ANNOTATION
to the dissertation for the degree of "Doctor of Philosophy" (PhD) in the specialty "8D05302 - Chemistry"

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Production of cellulose-based hydrogel materials from agricultural waste

Relevance of the topic. In recent years, due to climate change, global warming has been observed, and the lack of water resources has become a serious problem for the agricultural sector worldwide. In addition, there is a risk of land degradation due to droughts caused by both anthropogenic and climatic factors. This problem is also relevant for the Republic of Kazakhstan. The share of irrigated land in the structure of agricultural land in the country is only 0,7%, which emphasizes the urgent need to develop a new drought management strategy for the sustainable development of the agro-industrial sector. In addition, this problem demonstrates the need for domestic scientists to conduct in-depth research aimed at developing innovative materials to combat drought and increase crop yields.

The results of studies in recent decades confirm the importance of using polymer-based hydrogel materials against desertification, erosion, and improving the physical and chemical properties of soils. However, most studies aimed at ecological restoration of soils used synthetic polymers as superabsorbents. It is known that hydrogels obtained from synthetic polymers promote adhesion and salinization of soil particles, impair air permeability, negatively affect the development of the root system of plants and their absorption of nutrients, and also disrupt soil microflora and contribute to environmental pollution with microplastics.

Another pressing problem of our time is the pollution of water systems with toxic substances caused by the continuous growth of industrial activity, which accounts for about 20% of global water consumption. This has a serious negative impact on ecosystems and leads to a decrease in the availability of drinking water. Heavy metals are constantly released into the environment along with wastewater. The presence of heavy metal ions in such waters contributes to their further spread in ecological cycles, as well as accumulation in the organisms of animals, microorganisms and plants.

The rapid growth of the planet's population causes an increase in the production of agricultural raw materials in order to ensure food security. In this regard, millions of tons of waste accumulate annually in the agricultural sector. However, in most cases, effective recycling of this waste as an alternative raw material has not yet been established, and it is mainly used for the production of biofuels - as a source of energy from agro-industrial residues.

It should be noted that, despite the annual production of more than 75 million tons of cellulose fiber, most of it is still obtained from forest tree wood. In this context, the development of efficient technologies for processing and

extracting valuable components based on the principles of green chemistry, which provide for the rational use of agricultural waste rich in lignocellulosic compounds - such as cellulose, hemicellulose and lignin - is a key direction towards achieving sustainable development goals.

The unique properties of cellulose, such as high mechanical strength, gelation ability, water retention, sorption, thermal conductivity, low toxicity and high specific surface area, significantly expand the possibilities of its application for the production of various biocomposite materials. In particular, the synthesis of hydrogel materials based on cellulose and its derivatives, which have high water absorption capacity, biodegradability and the ability to sorb heavy metal ions, opens up broad prospects for their use in agriculture, medicine and the pharmaceutical industry.

To date, there are separate studies devoted to obtaining cellulose materials from agricultural waste. However, there are still no comprehensive studies aimed at optimizing the method for obtaining microcrystalline cellulose (MCC) from raw materials that include agricultural crops grown in Kazakhstan - such as sunflower, rice, wheat straw and husk, corn leaves and straw, soybeans, waste from the cotton processing industry. In addition, the processes of synthesizing nanocrystalline and nanofibrous cellulose from MCC and the subsequent production of composite materials based on them have been practically unstudied. In particular, among the entire volume of works, there are practically no studies on the processing of sunflower seed husks (SFH) for the purpose of obtaining nanocellulose materials. During the literature review, it was found that studies on the extraction of nanocellulose from sunflower seed husks (SFH) are limited.

To obtain cellulose, alkaline-acid treatments are usually used, which are less efficient from the ecological and economic point of view. This, in turn, creates a demand for alternative and environmentally friendly synthesis methods. Recently, researchers' attention has focused on the organosolvent method of biomass oxidation for cellulose production, based on the use of peracetic acid. One significant advantage is the potential for the delignifying agent to be reused multiple times. The reuse not only increases the economic efficiency of the production process, but also significantly reduces the environmental load. Peroxyacetic acid simultaneously acts as both an oxidizing agent and a solvent and ensures lignin decomposition by initiating the condensation process through electrophilic attack on the phenylpropane structure of plant biomass. Thus, it is possible to minimize the residual lignin content in cellulose and obtain a material with high quality characteristics. However, to date, glacial acetic acid has been used to obtain peroxyacetic acid. The possibility of significant reduction of its concentration has been established, which made it possible to develop a “soft” method that is more effective from the ecological and economic point of view. Nevertheless, further improvement of this method, in particular, reduction of the volume of peroxyacetic acid used for delignification to an optimal level that does not adversely affect the cellulose yield remains relevant.

The purpose of the dissertation. Development of hydrogel materials from cellulose obtained from agricultural waste, study of their physical and chemical properties and determination of the scope of application.

To achieve the set goal, the following tasks were completed:

1. Obtaining microcrystalline cellulose (MCC) from sunflower seed husks (Helianthus annuus L.) and rice husks (Oryza) grown in the Republic of Kazakhstan using organosolvent oxidation; studying its physicochemical properties and determining the yield.
2. Synthesis of hydrogels (MCChydrogel) based on MCC and water-soluble polymer (AAm), study of their physicochemical and kinetic properties.
3. Study of the soil moisture retention capacity and biodegradability of MCChydrogel.
4. Obtaining cellulose nanofibers (CNF) and nanocrystals (CNC) from cellulose raw materials and studying their physicochemical properties.
5. Study of sorption properties of hydrogels based on CNF, CNC and water-soluble polymer (AAm) in relation to Cu^{2+} ions.

Object of study: Microcrystalline and nanocellulose-based hydrogel materials derived from agricultural waste such as sunflower seed husk (SFH) and rice husk (RH) and their sorption properties.

Scientific and technical level of research and metrological support of research work. In the course of the research work, both classical and modern physicochemical methods of research were used. Quality indicators, particle size, charge, optical absorption, chemical structure, crystal structure, surface morphology and thermal stability of the MCC obtained by the improved "soft" organosolvent method, as well as CNF and CNC synthesized from it, were determined using physicochemical methods of analysis. These studies were carried out at the International and Inter-University Center for Nanoscience and Nanotechnology of Mahatma Gandhi University (India-686560, Kerala, Kottoyam), Nazarbayev University, the Laboratory of Engineering Profile of the Kazakh National Research Technical University named after K.I. Satpayev, as well as in the National Scientific Laboratory of Collective Use of the East Kazakhstan University named after S. Amanzholov. The quality parameters of MCC obtained by the improved "soft" organosolvent method were determined, namely: moisture content according to ASTM D1348-94 (2008), α-cellulose content according to ASTM D1103-60 (1977), residual lignin content according to ISO / DIS 21436, as well as hemicellulose content according to ASTM D5896 and ASTM 96 (2019) e1. The ash content (SiO_2) of MCC was studied by calcination in a muffle furnace (SNOL8.2 / 1100 L, Lithuania) and measuring the ash mass (SiO_2) on an analytical balance (SARTOGOSM LV 210-A, Russian). The particle size and zeta potential of micro- and nanocellulose were determined using a Zetasizer NanoZS 90 (Malvern, UK). The physicochemical properties of the obtained MCC and nanocellulose were studied, namely: optical absorption using a UV spectrophotometer (PE-5400UV, Russian), chemical structure using an IR spectrometer (FT-801 Simex Fourier spectrometer, Russian), crystal structure

using an X-ray diffractometer (X'PertPRO Malvern Panalytical Empyrean, the Netherlands), surface morphology using a scanning electron microscope (Quanta 200i 3D FEITM, the Netherlands), thermal stability using a differential thermogravimetric analyzer (LabSysevo Setaram, France).

The scientific novelty of the experimental results obtained is as follows:

1 The "soft" organosolvent method for extracting microcrystalline cellulose (MCC) from agricultural waste, such as sunflower seed husks (SFH) and rice husks (RH), has been improved by reducing the concentration of the delignifying agent, acetic acid. A comparative study of the influence of varietal characteristics of the raw material and the region of its cultivation on the quality indicators of MCC has also been conducted.

2 When MCC was extracted from SFH and RH husks using an improved “soft” organosolvent method in which the acetic acid concentration was reduced from 52% to 44%, the effective hydromodul was found to be 1:12 g/mL for SFH and 1:10 g/mL for RH.

3 Hydrogels were synthesized at a 1:1 ratio between MCC obtained from SFH and acrylamide monomer (AAm) using various crosslinking agents. It was found that with the addition of 10 mg of the crosslinking agent, the swelling degree of MCChydrogel in water was 1176%, which is the highest value of water absorption. It was found that MCChydrogel is saturated with moisture from the soil for 5 days, after 35 days it undergoes collapse with subsequent release of sorbed water back into the soil, and by the 77th day it loses up to 66% of its volume, undergoing biological decomposition.

4 A cellulose nanofibrous material was synthesized from MCC obtained from SFH by hydrolysis using formic acid (FA). It was found that the optimal hydromodulus for the MCC:FA ratio is 1:20 g/ml. A hydrogel sorbent was synthesized based on CNF with a yield of 71,09% and a zeta potential value of -15,8 mV, for which the ability to adsorb Cu^{2+} ions was studied. As a result, it was found that the HG_{CNF} hydrogel is capable of adsorbing 48,4% of Cu^{2+} ions from a model copper solution.

5 It was found that the hydrogel sorbent HG_{CNC}, synthesized on the basis of CNC, obtained from microcrystalline cellulose by the method of sulfuric acid hydrolysis, is capable of sorbing 51,5% of Cu^{2+} ions from a model copper solution.

The main provisions submitted for defense:

1. Improvement of the "soft" organosolvent method for extracting MCC from sunflower husk (SFH) and rice (RH) by reducing the concentration of acetic acid from 52% to 44% allows to reduce the effective hydromodule of raw materials:peroxyacetic acid to 1:12 and 1:10 g / ml for SFH and RH, respectively. In comparison with the Altayskaya SFH variety with a high fat content, namely 52-54%, the Belosnezhka variety with a low fat content, namely 33,7%, has an MCC yield of 50,69 ± 2% and, accordingly, a higher content of α-cellulose (67,53%). At the same time, to obtain MCC from the high-fat SFH variety, a relatively optimal amount of hydromodule is spent on 2 ml more. Thus, the sunflower husk variety (SFH) with low fat content

is a more efficient raw material for obtaining cellulose. Compared with microcrystalline cellulose (MCC) obtained from rice husk (RH) grown in the Almaty region (Bakanas settlement), the yield of MCC obtained from Kyzylorda rice husk (MSCC-RH) is 7,58% higher, while the optimal hydromodulus is 1:10 g / ml.

2. By improving the "soft" organosolvent method, MCC hydrogel was synthesized from SFH in a 1:1 ratio by weight with acrylamide monomer (AAm) using a crosslinking agent in an amount of 10, 15 and 20 mg. Among the hydrogels obtained, the $MCCHG_{10}$ sample with an MBA content of 10 mg had the best characteristics, demonstrating a swelling degree in water of 1176% and a mechanical strength of 27 MPa. The $MCCHG_{10}$ hydrogel is saturated with moisture in the model soil for 5 days, on the 35th day, releasing sorbed water back into the soil, collapses, and by the 77th day it is biologically decomposed, losing up to 66% of its volume.
3. An improved “soft” organosolvent method made it possible to obtain microcrystalline cellulose (MCC) from sunflower husk (SFH), which was subsequently hydrolyzed with formic acid (FA) to synthesize cellulose nanofibers (CNF); the effective hydromodulus of MCC:FA was 1:20 g/mL, the yield of CNF reached 71,09%, and the zeta potential value was -15,8 mV.
4. Hydrogels synthesized on the basis of CNC and CNF, obtained respectively by the method of sulfuric acid and formic acid hydrolysis of MCC extracted from sunflower husk (SFH) by an improved “soft” organosolvent method, sorb 51,5% and 48,4% of Cu^{2+} ions from a model copper solution, respectively.

Personal contribution of a doctoral student. In the process of completing the dissertation, the doctoral student independently analyzed literary sources, conducted experimental studies in accordance with the set goals and objectives, and performed a physicochemical analysis of the samples obtained. The "soft" organosolvent method for obtaining microcrystalline cellulose (MCC) from sunflower husk (SFH) and rice husk (RH) was improved by reducing the concentration of the delignifying agent - acetic acid. The synthesis of hydrogel sorbents based on nanofibrous (CNF) and nanocrystalline (CNC) cellulose obtained from MCC by acid hydrolysis was carried out. The theoretical and practical analysis of the results obtained was carried out, presented in the form of a dissertation.

Scientific and practical significance of the study

The practical significance of cellulose materials obtained from agricultural waste by an improved "soft" method that does not require additional processing and is based on reducing the concentration of the delignifying agent - acetic acid, is very high. The proposed method is characterized by low technogenic impact on the environment and environmental efficiency. Hydrogel materials based on cellulose nanofibrils and nanocrystals obtained by hydrolysis are biocompatible, prone to biodegradation, have high water-holding capacity and the ability to sorb heavy metal ions, which makes them promising for widespread use in the agro-industry -

as moisture-saving sorbents for arid soils, as well as in the pharmaceutical and medical industries and in the treatment of industrial wastewater. In addition, the obtained results have high potential for use as additional educational material and the basis for laboratory work in teaching disciplines such as chemical technology, physical and chemical research methods and chemistry of high-molecular compounds for students and postgraduates.

Relationship of scientific work with the research plan. The research work was carried out in accordance with the main scientific directions of the National Scientific Laboratory for Collective Use of the East Kazakhstan University named after S. Amanzholov and within the framework of grant financing of scientific and (or) scientific and technical projects: AP23490029 "Development of a multicomposite biohydrogel to increase soil moisture and fertility", AP19677542 "Obtaining "smart" edible nanocomposite packaging from waste of the agro-industrial complex of the Republic of Kazakhstan for storage and transportation of agricultural products" and AP19579302 "Development of an antibacterial and biodegradable moisture-retaining film for use as a coating for berry and vegetable crops".

Discussion of work. The main results of the dissertation research were presented and tested at the following scientific conferences:

1. «International conference on recent advancements in nanotechnology for sustainable development» (11th-12th November, 2022) Maharaja Agrasen University, India;
2. «International Hybrid Conference On Nano Structured Materials And Polymers. ICNP 2023» (12th-14th May, 2023) Mahatma Gandhi University, Kottayam, Kerala, India;
3. «International Conference on Polymers, Composites, Nanocomposites & Biocomposites-2023 (ICPCNB-2023)» (11th-13th December, 2023) Satbayev University, Almaty, Kazakhstan;
4. «International Conference on Polymers, Composites, Nanocomposites & Biocomposites-2024 (ICPCNB-2024)» (8th-10th November, 2024) Mahatma Gandhi University, Kottayam, Kerala, India.
5. «International Conference on Polymers and Nanomaterials (ICPN-2025» (21th -23th March, 2025) Mahatma Gandhi University, Kottayam, Kerala, India.

Publication of research results. Based on the results of the study, 4 scientific papers were published, including:

2 articles have been published in scientific publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan:

1. Journal «International Journal of Biology and Chemistry», Q4;
2. Journal «Chemical Bulletin of Kazakh National», Q4.

2 articles were published in publications included in the Scopus and Web of Science databases and having a non-zero impact factor:

1. «Journal of Polymer Science» - CiteScore-6.3, percentile - 73% Q2 IF=3.9;

2. «Journal of Polymer Science» - CiteScore-6.3, percentile - 73% Q2 IF=3.9;

Three abstracts of reports were published in the materials of international conferences.