneous particles size distribution (20-40 nm) obtained through agro-industrial waste were prepared and functionalized by in situ and post-grafting methodology, respectively, with alkoxysilanes with easy-cleaning properties and natural dye obtained through natural extracts, namely curcuma. Anatase TiO_2@SiO_2 spherical nanocomposites prepared by the sol-gel method, have also been developed. Subsequently, these functional nanomaterials and the organosilanes 1,4 – bis(triethoxysilyl)benzene (BTEB), Bis(triethoxysilylpropyl)disulfide (BTPD) and 1,2-Bis(triethoxysilyl)ethane (BTSE), were successfully incorporated into BCM, by in situ and post-grafting methodologies.

In the BCM functionalized with BTEB, BTPD and BTSE, spherical silica nanoparticles with porous structure and heterogeneous particle size, were formed on the cellulose fibers. The surface repellency of the functionalized BCM with silica nanoparticles containing easy-cleaning properties was remarkably enhanced. This BCM displaying phobicity to water, toluene, cyclohexane and artificial sweat. Specifically, the BCM functionalized by in situ and post-grafting with SiO_2@F_{13}TES, displayed a surface almost superhydrophobic (> 150°). Methyl violet 2B dye decomposition measurements showed that the BCMW-SiO_2@TiO_2 (BCM functionalized in wet state) presented a good self-cleaning performance showing fast Methyl violet 2B dye decomposition in 30 minutes. BCM with yellow-orange coloration from curcuma with good resistance to washing and high chemical stability have been developed.

This versatile biomaterial emerge as a promising substrate with high added value being able possibly allow their application in several areas.

Keywords: Functional bacterial cellulose membrane; organic-inorganic hybrids; silica nanoparticles; SiO_2@TiO_2 (Anatase) nanocomposites; sol-gel method; reuse of agro-industrial waste; easy-cleaning properties; photocatalytic activity; self-cleaning properties; natural-based color properties.

Resumo

Este trabalho descreve o desenvolvimento de membranas de cellulose bacterianas (BCM), econômicas e ecologicamente amigáveis com propriedades funcionais.

Nanopartículas de sílica esféricas com tamanho de partícula de cerca de 51 ± 4 nm, obtidas pelo método sol-gel e nanopartículas de sílica com tamanho de partículas heterogêneo, extraídas da casca de arroz, foram preparadas e funcionalizadas pelas metodologias *in situ* e *post-grafting*, respectivamente, com alcoxisilanos com propriedades easy-cleaning e curcuma. Nanocompósito de anatase SiO_2@TiO_2 preparado pelo método sol-gel, também foi desenvolvido.

Posteriormente, estes nanomateriais funcionais e os organosilanos 1,4 – bis(trietoxissilil)benzeno (BTEB), Bis(trietoxisililpropil)disulfeto (BTPD) and 1,2-Bis(trietoxissilil)etano (BTSE), foram imobilizados com sucesso na BCM, segundo as metodologias *in situ* e *post-grafting*.

Na BCM funcionalizada com os organosilanos BTEB, BTPD e BTSE, nanopartículas de sílica esféricas com estrutura porosa e distribuição de tamanho de partícula heterogêneo, foram formados nas fibras de celulose. A repelência da BCM funcionalizado com nanopartículas de sílica contendo propriedades de limpeza facilmente melhorada notavelmente. BCM apresenta fobicidade à água, tolueno, cicloexano e solução de suor artificial. Especificamente, a BCM funcionalizada com a amostra SiO_2@F_{13}TES segundo as metodologias *in situ* e *post-grafting*, apresentam uma superfície quase superhidrofóbica (> 150°). As medições de decomposição do corante metil violeta 2B, mostraram que a amostra BCMW-SiO_2@TiO_2 (BCM funcionalizada no estado molhada) apresentou um bom desempenho de auto-limpeza (decomposição do corante metil violeta 2B em 30 minutos). BCM com coloração amarelo alaranjado, proveniente da curcuma, com boa estabilidade química também foi desenvolvida.

Esse versátil biomaterial surge como um substrato promissor, com alto valor agregado, podendo ser aplicado em diversas áreas.

Palavras-Chave: Membrana de celulose bacteriana funcional; híbridos orgânicos-inorgânicos; Nanopartículas de sílica; Nanocompósito SiO_2@TiO_2 (anatase); método sol-gel; reutilização de resíduos agro-industriais; propriedades de fácil limpeza; atividade fotocatalítica; propriedades de auto-limpeza; propriedades de coloração natural.

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NOTATION AND GLOSSARY

List of abbreviations

AFM - Atomic Force Microscopy

BCM - Bacterial Cellulose Membrane

BTPD - Bis(triethoxysilylpropyl)disulfide

BET - Brunauer-Emmett-Teller

BTEB - 1,4 – bis(triethoxysilyl)benzene

BTSEENE - 1,2-Bis(triethoxysilyl)ethylene

BTSE - 1,2-Bis(triethoxysilyl)ethane

BCMW - Bacterial Cellulose Membrane Wet

BCMD - Bacterial Cellulose Membrane Dry

CA - Contact angle

CTAC - Aqueous hexadecyltrimethylammonium chloride solution solution

C_8TMS - Octyltrimethoxysilane

C_{16}TMS - Hexadecyltrimethoxysilane

Cur - Curcuma

CPMAS - Cross-polarization magic angle spinning

DLS - Dynamic Light Scattering

F_{13}TES - Tridecafluorooctyltriethoxysilane

FTIR-ATR - Attenuated Total Reflectance Fourier Transform Infrared

MNs - Mesoporous silica nanoparticles

MV - Methyl Violet 2B

NLDFT - Non-local density functional theory

PDI - Polydispersion indexes by DLS

PG - Post-grafting

RMN - Solid-State Nuclear Magnetic Resonance

SNs - Silica nanoparticles

SEM - Scanning Electron Microscopy

STEM - Scanning Transmission Electron Microscopy

TEA - Triethanolamine

TGA - Thermogravimetric Analysis

TEOS - Tetraethylorthosilicate

THF - Tetrahydrofuran

TEM - Transmission Electron Microscopy

Wt - Weight

XRD - X-ray Diffraction

XPS - X-ray photoelectron spectroscopy

XRFA - X-ray fluorescence

List of variables

A_{BET} - Specific surface areas

CrI – Relative degree of crystallinity

d_{DLS} - Average hydrodynamic diameters by DLS

d_{SEM} – Average particle size by SEM

d_{TEM} – Average particle size by TEM

d_{pore} - Pore size

$I002$ – Maximum intensity of the (002) plane diffraction

I_{am} – Intensity of the amorphous halo

V_{meso} - Porous volumes

CONTENTS

CHAPTER 1

Introduction

1. Introduction

1.1. Bacterial cellulose membrane

Cellulose ($C_6H_{10}O_5$) is a naturally occurring homopolysaccharide formed by a linear chain of monosaccharide β-D-glucose linked by β(1→4) bond. The repeting unit is cellobiose formed by the union of two glucose molecules (**Figure 1**) [1-3].

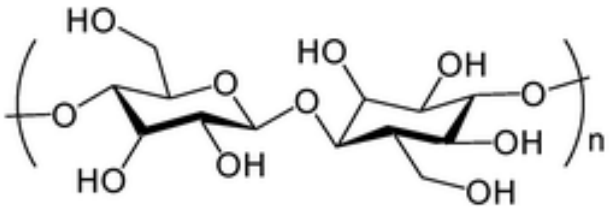

Figure 1 - Chemical structure of cellulose [2].

This biomaterial is obtained through the biosynthesis induced by a few strains of bacteria, including the *Gluconacetobacter xylinus* (formerly named *Acetobacter xylinus*). This microorganism is a gram-negative bacteria, non-pathogenic and non-photosynthetic, capable to convert glucose, glycerol and others organic substrates into cellulose within a few days [1, 2].

The biochemical process of cellulose synthesis by this microorganism consists of three main steps: (i) polymerization of glucose residues in β-1-4 glucan, (ii) extracellular secretion of linear chains, and (iii) organization and crystallization of glucan chains through hydrogen bonds and van der Waals forces [3]. The anhydroglucose units and various BC fibrils interact closely with each other to form a crystalline structure through internal and external hydrogen bonds, resulting in the compaction of fibers. After BCM synthesis, the membrane is further processed to remove bacterial cells, organic acids, salts as well as residual sugars and other components of the culture medium, which could be integrated within the cellulose network (**Figure 2**).

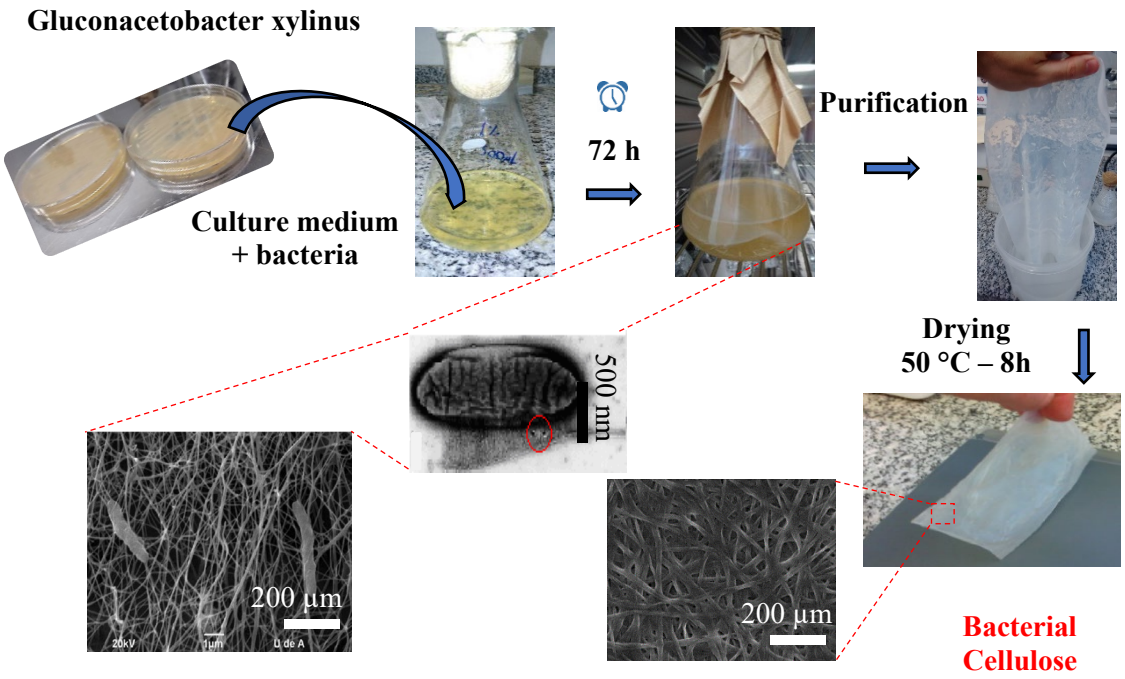

Figure 2 – Representative scheme of preparation of Bacterial Cellulose [own authorship].

Unlike plant cellulose, Bacterial Cellulose Membrane (BCM) is produced in the pure form, devoid of lignin, hemicellulose, pectin, or any other compound present in the plant pulp and does not contain components of animal origin. In addition, it has superior mechanical properties compared with plant cellulose (crystallinity – plant cellulose (56% - 65%) vs bacterial cellulose (65 – 79%) and young's modulus - plant cellulose (5.5 – 12.6 GPa) vs bacterial cellulose (15.0 – 30.0 GPa) [1-4].

The thin nanofibers of 20–100 nm diameter, with a large surface area per unit, combined with the hydrophilic nature of BC (hydroxyl groups), results in high water absorption capacity, better adherence, and increased moisture content. These properties, combined with the distinct physical and mechanical properties of the molecule, including its insolubility, rapid biodegradability, tensile strength, elasticity, durability, nontoxic and non-allergenic features, make BCM ideal for a variety of important applications in different fields including in the cosmetics area, as a stabilizer of emulsions, in the Medicine, as temporary artificial skin for therapy of burns and ulcers, among others areas [4, 5]. Indeed, with the presence of a large number of hydroxyl groups within their structure, these building blocks represent a unique platform for significant surface modification to graft a myriad of functional molecules using various chemistries, with

functional properties, namely, easy-cleaning and self-cleaning, make BCM ideal for the design of several functional products with high added value [5].

There are two main strategies to implant these modifications, in situ and post-grafting. In situ modification is to modify BCM during bacterial cell culture by varying the culture conditions, adding additional materials. In contrast, post-grating modification of BCM is carried out after the BCM has been formed (**Figure 3**) [5].

Figure 3 –Schematic representation of preparation of BCM modifications methods: (**A**) in situ and (**B**) post-grafting [5].

1.2. Silica

1.2.1. Properties and applications

Silica, SiO_2, is the most abundant chemical compound in the earth's crust (~ 60 wt%) [6]. The structural unit of silica is tetrahedron (SiO_4), in which each silicon atom, in central position, is coordinated by four oxygen atoms, joined by siloxane (Si-O-Si)

bridges. This arrangement allows the formation of a three-dimensional crystal lattice through the sharing of tetrahedral oxygen with neighboring groups. Silica contains silanol groups (Si-OH), (4-5 OH/nm^2 groups), giving it surface reactivity and sites of immobilization or efficient interaction/functionalization with various chemical species [6-8]. Si-OH groups can be classified into three types depending on how they are arranged: isolated silanols (where there is only one OH group attached to a silicon atom); vicinal (where there are two OH groups attached to two atoms) and geminal (in which two OH groups are attached to the same silicon atom), as shown in **Figure 4** [6-8].

Silica is a versatile material with a wide spectrum of applications for industry, improving the performance of the developed technologies and the products obtained due to its excellent properties such as thermal and mechanical stability, chemically inert, optical transparency and surface chemistry [6, 7].

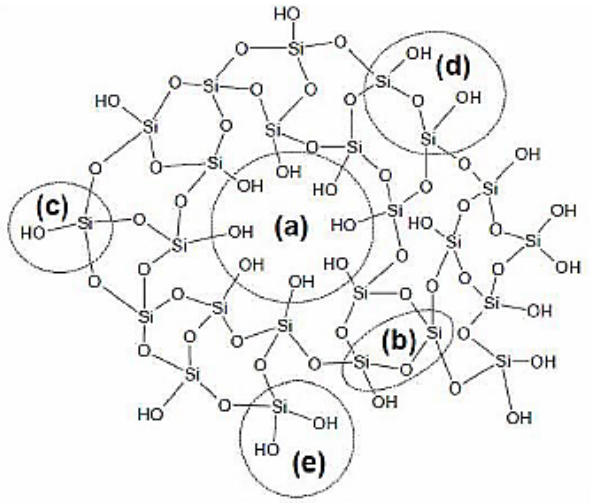

Figure 4 – Silica structure. (**a**) silica pore; (**b**) siloxane group; (**c**) isolated silanol group; (**d**) vicinal silanol group and (**e**) geminal silanol group [6].

1.2.2. Silica Source

Silica can be of natural or synthetic origin. They can be classified as natural crystalline silicas (ex: quartz), synthetic crystalline silicas (ex: Keatite), natural amorphous silicas (ex: biogenic silica and vitreous silica) and synthetic amorphous silicas (ex: fused silica, pyrogenic, precipitated, colloidal or gel) [9].

i. Synthetic amorphous silica – sol-gel method

Silica is synthesized through the sol-gel technological process. This process involves the synthesis of an inorganic polymer network at low temperatures, the gel being formed from a colloidal suspension or by hydrolysis and condensation of a precursor in solution [9-11]. The most commonly used precursors in the sol-gel method are metal or semi-metallic alkoxides, as they are easily hydrolyzable, soluble in organic media and easily purified [12]. The most widely used is tetraethylorthosilicate (TEOS), which being immiscible in water, requires the addition of an alcohol capable of homogenizing the solution [13].

This method involves hydrolysis and subsequent condensation of the precursor. In hydrolysis reactions, the alkoxide (OR) group of the precursor is replaced by the silanol group (Si-OH), forming in parallel an alcohol, due to the nucleophilic attack of the oxygen atom of the water hydroxyl group (**Figure 5A**). Condensation reactions form dimers, linear trimers, cyclic and polymeric species with siloxane bonds (Si-O-Si). These reactions may occur in aqueous medium when the network is formed with simultaneous production of water, or medium alcohol when an alcohol is produced (**Figure 5B** and **5C**). Hydrolysis and condensation reactions only occur in the presence of an acid or base catalyst as they are very slow and incomplete [10, 11].

The morphology and textural properties of the materials obtained are strongly influenced by several reaction parameters such as pH, temperature, reaction time, agitation, reagent concentration, nature and concentration of catalysts and type of solvent [10, 11].

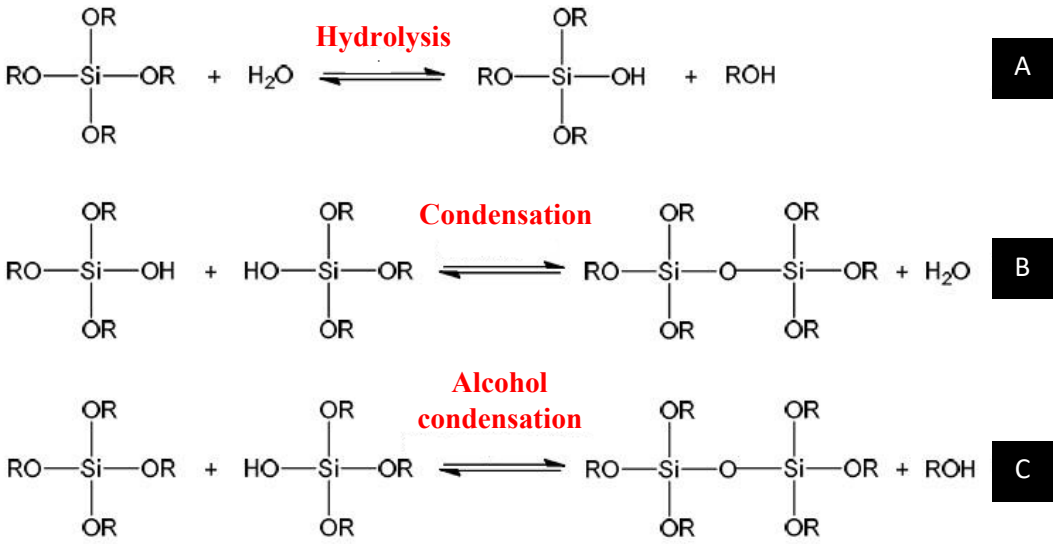

Figure 5 - Hydrolysis and condensation reactions that occur during the sol-gel method [13].

The sol-gel process presents as main advantages: the high purity and homogeneity of the inorganic materials and/or hybrid produced; the relatively low reaction temperature and the possibility of controlling the size and morphology of the particles as well as influencing the characteristics of the material through the experimental parameters such as reagent concentration, pH, temperature and reaction time [9, 14]. However, it also has some disadvantages leading to an environmental impact, namely: the toxicity and non-biodegradable reagents; use of catalysts; energy costs and high costs of reagents used during the process. The synthesis of TEOS is expensive and generates undesirable products such as hydrogen chloride gas [15] World production of TEOS is estimated to range from 23 thousand tons to 32 thousand tons a year [16].

Nowadays, other more economical and ecological possibilities emerge that include extracting silica from agro-industrial waste.

ii. Natural amorphous silica – biogenic silica

Biogenic silica is all the silica that is produced from living organisms such as plants and animals [17].

In general, the biosilification process occurs through the absorption and accumulation of the silicic acid monomer in the polymerization of monomeric units until formation of stable nuclei and spherical particles for formation of branched chains [18].

The bioaccumulation of silica by plants aims at increasing resistance against pathogenic fungi and improving the photosynthetic rate [19]. In all plants, silica is absorbed through the roots as orthosilicic acid $Si(OH)_4$. Due to its immunological and structural reinforcement character, silica is bioaccumulated mainly in the stems and leaves [19, 20].

1.2.3. Agro-industrial waste

The agro-industrial sector generates large amounts of solid waste resulting from processing, treatment of raw materials and disposal of its by-products. Handling and improper disposal in places such as soil, water and air can lead to pollution. This pollution causes problems that potentiate impacts on the environment and human health, because its high abundance, caused by excessive production, raises questions related to the accumulation of waste and consequent disposal in landfills.

Many of these agro-industrial wastes, considered without any commercial value, have silica in their composition. **Table 1** shows some abundant and biodegradable wastes as potential source of silica.

Table 1 - chemical composition of some agro-industrial wastes as a potential source of silica.

Waste		Ashes% (wt/wt)	SiO_2% (wt/wt)	Ref.
Rice	Peel	15,0-28,0	95,0-98,0	[21]
Peanut	Peel	3,1	27,7	[21]
	Straw	8,3		[22]
Coconut	Peel	3,1	69,3	[21]
Coffee		0,9-4,1	13,5-16,6	[21]
Wood		0,5	12,8	[23]
Bean	Straw	4,30	-	[23]
	Stem	4,61	-	[22]
	Pod	6,65	-	
Corn	Stem	3,43	-	[23]
	Leaf	3,53	-	
	Straw	1,58	-	
Olive	Pit	1,7	30,8	[24]
Sugar cane	Stem	3,23	-	[23]
	Leaf	3,45	-	[23]
Hazelnut	Peel	1,4	27,3	[24]
Nut	Peel	2,8	9,9	[24]
Wheat	Peel	9,9	43,2	[25]
Lupine bean	Peel	2-3	-	[25]

From the analysis of **Table 1**, it is possible to verify that the percentage of silica is higher in the rice husk ashes, therefore, this residue shows to be a great potential as an unlimited source of silica. The main constituents of the rice husk are cellulose, hemicellulose lignin (72-85% (wt/wt)) and silica (15-28% (wt/wt)). Generally, about 25% (wt/wt) of the rice husk is converted to ash whose composition is metal oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, K_2O), wherein about 85-90% (wt/wt) is SiO_2 amorphous [26].

The FAO (Food and Agriculture Organization) forecast for world rice production in 2018 was 772.5 million tons (1.3% higher than 2017), with 90% produced and consumed in Asian countries [25]. In Brazil, the estimated production for the same year was 12.1 million tons, which can generate about 435.0 thousand tons of silica, considering that the husks make up 22% of the rice and that they have an average content of 18% of silica [25].

1.2.4. Reuse of silica from agro-industrial waste

Different approaches have been developed for the extraction of silica from agroindustrial wastes. In order to obtain silica with a high degree of purity, a purification and heat treatment it is necessary.

The heat treatment conditions are defined by thermogravimetric analysis of the waste. Specifically, rice husk has an organic decomposition temperature of 700 ° C (see **chapter 4** – **section 4.1.2**).

Many authors have shown that rice husk purification treatment with HCl, HNO_3, H_2SO_4, NaOH and NH_4OH solutions, followed by heat treatment, has proven to be an effective way to remove impurities and metal oxides, producing completely white silica ash with a high purity (90-95% silica) [27-29]. Other forms include the direct extraction of silica in basic medium. Generally, the authors use a NaOH solution to obtain a silicate solution (precursor), followed by the addition of an acid (H_2SO_4) to precipitate the silica. [30].

In order to develop a more ecological and economical method and more effective in removing impurities and metal oxides, this work reports the development of a hydrothermal process to obtain silica from rice husk. Hydrothermal treatment will allows the expansion of the rice husk cellulosic fibers and solubilizes part of the lignin, contributing to the fast and effective access of the acid in the impurities [30].

1.2.5. Mesoporous silica nanoparticles

Mesoporous (pore diameter between 2 nm and 50 nm - classification according IUPAC (International Union of Pore and Applied Chemistry)) [26] silica nanoparticles are a class of versatile nanomaterials with tremendous potential for a broad spectra of applications, including catalysis [31], controlled drug delivery [32] and surface coatings [33]. Their high specific surface areas, ordered structure, and tunable pore sizes are some of their remarkable features. The ability to incorporate specific organic functional groups onto their surface through covalent bonding is another key parameter to engineer their properties in route to the target applications [31].

Bein *et al.*, developed a one-pot strategy for the synthesis of mesoporous silica nanoparticles with small size (40-60 nm), narrow particle size distributions, very high specific surface areas, and high colloidal stability. Their method is based on the use of a polyalcohol, triethanolamine (TEA) , which acts as a base, as a complexing agent for silicate precursors and as an encapsulator for mesoporous particles, thus regulating the

alkoxides hydrolysis/condensation rates and limiting the particles growth and aggregation [33].

1.3. Functional properties

Since the birth of nanotechnology, new challenges emerged in various areas of research toward the design of hybrid materials and technological processes [33]. The design of high performance functional materials with enhanced properties, has been the subject of intense research, offering promising improvements in a plethora of scientific and technological areas.

The silica nanoparticles is promising nanomaterial for the development of functional substrates with a view on a variety of technological applications owing to their remarkable properties, namely, adsorption capacity, optical transparency, high thermal, mechanical stability and tunable surface chemistry [33, 34].

1.3.1. Functionalization of silica nanoparticles

The surface functionalization of silicates can change the chemical and physical properties of these materials dramatically. There are two major ways to functionalize the surface of silica nanoparticles: co-condensation and post-grafting (**Figure 6**).

Post-grafting is a method to modify an assynthesized inorganic material surface by anchorage of functional groups to the surface of material. In the process of grafting silica nanoparticles, the surface silanol groups (Si-OH), which can be present in high concentration, act as convenient anchoring points for organic functionalization [33-35]. Surface functionalization with organic groups by grafting is most commonly carried out by silylation. The original structure of the porous support is generally maintained after grafting. In this method, the external surface is more accessible and is functionalized predominantly over the internal pore surface. The functional groups on the external surface are also more accessible in subsequent reactions, leading to reduced selectivities in processes that benefit from pore confinement [32-37].

Co-condensation method is another strategy to functionalize silica nanoparticles surface by sol-gel chemistry between tetraalkoxysilane and one or more organoalkoxysilanes with Si-C bonds. The co-condensation offers several advantages because it is an one-pot methodology, provides a more homogeneous distribution of the organic moieties throughout the material and controls the silica nanoparticles morphology. [31, 32, 35, 36].

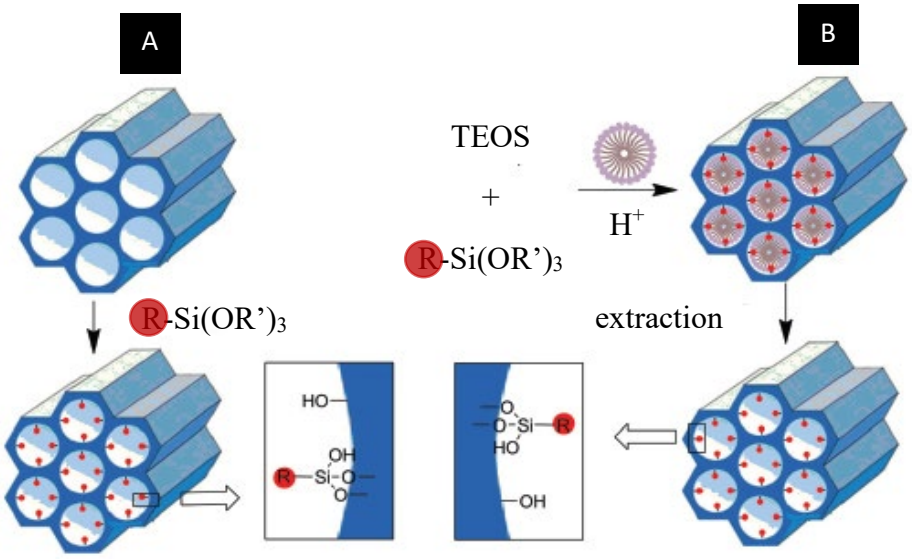

Figure 6 – Schematic illustration of the modification of MSNs by (**A**) post-grafting and (**B**) co-condensation methodology [35 and own authorship].

1.3.2. Easy-cleaning properties

One of the most fascinating property in nature is easy-cleaning properties, existing on the lotus leaf and butterfly wings, for example. This property is also known as lotus effect. The surface of these materials are always kept clean because they repel contaminants deposited therein. This action is possible due to the existence in the structure of lotus leaf of micro and nanoscale roughness and superhydrophobic epicuticular waxes with low surface energy (static contact angle > 150° and dynamic contact angle of 0°) (**Figure 7**) [37, 38].

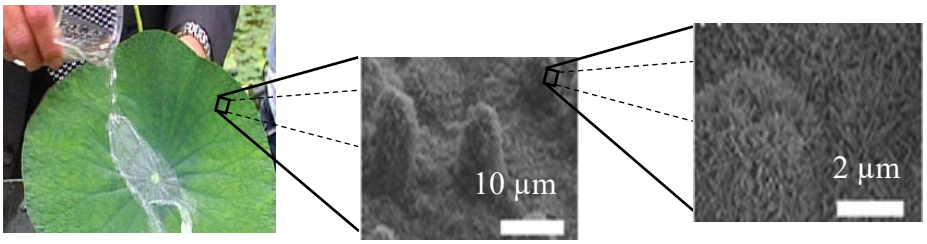

Figure 7 – Lotus leaf structure with easy-cleaning properties [37 and own authorship].

The requirements for the production of surfaces with easy-cleaning properties, it is the result of the synergy between two factors: an increase of the nanoscale surface roughness imparted for example by the silica nanoparticles combined with compounds with low surface free energy [33].

In this way, in the present work, to promote easy-cleaning properties, silica nanoparticles were functionalized by in situ and by post-grafting, with organosilanes with different surface energy and consequently with different degrees of easy of cleaning, to obtaining BCM with different degrees of repellency, for different applications. The organosilanes used were as follows: octyltrimethoxysilane (C_8TMS), hexadecyltrimethoxysilane (C_{16}TMS) and with fluoroalkoxysilane, the tridecafluorooctyltriethoxysilane (F_{13}TES) (see the structure of these organosilanes in **Table 2, chapter 2, section 2**).

BCM with easy-cleaning properties can be used as artificial temporary skin for wounds and burns, for example. BCM with this property, able to repel sweat, will provide greater cleaning and wound healing.

The easy-cleaning property is evaluated by measuring the contact angle (CA) between the drop of the test liquid and the substrate surface. If the CA is less than 90°, the surface is hydro/oleophilic (**Figure 8A**); between 90° and 150°, the surface is hydro/oleophobic (**Figure 8B**), equal or superior than 150°, the surface is superhydro/oleophobic (**Figure 8C**) [37, 38].

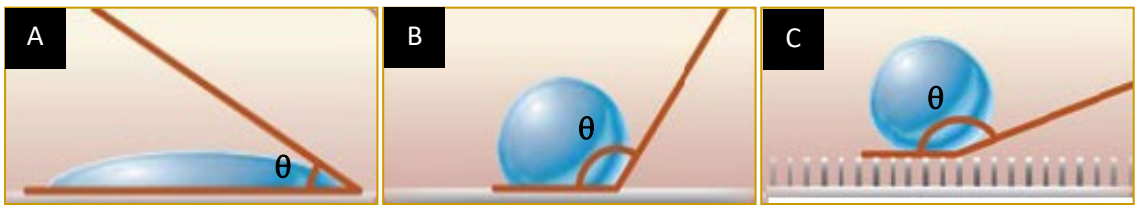

Figure 8 – Schematic representation of a surface (**A**) hidro/oleophilic ($0° < \theta < 90°$), (**B**) hidro/oleophobic ($90° < \theta < 150°$) e (**C**) superhidro/oleophobic ($\theta > 150°$) [37].

1.3.3. Self-cleaning properties

Substrates with self-cleaning technology have the capacity to degrade dirt, odour and microorganisms through a photocatalytic process (**Figure 9**), allowing a reduction of cleaning actions and increase of the durability of the substrates [39].

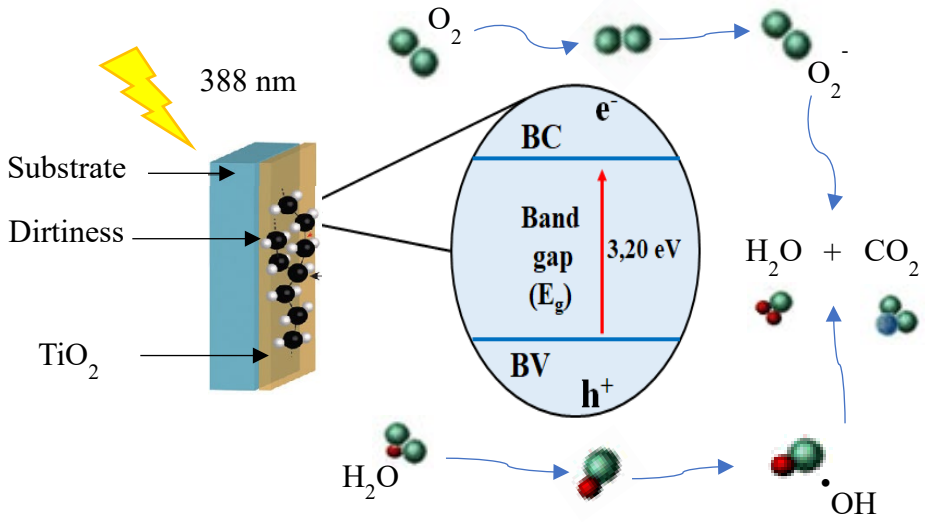

Figure 9 – Representative scheme of the photocatalytic process [own authorship].

The titanium dioxide (TiO_2) is the most used among the photocatalysts based on benefits-cost ratio, as well as due to its suitable electronic and optical properties and good chemical stability [40].

The Anatase TiO_2 has the highest photoactivity among different crystal phases of TiO_2, rutile and brookite (**Figure 10**) [41, 42]. The rutile phase is thermodynamically stable, but the metastable anatase phase that is generally formed at low temperature, for example, by sol-gel processing [43], transforms to rutile by heating or even by mechanical grinding [44]. The anatase-to-rutilo phase transformation (from a metastable phase to a stable one), is markedly influenced by the nature and the amount of cation impurities [44, 45] and anion impurities [46] present in the system, grain size [44], and preparation conditions such as reaction atmosphere. To resolve most of these problems, TiO_2 can be coated on the surface of thermally stable, low cost and high surface area core materials [46, 47]. SiO_2 is one of the best core materials for preparing the core@shell nanoparticles. SiO_2-TiO_2 heterogeneous system often exhibits better photocatalytic activity than TiO_2

alone [48] due to the improved stability of silica-supported anatase and presence of oxygen vacancies in the supported titania as well as due to the improved adsorption of the reactants near the active centers [49].

In the present work, the BCM with self-cleaning properties was developed by the immobilization of the SiO_2@TiO_2 nanocomposite in BCM.

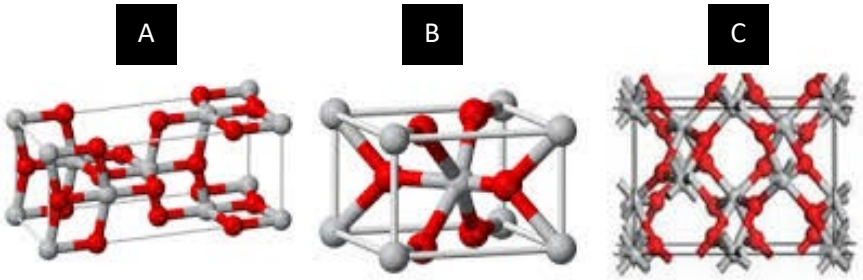

Figure 10 - Crystalline structures of titanium dioxide. A: Anatase, B: rutile and C: brookite [50].

1.3.4. Natural-based colored properties

Economic and environmentally friendly BCM with natural colored was another property developed. This functional BCM, with a view to being applied, for example, in the textile industry, as artificial textiles and highly absorbent materials, or in paper industry [51], overcome the limitations and environmental problems, namely the color fastness and the contamination of the effluents.

Currently it becomes imperative forward the industry for alternatives of dyeing more sustainable. In this context, this project intend to overcome these challenges, by the development of colored BCM of natural base, with high value added, through an innovative process, more economical and environmentally sustainable. These gains will be achieved by replacing synthetic dyes by natural dyes, that will be covalently bonded to the BCM through silica nanoparticles, obtained from agro-industrial waste.

Silica nanoparticles acts as linker between dye and the BCM structure, and allow to obtain better color parameters, such as uniformity, intensity and solidity [52, 53].

The natural dye used in this project was the curcuma. Curcuma (**Figure 11A**) is a yellow-orange, aromatic substance extracted from the plant named Crocus Sativa. The

coloring matter exists in the plant stamens. The yellow-orange color is due to crocin, which is a glycosated carotenoid, whose aglycone is crocetin (**Figure 11B and 11C**) [54, 55]. This dye is one of the most powerful chemopreventive and anticancer agents. Its biological effects range from antioxidant, anti-inflammatory to inhibition of angiogenesis and is also shown to possess specific antitumoral activity [41]. These properties will add value in the BCM, extending therefore their use to a wide range of highly sophisticated applications.

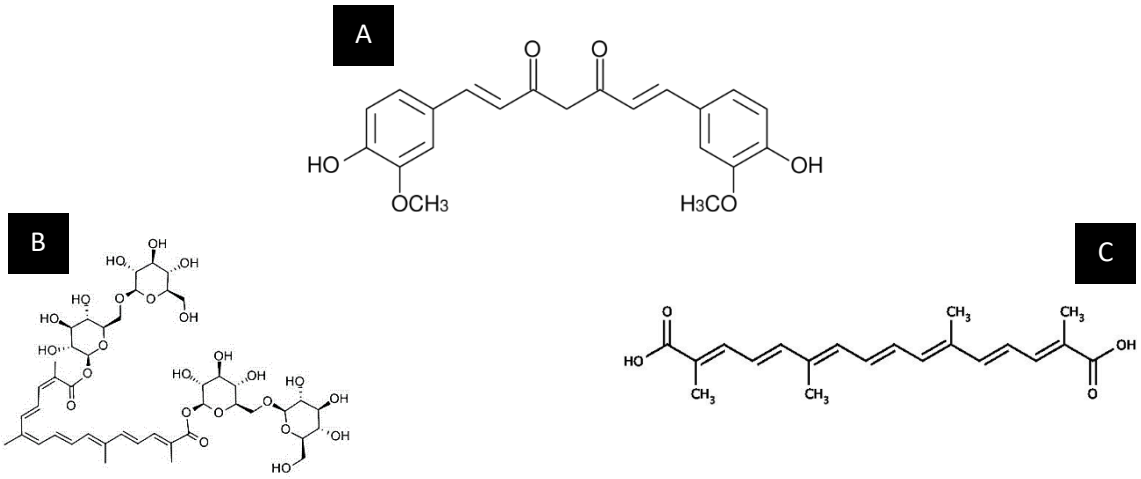

Figure 11 - Chemical structure of (**A**) curcuma (**B**) crocin and (**C**) crocetin.

CHAPTER 10

General Conclusion

10. General conclusions

The objectives proposed for the project have been achieved and the execution of the activities proceeded as planned.

The spherical silica nanoparticles with average particle size around 51 ± 4 nm, narrow size distribution, wormhole-type mesoporous structure and high porosity were successfully synthesized and functionalized by in situ with organosilanes C_8TMS, C_{16}TMS and F_{13}TES by sol-gel method.

The hydrothermal process allowed to obtain silica with a higher purity (99.7 % (wt/wt)) than reported in the literature by conventional methods (90-95 % (wt/wt)). The silica obtained are composed of nearly spherical nanoparticles with heterogeneous particles size (20-40 nm) and exhibit mesoporous structure and high porous structure. The SiO_2-rice were successfully functionalized with organosilane F_{13}TES and curcuma.

The SiO_2@F_{13}TES and SiO_2@F_{13}TES-rice present excellent easy-cleaning properties, displaying phobicity to water (threshold of superhydrophobicity), toluene, cyclohexane and artificial sweat, whereas the pristine silica nanoparticles (SiO_2 and SiO_2-rice) presented philicity to these liquids.

Regardless of the functionalization method (in situ vs post-grafting) and the method of obtaining silica nanoparticles (sol-gel method or from rice husk), the easy-cleaning properties obtained are very similar (SiO_2@F_{13}TES and SiO_2@F_{13}TES-rice). Anatase TiO_2@SiO_2 spherical nanocomposites, with average particle size around 60 ± 5 nm, prepared by a sol-gel method, have also been developed.

These hybrid nanomaterials were successfully incorporated into BCM by in situ and post-grafting. The size and morphology of these nanomaterials remained constant after immobilization on the BCM. BTEB, BTPD and BTSE were successfully incorporated into BCM by in situ. After immobilization of these different organosilanes on the cellulose, spherical silica nanoparticles with porous structure and heterogeneous particle size, were formed on the cellulose fibers.

The surface repellency of the functionalized BCM with silica nanoparticles containing easy-cleaning properties was remarkably enhanced. Specifically, the BCM functionalized by in situ and post-grafting with SiO_2@F_{13}TES, displayed a surface almost superhydrophobic (> 150°). The repellency properties of functional BCM reveals are better to those obtained by the respective immobilized nanoparticles. Furthermore, regardless of the immobilization method used, the contact angle values were similar.

BCM displaying self-cleaning properties have been prepared by incorporation of SiO_2@TiO_2 nanocomposite in BCM. Methyl violet 2B dye decomposition measurements showed that the BCMW-SiO_2@TiO_2 (BCM functionalized in wet state) presented a good self-cleaning performance (fast Methyl violet 2B dye decomposition in 30 minutes).

The functional BCM also presented a good resistance to washing with high chemical stability and the original features, color and texture were maintained.

The good properties acquired in this versatile biomaterial open the way to obtain functional BCM which will find applications in several areas. The results obtained in this project, will open new avenues for the design of smart and innovative cellulose membrane.

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