

# Production of Microcrystalline Cellulose Aerogels by Supercritical Gel Drying, for Water Remediation

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Dye abundance in industrial wastewater is emerging as a critical issue in chemical engineering, due to their harmful impact on natural ecosystems equilibrium. Adsorption is a cost-effective and flexible unit operation to perform: however, its outcomes rely on the choice of the sorbent. Indeed, the adsorbent should expose large surface areas, to optimize the performance-to-size ratio; it should be selective, and affine with the molecule to remove from the sludge. Moreover, it should be low-cost and biodegradable. Cellulose meets these last requirements: in this work, it has been processed by supercritical drying, in order to improve network interconnectivity and enhance active sites availability. The present research focuses on the efficacy of microcrystalline cellulose on removing different dyes, as well as the effect of supercritical drying operating conditions on adsorption performances, as well as. The present study outlined that the lower the carbon dioxide density is, the more likely is for the adsorption to worsen. Moreover, pristine cellulose results to be affine with cationic dyes, rather than anionic; on the other hand, adsorption is less favourable for linear molecules rather than more compact ones.

## 1. Introduction

Water contamination is a critical issue that arouses concern in both industrial and researchers. Numerous contaminants are reported to be detrimental to water health, but the most discussed ones are the emerging contaminants (Arman et al., 2021). Namely, this class of species – that comprehends pharmaceutical and cosmetic products, synthetic pesticides and herbicides, flame retardants, etc. – is wide, and is characterized by not being limited by a proper legislation that controls their introduction in industrial wastewater (Parida et al., 2021). Among the emerging contaminants, synthetic dyes – if improperly disposed of – cause eutrophication, poor oxygen and light transmission, and ecosystem irreversible alteration. Moreover, they are detrimental also to human health: most of the synthetic dyes bring about inflammatory, carcinogenic, and toxic effects, apart from abdominal, mental, and digestive apparatus disorders (Sahu and Poler, 2024). Due to the concerns aroused from the effects of synthetic dyes, researchers put effort in outlining the most effective strategy to remove these contaminants from industrial wastewater. Several processes are explored, spanning from biological to chemical methods: however, most of these strategies result in slow kinetics (i.e., large volume reactors), production of sludge, or generation of toxic intermediates (Solayman et al., 2023). In contrast, physical methods are already widespread in industrial contexts. Physical methods encompass all the strategies that rely on mass transport phenomena, thanks to which the contaminant is localized onto a solid phase or in a tank: in this way, dye disposal is reliable and controlled (Slama et al., 2021). Among physical processes, adsorption stands out for its flexibility and scalability (Yagub et al., 2014). Adsorption is a fluid-solid mass exchange, during which a molecule in the fluid phase moves towards the solid (sorbent) surface (Rathi and Kumar, 2021). Intense efforts are put by researchers into exploring the effectiveness of adsorption towards dye removal (Phuong et al., 2021; Nguyen et al., 2021; Amon and Chosel, 2021). It is given that the larger the adsorbent specific surface area is, the enhanced is mass transfer from the fluid to the solid phase.

Aerogels are an innovative class of materials, that are renowned for being highly porous, lightweight, and for exposing large internal surface areas (Idumah et al., 2021). This last feature is bound to the existence of open and interconnected frameworks on the nanoscale, that enhances also surface chemistry and active sites

availability for adsorption purposes. Moreover, aerogels characteristics can be even extended to biodegradability and eco-friendliness – key factors in process circularity – provided the utilization of biopolymeric raw materials, like cellulose, chitosan, alginate, carrageenans, etc. (Dassanayake et al., 2021). However, to produce biopolymeric-based aerogels, a drying step must be performed on the starting hydro- or solvogel: namely, the liquid must be removed from the solid skeleton (Basak and Singhal, 2023). Biopolymeric-based gels are delicate structures, that easily collapse during drying. Supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) gel drying is appointed as the most effective strategy to preserve the nanostructured network (Li et al., 2022), since supercritical fluids feature gas-like diffusivities and negligible surface tension: there is no liquid-vapor meniscus and no tension is applied onto the nanopores surface, then, avoiding structural collapse (Mißfeldt et al., 2020). Among the different biopolymers that exhibit gelling properties, in this work attention is focused on cellulose, that is the most abundant biopolymer on Earth. Cellulose is a polysaccharide made out of the repetition of  $\beta(1 \rightarrow 4)$  linked d-glucose units (Srasri et al., 2018). It can be easily extracted from raw or waste materials, making it appealing from an ecological point of view (Ventura-Cruz and Tecante, 2021).

The present research has been devoted to producing cellulose-based aerogels via SC-CO<sub>2</sub> drying, and to testing them to remove two kinds of cationic dyes (crystal violet – CV – and methylene blue – MB), that differ for steric hindrance. Moreover, sorbent selectivity was also assessed, by mixing MB and methyl orange (MO): the latter is a linear anionic dye. Moreover, attention was paid also to the effect of SC-CO<sub>2</sub> gel drying operating conditions – namely, operating pressure, so carbon dioxide density – on dye removal.

## 2. Materials and Methods

Aerogels were produced via supercritical drying, characterized and used for CV, MB, and MO adsorption.

### 2.1 Materials

Microcrystalline cellulose (MCC) was purchased from Macherey-Nagel (Duren, DE). Ethanol was obtained from Carlo Erba Reagenti. Distilled water was produced in a home-made distillation column. Crystal violet, methylene blue, and methyl orange, were bought from Thermoscientific.

### 2.2 Gel preparation

A 4% w/v cellulose solution was prepared in an 8% w/v NaOH/water solvent. Once complete MCC dissolution was ensured, the resulting solution was poured into steel molds and put into an oven set at 50 °C for 3 hours; after the solidification step, gelation was achieved using a cold-water bath as non-solvent. The gels were left to settle overnight. Water was gradually swapped from the hydrogel using ethanol/water solutions, at gently increasing ethanol concentration. 10%, 30%, 50%, 70%, 90% v/v exchanges were set to last for 1 hour; the last exchange – namely, the one with pure ethanol – was prolonged overnight. At the end of this procedure, MCC solvogels were obtained.

### 2.3 Supercritical drying

Drying experiments were carried out in a laboratory scale setup. It consists of a 200 mL high-pressure vessel, prior to which a refrigerating bath (Julabo, mod. ED-F38), a high-pressure pump (Gilson, mod. 146562), and a pre-heater are located, to achieve supercritical conditions. Then, a micro-metering valve (Milli-Mite 1300 Series HOKE) and a separator allow CO<sub>2</sub> decompression and its separation from the ethanol extracted from the solvogel. Pressure along the line were monitored using type J thermocouples and test gauges. Temperature was controlled on the vessel and on the pre-heater by means of PID controllers (Watlow, mod. 63), coupled with heating bands and type J thermocouples. CO<sub>2</sub> flow rate was monitored through a calibrated rotameter. The drying experiments were conducted at different operating pressures (12, 15, and 20 MPa), while temperature and CO<sub>2</sub> flow rate were kept constant at 40 °C and 0.8 kg/h, respectively. Drying time was 7, 5, and 4 hours for the experiments conducted at 12, 15, and 20 MPa. Depressurization rate was set at 0.2 MPa/min, so that the system could be gently brought to atmospheric conditions to avoid cavitation and nanostructure collapse.

### 2.4 Morphological analysis

Morphological analysis was carried out by Field Emission Scanning Electron Microscopy (FESEM, Carl Zeiss Supra 35), after the samples were cryofractured in liquid nitrogen and coated with gold using an Agar Auto Sputter Coater (mod. 108 A, Stansted, UK) operated at 40 mA for 180 s.

### 2.5 Adsorption experiments

Adsorption experiments were carried out batch-wise, at 300 rpm as agitation speed and at room temperature, employing an adsorbent dosage of 1 g/L. The experiments were carried out at spontaneous pH: namely, 10 ppm dye solutions were prepared and immediately used for adsorption, not adjusting their acidity/basicity. Dyes

concentration was monitored at regular intervals of time, using a UV-Vis spectrophotometer (Mod. Cary 60, Varian, Palo Alto, CA, USA). Detection wavelengths were 590, 665, and 460 nm for CV, MB, and MO, respectively. Adsorption experiments were carried out on solutions of single dyes, while to investigate process selectivity also on the mixture MB-MO, whose respective concentrations were set to be equal to 10 ppm each. Removal efficiency was calculated as the ratio between the adsorbed amount of dye and its initial concentration.

### 3. Results and Discussion

In this work, research has been organized followingly: MCC aerogels were produced via SC-CO<sub>2</sub> drying performed at 20 MPa and 40 °C – to which corresponds a CO<sub>2</sub> density of about 0.84 g/cm<sup>3</sup>. The produced aerogels were observed by means of FESEM analysis, thanks to which nanostructure could be explored. Then, MB and CV adsorption experiments were conducted as explained previously; also, MB+MO solutions were prepared, and selective adsorption assessed. Finally, a section of the work was dedicated to assessing how drying conditions affect dye uptake: in this context, CV has been used as model dye.

#### 3.1 Aerogel characterization

For adsorption purposes, it is crucial to assess whether the sorbent offers an open path to the dye to intrude or not. Indeed, both aerogel surface and cross-section play a role in this context: surface openness determines if the dye can penetrate inside the inner structure, so employing the available internal active sites; cross-section, instead, defines the regularity of the nanostructure itself. The collected images are reported in Figure 1 and Figure 2.

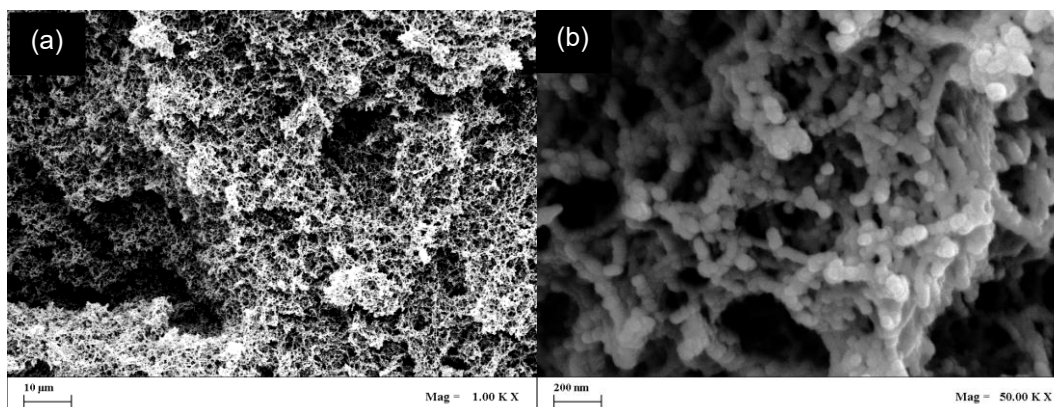


Figure 1: FESEM images of 4% w/v MCC aerogel cross-section obtained at 20 MPa and 40 °C, at different magnifications: (a) landscape; (b) detail

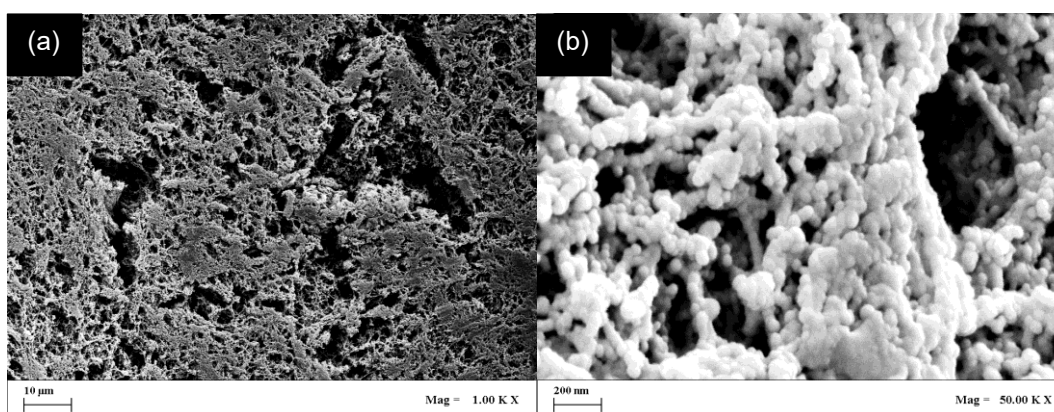


Figure 2: FESEM images of 4% w/v MCC aerogel surface obtained at 20 MPa and 40 °C, at different magnifications: (a) landscape; (b) detail

By comparing Figure 1a and Figure 2a, it is evident that the external surface is more prone to structural compaction, rather than the internal section. This densification trend is confirmed by looking at Figure 1b and

Figure 2b, relative to nanoscale observations: aerogel surface is denser than the cross section, also on the nanoscale. There are some morphological domains that evidence a tendency to coagulate into thicker bands, but overall, both observation points display structural homogeneity and interconnection. Cellulose chains organize in space somehow in-between a fibre-like and nanoporous structure: landscape observations resemble more a fibrous structure, whereas the in-detail analysis features a porous-like configuration. These MCC aerogels, produced by SC-CO<sub>2</sub> drying at 20 MPa and 40 °C, display a characteristic hierarchical morphology open and interconnected in every observation point.

### 3.2 Dye adsorption

Once it is proved that the produced MCC aerogel is eligible for the meant purposes, adsorption experiments were carried out in the conditions enunciated earlier: the obtained results are collected in Figure 3.

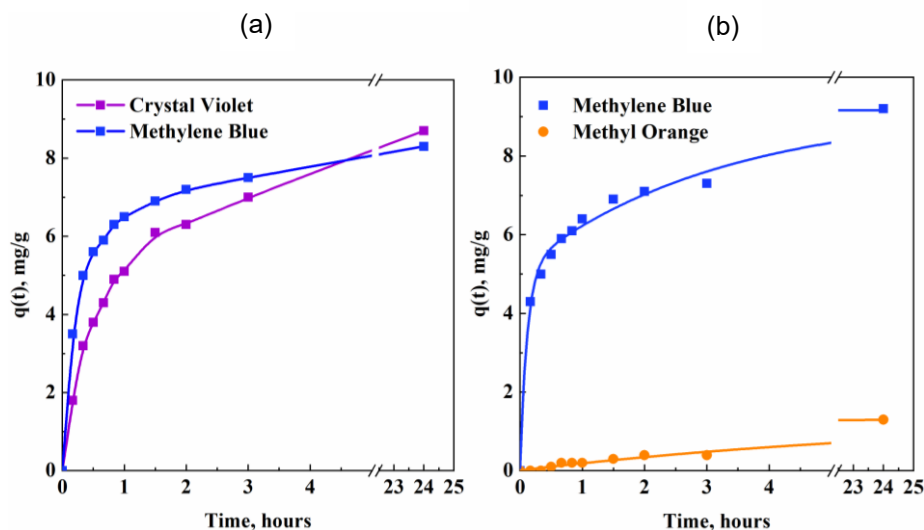


Figure 3: Adsorption experimental points of: (a) CV and MB; (b) MB+MO mixture

As it can be seen from Figure 3a, in the first moments of adsorption it seems that MB removal is much more efficient than CV; however, at some point of the process, there is a crossover between the two curves. A possible explanation to this behaviour is: MB is a linear molecule, that easily intrudes inside the aerogel nanostructure, differently from CV, that has a greater steric hindrance. For this reason, MB adsorption takes place at a faster rate than CV. On the other hand, the location of the positive charge on the organic moiety changes from dye to dye. The equilibrium point, collected after a contact time of 24 hours, should be associated with the active sites available within the inner part of the sorbent: in this position, dye molecules dispose themselves differently because of their steric arrangement. Molecules are arranged onto the sorbent surface in the configuration energetically more stable: it is possible that MB linear molecules tend to exert some reciprocal repulsion towards each other, leading to lower adsorbed amounts in equilibrium conditions. Therefore, at spontaneous pH, MB adsorption is slightly less favourable than CV, although  $\eta$  values are quite high for both: respectively, they are 83% and 88%, meaning that MCC aerogel is an effective sorbent for cationic dyes, despite of their steric hindrance. Respectively, the  $q_{eq}$  values are 8.3 mg/g and 8.8 mg/g. These values are consistent with literature works: for instance, some cellulose-based composites showed a MB adsorption capacity of about 1.5 mg/g – starting from a 10-ppm solution (Luo et al., 2021); whereas, cellulose obtained by acid activation of banana pseudo stem were tested for CV removal, resulting in an adsorption capacity of 9.8 mg/g from 20-ppm solutions. On the other hand, by looking at Figure 3b, it is evident that the MCC aerogel is much more affine with cationic dyes rather than anionic ones; however, the presence of methyl orange seems to have a positive effect on MB adsorption. MB removal efficiency increases from 83% in the single dye experiment, to 92% in the mixed-dye experiment. It is possible that MB and MO interact with each other, having opposite charges, and this charge neutrality helps the complex to unlock other kinds of interactions with the MCC active sites (e.g., van der Waals). Nevertheless, MO uptake is poor: its removal efficiency stops at 8%, proving that MCC – in its unmodified form – is much more efficient towards cationic dyes rather than anionic.

### 3.3 Effect of drying pressure on adsorption

In this work, the effect of SC-CO<sub>2</sub> drying operating pressure on dye uptake was also investigated. Three different operating pressures were used to produce MCC aerogels, namely: 12, 15, and 20 MPa, to which correspond a CO<sub>2</sub> density of 0.72, 0.78, and 0.84 g/cm<sup>3</sup>. The adsorption experiments were carried out on CV as model dye, and the results are collected in Figure 4.

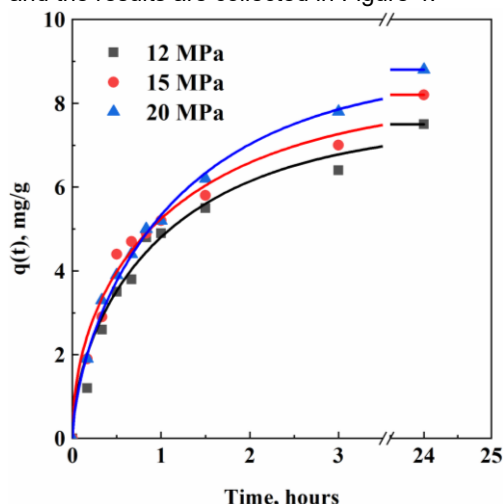


Figure 4: CV adsorption using MCC aerogels dried at 12, 15, and 20 MPa

Figure 4 evidences that the larger is the operating pressure, the more efficient is CV adsorption: removal efficiency increases from 75% to 88% when drying pressure moves from 12 to 20 MPa. What stands behind this result is associated with extraction/evaporation phenomena during supercritical drying. Supercritical gel drying can be associated with an extraction process, in which the supercritical fluid plays the role of the extraction solvent. As mentioned earlier, the main advantage that contributes to SC-CO<sub>2</sub> standing out is the fact that there is negligible surface tension exerted on the nanopores walls, avoiding their collapse. However, when lower pressures are employed, CO<sub>2</sub> density decreases as well as its solvent power: in such circumstances, the effect of ethanol evaporation begins to weigh more on solvent removal, dampening the beneficial effects of supercritical fluids utilization. Therefore, lower operating pressures imply that ethanol evaporation potentially leads to partial collapse of the weaker nanopores, resulting in fewer active sites available for adsorption. Moreover, it should be considered that longer drying times are needed when CO<sub>2</sub> solvent power is lower: not only does working at 20 MPa lead to improved adsorption performances, but it also means that the process takes up less time, which is appealing from a scaling-up point of view.

## 4. Conclusions

In conclusion, MCC aerogels – produced via SC-CO<sub>2</sub> gel drying – are proved to be effective sorbents for water remediation purposes. FESEM images showed that the aerogels produced operating at 20 MPa and 40 °C are morphologically hierarchical, open and interconnected, apart from being nanostructured. The availability of said nanostructure results in large removal efficiencies for cationic dyes, like MB and CV, that amount respectively at 83% and 88% at spontaneous pH, using only 1 g/L as adsorbent dosage. Also molecules steric hindrance plays a role in dye uptake, leading to the conclusion that linear dyes adsorption is less favored with respect to other kinds of molecules. Moreover, the aerogel is much more effective towards cationic dyes rather than anionics, proved by the large difference in calculated removal efficiencies. Overall, cellulose-based aerogels can be considered as promising materials for contaminant removal: low amounts of materials are needed to yield high removal efficiencies, evolving this technology towards process intensification and scale-up.

### Nomenclature

$q(t)$  – Adsorbed amount of dye per unit adsorbent, mg/g

$q_{eq}$  – Adsorbed amount of dye per unit adsorbent at equilibrium, mg/g

$\eta$  – removal efficiency, %

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