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INVESTIGATION OF BACTERIAL CELLULOSE-BASED HYBRID AEROGELS AS CONSEQUENCE OF DRYING TECHNIQUES AND FUNCTIONALIZATION

Ph.D. Thesis

LEONARDO MARCHIORI

Araraquara
2026

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INVESTIGATION OF BACTERIAL CELLULOSE HYBRID AEROGELS AS CONSEQUENCE OF DRYING TECHNIQUES AND FUNCTIONALIZATION

Thesis presented to the Institute of Chemistry, São Paulo State University (UNESP), Araraquara, to obtain the Ph.D. title in Chemistry.

Supervisor: Prof. Dr. Sidney José Lima Ribeiro

Co-supervisor: Prof. Dr. Elias Ferreira Paiva Neto

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LEONARDO MARCHIORI

INVESTIGAÇÃO DE AEROGÉIS HÍBRIDOS BASEADOS EM CELULOSE BACTERIANA DECORRENTE DE TÉCNICAS DE SECAGENS E FUNCIONALIZAÇÃO

Tese apresentada à Universidade Estadual Paulista (UNESP), Instituto de Química, Araraquara, para obtenção do título de Doutor em Química.

Orientador(a): Prof. Dr. Sidney José Lima Ribeiro

Coorientador(a): Prof. Dr. Elias Ferreira Paiva Neto

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IMPACTO POTENCIAL DESTA PESQUISA

Esta tese pode ter impactos relacionados aos Objetivos de Desenvolvimento Sustentável (ODS) da ONU, como o ODS 9, que se preocupa com indústria, inovação e infraestrutura. Aerogéis são uma temática de grande relevância tanto nas tecnologias energéticas, como baterias de alto desempenho, como isolantes térmicos, necessários em diversos países com grande potencial na redução do gasto com aquecimento.

POTENTIAL IMPACT OF THIS RESEARCH

This thesis can have an impact related to Sustainable Development Goals (SDG) from the UN, especially SDG 9, related to industry, innovation, and infrastructure. Aerogels are a highly relevant topic in energetic transition to new technologies, like high-performance batteries, as well as thermal insulating materials, needed in countries across the globe, posing a high cost-/energy- reduction with heating.

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Campos, A.L., *Aerogéis Híbridos de Celulose Bacteriana/Organosílica modificados com Azul da Prússia e Oxicloreto de Bismuto para Purificação Foto-Assistida de Água*. 2024. Orientador: Elias Paiva Ferreira Neto. Trabalho de Conclusão de curso (Graduação em Química). – Universidade Federal de Santa Catarina (UFSC), Florianópolis.

SCIENTIFIC EVENTS PARTICIPATION

XXIII Brazilian Materials Research Society Meeting (SBPMat), 2025 (Salvador, Brazil), oral presentation entitled Investigating Photocatalytic Degradation of Nanocellulose Supports for Enhanced Water Purification Technologies.

VI Iberoamerican Conference on Advanced Oxidation Technologies (CIPOA), 2024 (Florianópolis, Brazil), oral presentation entitled Mesoporous nanocrystalline TiO2 deposited on bacterial nanocellulose membrane scaffolds through a low-temperature method: An active membrane for methylene blue photocatalytic degradation.

VI Iberoamerican Conference on Advanced Oxidation Technologies (CIPOA), 2024 (Florianópolis, Brazil), poster entitled Hybrid bacterial cellulose@SiO2-TiO2 hybrid

aerogel for in-flow photo-assisted removal of water contaminants

XXII International Sol-Gel Conference, 2024 (Berlin, Germany), oral presentation entitled Effect of drying methods on the structure and properties of bacterial nanocellulose/MoS_2 hybrid gel membranes and beads for enhanced adsorption and photocatalytic applications.

6th International Seminar on Aerogels, 2022 (Hamburg, Germany), poster entitled Photocatalysts supported on bacterial cellulose aerogels for environmental applications.

7th International Summer School on Aerogels, 2022 (Cologne, Germany)

XVII Brazilian Materials Research Society Meeting (SBPMat), 2018 (Natal, Brazil), poster entitled Titanium dioxide micromotors - Applied to remove emerging contaminants.

XVI Brazilian Materials Research Society Meeting (SBPMat), 2017 (Gramado, Brazil), poster entitled Calcium carbonate micromotors for drug delivery presented.

INTERNATIONAL EXPERIENCE

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September, 2023 – December, 2023
Project: Surface modifications on bacterial cellulose and cellulose nanocrystals for environmental applications
Department of Molecular Science, Swedish University of Agricultural Sciences, Uppsala, Sweden
Cooperation: Prof. Dr. Gulaim Seisenbaeva

November, 2019 – March, 2020
Project: Titanium-based micromotor applied to emerging contaminants removal
Nanoengineering Department, University of California San Diego, San Diego, United States of America
Cooperation: Prof. Dr. Joseph Wang

I would like to dedicate this PhD thesis to my parents for their support in my academic life and pursuit of my research goals.

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“There is no difference between Time and any of the three dimensions of Space

except that our consciousness moves along it.”

The Time Machine,
H.G. Wells

RESUMO

A compreensão da microestrutura de aerogéis, mantida intacta pela secagem supercrítica, impacta suas propriedades para além de sua composição química. Atualmente, são imprescindíveis em diversas indústrias, como de isolantes térmicos, baterias de alta eficiência e aplicações aeroespaciais. Entretanto, é um material onde muito foi produzido rapidamente, deixando alguns estudos básicos cruciais pendentes. Em contrapartida, a celulose é polímero natural estudado há décadas, é formado por unidades de glicose e obtido de diversas formas, onde a bacteriana resulta no biopolímero de maior pureza e cristalinidade. Composta por fibras entrelaçadas, as quais possuem diâmetro nanométrico e comprimento micrométrico, materiais feitos de celulose bacteriana possuem resistência mecânica, alta flexibilidade, poros interconectados e relativamente alta área superficial. Por conta destas propriedades, transformá-la de gel para aerogel, mantendo as características morfológicas, é de grande interesse em diversas áreas, como adsorção e catálise, onde fenômenos de superfície e transporte de massa são altamente relevantes. A celulose em si não apresenta grande capacidade de sorção para diferentes moléculas ou mesmo atividade catalítica, mas quando associada a nanomateriais, sendo ela utilizada como suporte, por exemplo, abre novas opções para o uso destes nanomateriais. Além do melhor aproveitamento das propriedades da celulose, usando-a na forma de aerogel, a possibilidade de utilizá-la na forma de membranas ou partículas quase esféricas permite seu uso tanto em sistema em fluxo como em sistemas de partículas suspensas, facilitando a recuperação do material. De fato, a recuperação é um dos principais fatores limitantes quanto ao uso de nanomateriais quando usados sem suporte, além da reconhecida toxicidade intrínseca dos mesmos, associado ao tamanho. Por conta do sinergismo existente entre os estudos de celulose, aerogel e nanomateriais, a presente tese se inicia focando nas diferentes propriedades observadas quando o material é obtido aplicando diferentes formas de secagem, e avaliando suas diferentes propriedades superficiais, como sorção e fotocatálise. Explorando lacunas na literatura de aerogéis, tanto em sua definição como em seus estudos mais fundamentais, foi proposta uma definição atualizada de aerogéis, bem como sua interpretação. Tendo explorado a consequência da preparação dos géis, o próximo capítulo da tese buscou explorar como um gel de sílica

crescido na celulose, formado por dois precursores alcóxisilanos, poderia afetar propriedades funcionais de sorção e seletividade. Enquanto um dos precursores possuía quatro grupos hidrolisáveis, resultando somente em uma estrutura de óxido de silício, um dos grupos alcoxi do outro precursor era substituído por uma cadeia orgânica que continha um grupo etilenodiamina. Apesar do primeiro precursor apenas resultar em uma superfície com grupos hidróxidos, o segundo atribuía grupos complexantes e adsorventes de metais. Por fim, após estudar como o material poderia ser preparado e a funcionalização do mesmo, aerogéis de celulose recobertos com titânia foram utilizados para analisar a estabilidade química da celulose frente à fotodegradação. A titania, que possui propriedades oxidativas quando irradiada com luz ultravioleta, ao recobrir a celulose, mostrou-se capaz apenas de induzir a oxidação não apenas de moléculas orgânicas, mas também da própria celulose, sendo essa demonstração um resultado inédito na literatura. Por fim, os resultados obtidos nesta tese abordam aspectos fundamentais de aerogéis de celulose in diferentes aspectos, desde a biossíntese à preparação dos géis secos. Ressaltando a funcionalização com géis baseados em sílica, para aplicações diversas, e por último apresenta o primeiro estudo comprovando a oxidação da celulose por um processo fotocatalítico. Assim, a tese contribui não somente para o estudo e compreensão da celulose, mas para a ciência dos materiais de forma geral.

Palavras-chave: Propriedades sol-gel; Redes de polímeros; Semicondutores; Sílica gel; Fotocatálise; Secagem por congelação.

ABSTRACT

Aerogel's microstructure, kept intact by supercritical drying, affects its properties beyond its chemical composition. Nowadays, aerogels are essential in different industries, like thermal insulation, high-efficiency batteries, and aerospace applications. Nevertheless, aerogels rapidly reach mass production, while their fundamental studies and particularities were partially left behind. On the other hand, cellulose is a natural polymer that has been studied for decades, composed of glucose units, and can be obtained by different approaches, but via bacterial production yields a higher purity and crystallinity biopolymer. Structured by intertwined fibers, which possess nanometric diameters and micrometric length, materials based on bacterial cellulose have mechanical strength, flexibility, interconnected pore structure, and relatively high surface area. Due to its properties, transforming bacterial cellulose gel to aerogel, preserving its morphological features, is of great interest to a vast range of applications, adsorption and catalysis are examples. Cellulose itself does not show great adsorption capability for different molecules, nor for catalysis, but it can be associated with nanomaterials as a support, enhancing nanomaterial applications. Taking advantage of cellulose properties, they can be employed as membranes or sphere-like particles, allowing in-flow applications and suspended particles, achieving feasible recovery, contrasting nanomaterials' common drawback, aside from the nanoscale-related toxicity. Arising from synergism between cellulose, aerogels, and nanomaterials studies, the thesis starts with a focus on the different properties obtained when obtained the biopolymer is dried under different drying techniques, and evaluating their surface properties as well as their adsorption and photocatalytic applications. Analyzing literature gaps on aerogels, both on definition and fundamental studies, it was proposed an updated aerogel's definition, as well as its interpretation. After exploring the influence of drying technique on gels' preparation, the next chapter aimed to explore how a silica-based gel grows onto bacterial cellulose, a gel formed by two different alkoxy-silane precursors, impact aerogel's REE sorption and selectivity. One precursor had four hydrolysable groups, and the other had an organic chain substitution, guarantying ethylenediamine functionalization. While the first precursor could only result in silica oxide structure, presenting surface metalol groups, the other precursor had metal-coordinating and adsorbing groups, guiding their

application. Lastly, after studying means of materials preparation with drying technique and functionalization, bacterial cellulose aerogels were coated with titania and were applied to investigate the chemical stability of bacterial cellulose. Titania, a known oxidizing material upon ultraviolet light irradiation, once coating cellulose fibers, is capable not only of oxidizing organic molecules, but also of oxidizing cellulose itself, the inner material used as support. Result never seen in literature. Finally, the results obtained on this thesis abord bacterial cellulose aerogels in different aspects, from its biosynthesis, to preparation of the dried gels. Given highlights to the functionalization with silica-based gel, for distinct applications, and lastly shown the first study of bacterial cellulose oxidation under a photocatalytic process. Contributing not only with cellulose studies, but to material science as a broader area.

Keywords: Sol-gel properties; Polymeric networks; Semiconductors; Silica gel; Photocatalysis; Freeze-drying.

Resumo expandido em português

Descobertos há aproximadamente 90 anos, os aerogéis tiveram um começo comedido. Apesar disso, o interesse industrial já se apresentou rapidamente, em menos de 10 anos de seu descobrimento, resultou na criação e venda de patentes, e já havia produção em escala industrial. Apesar disso, o alto custo de produção e a lentidão com que eram produzidos faziam-nos materiais de alto valor agregado, mas devido à falta de um material competitivo, sua comercialização foi bem sucedida, principalmente na área de isolamento térmico. Com o surgimento dos plásticos, apesar de serem menos eficientes como isolantes térmicos, possuíam uma produção mais rápida e de menor custo, sendo mais competitivos financeiramente que os aerogéis, superaram sua demanda e substituíram-no no mercado. Esses fatores foram derradeiros para o quase desaparecimento dos aerogéis, que não obstante de sua decadência, ficaram conhecidos por serem materiais exóticos e inovadores, apesar de pouco aplicáveis.

As propriedades dos aerogéis estão intimamente atreladas a dois fatores, sua composição química e sua microestrutura, que é determinada pela forma com que o gel é seco para transformar-se em aerogel. De acordo com seu descobridor, aerogéis são géis onde o solvente confinado pela estrutura sólida do gel foi substituído por ar, sem que a estrutura do gel tenha sido alterada, por encolhimento ou quebra. No artigo onde foram anunciados pela primeira vez, mas também pelas décadas seguintes, aerogéis eram obtidos quando o solvente era extraído por secagem supercrítica. Diferente dos métodos de secagem comumente utilizados, seja de retirar o solvente utilizando a transição das fases líquido-vapor (evaporação) ou por sublimação (liofilização), a qual é necessário o congelamento do solvente previamente, seguido por sua sublimação, realizando a transição sólido-vapor. Com essa nova técnica, o solvente era inicialmente aquecido até seu ponto crítico, onde se torna um fluido supercrítico, e depois este fluido era transformado em gás. Com isso, os géis eram submetidos a um processo de quase-zero pressão capilar, fazendo com que a estrutura do material seco fosse mantida quando comparada ao gel úmido.

O desenvolvimento de aerogéis nas três décadas seguintes foi modesto, eram estudos majoritariamente feitos por empresas, e sendo assim, ocasionou pouco acréscimo à literatura em sua forma ampla, com o conhecimento mantido como

segredo industrial. Entretanto, algumas dessas patentes geradas tiveram relevância e foram efetivamente exploradas de forma mais ampla após os anos 2000. Sendo um material incipiente, caro e exótico, encontrou lugar em uma aplicação específica no final da década de 1980, detecção e estudo da radiação emitida em reatores nucleares. Os aerogéis de sílica produzidos para esse fim, além da conhecida capacidade de performar como isolante térmico, também usufruíram do índice de refração destes que poderiam ser obtidos com rigoroso controle e precisão. Assim, a combinação destas propriedades, sem que o custo fosse um fator limitante neste momento, atingiu os pré-requisitos propostos pelos autores e permitiu o estudo da radiação de Cherenkov.

A aplicação dos aerogéis no reator nuclear foi um marco em sua história, não somente por trazer uma nova possibilidade de aplicação, mas como o renascimento para pesquisa na área de forma mais abrangente. Esse fenômeno se deu pelo encontro entre dois cientistas, um pesquisador, envolvido na produção dos aerogéis de sílica para o reator nuclear, e outro, professor universitário. Neste encontro, o pesquisador entregou um dos aerogéis produzidos ao professor, o qual seguiu com o material para análises distintas, medindo diversas propriedades ao seu alcance. Afinal, era um material exótico e pouquíssimo explorado na literatura. Muitas publicações surgiram desta interação, ambos se tornaram referência na área de aerogel e publicaram diversos trabalhos relacionados às propriedades dos aerogéis.

Deste ponto em diante, muitos estudos fundamentais e aplicados foram produzidos. No decorrer da história dos aerogéis, houveram outros momentos de grande transformação para literatura na área, como a substituição do silicato de sódio por alcóxidos, sínteses sol-gel em duas etapas, secagem com CO_2 supercrítico ao invés do solvente nativo da síntese, descobrimento de aerogéis orgânicos e de carbono, gelificação assistida por epóxido, efeito *spring-back* e muitos outros. Todos foram vitais para alcançar o estado da arte atual, em que aerogéis são amplamente aplicados, estudados e comercializados. Apesar de terem começado sua trajetória na área de isolantes térmicos, área de maior relevância industrial ainda hoje, tem-se estima de que os aerogéis serão materiais fundamentais para a transição energética. Onde desenvolvem papel importante não somente na indústria de isolantes, mas também para composição de baterias de alta eficiência, catalisadores e até exploração espacial.

Uma grande área que também se beneficiou com o advento dos aerogéis foi a área de polímeros, mais especificamente para esta tese, a celulose bacteriana. A celulose é um dos polímeros mais abundantes no planeta, sendo encontrada em todas as plantas, como componente importante da parede celular, mas também presente em fungos e bactérias. Por ter majoritariamente uma função estrutural nas plantas, a celulose é comumente encontrada junto a outros polímeros, como hemicelulose e lignina. A celulose em si é formada por unidades de glicose conectadas por ligações β1-4, formando longas cadeias poliméricas lineares. Por ser constituída de unidades de glicose, cada monômero possui três grupos hidroxilas, permitindo à cadeia de celulose formar diversas ligações de hidrogênio, tanto ligações intracadeias, quanto intercadeias. E apesar de ser um polímero repleto de grupos hidroxila, não é um polímero solúvel em água, nem na maioria dos solventes comuns, característica resultante das inúmeras ligações de hidrogênio formadas entre as próprias cadeias de glicose, que originam as fibras de celulose.

Devido às fortes ligações que podem ser formadas entre as cadeias de celulose, o material pode se organizar, se estruturando e apresentando cristalinidade. Ainda que as plantas sejam as maiores produtoras de celulose, a presença de outros polímeros que compõem a celulose vegetal faz com que a celulose resultante dessas fontes apresente uma cristalinidade reduzida. Em contrapartida, a celulose produzida por bactérias, por não possuir uma função estrutural, mas terem a função de protegerem à radiação ultravioleta, apresenta alta pureza e alta cristalinidade. Logo, a obtenção de celulose bacteriana se faz vantajosa por evitar etapas de extração e purificação, o que acresceria ao custo do processo.

Por ser formada por fibras micrométricas de diâmetro nanométrico, também é chamada de nanocelulose; ela apresenta propriedades como alta retenção de água, flexibilidade, alta porosidade, poros conectados, resistência mecânica, biocompatibilidade e biodegradabilidade. Quando associado à produção por bactérias, as quais produzem a celulose partindo de precursores de baixo valor agregado, também atribui às interessantes características da celulose a de ser um material de baixo custo. Portanto, unir os estudos da celulose bacteriana aos estudos de aerogéis permite aproveitar o arranjo estrutural das fibras produzidas pelas bactérias e, com isso, aperfeiçoar aplicações onde área superficial e porosidade sejam fatores cruciais, como em tecnologias de adsorção e catálise.

Após a contextualização dos tópicos principais, o primeiro estudo apresentado na tese aborda a interface entre estes tópicos, onde géis híbridos de celulose bacteriana com sulfeto de molibdênio foram secos de diferentes formas, e suas propriedades foram exploradas em termos de adsorção do corante azul de metileno e fotocatálise do mesmo corante. Inicialmente, foi desenvolvido o crescimento da celulose em duas morfologias diferentes, a de membranas e a de partículas esferoidais de celulose, sendo a obtenção em membranas já estabelecida no grupo. Assim, a obtenção das partículas esferoidais de celulose precisou ser estudada nas condições disponíveis, utilizando a linhagem de bactéria disponível. Portanto, com aprofundamento bibliográfico e estudos empíricos, os parâmetros para síntese das partículas foram obtidos e padronizados para o contexto do grupo.

Com o procedimento para obtenção das duas morfologias de celulose bacteriana estabelecido, ambas foram submetidas ao recobrimento com sulfeto de molibdênio por via hidrotérmica, que já havia sido feito para as membranas, mas fora necessário adaptá-lo para as partículas. Seguidamente, ambas as morfologias, contendo ou não o semicondutor, foram secas por evaporação do solvente, liofilização e secagem supercrítica com CO_2, obtendo respectivamente xerogel, criogel e aerogel. Os materiais foram caracterizados por diversas técnicas, como difração de raios X, microscopia eletrônica de varredura e adsorção de nitrogênio, mas também foram testados em ensaios de filtração, adsorção máxima e fotocatálise.

Os resultados obtidos pelas técnicas de microscopia e adsorção de nitrogênio apontaram para resultados similares, onde as amostras liofilizadas possuem resultados intermediários aos obtidos por evaporação do solvente (resultados inferiores) e obtidos por secagem com CO_2 supercrítico (superiores). Entretanto, enquanto as membranas liofilizadas apresentam resultados próximos às membranas obtidas por secagem supercrítica (aerogel), as partículas liofilizadas se aproximam das partículas secas por evaporação do solvente, (xerogel). As amostras, após secagem supercrítica, apresentam as fibras da celulose dispersas e notável espaçamento entre elas, mas as amostras onde o solvente foi evaporado apresentam um colapso estrutural, provocando perda de área superficial e porosidade. Assim, a denotando a manifestação dos efeitos de pressão capilar, promovendo o colapso da estrutura na remoção do solvente. O xerogel das partículas com o semicondutor se destacou neste momento, dentre todas amostras sintetizadas, essa foi a única que

apresentou reorganização das lamelas da fase inorgânica, ao invés de estarem paralelas, as lamelas se organizaram em uma estrutura similar a uma flor.

Para remoção de corante azul de metileno, o aerogel das partículas apresentou resultados superiores a todos, o que pode também ser relacionado à maior área superficial, enquanto o criogel e xerogel das partículas apresentaram resultados bastante inferiores. Para as membranas, os criogéis, apesar de terem resultados próximos dos aerogéis, não foram possíveis a obtenção de membranas liofilizada integras, extinguindo a possibilidade de compará-las quando utilizado o reator em fluxo. Devido aos aerogéis apresentarem uma estrutura mais porosa e de maior área superficial, apresentaram melhores resultados, estes que são comparáveis não apenas entre si, mas também a outros materiais baseados em celulose ou em sulfeto de molibdênio.

Após este estudo na interface entre aerogéis e celulose, géis de sílica foram produzidos e secos de diferentes formas, visando melhor compreender conceitos fundamentais na secagem dos géis. Buscando não somente preencher lacunas na literatura na área de ciência dos aerogéis, mas também contornar a dificuldade de se obter uma membrana integra seca por liofilização. Muitos artigos classificam seus próprios géis como sendo aerogéis sem um critério específico, como quando os géis são liofilizados e mantêm a forma, por exemplo. Assim, a secagem acompanhada do estudo dos géis de sílica, além do que já é apresentado neste primeiro capítulo de resultados, servem como base para mostrar que, mesmo géis obtidos da mesma forma, mas secos de formas diferentes, principalmente quando é necessário congelamento, devem ser classificados diferentemente. Onde o congelamento é necessário, a formação da fase sólida do solvente no interior da estrutura causa distorções à rede polimérica que não podem ser preditas, sendo dependentes do solvente utilizado e da forma que o congelamento é conduzido na própria rede polimérica. Por consequência, uma definição para diferenciar aerogéis, criogéis e xerogéis, mas também a inclusão do termo liogel, é proposta buscando uma melhor descrição do material, onde o nome reflita a forma que o material foi obtido.

Seguidamente, o próximo capítulo da tese descreve a formação de um gel formado por diferentes proporções de precursores alcóxisilanos, e o impacto resultante no aerogel de celulose que é recoberto. Os precursores utilizados foram chamados de sílica inorgânica (TEOS), qual possui os quatro grupos alcóxi

hidrolisáveis, e o precursor chamado de organosilica (EDAS), onde um dos quatro grupos hidrolisáveis, foi substituído por um grupo propiletilenodiamina. Assim, as mudanças provocadas pela combinação de precursores de sílica foram avaliadas em relação às características morfológicas e adsorção de metais, capacidade reconhecida nos grupos etilenodiamina. Utilizando a síntese sol-gel em duas etapas, e mantendo todas as condições de síntese com exceção da proporção de sílica inorgânica e organosilica, originaram-se amostras denominadas H1 à H5. Onde H1 denomina o híbrido obtido somente com TEOS, qual a gradativamente substituída até a amostra H5, que é formada integralmente pelo precursor EDAS. Com isso, os aerogéis H1 obtidos apresentavam em sua superfície grupos óxidos e hidróxidos de silício, até H5, que majoritariamente possui grupos etilenodiamina ancorados nos silícios. Embora apenas um dos quatro grupos do precursor de sílica tenha sido substituído, a distinção entre as amostras foi observada em distintas escalas, desde a técnica de microscopia, até ensaios de sorção realizados com solução multielementar de terras raras.

Pelas imagens de microscopia eletrônica, evidencia-se o contraste gerado pela mudança na proporção entre os precursores, onde da amostra H5 até a amostra H1, as fibras da celulose são gradualmente mais recobertas, na qual uma imagem de H5 é similar à celulose pura, enquanto a de H1, grandes aglomerados de nanopartículas de sílica estão presentes. Esta interpretação é amparada pela técnica de gravimetria, que segue a mesma tendência, a amostra H1 com alta massa residual após a combustão da matéria orgânica, e amostra H5 com baixa massa residual. Ademais, devido à rota sintética, o TEOS resulta em um gel poroso e de alta área superficial, o que é observado na adsorção de nitrogênio, que acompanha a tendência. Onde o híbrido com maior área superficial é H1 e decresce até H5, apesar das amostras H3 à H5, possuírem valores similares. Apesar disso, somente com a técnica de RMN de ^{29}Si foi possível confirmar a presença dos grupos silanos na amostra H5. Combinando os resultados obtidos por essa técnica, com os resultados de análise elementar, observou que a quantidade de nitrogênio em cada amostra, oriunda do precursor EDAS, não é diretamente proporcional à sua fração molar, mas sim possui um máximo na amostra H3.

A explicação para essa variação da quantidade nominal de nitrogênio, é associada ao TEOS promover um local alternativo para o ancoramento de novas

espécies. Considerando que a celulose tem sítios ativos limitados, a área superficial gerada pela rede porosa do TEOS, favorece a incorporação de outras espécies, como o EDAS. Entretanto, a celulose parece ter um limite de fração inorgânica que pode comportar, enquanto existe um equilíbrio entre quantidade de TEOS presente e quantidade de EDAS que pode ser incorporado. Como a sorção é dependente da quantidade de nitrogênio presente, os grupos etilenodiamina, os resultados obtidos seguem o que foi observado na análise elementar. Onde a amostra H3 apresentou a maior capacidade de sorção, e amostra H1, apesar de possuir a maior área superficial, apresentou a capacidade de sorção quase insignificante para a maioria dos cátions analisados. Entretanto, como a amostra H3 sorveu praticamente todos os cátions em solução, ela não pode ser estudada frente à sua seletividade nessas condições. Já as outras amostras, todas apresentam alta sorção para o Sc, mas a enquanto H1 sorve também os lantanídeos mais pesados (Yb e Lu), a amostra H2 tem uma seletividade crescente conforme o cátion é mais pesado. Enquanto isso, H4 e H5 apresentam sorção moderada para todos os íons estudados.

Em seguida, as amostras foram testadas para o crescimento de prata *in situ*, demonstrando a multifuncionalidade dos aerogéis híbridos desenvolvidos. Como observado visualmente, mas suportado por medidas de DRX, as espécies de prata formadas eram dependentes da fração TEOS:EDAS de cada amostra. Enquanto a amostra que possuía predominantemente TEOS, crescia cloreto de prata, nas amostras que possuíam maior fração de EDAS tinham também um crescimento de prata metálica. Esse fenômeno foi associado à capacidade dos grupos amina não somente adsorverem os íons prata, fornecendo um ponto de nucleação das espécies de prata, mas também de reduzirem o cátion prata a prata metálica. Estes híbridos recobertos com prata, podem ser aplicados tanto para fotocatálise, como também como curativos antibactericidas. Dessa forma, a sorção de lantanídeos, associada com o crescimento seletivo de espécies de prata, denotam a versatilidade e controle dos híbridos formados quando se varia a fração molar dos precursores de silício. Assim, demonstrando que os aerogéis desenvolvidos por um processo sol-gel de duas etapas podem ter aplicações diversas, mas também serem utilizados como plataformas para modificações futuras, como em funcionalização por reações orgânicas ou crescimento de outras espécies além da prata.

Por fim, no último capítulo da tese, utilizando diferentes técnicas de caracterização, buscou-se averiguar diferenças geradas pelo processo fotocatalítico ou irradiação ultravioleta nos aerogéis de celulose. Utilizando-se de membranas de atividade fotocatalítica já conhecidas, membranas inteiras, mas também fragmentos das mesmas, foram estudados antes e depois da irradiação. Apesar de nenhum efeito ter sido observado nas membranas, seja na técnica de DRX ou FTIR-ATR, as amostras fragmentadas apresentaram drásticas mudanças nos espectros de micro-FTIR após a irradiação. Para mensurar os efeitos, as bandas da região de interesse dos espectros (1800 – 1300 cm^{-1}) foram deconvoluídas em suas componentes vibracionais, um índice de oxidação foi criado para quantificar e comprar o efeito entre as amostras. Por este índice, foi possível observar que todas as amostras sofreram oxidação após irradiação, mesmo as amostras de celulose pura e celulose com sílica (BSR2) tiveram um aumento. Já para as amostras com fotocatalisador (titania), o aumento do índice de oxidação foi expressivo, destacando que o fotocatalisador oxida sim o material de suporte. E, enquanto a hipótese anterior era de que a camada de sílica entre a celulose e a titânia pudesse proteger a celulose, aumentando a atividade fotocatalítica do material, foi observado que o BSR2@TiO_2 apresentou o maior valor deste índice, indicando que a sílica não desempenha papel de proteção à celulose.

De maneira breve, o primeiro capítulo avalia a forma de secagem dos géis híbridos baseados em celulose, além da descrição do desenvolvimento da produção de partículas de celulose esferoidais pelo nosso grupo. O segundo capítulo foca na modificação e funcionalização de aerogéis de celulose. O recobrimento de celulose por géis de sílica formados por TEOS e EDAS, onde o controle da proporção entre os precursores atribui ao aerogel híbrido diferentes propriedades. Este controle garante diferenças desde a gelificação, a testes de sorção e crescimento de espécies de prata, além de poder ser aplicado para fotocatálise e bactericida. Por fim, o último capítulo aborda os aerogéis modificados de celulose bacteriana após um processo fotocatalítico, mostrando, pela primeira vez na literatura, que a fotocatálise também oxida a matriz de celulose.

Assim, a tese aborda aspectos fundamentais da síntese sol-gel aplicada ao desenvolvimento de aerogéis híbridos baseados em celulose bacteriana. Onde os estudos começam desde a produção da celulose à sua respectiva funcionalização, aplicação e consequência dessa aplicação para a matriz biopolimérica.

Desenvolvendo, assim, um trabalho amplo centrado na celulose bacteriana, mas que apresenta impactos diretos nos estudos de celulose, nas sínteses sol-gel, mas também no campo de aerogéis e na ciência dos materiais, como um todo.

LIST OF SYMBOLS AND ABBREVIATIONS

AOP	Advanced oxidation processes
ASAP	Accelerated surface area and porosity system
ATR	Attenuated Total reflectance
BC or BNC	Bacterial cellulose
BCM	Bacterial cellulose membranes
BCS	Bacterial cellulose sphere-like
BET	Brunnauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
DOx	Degree of Oxidation
EAG	Epoxide assisted gelation
ED	Evaporation drying
EDAS	*N*-[3-(trimethoxysilyl)propyl]ethylenediamine
FD	Freeze-drying
FWHM	Full width at half maximum
HD	Heat Drying
HS	Hestrin-Schramm
Hx	Hybrid samples composed of TEOS and/or EDAS
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene Blue
NMR	Nuclear magnetic resonance
OSSD	Organic Solvent Sublimation Drying
P_c	Critical pressure
REE	Rare earth element
RMSE	Root mean square error
SCD	Supercritical Drying
SEM	Scanning Electron Microscopy
SD	Sublimation Drying
T_c	Critical temperature
TEOS	Tetraethylorthosilicate
TGA	Thermogravimetric Analysis
UV	Ultraviolet light
XRD	X ray diffractometry

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1. Aerogels

“Whipped egg whites or solid bubble bath are the closest in appearance to aerogels.” This statement was made by Hüsing and Schubert in 1998 as an initial representation of what aerogels are.[1] Although a very illustrative approach to aerogels' most signature characteristic, “the air-composed” material, one must bear in mind that aerogels’ special feature refers to their nanostructure composition and its direct consequences on the macroscopic properties of the materials. Their overall properties are composition dependent, so they vary along with nanostructure elements, but many are of great interest to aerogel research field nowadays. Aerogels can exhibit properties ranging from high specific surface area, high porosity, and ultralow density, to ultralow heat conductivity, electrical conductivity, superelasticity, mechanical durability, optical transparency, superparamagnetism, and numerous others alone, or even taking advantage of enhanced properties due to their combination.[2]

On their first appearance, in 1931, in a Nature paper published by Kistler alone,[3] Kistler coined the term *aerogels*, thus classifying the materials he produced as such, and determined that they were gels where liquid was replaced by air. At this moment, Kistler’s interests were to better understand how liquids would permeate and diffuse into jellies, but after observing that gel could retain its structure independent of the liquid they were bathed in, his interests grew on how to remove the present liquid without affecting the gel’s structure. After the common observation of collapse upon simple solvent evaporation, causing shrinkage, studying led him to elaborate a hypothesis that using a supercritical drying equipment would be able to diminish the capillary forces on the material, hindering the collapse. Using a pressurized reactor borrowed from a fellow researcher, he investigated his hypothesis, and this short paper from 1931, where he reports the successful achievements on said hypothesis, is considered to be the official start of aerogels research, and Samuel Stephens Kistler is considered the founder of aerogel materials. Now, aerogels can be seen as presenting different morphology, properties, and composition, unimaginable to their first production, as displayed in Figure 1.

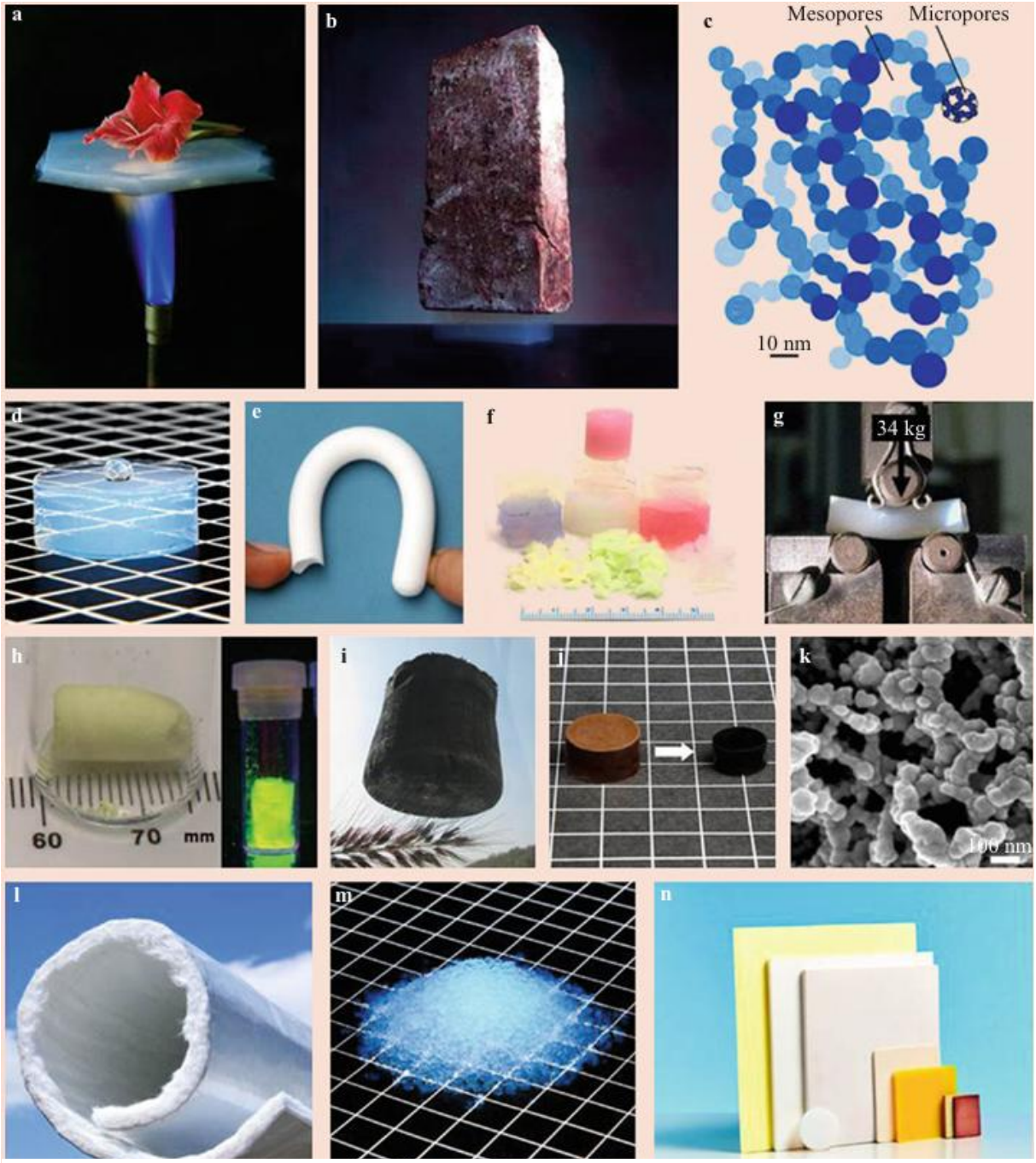

Figure 1 – Representative of the diversity in aerogels science. (a) "The Flower" is a silica aerogel monolith protecting a flower from a flame; (b) >98% porous silica monolith under a brick 1000 times heavier; (c) general illustration of aerogel with its string-of-pearls microstructure; (d) Silica aerogel functionalized with hydrophobic trimethylsiloxyl groups; (e) Silica aerogel functionalized with methyltrimethoxysilane for flexibility; (f) Lanthanide salts made to oxide aerogels by epoxide gelation; (g) Silica aerogel reinforced with crosslinked polymer; (h) Photoluminescent quantum dot aerogel made from cadmium sulfide; (i) Graphene aerogel on a dandelion (Least dense solid, Guinness World Records);(j) Organic aerogel made from polymeric resorcinol-formaldehyde and its carbon aerogel derivate; (k) Aerogel-like silver structure obtained from physical vapor deposition; (l) Silica aerogel reinforced by fibers, Cryogel® Z; (m) Aerogel particles Lumira® LA1000; (n) Polymeric aerogel panels, Airloy®.

Source: Image and description obtained from reference.[2]

Even though in the first aerogel article, Kistler already reported the production of a wide range of different aerogel compositions, ranging from inorganic (silica, alumina, titania, metal oxides and hydroxides) to organic (cellulose, gelatin, agar, egg albumin),[3] Silica aerogels were the first to gain industrial interest, and by the end of 1930s were already mass produced. These silica gels were produced from sodium silicate (also known as water glass), resulting in a very porous powder material that was widely used as a thermal insulator for refrigerators and pipelines. While yielding great results, they began to lose market when polymers and plastics appeared in the market, mainly due to their lower production costs when compared with silica aerogels.[2] Aerogels produced at this moment took weeks to be ready, had the high-alkaline sodium silicates as precursor, and the industrial-scale supercritical drying equipment to obtain them used methanol as drying solvent, since it was also the synthesis solvent, but different solvents had been explored by this time.[2]

Sodium silicate gels had gelation restricted to high acidity media, and generated different sodium salts that required abundant solvent washes to be removed. The combination of acidic media and high salt concentration was not only harmful to the equipment used, but also yielded gels with reduced transparency and increased hydrophilicity.[4] A significant revolution came to the aerogels area more than 30 years after its first appearance, in 1960s, different sources of silica were discovered and used as a substitute for the cheap and easy-to-obtain sodium silicate.[5] Standard Oil Co. industry was the first to develop this new route, using tetraethylorthosilicate (TEOS) as a precursor; their synthesis could proceed in ethanol, with water and a catalyst for condensation and hydrolysis, resulting in a significant reduction of both the gelation time and the amount of solvent exchanges needed before supercritically drying the material.[6]

The use of alkoxides began as an alternative to reduce time on gel production, but they became an important ally in aerogel research. Alkoxides allowed scientists to explore how the gels were formed by following the condensation and hydrolysis reactions. From their first discovery up to decades later, aerogels were perceived as an exotic material, with interesting properties, fascinating appearance, and production methodology, but their high costs and lack of direct competitive application caused them to be famous, still without great interest emerging either from academy or industry. Owing to these precursors' change, highly optical transparency was achieved

in aerogel, and combined with low and tunable refractive index from silica materials (from 1.007 to 1.24),[7] by the end of 1970s, these new exotic materials emerged as a candidate for the detection of high-energy particles in a nuclear reactor, while simultaneously providing thermal isolation.[8,9]

Prof. Max Scheer was one of the researchers responsible for producing the silica gel tiles used for nuclear radiation detection. During his visit at the end of 1970s to the University of Würzburg, he met Prof. Jochen Fricke, whose main interest at that moment was the development of opaque thermal superinsulation materials. On the occasion, Prof. Scheer gave Prof. Fricke a sample of his produced transparent superinsulation silica aerogel, and the curiosity on the exotic material led him to initiate a characterization series on the gifted tile, observing its structural, thermal, optical, and acoustic properties.[2] This cooperation gave them a vast number of publications, and a strong understanding of aerogel's main properties we refer to nowadays.

After proper characterization and publication of silica's aerogel properties, these papers drove an increase attention of other researchers from different fields, who saw not only potential applications for them, but mainly saw an opportunity to incorporate this material preparation procedure to their own materials, combining their already known gels with supercritical drying methodology, enhancing their properties, and aiming for desired aerogels' attractive properties. As Kistler wrote in the last paragraph of his first paper in 1931, "So far, we have prepared silica, alumina, nickel tartarate, stannic oxide, tungstic oxide, gelatine, agar, nitrocellulose, cellulose, and egg albumin aerogels and we see no reason why this list may not be extended indefinitely".[3]

Another important moment in aerogel research came at the end of 1980s, when Pekala developed RF aerogels.[10] Upon reacting resorcinol (R) and Formaldehyde (F), Pekala showed a gel where the solid network was exclusively made of organic compounds. Aside from being the first to display an organic aerogel, he also showed in this paper that heating the aerogel under a non-oxidative atmosphere, one could transform the organic aerogel to a carbon aerogel. On a single paper, he started two important research branches of aerogels we know nowadays, organic and carbon aerogels, similar to Figure 1j. Although organic aerogels were a new idea, carbon aerogels got a higher spotlight, especially today, due to their electronic properties and their possibilities of being applied for renewable energy and batteries.[11]

In 1990s, while it may seem of small relevance at first, the use of epoxide compounds as gelling agents reappeared at Lawrence Livermore National Laboratory (Livermore, USA), opening a vast horizon to aerogel science.[12] From this moment on, gels from widely different sources could be produced, enabling different solutions to be gelled by EAG (epoxide-assisted gelation), and thereafter dried via supercritical drying to obtain aerogels.[13,14] Though alkoxides had gained much attention, due to the creation of new and bimetallic gels, most precursors were expensive or difficult to obtain, and the condensation reactions generally led to denser aerogels, hindering the potential. Aerogel synthesis initially made using salts reemerged as an attractive possibility, since epoxide gave them an alternative to control their fast hydrolysis. The epoxide acts as a proton scavenger, slowly increasing the pH of the solution, thus slowly transforming the hydrated metal centers ($M–OH_2$) to metalol groups (M–OH), and these more reactive metalol groups will be responsible for undergoing further reactions.

Especially after these three crucial moments in aerogels' history, use of alkoxides (1960s), creation of binary oxides and organic aerogels (1980s), and use of epoxides as gelling agents (1990s), but including interests of aerogels for specific applications where large amount of money is invested, like aerospace and oil industries (2000s),[15–17] one can comprehend the development of aerogels through time, represented in Figure 2, which displays the yearly publications on aerogels by year.

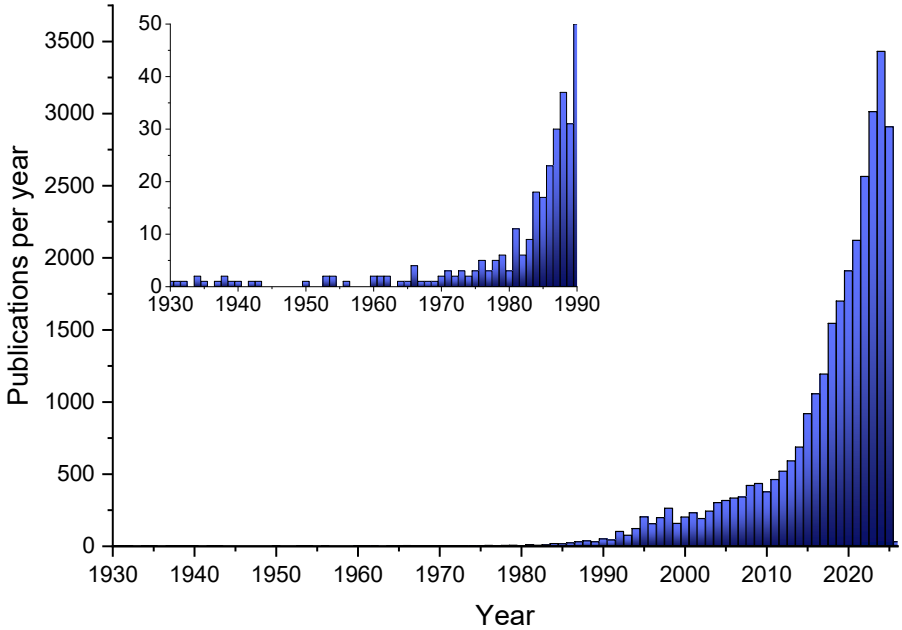

Figure 2 - Annually publications on Aerogels
Source: Data obtained from Scopus website, with "aerogel" as keyword, on September 10th, 2025.

Nowadays, aerogels are already produced on an industrial scale by companies like Aspen Aerogels, BASF, Cabot Corporation, Aerogel Technologies, Shanghai Aerogelzone Technology, and more. Nevertheless, there are still bottlenecks and difficulties to overcome, such as high precursor prices and the feasibility of the drying technique employed. Top markets for aerogels are thermal insulators, due to their heat resistance and high porosity, and high-efficiency batteries, due to aerogels with high electrical conductivity, interconnected pores. As properties are controlled by materials' composition, they can be controlled to suit the application,[18,19] so aerogels can be applied in a vast different fields.[17,20–22]

1.1.1. Definition of aerogel through time

As mentioned before, Kistler already coined the term *aerogels* in his initial paper, and defined them as "a gel where the liquid inside was exchanged to air", matching the illustrative description made by Hüsing and Schubert[1] at the beginning of this chapter. Nowadays, this description is quite simplified for different reasons presented below. Since the term *gel* was not properly defined by Kistler's first publication on aerogel, this may be the reason Kistler used the term *jelly/jellies* throughout his paper. As one can

observe in literature, in 1930, there was a paper where the author states the difficulty of defining gel, affirming that it was a much simpler task to recognize them visually than it is to define them, but a definition was not agreed upon.[23]

IUPAC, being the most renowned international entity responsible for defining technical terms for the general chemistry field, defines a gel as “a non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid”.[24] This definition is not completely updated with nowadays literature, understood when seen that this was established in 2007 and had no updates. Since the description made by IUPAC is outdated, another good reference for the gel’s description can be found in 2015 Sol-Gel Handbook, and even though it is 10 years old, it describes the gel state more properly. According to it, the gel is a continuous solid network, porous and three-dimensional, surrounding and supporting a continuous phase.[25]

It is interesting to bring to the discussion the book Nano Design for Smart Gels from 2020, where authors stated that the concept of gel formation strongly relies on physicochemical concepts inherited from colloidal sciences.[26] These concepts unfold through microscopic structure, the nature of the gelled medium, and the physicochemical resulting properties. Later, the authors define gels as belonging to two major classes depending on their gelling process, either polymeric or colloidal gel. Polymeric gels are obtained when sols are gelled chemically, either by in situ polymerization or chains interconnection induced by covalent bonds. While colloidal gels are either obtained by physical process, where physical or intermolecular noncovalent interaction leads to agglomerate organization. A rheological view of gels, like the shear rate and viscosity, is long known in literature[27–29] and helped guide through this newer definition, unifying organic and inorganic gels, because it considers both their polymeric and particulate natures.

Sometimes redundantly called wetgels, gel growth is commonly described by a cluster aggregation theory, entitled percolation, which is especially useful when describing inorganic matrices. On this model,[30] it is proposed that hydrolyzed and condensed particles aggregate to form bigger structures (clusters), and these clusters, diffused in the liquid media, can assemble, generating more complex structures, and upon many clusters and particles combined and gathered, it will result in the random three-dimensional solid gel network. This aggregation can be followed by an increase

in the solution's viscosity or even by time-resolved X-ray scattering for example, which indicates the transition from sol to gel phases.[31]

When Kistler coined the term aerogel, it mostly did not correlate with a specific material, depending solely on methodology to obtain the dried gel, so the composition of the material was not important; it was more about the means the dried specimen body was obtained. Although different composition matrices were produced, silica aerogels were first to gain commercial and industrial interest, almost exclusively for thermal isolation applications. Since they were brand-new materials, it is easy to understand that the word aerogel became associated with mesoporous silica materials made from water glass and then supercritically dried, thus becoming synonymous.[32,33] As described before, aerogels' history underwent a series of revolutions, resulting in a need of readaptation on the term aerogel, to be inclusive to those new aerogels which were arising, from silica alkoxides to organic, and polymeric for example, but initially this "adaption" was merely a formal return to what was state by aerogel's founder, which classify the material independent of its composition.

Despite its return close to its original definition, the material became, as still is up to this date, a hot topic with increased interest arising from academic fields, start-ups, and industries; hence, some authors chose to call their material aerogel to increase attention to their article or product, surfing this trend.[34] Thus, the increase use of the word aerogel without a proper definition, combined with innovation in sample preparing/drying, leads to incorrect classification and confusion. Particularly to this theme, the term could be mistaken with other existing terms, such as cryogel, which initially referred to a gel that was freeze-dried or a solution that was only made into a gel via freezing (cryo) methodology. In this way, the difference was very straightforward, led by its drying definition, it was material independent, where a xerogel (meaning a dry, "*xeros*" in Greek) would be obtained if the solvent was evaporated (with or without changes in pressure or temperature); and a cryogel (meaning an ice/cold, "*kryos*" in Greek) would be obtained if the material was freeze-dried.[34] More about the proper description of specific drying techniques, refers to section 1.3. Drying technologies.

In 1944, Kistler himself already filed a patent that later helped push the boundaries of aerogel's definition. He proposed creating hydrophobic silica monoliths by making the gels using organic solvents instead of water.[35] Since organic solvents

have less surface tension than water, they cause less structure collapse, which allows aerogel-like materials to be synthesized without solvent exchange, and to be more easily dried. This advance and new understanding of solvent-structure correlation led industries to start producing aerogels with reduced costs and at an increased speed.[36,37] Later, even called xerogels by the patent authors, a major advance was published by Deshpade, Smith, and Brinker was seen who proposed a surface chemical modification on silica aerogels, functionalizing the material after gelation with organic groups to diminish solvent-solid interaction, leading to a high reduction in shrinkage upon solvent evaporation.[38] The achieved effect, as suggested in 2001 by Land, was a spring-back effect, where the gel initially shrank and later returned closely to its wet gel size.[39] By this phenomenon, the solid network did not lose its structure, its flexibility allowed it to withstand to solvent's action without breaking, and later it regained its integrity. Therefore, they were creating aerogels without supercritical drying, just by evaporation of the solvent.

With more advances in this field, the term aerogel grew and came to be more attention-catching compared with the others, like cryogel, xerogel, lyogel, and oleogel; thus, it ended up being considered as a more "prestigious" material, with better properties than the others. As a consequence, this nomenclature misleads about the way to obtain the material, being focused more on its properties, rather than on its preparation, as initially proposed.[34] Bearing the difficulty in classification, what exactly is an aerogel, arising from advanced sample preparation methodologies, for example, IUPAC published an official definition also in 2007.[24] They define aerogel as a "gel comprised of a microporous solid in which the dispersed phase is a gas", with the addition of "Note: Microporous silica, microporous glass, and zeolites are common examples of aerogels". It is interesting to underline the problem of this definition, mostly because it implies that classical silica aerogels would not fit into this category. Therefore, different groups proposed their own definitions for the aerogels,[40–42] aiming for a standardization and guide for future research, but as observed from these articles, being from 2006, 2010, and 2017, respectively, it is clear that no consensus was achieved, either by lack of reach of the article or fundamental theoretical disagreement.

Discussing them in chronological order, Hüsing and Schubert in 2006[40] had a precise and restricted definition. They define aerogels as materials possessing density from 0.004 to 0.500 g cm^{-3}, resulting from the large open pores solid with high specific

surface area. Highlighting that these properties imply low thermal conductivity, low sound velocity, and high optical transparency, among others not cited. In this paper, the authors combine this description with an adaptation to Kistler's idea, stating that aerogels are materials in which the porous solid structure is preserved when the liquid in the pores is replaced by air, but emphasize that the degree of structure's preservation is not clearly known. This update shows an improvement to aerogel's definition; they already indicate that classifying exclusively by supercritical drying is not enough, and that classifying by porous structure can lead to inclusion of different materials not previously included, like molecular sieves and zeolites. Thus, upon making the definition, the authors themselves point out gaps in their definition. It is worth mentioning that their definition excludes aerogels, which are opaque, with different densities, and even stating that large pores and high specific surface area are needed, they do not cite numbers, leaving a subjective definition open to interpretation.

Written by Leventis and co-authors in 2010,[41] the second article cited here that brings a contribution does not have the explicit definition of aerogel as the core of the scientific discussion, as the definition is explored in its support information, but it is evident that the researchers are concerned with the topic. They began criticizing IUPAC's definition of aerogel, and based on IUPAC's gel definition, propose an updated version, and after realizing that this new definition could be confused with foam or xerogel definition, they mention their differences and, without delay, propose an updated version. Here, authors suggest that "aerogel is an open non-fluid colloidal network or polymer network that is expanded throughout its whole volume by gas, and is formed by the removal of all swelling agents from a gel without substantial volume reduction or network compaction." With this definition, they were not as specific as prior definitions, but this definition lacks one of the main characteristic goals for aerogel, a highly porous network; thus this definition can also classify low surface area, and dense materials characteristics as aerogels.

To bring another example, a paper led by Eychmüller and co-authors brought in 2017 a definition on a review article, though they focus their paper on inorganic aerogels, their view is broad and important for general cases.[42] On this review, they start with a discussion about what a gel is, and then bring the definition as it follows: "An aerogel is a solid with meso- and macropores with diameters up to a few hundred nanometers and a porosity of more than 95% in which the dispersed phase is a gas."

While they declare that this definition includes all aerogel materials within their review, they also admit that aerogel materials are still challenging to precisely define. Moreover, none of these three definitions given so far are the official one, given by IUPAC in 2007,[24] and even being the official definition, it is clear by the unofficial definitions given so far that the community vastly disagrees with it.

A widespread standard definition is of utmost importance, so researchers are critical to write, interpret, and analyze articles published by other researchers. A recent example of an academic mistake can be seen by Bhuyan and Jeong in the journal *Gels* (Impact factor 5.3, in November 2025), volume 10, issue 9, published in 2024, where they state “when the gel contain high porosity with extended mechanical strength and a higher surface area for greater adsorption capacity, they are termed aerogels”.[43] Only after the discussion made so far, it is already possible to point out inconsistencies stated by authors, like the need for extended mechanical strength and greater adsorption capability. Aerogels have been known for a long time as fragile materials, and most inorganic aerogels still have this drawback. While adsorption capacity relies extensively on the adsorbate (material or compound to be adsorbed) interactions with the material’s surface, regardless it consists of an aerogel or not.

So far, no definition has been widely accepted throughout scientific community, or an updated version of IUPAC has not been found, and although Hüsing and Schubert's proposal in 2008 is the accepted, since it is more precise, it does present gaps, and points which could be improved to include the recent gel advances, related to more than 15 years of progress. Thus, there is still room for work to be done in this regard, where a proper definition of the material is needed to both categorize and classify them accordingly. A good reflection of this problem can be seen in an aerogel review paper published by Takeshita, Mine, and Ono in 2025, where they present Figure 3 to highlight the disorientated knowledge in the literature about it.[34] The discussion about the definition of aerogel, like other dried gels, is deepened later during this thesis in chapter 2.4.7.

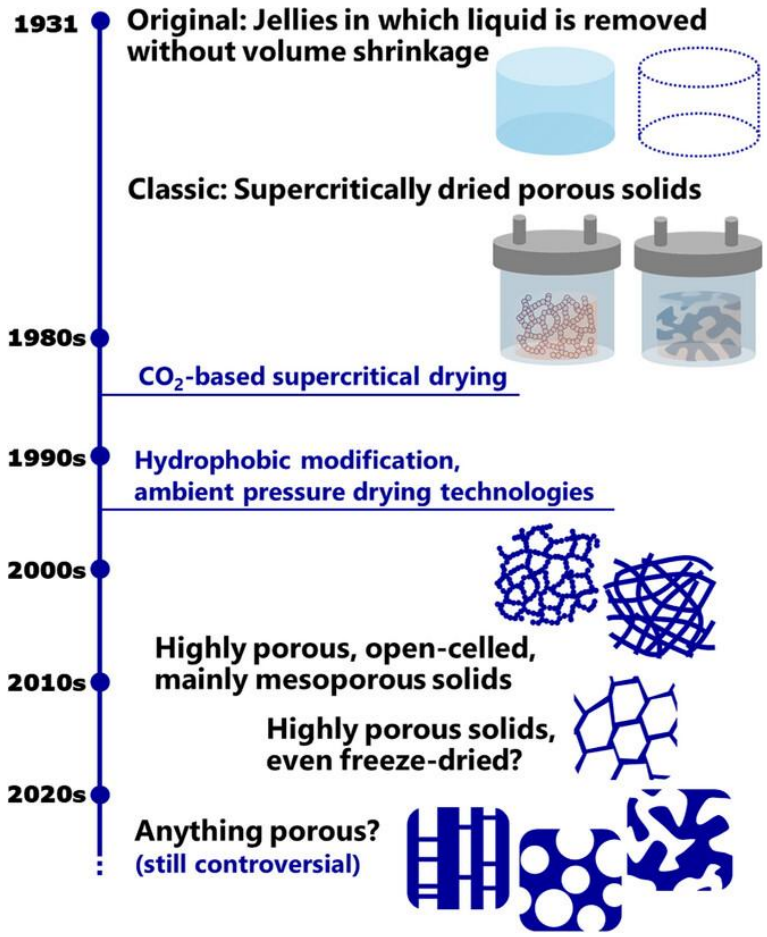

Figure 3 – Timeline of aerogels definition by literature consensus
Source: Figure from reference[34]

Even with the vast growth of aerogels field described in previous sections, majority of aerogels, but mostly inorganic ones, have two major flaws: extensive solvent exchange steps before proper drying technique is employed, and gel mechanical fragility, especially after drying. Though literature shows ways to improve dried gels' fragility, like adding polymers to gels' matrix, it usually implies exchanging one or more properties to increase mechanical resistance, creating a compromise between the desired activity and mechanical resistance. Therefore, a pristine dried gel with high activity and high mechanical strength is a goal for many researchers.

1.1.2. Aerogels today

Massive progress in the field could be seen in each decade, including recent years. Today, one can find in the literature aerogels made from different starting materials, like protein as the solid network,[44] but also advanced production techniques, like aerogels made via additive manufacturing.[45] Despite limitations presented before, nowadays aerogels are already commercially available with a competitive cost, but much has changed from the initial synthesis. Springer Handbook of Aerogels collected information from aerogel industries both via literature and via questionnaires directly sent to companies. The summary of these data is published in the 1st and 64th chapters, and will shortly be described here.[2]

Collins, Zhao, Wang, Griffin, Steiner III, 64th chapter authors, underline that aerogel commercialization had four main obstacles to overcome before achieving relevance in the market. First was the manufacturing process, mostly concerning the supercritical drying; second was material feedstock, restrictions about precursors; third was material durability, since aerogels-of-interest produced so far were brittle in its majority; and fourth was market history, which had many ups and downs. As aforementioned, drying technique was as fundamental to aerogel science as it was a drawback to increase production scale, but the substitution for CO_2 as solvent allows industries a safer and cheaper process (due to lower temperature and pressure needed to achieve supercritical state), even with required solvent exchange steps. Not restricted to changing the supercritical solvent, but also the discovery of aerogel production from solvent evaporation, due to organic solvent and the material's functionalization, permits a more fitted industrial production methodology. Thus, improving drying of gel itself is still a notable area of interest for industries, its development has already made aerogel commercialization at an industrial scale.

Currently, close to 50% of the aerogel's final price is related to its precursor's price, and even with advances in alkoxide synthesis, instead of being salt-restricted, the starting material still possesses chemical stability issues, as well as susceptibility to air humidity. Even reaching for new compounds as precursors, the aerogel industry is strictly dependent on alkoxide industry and its advances. The third obstacle for aerogels business, although mechanically strong aerogels are present in literature, they have not achieved industry-wide production, and the materials produced so far are brittle silica. To overcome the challenge of using pristine aerogel monoliths, either

aerogels are applied as powder-like, as filling between walls or around oil pipes, or they are incorporated onto other materials, like fiberglass, and can be used as an improved thermal isolating sheet.

Market-wise, as described during the brief history of aerogels, aerogels had a strong beginning, with Kistler securing patents to processes, and after Monsanto started producing, but since the insulating market of aerogels was quickly overcome by plastic, it had a fast decline.

1.2. Bacterial Cellulose

Considered one of the most plentiful biopolymers in the world, cellulose is widely found in nature, being the main component in plant cell walls, and most of this biopolymer is found to be combined with hemicellulose and lignin.[46] Being a renewable source and vastly available, this abundant biopolymer has two main sources, lignocellulosic biomass and an extracellular side-product of bacterial biosynthesis, as represented in Figure 4.

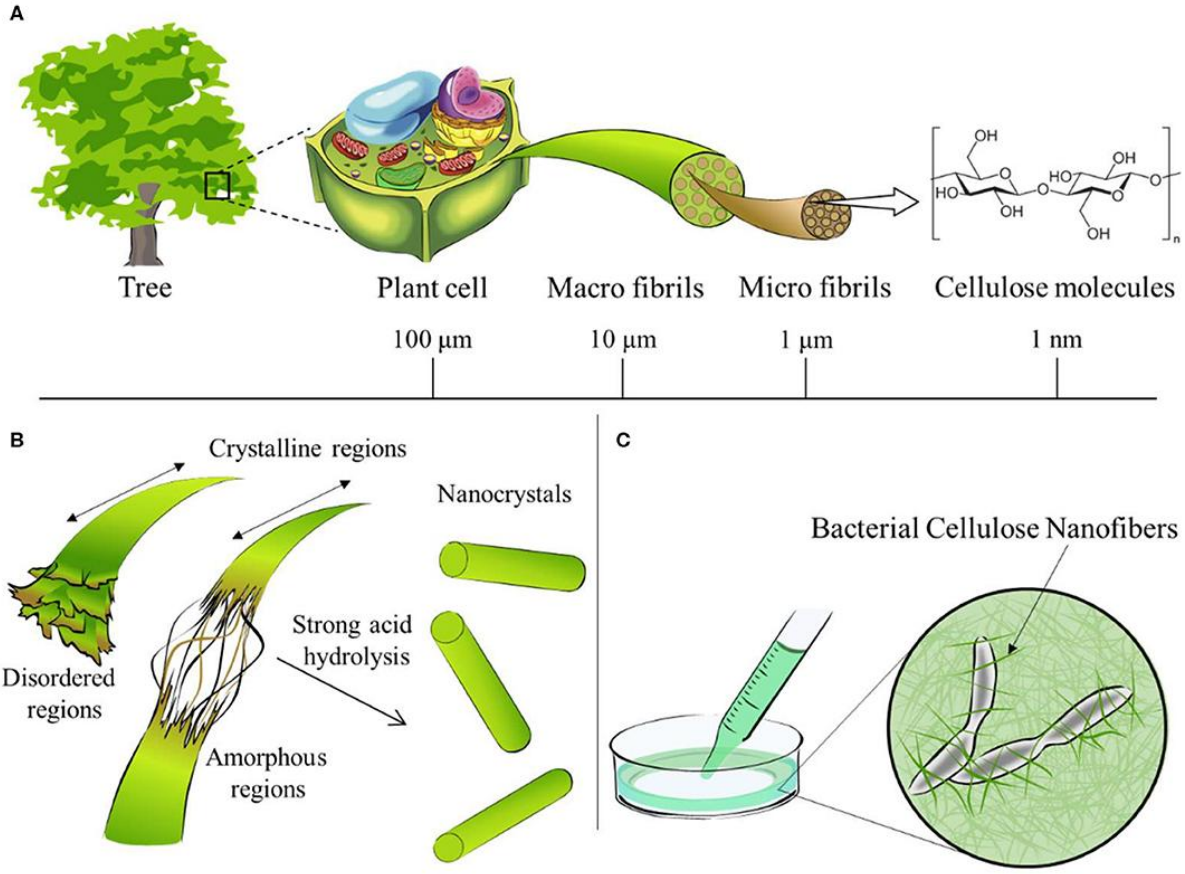

Figure 4 – (A) Diagram displaying the hierarchal structure of plant cellulose, from micro scale to cellulose fibers and glucose polymer; (B) Display of nanocrystal extraction via acid attack to cellulosic fibers; (C) Cellulose fibers obtained from bacteria culture media.
Source: Figure from reference.[47]

Lignocellulosic biomass is a good cellulose source; they are natural material and usually can be obtained from different residues or wastes, like sugarcane bagasse residues or wood industry wastes. As a result of its low price and renewable feature, lignocellulosic biomass residues are of increasing interest as a potential cellulose source, thus commonly explored in literature.[48] As forementioned, cellulose in plant residues is often found accompanied by its two other polymers, hemicellulose and lignin, thus decreasing cellulose content and providing a less pure material. To overcome this problem, pretreatment methodologies of these blends were developed and focused on either obtaining a higher cellulose content or less cellulose loss.[47] But since these polymers are alike, the advantages of a green and renewable source can be matched with the harmful reagents used for purification and extraction steps.[49]

Aside from cellulose obtained from lignocellulosic biomass residues, bacteria are another common cellulose source. Being a side product of some bacteria strains and it is produced for their sun-protection, rather than structural needs like lignocellulosic materials, as consequence they have no necessity to incorporate hemicellulose or lignin in the produced fibers, resulting in a pure cellulose production with higher crystallinity.[50] The cellulose produced by bacteria, also called bacterial cellulose (BC) or bacterial nanocellulose, is produced as a membrane on the liquid-air interface where bacteria grow. In this manner, the membrane must have exquisite oxygen transport properties, so the aerobic bacteria in the liquid are not suffocated, meanwhile creating UV protection.[51] A summary of different cellulose names, sources, and resulting morphologies can be observed in Table 1.

Table 1 – Comparison between cellulose types, with respective names and physical characteristics.

Type of nanocellulose	Synonyms	Typical sources	Formation and average size
Nano- or microfibrillated cellulose (NFC/MFC)	Micro-fibrillated cellulose, nano-fibrils, and micro-fibrils, nano-fibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax	It can be extracted from cellulose chains using a mechanical process to cleave the fiber into a nanometer-sized diameter. Diameter: 5 – 60 nm Length: several micrometers
Nanocrystalline cellulose (NCC)	Cellulose nano-crystals, crystallites, whiskers, rod-like cellulose, microcrystals	Wood, cotton, hemp, flax, wheat straw, mulberry bark, ramie, Avicel®, tunicin, cellulose from algae and bacteria	It can be extracted from cellulose chains using acid hydrolysis of amorphous region and leaving only crystalline region. Diameter: 5 – 70 nm Length: 100 – 250 nm (from plant celluloses)
Bacterial nanocellulose	Bacterial cellulose, microbial cellulose, bio-cellulose	Low-molecular weight sugars and alcohols	Bacterial synthesis Diameter: 20 – 100 nm Different types of nano-fiber networks

Source: Table from literature.[52]

Since cellulose production is relatively cheap and has many sources, both renewable biomass and produced, like bacterial cellulose or cellulose nanocrystals, these materials are explored as a way to future technologies, from health sciences to technological fields, from smart patches to precise sensors.[53,54] Cellulosic materials are even coming for to aid recent years' emergences, being explored as a plastic alternative[55] to fuel-transition technologies, being explored as energy storage

materials, conductors, and isolators, all derived from its tunable properties and respective functionalization.[56] Since our research group, led by Professor Sidney Ribeiro, has know-how on bacterial cellulose production and application, due to its own production facility and many articles published throughout the years,[57–61] a deep discussion and comparison between plant and bacterial cellulose is not in the scope of this thesis, and it can be found elsewhere.[48] Consequently, the discussion henceforth will focus on bacterial cellulose, unless specified.

1.2.1. Physico-Chemical Properties

A closer look to cellulose structure composition shows a material that is made of long fibers, which are created by an organization of smaller fibers, and these smaller fibers are an assembly of even smaller fibers, that are an organization of anhydro-β-D-glucose polymeric backbone, as seen in Figure 5, where glucose units are chemically bonded by β(1→4) glycosidic bonds to form the linear polymeric structure. Despite three hydroxyl groups on each glucose unit, the majority of them are interacting strongly with a nearby glucose chain via hydrogen bond, causing these hydroxyl groups to be unavailable to other kinds of interactions (Figure 5B). These occupations lead cellulose chains to be resistant to interacting with most solvents, and although it has high interaction with water, its chains are not water-dispersed, nor are they affected by it.[62]

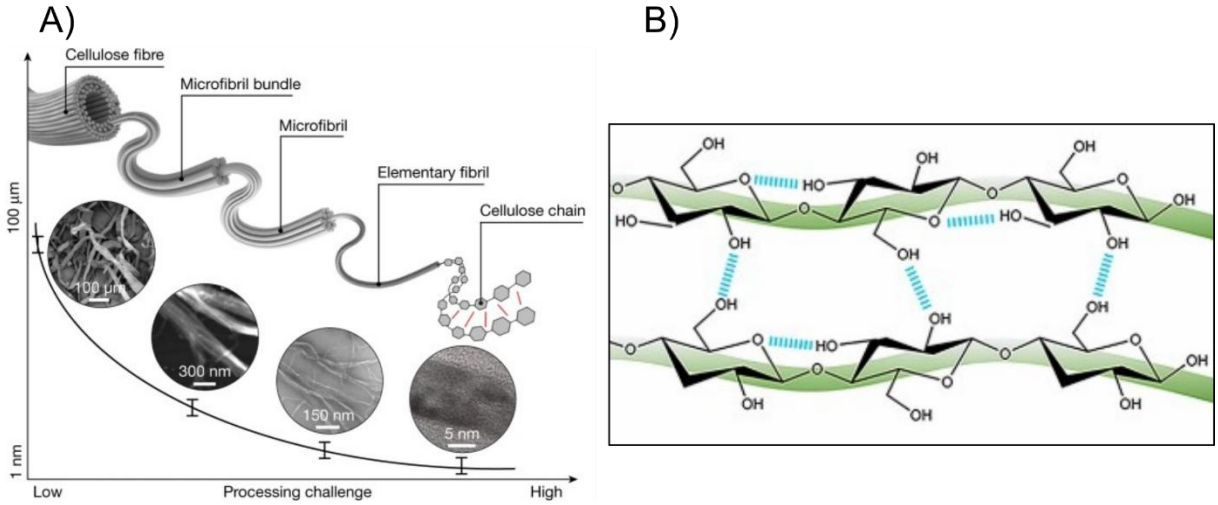

Figure 5 – (A) Hierarchy of cellulose fibers organization with respective SEM images as example. (B) The molecular structure organization with noted interactions between two fibers of cellulose.
Source: Images adapted from literature.[56,63]

The degree of occupation of these hydroxyl groups, or how strong the interaction inter- and intrachain of glucose units, results in the degree of organization of the polymer, thus it implies directly on its crystallinity. Where more interchain bonds are observed, a more organized linear structure occurs, thus a more crystalline region of cellulose is formed. For this reason, the higher crystalline region will be more chemically stable when compared to its less crystalline, or amorphous, region.[64] The balance between crystalline and amorphous regions also dictates further features of obtained cellulosic material, from reaction active sites availability to optical properties.[65]

As shown in Figure 6, cellulosic materials are composed of long fibers, but upon analyzing these materials via microscopy, the fibers are naturally aligned, causing a intertwined complex network, resulting in a structure that guarantees cellulose, specially bacterial cellulose, most of their known properties, like relatively high surface area for a biopolymer, interconnected pore structure, macroporous, high mechanical strength, high Youngs Modulus (15-35 GPa), high tensile strength (200-300 MPa), biodegradability, water retention, gas transport, abundant hydroxyl groups on its surface [50,62,66] Summarizing, the combination of all properties mentioned, low-cost, green biopolymer, non-toxic, and physical stability, made evident how cellulose-based

materials are competitive to supply nowadays demand for promising, multifunctional, technological materials.

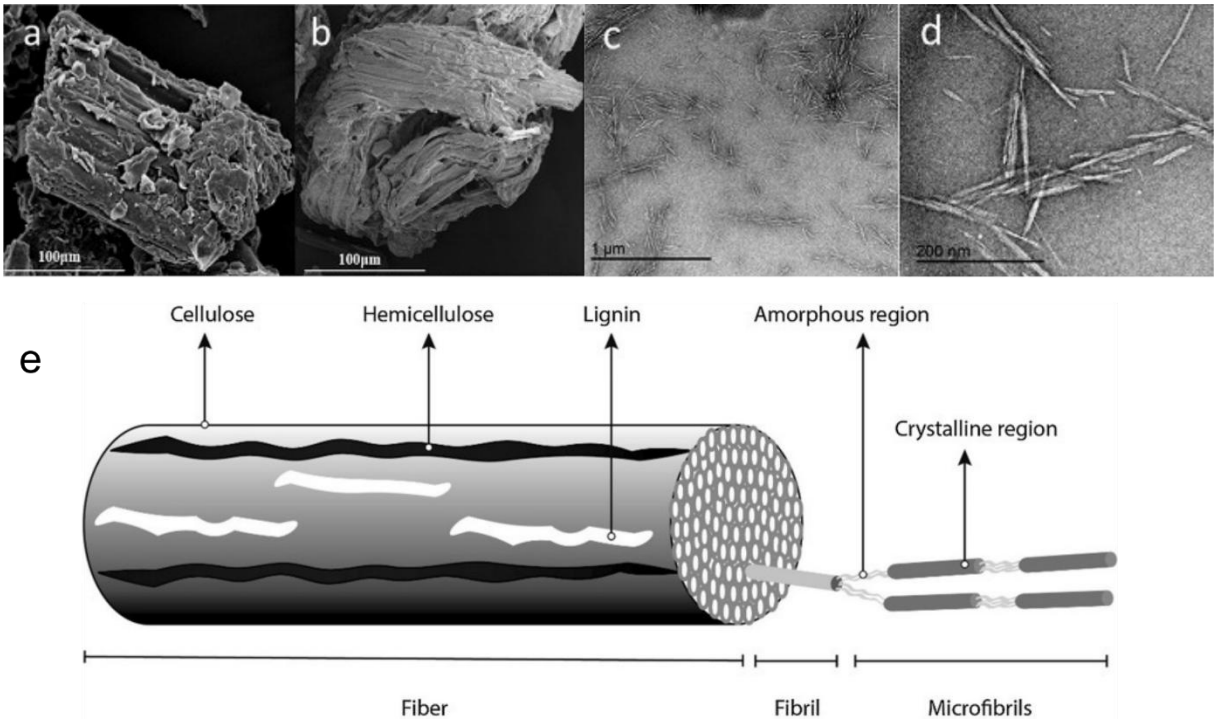

Figure 6 – From corn stalk to purified cellulose and cellulose nanocrystals. (a) raw corn stalk cellulose precursor; (b) cellulose purified from corn stalk (c-d) cellulose nanocrystals after acid treating purified cellulose; (e) schematic of structure organization of cellulose. Neglecting the presence of hemicellulose and lignin on (a) and (e), similar organization is expected for bacterial cellulose.
Source: images from references, (a-d)[47] and (e).[48]

Regardless of abovementioned properties, the final characteristics attributed to cellulose are strongly dependent on its production methodology, hence it is important also to discuss the general concepts of this polymer biosynthesis.

1.2.2. Production methodologies, from laboratory to industrial scale

There are bacterial strains capable of producing cellulose, like *Agrobacterium tumefaciens, Rhizobium leguminosarum, Escherichia coli,* and others. As expected, each of these strains has its unique characteristics, but *Komagataeibacter xylinus* strain is mostly used due to its higher yield and acceptance of different carbon sources.[67] This bacterial strain, formerly classified as *Gluconobacter*, is rod-shaped,

without flagella, it is found in warm and humid regions, and where foods, fruits, and vegetables are fermented.[68] When glucose is used as a carbon source by *K. xylinus*, it will require the least chemical transformations to obtain final product, cellulose biosynthesis. Then it can be summarized into four steps: phosphorylation, isomerization, conversion to uridine glucose diphosphate, and polymerization of uridine glucose diphosphate to form the known cellulose structure. The bacteria will then extrude cellulose chains around 1.5 nm thickness, which organize via Van de Waals interactions and hydrogen bonding to form the thicker fibers,[67] as represented in Figure 7.

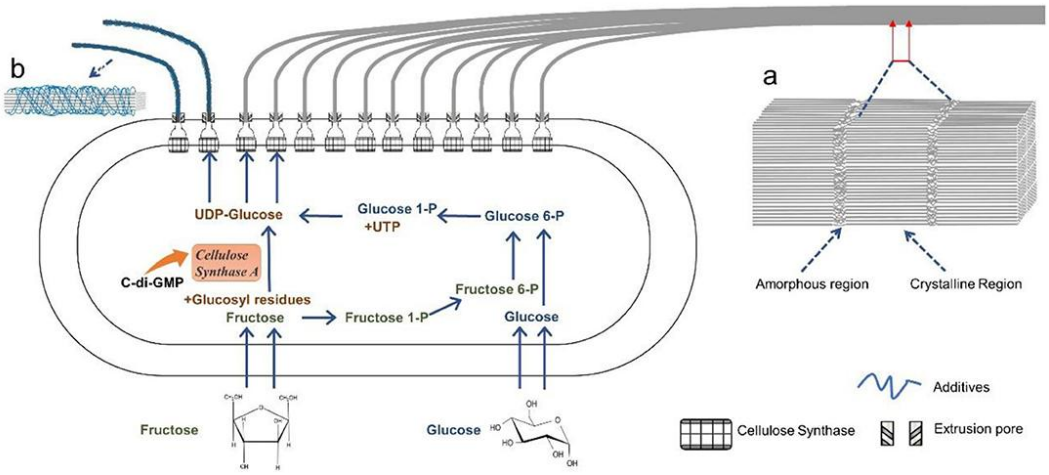

Figure 7 – Schematic of cellulose biosynthesis closely looking at steps inside the bacteria cell, displaying difference between (a) ribbon-like synthesis and (b) loosely-gathered productions, which can be influenced by additives.
Source: image from reference.[69]

With the cellulose fiber formed, it will float to the liquid-air interface, and since the bacteria has no way of controlling its movement, the fiber's producing bacteria gather with other bacteria on the solvent's surface, causing the produced fibers to form a random complex intertwined three-dimensional network, resulted from the random movement from cellulose production,[69] providing bacteria a UV-protective-membrane layer where oxygen and humidity conditions allows them a safe place to thrive.[70] While bacteria can generate this controlled environment for their protection and growth, the conditions when artificially cultivating them to produce cellulose are already favored for their development, hindering their strive for survival, since temperature and humidity

are usually controlled to best stimulate their yield. Thus, the controlled environment where they are cultivated allows researchers to explore different approaches for bacterial cellulose's obtention, vis-à-vis the static (more traditional) and dynamic growth methodologies.

Initial steps of production are shared among the two growth methodologies, where starting from bacteria activation in solid media, if the bacteria is storage in a freezer of fridge for example, followed by transference of formed colonies to liquid media, where they should have a rapid increase in cell's number, and after a dilution to desired amount of bacteria, the cells are expected to produce cellulose in a set period that could take hours to days. The last step, where they are allowed to biosynthesize the cellulose, lies in the difference between the methodologies. In the static methodologies, the bacteria are cultivated in flasks or trays, which are kept without agitation and allowed to grow undisturbed, resulting in a membrane shaped according to the vessel's liquid-air surface geometry. On the other hand, the dynamic methodologies place the diluted bacteria into flasks that are commonly agitated on an orbital shaker, and instead of acquiring its shape, due to fluid convection, the heavier bacteria agglomerates, caused by cellulose production and fiber entanglement, are transported from the surface to the interior of the fluid, and this process leads to sphere-like particles being formed.[66,69]

Static strategy presents fewer process variables to change during the bacterial growth, roughly one can interfere with growth time, ambient temperature, and relative humidity, aside from vessel's shape and liquid-air ratio. However, the dynamic strategy presents same variables, but includes the solution's total volume, flask's volume and geometry, and agitation speed. To make it more complicated, the stress generated on the cells during agitation can cause undesirable mutations or cell death, leading to lower yield or no BC's production. Hence, of the bacteria capable of producing cellulose, only partially are suitable for production under dynamic conditions.[71]

Because cellulosic materials are highly desired for newer technologies, industrial production is required, which overall prefers dynamic processes over static processes, but the development and design for BC's obtention scale-up reactors are challenging, mostly because the biopolymer attaches to the stirring mechanisms or the reactor's walls, inhibiting a homogenous production. Thus, most bacterial cellulose

scale-up productions are made using smaller batch systems incorporated in the dynamic flow production chain.[72]

The bacterial cellulosic raw material obtained from either static or dynamic methodologies, as mentioned before, contains a significant number of bacterial cells within, although not harmful microorganisms, which must be removed prior to any other uses. The most common method for purification of the biopolymer is via heated alkaline solution treatment, a diluted NaOH solution (0.1 to 0.2 M) heated up to no more than 90 ºC, for less than an hour. This mild process is enough to inactivate present cells, and with water washing aid to neutralize the pH, remove the cells that could be found throughout the polymer.[48,56] The purification step is the final step for bacterial cellulose production; from this point onward, changes and adaptations are made to suit the user's interest.

It is important to highlight that, even though bacterial production is well stablished in literature, there is plenty of room for improvements, such as using residue as carbon source for bacteria growth, using only enzymes from the bacteria and not the cell itself to increase yield, designing new reactors that could optimize production, and other possibilities that does not belong to the scope of this thesis, but the reader can found elsewhere.[73,74]

1.3. Drying technologies

Although some materials can be applied as "never-dried" state, this is not true for most materials, especially in the aerogel research area. Commonly neglected in many research fields, the drying technique employed to obtain the final product is crucial to achieving the highest effectiveness that the developed material is capable of. Without restriction, all materials developed by researchers must undergo characterization techniques to be properly understood, and most techniques require the material to be applied in a dry state, so the solvent does not interfere with either the measurement or the equipment itself. Therefore, the chosen drying methodology will impact how close the observed characterization result will be to the sample before drying. If a sample is to be applied as dried powder for example, and a high-temperature induced solvent evaporation is part of the obtention methodology (i.e., drying or annealing), then the characterized material will be the same as applied one,

but its specific surface area and porosity properties are expected to be reduced, reducing as well any further surface-related phenomena.

Loss of surface properties due to high heat treatment can be associated with the coalescence effect, which is independent of the material being previously submerged in solution. It is related to giving enough energy for the solid to rearrange into a more stable morphology, which usually implies removing microporous or even mesoporous to create a structure with lesser surface energy.[75] While the coalescence effect is very interesting, it is described by Gibbs-Thomson equation,[76] and this chapter focuses on the effect caused by solvent removal, which is governed by a simpler description than for solids, since it centers on the liquid-air interaction, and the solid as a lesser element. While a simpler equation, the Kelvin equation used to describe the liquid-air interface is fair and gives enough description of the concepts illustrated here.[77]

Lord Kelvin's equation, a specific case from Laplace's equation, describes the capillary pressure exerted on a surface (P_{cap}) where the curvature is characterized by a radius (r), but this equation is also fluid dependent, so it also depends on the fluid's surface tension (γ).[77] Figure 8 has the mathematical representation Kelvin equation, but also shows a visual representation of the resulting interaction between solid and liquid with air interaction. This mathematical approximation is known to calculate the meniscus radius, but it is also known to describe capillary pressure, the central phenomenon of this chapter.

$$P_{cap} = -\frac{2\gamma}{r}$$

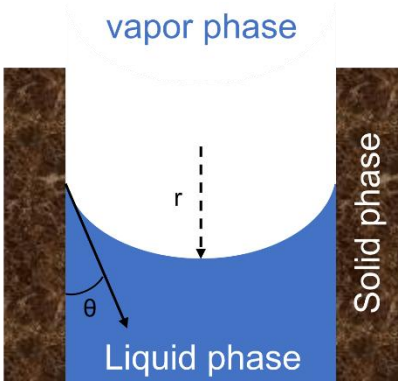

Figure 8 – Mathematical description and visual representation of pressure applied on solids surface by the liquid.
Source: Adapted from reference.[77]

The same straightforward explanation given to justify the meniscus formation, will help in explaining the capillary pressure effect. As the liquid and solid interact, attraction or repulsion can happen between them, a positive meniscus is seen in case of attraction (as shown in Figure 8), while a negative meniscus is seen in case of repulsion. On positive meniscus, as attraction exists between solid and liquid phases, there is also attraction happening into liquid phase itself, hence capillary effect is already there. Governed by surface tension of the fluid, there is a force pulling the solid's surface to meniscus center that is inversely proportional to the radius of the meniscus and directly proportional to the fluid's surface tension, thus as higher the fluid's surface tension is, the stronger is this pressure, and as smaller the radius of meniscus – and here we can understand it as porous size – the higher will be the resulting pressure onto solid's surface.

On daily basis these effect is not usually perceived, since it consists of a macro scale with at least dozens centimeter-size meniscus, but for porous materials, where the porosity is in the range of microporous (<2 nm) to mesoporous (2 - 50 nm) or macroporous (> 50 nm), according to IUPAC,[78] the forces exerted by the liquid are strong enough to collapse the solid's structure, extinguishing gradually its specific surface area by hierarchal eradication of material's porous network. Therefore, knowing the solid's characteristics and research goals, is imperative to apply a proper drying technique that will match the means and the ends.

Roughly, drying techniques can be divided into three categories related with the main phenomena involved in the phase transition from liquid to gaseous phase, as observed in Figure 9, the sublimation drying (SD), evaporation drying (ED), and supercritical drying (SCD). Meanwhile there are authors who chose to classify the drying techniques according to temperature[42] or to pressure,[79] this can lead to uncertainty and misclassification, because it can happen for a solvent's evaporation to be aided by vacuum pump at room temperature (lower pressure, but mostly not lower enough to cause sublimation), but it can also happen an evaporation of solvent quicken by temperature's increase (higher temperature, which can be higher than regular employed by supercritical drying without having the supercritical condition).

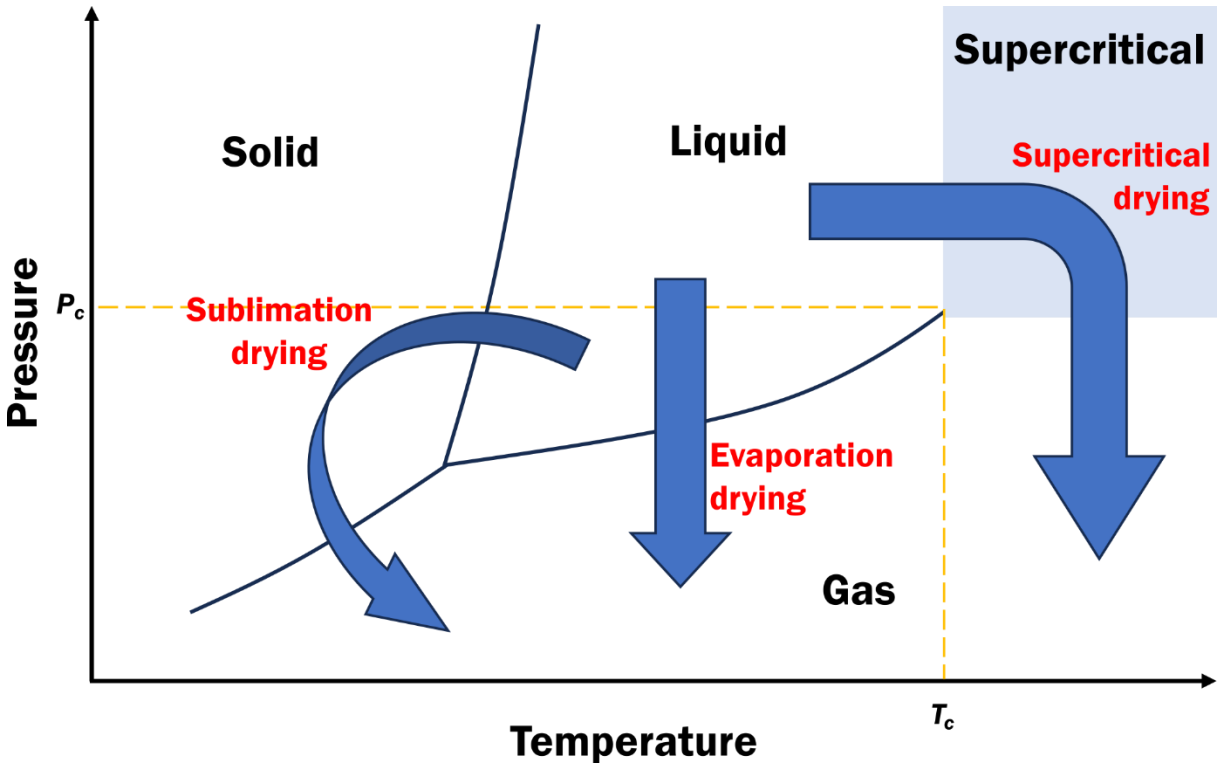

Figure 9 – Generic phase diagram for a substance evidencing the phase transitions which can undergo to be extracted from a gel when used as a solvent. In red are the drying techniques, and the area in blue denote the supercritical state, marked after critical pressure (P_c) and temperature (T_c) are achieved.
Source: image made by the author.

Most commonly employed drying technique is ED, it is the cheapest and it can be done without any equipment, where the sample's solvent is just left to evaporate on its own by the solvent's volatility, and it is usually speed up by heating or by placing the gel into a lower pressure chamber. Raise in temperature or reduction in pressure are not needed for the obtention of a dried material via evaporation, these are options to speed up the process. Opposed by its simplicity and feasibility, is its susceptibility to capillary pressure, since it involves the direct transition from liquid to gaseous phase, menisci are formed throughout samples' surface by these two phases interface, and it is capable of causing great trouble to the materials surface if not properly prepared for that.[39] Even under this drastic pressure exerted onto the sample's body, there are materials which are either physically stiff to withstand this pressure or underwent chemical modifications which prepare the surface to repel the solvent or attribute flexibility enough to spring back to its original size.[80,81] The chemical modifications were

mostly explored when aerogel and sol-gel fields overlap, due to numerous studies about precursors synthesis, kinect, reactivity, and others, made in sol-gel area beforehand and were adapted to overcome aerogel's challenges,[36,37] but they are relatively new to literature.

Inspired by ancestry knowledge on food conservation developed by Andine region people, where food was left on cold high mountains to dehydrate,[82] freeze-drying is the representant of the SD, the second most used technique to remove solvent, vastly used in industries as well.[83] This technique requires the sample and solvent to be frozen and placed in a very low-pressure environment, where temperature needs to be kept low enough so the solvent will not unfreeze and pressure needs to induce the sublimation on the solvent. For freeze-drying, also called lyophilization, although it is not a rule to use water as solvent, most systems are built aiming on water removal, but more robust equipment can work with lower pressure and temperature, making them capable of removing small organic solvents, like methanol or ethanol.

Since the starting point in lyophilization is freezing the sample, it brings the novelty of working under solid-gas phases system, which dismiss the most significant drawback of evaporation, the pores collapsing caused by capillary pressure onto materials walls when menisci are formed inside its cavities. While on one hand it solves a significant problem from before, on the other hand it creates another attention point usually neglected, which is the effect caused by ice formation into and onto the sample.[84] Considering water as the most common solvent for SD, it is important to pay attention to its anomalous expansion behaviors under this regime of temperature, causing the water inside the specimens porous framework to expand, and a more drastic effect is seem when the ice crystals break the materials structure, forcing unorganized channels inside the material or even fragmenting it.[85] Moreover, this solidifying step can as well be used to researchers advantage, like for gelation induced nanoparticle gels or creating oriented porous systems with freezing.[86,87] Furthermore it allows the obtention of different gels without using a crosslinker of gelling agent, just relying on materials' self-assembly.[88,89] Nevertheless, the effects done by freezing to gels, being obtained by different methods, are mostly unknown or not measured.

There are authors who take advantage of the freezing part, where sometimes it is when the gel is obtained, to also employ a drying technique intermediate between

freeze-drying and regular solvent evaporation, called Organic Solvent Sublimation Drying (OSSD).[86,90] To apply this technique, initially, the sample (solution or wet gel) is frozen, then it is placed inside a lower-pressure chamber, where the solvent will be removed. According to the authors, even though the main removal process is evaporation of the solvent, sublimation happens on the immediate samples' surface, which is kept frozen by the cooling effect caused by the evaporation of outer layer of solvent, as shown in Figure 10. Using this technique, results have proven to be better than relying exclusively on evaporation of the solvent, also cheaper than freeze-drying, this presents an optional way to dry a sample when evaporation's results are not satisfactory and a freeze-drier, or other techniques, are unavailable.

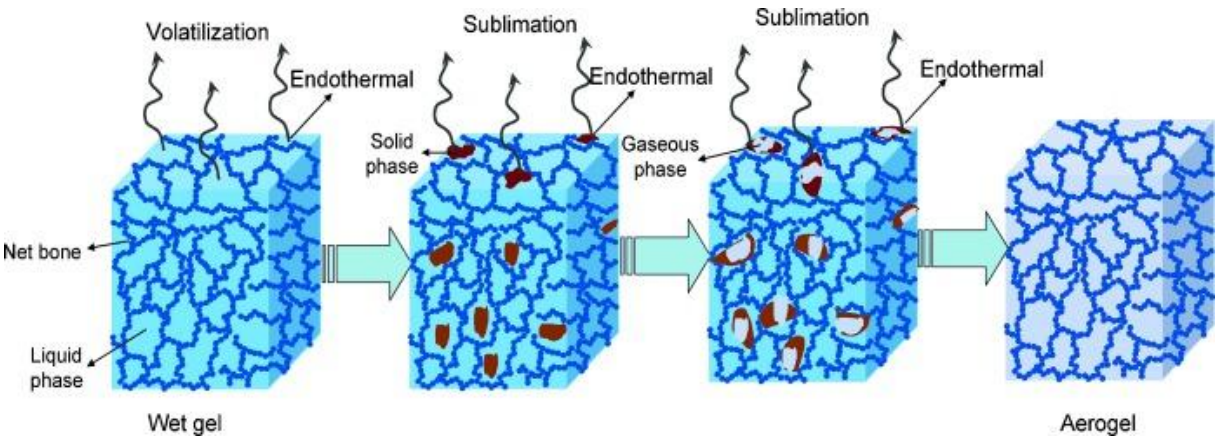

Figure 10 – Schematic on Organic solvent sublimation drying (OSSD) procedure from frozen gel to dried gel.
Source: image from reference.[86]

Avoiding problems caused by ice formation and capillary pressure, supercritical drying, also called supercritical solvent extraction, via temperature increase on a closed system, the wet sample with its solvent is allowed to undergo a pressure rise, where a phase transformation throughout the whole chamber is observed. When transforming from liquid to supercritical fluid, the solvent causes no capillary pressure onto the material, due to its phase-transformation nature, not a phase interface as evaporation or sublimation. A similar process is observed when the fluid transforms from supercritical to gaseous state, a phase transformation that does not generate an interface, and can be removed from the sample and chamber without harming the porous structure. Since this process generates the least capillary stress, it is also

considered a “zero-capillarity” pressure process, which is considered to preserve the most porosity.[34] Different solvents can be used for supercritical drying, as long as the equipment can achieve the solvent’s critical point, as shown in Table 2.

Table 2 – Minimum pressure and temperature required for certain solvents to achieve supercritical conditions

Fluid	Critical temperature / ºC	Critical pressure / bar
Water	374	221
Ethanol	241	61
Methanol	239	81
Acetone	235	47
Hexane	234	30
Toluene	319	41
Chloroform	263	55
Benzene	289	49
Phenol	421	59
CO_2	31	74

Source: Values obtained from CRC Handbook of Chemistry and Physics, 2005[91]

The possibility of using the samples' solvent is tempting and attractive, but the high temperatures and pressures required to reach the supercritical point of some substances hinder its applicability. Under supercritical conditions, either the solvent can become corrosive, or it can be dangerous to work with it, like water and ethanol, respectively.[92] To avoid these problems that grow acute as the scale expands, the use of a less harmful reagent with lower critical point conditions is desired, and carbon dioxide was highlighted, which combines its relatively lower health risks with moderate supercritical pressure and low supercritical temperature.

Considering that in normal conditions of temperature and pressure conditions CO_2 is a gas, the desired material’s synthesis cannot use the gas as a solvent, so an alternative solvent must be used prior to the drying. Since a different solvent will be used for the synthesis and drying, the synthesis solvent will need to be removed prior to achieving supercritical conditions; otherwise, different supercritical conditions will be required. Consequently, the option for the solvent cannot be random; it must be a solvent that is miscible with liquid CO_2, so it can be replaced as a first step of the drying

procedure. Solvents like ethanol, acetone, and acetonitrile are miscible with liquid CO_2 and present good results as a solvent that can be exchanged. Different from lyophilization, which is solvent restricted by the equipment, but mostly done in water, supercritical drying technique gives more opportunity for solvents to be worked on.

As a control to supercritical drying, or as an alternative, literature shows articles using liquid CO_2 (L-CO_2)[93] or subcritical CO_2 drying,[94] exploring the role of undergoing the supercritical phase transition, and not only using CO_2. The idea in the first technique is to exchange the sample's solvent for L-CO_2, and then slowly remove the pressure achieved to obtain liquid carbon dioxide. For the subcritical drying, the technique is similar, but a higher pressure is expected, when compared with just the exchange of solvent to CO_2, but not high enough to cause a supercritical state, therefore its name. The phase transition is yet from liquid to gaseous, but starting at a higher pressure or higher temperature. For both, even with L-CO_2 presenting low surface tension, an important factor contributing towards evaporation positive results, it still relies on evaporation of solvent, resulting in structure collapse.

Supercritical drying overall produces the best results when surface area and porosity are the goal, but its larger-scale application has drawbacks when compared with other demonstrated so far, which already have industrial-scale options. However, progress has been made recently to increase the scalability of supercritical drying processes,[2] allowing researchers and companies to envision a future where this methodology can be broadly applied. Table 3 and Figure 11 are summaries of the discussion exposed so far in this subchapter, highlighting the advantages and disadvantages of drying techniques.

Table 3 – Comparison between the most common drying techniques, displaying their overall advantages and disadvantages.

Drying method	Advantages	Disadvantages
Ambient Pressure Drying	Low cost Energy saving Compressive strength is higher	Causes shrinkage Form solid films The matrix is compact (aerogel density > 0.1 g/cm^3) Extra step required for matrix modification Requires a lot of hydrophilization agents Higher thermal conductivity Reduction in optical transparency
Supercritical Drying(high temperature)	No solvent exchange required Very minimal structure damage Risk of side reaction with solvent Dangerous when using a solvent other than CO_2	Low solubility of CO_2 in water Time consuming Energy intensive High toxicity hazard and explosive risks
Supercritical Drying (CO_2)	It has good compatibility with most types of gels Due to lower operating temperature, it has lower explosion risks Finding a compatible solvent that is miscible with CO_2	Low solubility of CO_2 in water Time consuming Energy-intensive due to CO_2 compression process
Freeze-drying	Less Shrinkage Narrower pore size distribution Economical Generally quicker due to lack of solvent exchange	Long processing time High energy consumption Change in volume (due to ice crystal) Crystallization of solvent in pores Chance of producing a more brittle aerogel

Source: Adapted from reference[92]

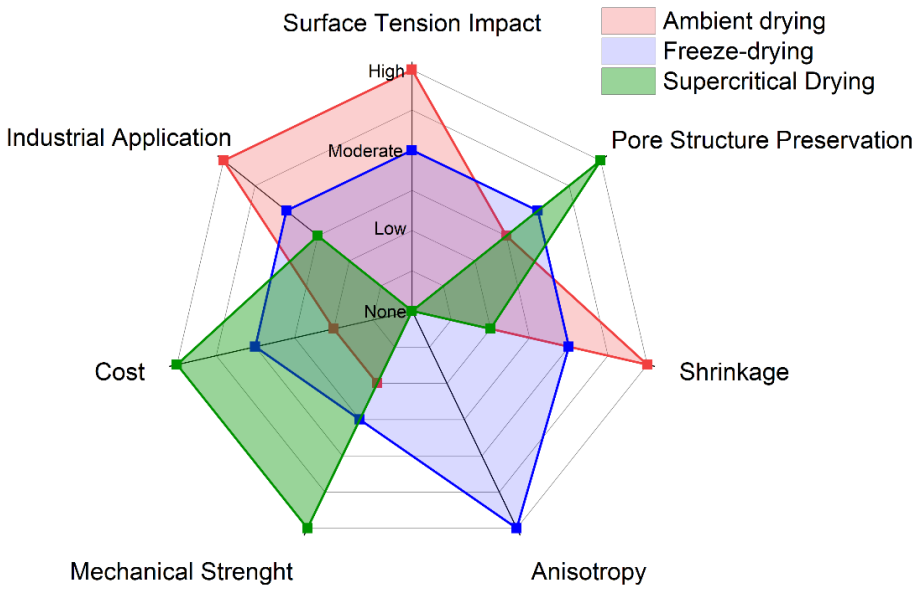

Figure 11 – Schematic representation of advantages and disadvantages of Supercritical drying, Freeze-drying (lyophilization), and ambient drying.
Source: Adapted from reference[75]

Therefore, a fundamental study of dried gels (xerogels, cryogels, and aerogels) is central to understanding how to accordingly process new gels, or even comprehend how the gelation process can be achieved. Regardless of the drying technique employed, it can be focused on the application, balancing the cost and desired properties. A deepened study becomes necessary, better comprehending how gels behave when submitted to each drying regime, and how the same material's properties can be modified by drying techniques.

1.4. Objectives

After an introduction mostly about aerogels and bacterial cellulose, this thesis aims to solve literature's gaps in the interface between these topics, hence, bacterial cellulose aerogels, and their applications, but not limited to it. Starting with an exploratory study to confront literature with new data directly comparing drying techniques, followed by hybrid aerogels applied to sorption and photocatalysis,

relevant topics to nowadays problems, and lastly the consequences to the material itself after photocatalytic tests.

In chapter 2, the work gives literature with a comparison between hybrid aerogels when different drying techniques are employed their direct consequences on surface properties. Continuous studies challenge the literature in the pursuit of investigating many ways of obtaining a dried gel, using monolithic samples, and obtained gels could be compared under the same conditions, and a fundamental study on the transition from gel state to dry state could be observed, along with its observable consequences.

After highlighting the importance of drying technique, CO_2 supercritical drying was employed to prepare hybrid multifunctional aerogels, shown in chapter 3. These aerogels were employed for rare-earth sorption and photocatalysis. Molecularly controlled silica growth and functionalization allowed authors to create a material for cation sorption. Due to sorption capabilities, the hybrid membranes also have proven useful to regulate silver's incorporation, vastly increasing the range of applications.

Lastly, considering the non-specific oxidation of photocatalysis processes, summed with the vast use of support frameworks for oxidative-promoting materials, chapter 4 brings criticism to its own thesis, having the goal of exploring if there is any detected damage to support materials during oxidation process. To meet this goal, bacterial cellulose coated with titania gels was analyzed under photocatalytic conditions, without analyte or contaminant, to fully focus on support and photocatalyst interaction's consequences, and assess if the support can be applied for long-term uses.

To achieve these broad purposes described above, specific objectives were created in order to guide the development of this thesis. Hence, smaller goals were planned as key points to obtain data to support the proposed hypothesis; those goals are described below:

A) Develop a reproducible dynamic growth methodology of bacterial cellulose to grow sphere-like support material;
B) Compare surface properties of obtained bacterial nanocellulose materials coated with MoS_2, and test for sorption applications, after different drying techniques were employed;

C) Dry gels under different solvent systems, employing supercritical drying, freeze drying, and ambient pressure drying, comparing results via nitrogen sorption;
D) Develop a hybrid BC/Silica aerogel membranes (referred to as Hx) with controlled functionalization based on inorganic (TEOS) and organic (EDAS) silica precursors ratio;
E) Evaluate the ethylene diamine functionalization of Hx based on rare-earth sorption, measuring cation selectivity and sorption isotherms models;
F) Based on highly photoactive BC/TiO_2 and BC/SiO_2/TiO_2 aerogels, perform photocatalysis experiments exclusively with water and photocatalytic membrane under UV;
G) Investigate changes in aerogels via structural and vibrational characterization techniques to uncover changes in bacterial cellulose structure after a non-specific oxidation process was performed.

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