

Nanoporous Cellulose Aerogels for Methylene Blue Removal from Wastewater

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Nanotechnology offers a powerful tool to overcome the issue of clean water shortage. In particular, dyestuff abundance in industrial wastewater pollutes the environment and can affect negatively even human health, entering the food chain. Indeed, adsorption represents a good strategy for dye withdrawal, and this unit operation could be optimized by using nanostructured sorbents, like aerogels, that show remarkable properties in terms of active sites availability, large surface area, low density, etc. In this work, microcrystalline cellulose aerogels were produced employing the sol-gel route followed by supercritical gel drying, combining the utilization of a bio-based source with a both highly performing and eco-friendly process. The produced aerogels were characterized and tested batchwise for methylene blue removal from water, exploring the effect of initial pH and sorbent regeneration on process efficiency; the maximum removal efficiency, in the range of the adopted operating conditions, was about 90%. Eventually, the experimental data were described using kinetic models, that further proved that cellulose aerogels are promising candidates for cationic dyes removal from aqueous solutions.

1. Introduction

Nanotechnology-based approaches are rapidly stepping foot into numerous industrial scenarios. The appeal that revolves around nano-scaled materials stems from the enhancement of their properties with respect to their bulk counterpart: biological, chemical, and physical attributes are significantly amplified, meaning that it is possible to achieve larger performance-to-size ratios using this kind of innovative products. Due to their versatility, nanotechnologies are weighing in the rapid development of several applicative fields, ranging from biomedicine and healthcare, to automotive, agriculture, cosmetics, food, etc. (Malik et al., 2023). Particularly, nanotechnologies can be harnessed in the environmental field, with a special view to water remediation. Water contamination is causing its non-negligible shortage, that results in being an urgent issue discussed by researchers and industry parties.

Usually, wastewater treatment plants are defined into three main process categories, namely: primary, secondary, and tertiary treatments. Tertiary treatments are designed to remove contaminants traces from the stream resulting from secondary units, in order to bring their concentrations down to legislation limits. In the frame of tertiary treatments, adsorption is recognized as an easy, flexible, and cost-effective alternative to remediate contaminated streams (Yagub et al., 2014). However, the choice of the adsorbent material should be tailored on the specific contaminant – or on their mixture – to guarantee favourable interactions between the solute and the solid surface, and, consequently, good removal rates. Although adsorption is a state-of-the-art unit operation, it is possible to rearrange the way it is designed by employing nanotechnologies. Among the wide plethora of nanomaterials, the way-to-go choice relies on 3-D nanostructured materials, which are basically solid materials featuring nano-sized pores (Burakov et al., 2018). Indeed, 3-D nanostructures, such as aerogels, encompass interesting properties for adsorption purposes (Garg et al., 2025), such as large specific surface areas and porosity, very low density, and regular and hierarchical morphology (James and Yadav, 2022). It is possible to obtain this kind of adsorbent by means of a bottom-up approach combined with the utilization of supercritical fluids-assisted technologies, namely the following steps are to be followed: the sol-gel route is carried out in such a way that a three-dimensional hydrogel is obtained. Once water is swapped with an organic

solvent – i.e., ethanol – to obtain a so-called “solvogel”, supercritical CO₂ gel drying is performed to extract the liquid phase from the gel. Eventually, the aerogel is produced, retaining the nanostructured features of the starting gel thanks to the characteristic near-zero surface tension and gas-like diffusivity of supercritical CO₂ (SC-CO₂). Other kinds of drying techniques, such as freeze-drying or air drying, inevitably lead to the structural collapse of the nano-sized pores, due to the templating growth of ice crystals or to large liquid-vapor interface tension, respectively (Machado et al., 2025). Indeed, SC-CO₂ gel drying represents the most effective way not to sacrifice the nano-scale properties of the adsorbent materials; moreover, supercritical CO₂ is cheap, eco-friendly, non-toxic, and non-explosive, thus places well in an industrial scenario. The potential of supercritical gel drying can be even enhanced when performed on bio-based gels (Demina et al., 2024). Indeed, some biopolymeric aerogels were produced, and their effectiveness towards dye removal demonstrated (Mazzeo et al., 2021). In particular, cellulose is a polysaccharide consisting of the repetition of $\beta(1\rightarrow4)$ linked D-glucose units: it is the most abundant biopolymer on Earth, and its sources can vary from both natural resources and industrial wastes (Riseh et al., 2024). Overall, it could be interesting to investigate the utilization of nanostructured cellulose-based aerogels for adsorption purposes. In this work, microcrystalline cellulose (MCC) aerogels have been produced by means of supercritical gel drying, and used to assess their effectiveness towards dye removal. More specifically, methylene blue (MB), that is a cationic dye – meaning that the colour-bearing part is also positively charged – has been chosen as model dye to carry out a first screening of aerogel performances.

To accomplish this aim, aerogels Point of Zero Charge (PZC) has been calculated, to overview its affinity towards cationic dyes; adsorption has been carried out by investigated dyed solution pH, and eventually reusability studies were conducted. Kinetic analysis was also conducted to indirectly extrapolate information on sorbate-sorbent interactions. Eventually, the main goal is to prove that bio-based nanostructured materials are promising candidates for wastewater treatment purposes, moving a step towards the affirmation of nanotechnologies in industrial scenarios.

2. Materials and Methods

MCC-based hydrogels were produced, then subjected to solvent exchange and eventually to supercritical drying. Aerogels were characterized in terms of morphology and PZC, and tested toward MB removal.

2.1 Materials

MCC was acquired by Macherey-Nagel (Duren, DE). Glacial acetic acid, sodium hydroxide (NaOH), and urea were bought from Sigma Aldrich (St. Louis, MO). Ethanol was bought from Carlo Erba Reagenti (Chaussée du Vexin, FR). Methylene Blue was purchased from ThermoScientific (Kandel, DE). Carbon dioxide was supplied by SON (Società Ossigeno Napoli).

2.2 Hydro/solvogel preparation

MCC hydrogels were prepared followingly: a 4% w/v MCC solution was obtained by solubilizing a calculated amount of polymer in a pre-cooled aqueous solution of NaOH/urea (respectively, 7% and 12% w/w). The so-formed sol was poured into steel molds, and immersed into a 3 M acetic acid aqueous solution for regeneration. Once a stable gel was formed (i.e., acetic acid diffused down to the center of the sol), aging was carried out for stabilization. The hydrogel was thus washed repeatedly with distilled water to remove residual salts, and subjected to a stepwise solvent exchange using water/ethanol solutions, having progressively higher ethanol concentration (10, 30, 50, 70, 90, and 100% v/v). This strategy was employed to avoid solvent exchange-induced structural damages (Dirauf et al., 2021). Each step was set to last 1 h, exception made for the last one that lasted overnight to guarantee complete water removal and substitution with ethanol. Eventually, solvogels were obtained.

2.3 SC-CO₂ gel drying

Supercritical gel drying was carried out in a lab-scale high-pressure plant. Such plant consists of a 200 mL stainless steel vessel, in which solvogels were loaded for drying experiments; CO₂ is stored in liquid-vapor equilibrium; then it passes through a refrigeration bath (Julabo, mod. EH-F38) to guarantee complete transition to the liquid state prior to being pumped by a high-pressure pump (Gilson, mod. 146562). Supercritical condition is achieved by means of a pre-heating volume: this purposed is accomplished using heating bands. Supercritical CO₂, then passes through the drying vessel, where ethanol is extracted. CO₂-ethanol mixture is then depressurized using a micro-metering valve (Milli-Mite 1300 Series HOKE), and a following separation vessel. Pressure is monitored along the line using manometers, whereas temperature is read and adjusted automatically thanks to the combination of Type J thermocouples and heating bands, coupled by PID controllers (Watlow, mod. 63). CO₂ flow rate was continuously monitored using a rotameter. The operating conditions

chosen for the drying experiments were: 20 MPa and 40 °C, setting CO₂ flow rate at 0.8 kg/h. Once the experiment was over, the system was slowly brought to atmospheric pressure using a depressurization rate of 0.2 MPa/min. Drying experiments were replicated at least three times before characterization and utilization, to guarantee process reproducibility.

2.4 FESEM analysis

MCC aerogels morphology was investigated by means of Field Emission Scanning Electron Microscopy (FESEM, Carl Zeiss Supra 35). Samples were coated with a thin layer of gold, employing an Agar Auto Sputter coater (mod. 108 A, Stansted, UK). Different observation points were chosen for each sample, to guarantee sample morphological homogeneity.

2.5 PZC measurement

The point of zero charge was evaluated as the point at which the sorbent surface bears no net charge. Namely, a saline solution was prepared, and its pH adjusted to a known value using HCl or NaOH aqueous solution. 20 mg of aerogels were located in 50 mL of solution, and the final pH was measured after a settling time of 24 h. Eventually, the difference between initial and final pH was calculated and plotted vs. solution initial pH: PZC was evaluated the initial pH value at which the difference between initial and final pH was null.

2.6 Adsorption experiments

Each adsorption experiment was carried out employing 1 g/L as adsorbent dosage for a first efficiency assessment, at room temperature and using a stirring rate of 300 rpm. MB initial concentration was set equal to 10 ppm for each experiment. Solution initial pH was adjusted using 0.1 M solutions of either NaOH or HCl. MB concentration was monitored at regular intervals of time using a UV-Vis spectrophotometer (Mod. Cary 60, Varian, Palo Alto, CA, USA), set to read the samples at a wavelength of 665 nm. In the range of pH and concentration tested, there was no significant absorbance difference: the calibration curve was considered viable for every measurement.

Reusability studies were carried out by adsorption-desorption cycles; once concentration reached a plateau value, the sorbent was washed with a 1 M HCl aqueous solution to favour desorption; this procedure was repeated until the sorbent could not be spent anymore. Removal efficiency was calculated as the ratio between the difference of initial concentration and final concentration over initial concentration.

3. Results and Discussion

Prior to utilization, the sorbent was characterized.

3.1 MCC aerogel morphology

Cellulose inner morphology depends strongly on the regeneration method. Figure 1 reports both a low magnification and a high magnification image of the produced aerogel.

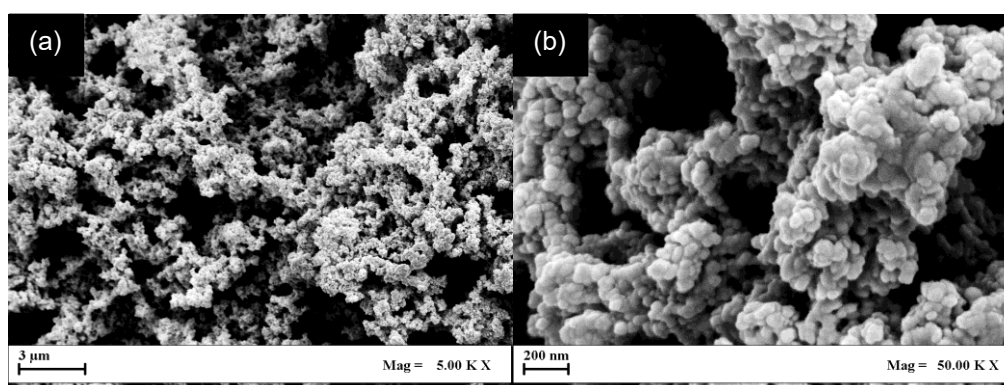


Figure 1: FESEM images of 4% w/v cellulose aerogels at: (a) low magnification; (b) high magnification

Looking at Figure 1a, it can be observed that MCC polymer chain organize in space in a tightly packed coagulated structure, leaving space for large macrovoids. Indeed, this result is consistent with the adopted regeneration strategy: the acetic acid strength forces the macromolecules the rearrange themselves immediately in a compact structure. Nevertheless, the nanoporous structure is not sacrificed, as it is shown in Figure 1b. The primary MCC coagulated particles still offer nano-sized pathways for the dye to intrude. Overall,

this kind of morphological organization is favourable for adsorption purposes: the macro-sized pores allow rapid water intrusion, whereas the nanopores present inside the thick band can offer numerous active sites for the dye to bind to. Indeed, the existence of the nanostructure is further proof of the potential of supercritical gel drying; this kind of hierarchical organization is achievable only by means of supercritical fluids, which do not exert any tension onto the gel nanopores.

3.2 Point of Zero Charge

As mentioned before, it is crucial to assess the adsorbent surface charge, in order to understand to what species the solid is more affine with. Adopting the procedure explained in the Materials and Methods section, a plot of (ΔpH) $pH_i - pH_f$ was obtained (Figure 2).

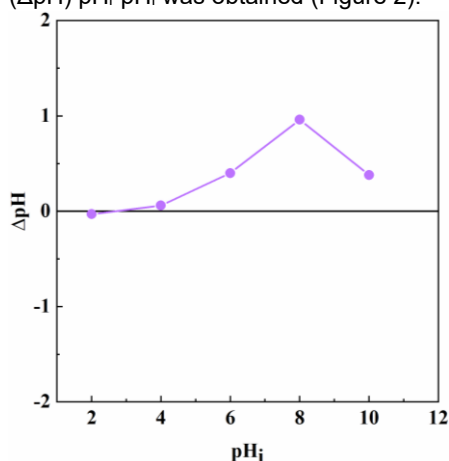


Figure 2: ΔpH vs. pH_i

As shown in Figure 2, the point at which the sorbent surface bears no charge corresponds to pH_i equal to 2.7: for pH values larger than the PZC, cellulose surface becomes negatively charged, whereas for $pH < 2.7$ an accumulation of positive charge is observed. Therefore, for $pH > PZC$, the negative charges on the aerogel surface set electrostatic interactions with positive charge-bearing molecules. Overall, being the goal to remove methylene blue, that is cationic, it can be concluded that this cellulose-based sorbent is an eligible candidate for such purpose.

3.3 Effect of solution pH

In wastewater treatment, solution pH is a crucial parameter that affects adsorption performance. In this scenario, different pH values were considered, namely: 4, 6, 8, 10. The removal efficiency points vs. solution pH are reported in Figure 3.

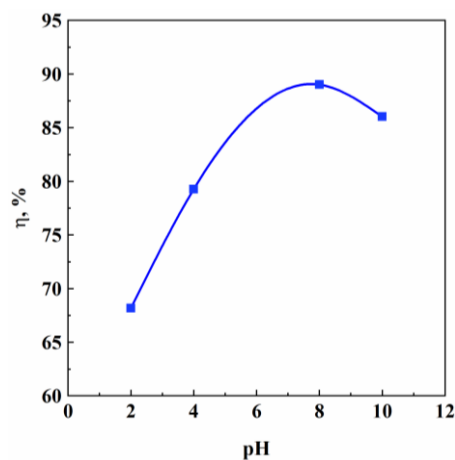


Figure 3: MB removal efficiency vs. pH

The experimental data collected in Figure 3 show an increasing trend when moving from acidic pH values to basic ones. Indeed, this observation is coherent with the PZC values: for pH values larger than 2.7, the adsorbent surface charge is negative, meaning that it is affine with MB molecules. The more the initial pH increases, the more intense are the interactions between the two species (i.e., its charge density increases). This trend is valid up until pH=8, to which corresponds the maximum observed η value (i.e., about 90%). After this pH value is passed over, removal efficiency worsens, due to an excessive accumulation of negative charge that plays a competing role with respect to the dye molecules. Such large values of removal efficiency can be attributed to the sorbent nanostructure (i.e., availability of active sites): cellulose offers only hydroxyl groups for binding, and the fact that the dye is so easily removed is related to the presence of open and interconnected polymeric networks on the nanoscale. Overall, the optimal pH for adsorption is equal to 8, to which almost all the dye can be removed from the starting solution. However, in a real-case scenario, other contaminants could coexist, possibly altering the optimal adsorption conditions.

3.4 Kinetic analysis

A brief kinetic analysis was carried out on the adsorption dataset corresponding to pH=8. Two of the most widespread kinetic models were considered, namely: pseudo-first order (PFO) and pseudo-second order (PSO) equations (Benjelloun et al., 2021). Table 1 reports the results of this mathematical analysis.

Table 1: PFO and PSO fit parameters

Model	Parameter	Value	R ²
PFO	Q _{eq} , mg/g	58.68	0.231
	K ₁ , min ⁻¹	4.66 E-5	
PSO	Q _{eq} , mg/g	9.28	0.999
	K ₂ , g (mg min) ⁻¹	0.0066	

The R² values reported in Table 1 provide information about the goodness of the fit of the PSO model, rather than the PFO one; indeed, it is well known that this kinetic model is somehow related to the intensity of the interactions between the adsorbate and the adsorbent. The fact that the PSO model describes so well the experimental data is related to MB and MCC aerogels active sites being intensely interacting with each other, to the boundary of chemisorption. Indeed, kinetic analysis through PFO and PSO models indirectly provides information on sorbent-sorbate interaction, proving that in this case the choice of employing cellulose for MB removal is correct.

3.5 Adsorbent reusability

With a view to reduce raw material consumption, MCC aerogels were also tested to be reused, following the procedure mentioned in the Materials and Methods section. The results are reported in Figure 4.

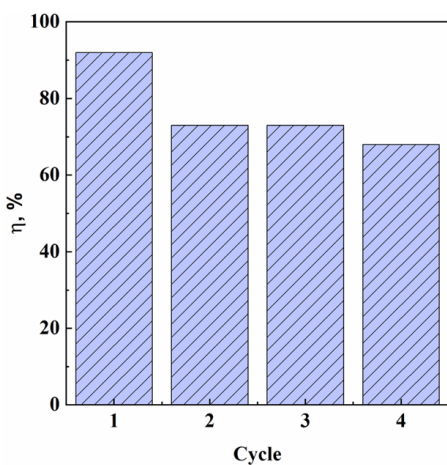


Figure 4: MCC aerogel reusability

The columns reported in Figure 4 show that there is rather a rapid decay of removal efficiency during the adsorption-desorption cycles: η dampens from about 90% to about 70%, although this decrease is smoother cycle after cycle. However, this loss of capacity should not be attributed to active sites saturation, but much rather to material loss during desorption in acidic media. Some cellulose fragments were observed during this procedure, meaning that even though aerogels active sites were freed from MB molecules, others were lost in the process, leading to the result of losing removal efficiency. Operating this way, cellulose aerogels can last up to 4 cycles, after which there was almost no more available sorbent. Overall, cellulose aerogels can be considered as reusable materials, although some adjustments should be made in the future to improve their mechanical stability, like filler addition or tailoring pore size.

4. Conclusions

In conclusion, this research proves that MCC aerogels, produced by supercritical drying, represent an effective solution for water remediation. Indeed, FESEM analysis proved that the adopted technique allows for the generation of an open and interconnected polymeric pathway, whereas the low value of PZC (2.7) indicates that this sorbent is particularly compatible with cationic molecules. Optimization of solution pH led to the promising result of removal efficiency of 90%, achievable thanks to the existence of the nanostructure; PSO model, moreover, suggested once again that MCC aerogels can be spent for MB removal, due to the presence of strong chemical interactions between the respective active sites. Lastly, the produced aerogels can be spent for 4 adsorption-desorption cycles, leading to believe that this sorbent can be regenerated, improving its appeal from an industrial application. Overall, the combination of supercritical fluid processing and nanotechnology yields materials with a large performance-to-size ratio, opening the doors towards the rearrangement of conventional processes through innovative techniques.

Nomenclature

K_1 – kinetic constant PFO, min^{-1}	pH_f – final pH, -
K_2 – kinetic constant PSO, $\text{g} (\text{mg min})^{-1}$	Q_{eq} – adsorption capacity at equilibrium, mg/g
pH_i – initial pH, -	η – removal efficiency, %

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