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Preparation of cellulose nanocrystals in water–aprotic solvent mixtures

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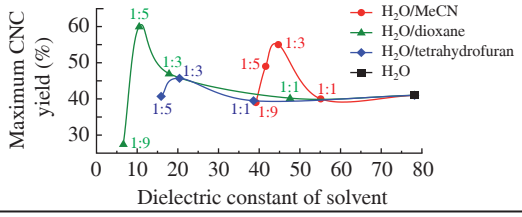
The effect of mixtures of water and aprotic solvents such as tetrahydrofuran, dioxane and acetonitrile on the production of cellulose nanocrystals (CNCs) by hydrolysis with sulfuric acid was investigated. Addition of an aprotic solvent to water increases the yield of CNCs and reduces the required acid concentration.



Keywords: cellulose nanocrystals, hydrolysis, yield, aprotic solvent, dielectric constant.

Cellulose nanocrystals (CNCs), which are virtually defect-free crystalline rod-shaped particles, can be isolated from cellulose fibers by acid hydrolysis.[1] The sizes of these nanocrystals vary from approximately 100 to 1000 nm in length and from 5 to 50 nm in diameter, depending on the acid hydrolysis conditions and the type of feedstock used. CNCs are currently attracting considerable interest among materials scientists due to their abundant availability and environmental friendliness, as well as their unique combination of physical and chemical properties, including non-toxicity, biocompatibility, biodegradability, high specific surface area, high elastic modulus and extensive possibilities for surface modification.[2]

The production and properties of CNCs are extensively detailed in numerous monographs and review articles.[3,4] The standard method for producing CNCs involves hydrolysis of cellulose-containing materials using 62–64% H_2SO_4 at temperatures from 45 to 50 °C. Typically, the yield of CNCs in this process does not exceed 30–40%.[5–7] Despite the relatively high cost of CNC isolation, it should be recognized that at present there is no real alternative to the sulfuric acid hydrolysis method. Nevertheless, researchers continue to explore new methods and approaches in this area.[8]

Depolymerization of cellulose by acid hydrolysis is initiated by the cleavage of glycosidic bonds in the cellulose macromolecule due to protonation of the glycosidic oxygen.[9] This process requires harsh conditions such as the use of strong acids and high proton concentrations.[10] Moreover, protonation of the glycosidic oxygen alone is not sufficient to trigger the hydrolysis process. Hydrolysis also requires conformational changes in the glucopyranose units of the cellulose macromolecule to overcome structural factors (such as hydrogen bonding) and electronic factors (such as anomeric effects) that hinder the process.[11] In aqueous media, the glucopyranose rings in the cellulose macromolecule typically adopts the most energetically favorable 'chair' conformation. This conformation, along with intramolecular hydrogen bonds, restricted rotation around the glycosidic bond and its equatorial orientation (the exo-anomeric effect), significantly increases the activation energy required for hydrolysis. Protonation of the glycosidic oxygen diminishes the exo-anomeric effect and causes elongation of the glycosidic bond. Subsequent conformational changes in the glucopyranose units of the cellulose macromolecule occur under the influence of cellulose solvation by the solvent.[12] Being a polar solvent, water enhances the exo-anomeric effect. In solvents with lower dielectric constants, conformations other than the 'chair' conformation are stabilized, which reduces the exo-anomeric effect and promotes the cleavage of glycosidic bonds.[13] Thus, a low dielectric constant of the solvent may contribute to the stabilization of conformers that facilitate the hydrolysis process.

Previously, we investigated the conditions for the preparation of CNCs in polar protic solvents such as aliphatic alcohols[14,15] and in mixtures of 1-butanol and benzene as a non-polar aprotic solvent.[16] In this work, we examined the effect of the composition of mixtures of H_2O and aprotic solvents including tetrahydrofuran (THF), dioxane and acetonitrile (MeCN) on the production of CNCs *via* hydrolysis with H_2SO_4.

The preparation of CNCs in these H_2O–aprotic solvent mixtures was carried out under identical conditions at a temperature of 50 °C and vigorous stirring for 2 h with different concentrations of sulfuric acid[17] (for details of the synthesis and characterization of CNCs, see Online Supplementary Materials).

Figure 1 shows the dependence of the CNC yield on the concentration of H_2SO_4 in H_2O–dioxane, H_2O–MeCN and H_2O–THF mixtures with different component ratios (indicated on the graph), as well as in pure H_2O for comparison.

The obtained data indicate that the composition of the H_2O–aprotic solvent mixtures significantly affects the process of CNC isolation. For all the studied mixtures, an increase in the proportion of aprotic solvent shifts the range of H_2SO_4 concentrations for CNC isolation toward lower values compared to pure H_2O. Additionally, for each mixed solvent, there exists an optimal concentration of H_2SO_4 at which the maximum CNC yield is achieved.

In 1 : 5 H_2O–dioxane and 1 : 3 H_2O–MeCN mixtures, the yield of CNCs is significantly higher than in pure H_2O, reaching 60 and 55%, respectively, at an H_2SO_4 concentration of approximately 55 wt% (see Figure 1). The CNCs obtained in maximum yield using H_2O–MeCN, H_2O–dioxane and H_2O–THF mixtures exhibit properties such as chemical structure, shape, size, charge, degree of crystallinity and degree of polymerization that are similar to those of CNCs produced by standard hydrolysis with H_2SO_4 in water (see Online Supplementary Materials).

It is important to note that in pure dioxane, MeCN and THF, as well as in mixtures with their high content (for example, in a 1 : 9 H_2O–THF mixture), it was not possible to isolate CNCs under the indicated experimental conditions. In these cases, either large micrometer-sized particles are formed if the concentration of H_2SO_4 is below

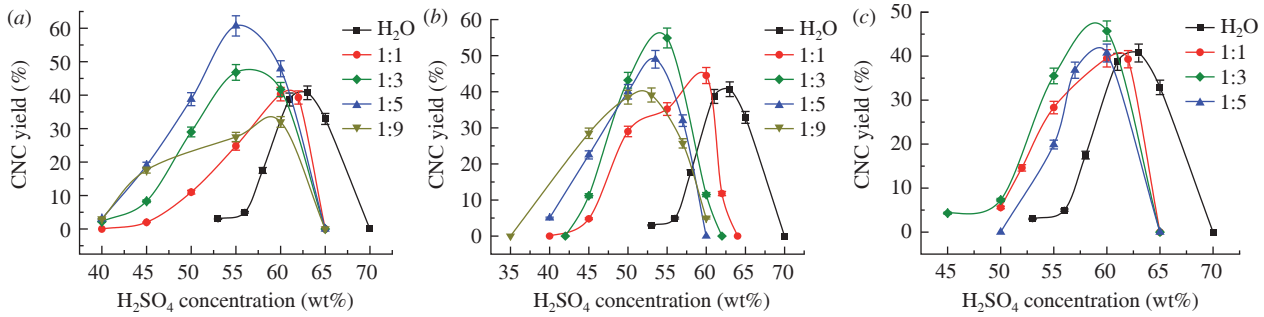


Figure 1 Dependence of the yield of CNCs on the concentration of H_2SO_4 in mixtures of H_2O and (*a*) dioxane, (*b*) MeCN or (*c*) THF. The numbers in the mixture designations on the graph indicate the H_2O/solvent weight ratio. Data on the CNC yield in pure H_2O are included for comparison.[14]

65 wt%, or water-soluble products of cellulose depolymerization are formed if the concentration of H_2SO_4 is above 65 wt%.

An increase in the proportion of aprotic solvent in mixtures with H_2O leads to a decrease in the dielectric constant of the mixture. To evaluate the impact of different environments on the hydrolysis of cellulose with H_2SO_4 during the production of CNCs, we compared two indicators: the maximum yield of CNCs in each solvent and the concentration of H_2SO_4 at which this maximum yield was achieved.

Figure 2(*a*) clearly shows that the optimal H_2SO_4 concentration corresponding to the maximum CNC yield for the studied H_2O–aprotic solvent mixtures is largely independent of the dielectric constant of the medium, falling within a relatively narrow range of 55–62%. This range aligns well with the H_2SO_4 concentrations typically used to produce CNCs via hydrolysis with H_2SO_4.[18]

In contrast, the relationship between the maximum CNC yield and the dielectric constant of the studied mixtures is much more complex. For each aqueous mixture (H_2O–dioxane, H_2O–THF and H_2O–MeCN), there is a local maximum of the CNC yield that corresponds to a specific mixture composition and dielectric constant. For H_2O–dioxane, H_2O–THF and H_2O–MeCN mixtures with dielectric constants of 10.5, 20.4 and 44.7, the maximum CNC yields are achieved at the optimal component ratios of 1 : 5, 1 : 3 and 1 : 3, respectively [Figure 2(*b*)]. In this context, the optimal H_2SO_4 concentrations corresponding to these maximum CNC yields vary only slightly, as noted earlier [see Figure 2(*a*)].

In summary, CNCs were synthesized in a mixture of H_2O and aprotic solvents THF, dioxane and MeCN. Analysis of the physicochemical properties of the synthesized CNCs revealed that their characteristics are similar to those of CNCs produced by standard hydrolysis with H_2SO_4 in an aqueous medium. The influence of the dielectric constant of the solvent on the optimization of the CNC production process was also demonstrated. For all the studied mixtures, an increase in the proportion of the aprotic solvent shifts the range of H_2SO_4 concentrations for the efficient isolation of CNCs toward lower values compared to pure H_2O. In a 1 : 5 H_2O–dioxane mixture and a 1 : 3 H_2O–MeCN mixture, the CNC yield is significantly higher than in pure H_2O, reaching 60 and 55%, respectively, at an H_2SO_4 concentration of approximately 55 wt%.

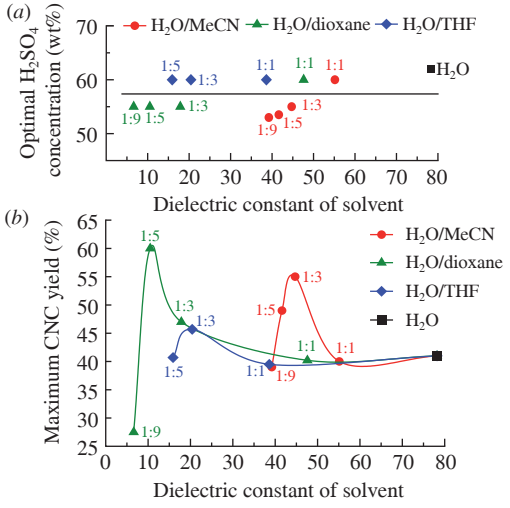


Figure 2 Dependences of (*a*) the optimal concentration of H_2SO_4 and (*b*) the maximum yield of CNCs on the dielectric constant of mixtures of H_2O and aprotic solvents MeCN, dioxane or THF.

This work was carried out using equipment at 'The Upper Volga Region Center for Physical and Chemical Research' (Ivanovo, Russia).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7788.

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