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Processing of Cellulose in Sub- and Supercritical Fluids, Cryotropic Gelation, and Drying

Abstract

In accordance with Decree No. 145 of the President of the Russian Federation dated February 28, 2024, "On the Strategy for Scientific and Technological Development of the Russian Federation," one of the priority areas is the transition to advanced technologies for creating high-tech products based on the application of new materials. Such materials include nanostructured materials based on biopolymers. Cellulose, being one of the most abundant renewable biopolymers, has great potential for use as an alternative to synthetic polymers.

Currently, the production of nanocrystalline cellulose (NCC) in Russia is predominantly at the stage of scientific research. This work investigates and develops a cellulose processing technology using hydrolysis in subcritical water. The proposed approach is promising for producing high-quality cellulose for a wide range of applications.

Highly porous cellulose-based materials are of particular interest due to their high specific surface area and large pore volume, combined with biodegradability and biocompatibility. Furthermore, a significant amount of cellulose-based waste produced worldwide remains a largely untapped resource. This work presents the development of technologies for processing cellulose and paper waste to produce highly porous materials.

As part of the dissertation research, technologies have been developed for producing various functional cellulose-based materials: nanocrystalline cellulose, cellulose-based aerogels, and highly porous materials from recycled paper waste.

This work was carried out under Agreement No. 075-03-2025-355/4 of April 29, 2025, between the D.I. Mendeleyev University of Chemical Technology of Russia and the Ministry of Science and Higher Education of the Russian Federation for the performance of work on the topic "Hierarchical Porous Materials for Personalized Implants and Medical Devices" (unique identifier: FSSM-2025-0007).

The aim of the study was to develop processes for the processing of cellulose in sub- and supercritical fluids and the production of nanostructured materials based on it.

Tasks:

1. Experimental investigation of the cellulose processing in subcritical water. Study of the influence of process parameters on the product yield and its characteristics.

2. Investigation of the aerogel production process using supercritical drying with varying approaches to cellulose gelation (chemical cross-linking, cryotropic gelation, pressure-induced gelation). Study of the effect of initial component concentrations and process parameters on the structure of the aerogels.

3. Investigation of the process of recycling paper waste to produce a highly porous cellulose-based material. Analytical studies of the obtained samples; evaluation of factors affecting the sample characteristics. Assessment of the effectiveness of the obtained materials as oil sorbents.

4. Development of a cellular automaton model for the process of oil sorption by highly porous cellulose-based materials.

5. Calculation of the economic costs for the processes of producing highly porous cellulose-based materials from secondary raw materials for semi-industrial scale production.

Scientific novelty.

The influence of the cellulose processing parameters in subcritical water on the yield of nanocrystalline cellulose was investigated. The relationships between the NCC characteristics and the process parameters (temperature, pressure, time) were established. A regression equation reflecting the influence of the process parameters on the NCC yield was obtained.

Mechanisms for the formation of cellulose-based aerogel structure, depending on the gelation approach, are proposed.

The influence of ultrasonic treatment applied at the stage of cryotropic gelation on the structure and morphology of cellulose-based aerogels after supercritical drying was investigated.

The kinetic dependencies of the cellulose solution freezing process, including with the use of ultrasonic treatment, were established.

The kinetic dependencies of the oil sorption process from the water surface by highly porous materials at varying cellulose concentrations were established.

A cellular automaton model of the oil sorption process by highly porous cellulose-based materials was developed.

Practical significance.

A method for producing nanocrystalline cellulose using a hydrothermal process of cellulose treatment in subcritical water has been developed.

Methods for producing aerogels using supercritical drying with varying approaches to cellulose gelation (chemical cross-linking, cryotropic gelation, pressure-induced gelation) have been developed. Cellulose-based aerogels that can be used as matrices for cell culture and systems for the delivery of active pharmaceutical ingredients have been obtained.

A process for recycling paper waste to produce hydrophobic, highly porous cellulose-based materials has been developed. The effectiveness of hydrophobic, highly porous cellulose-based materials as oil sorbents has been demonstrated.

Results of computational experiments on the kinetics of oil sorption by highly porous materials using the developed cellular automaton model have been obtained.

An economic calculation for the processes of producing highly porous cellulose-based materials from secondary raw materials for semi-industrial scale production has been performed.

The main provisions for the defense.

Results of experimental studies on the processing of cellulose in subcritical water.

Mechanisms of cellulose-based aerogel structure formation depending on the gelation approach used. Kinetic dependencies of cellulose solution freezing, including with the application of ultrasonic treatment. Results of experimental studies on the production of cellulose-based aerogels using supercritical drying.

Results of the investigation into the process of recycling paper waste to produce hydrophobic, highly porous cellulose-based materials. Experimentally proven application of highly porous cellulose-based materials as oil sorbents and environmental remediation agents.

A cellular automaton model of the kinetics of oil sorption from the water surface by highly porous materials.

Results of the economic calculation for the processes of producing highly porous cellulose-based materials from secondary raw materials for semi-industrial scale production.