ABSTRACT

of thesis research for the degree of Doctor of Philosophy (PhD)
6D060600-Chemistry

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Obtaining and studying the properties of nanocellulose materials from nonwood plant raw materials

Research relevance. Currently, the availability, biocompatibility and biodegradability of cellulosic materials are the main factors for their use in various industries. Therefore, the production of cellulose fibers and nanocrystals from various types of raw materials is of scientific and industrial interest. The main reason for this is the physical and mechanical properties, economic efficiency and susceptibility to modification of nanocellulose materials. The ordered crystal structure of nanocrystalline cellulose (NCC) particles ensures their high strength. This creates the prerequisites for using the NCC as a key component of the stabilization system. In addition, the use of NCC as a filler in polymeric materials, in addition to improving their mechanical properties, makes it possible to control moisture absorption, optical and sorption, as well as biological destructive properties. This paves the way for the widespread use of NCC-based composite materials in the food, pharmaceutical, light and chemical industries and medicine.

The scarcity of wood resources, which is the main source of cellulosic materials, has led to the search for alternative sources of raw materials. They are known to include the biomass of annual plants. The main advantages of using annual plants in the production of cellulosic raw materials are the endless supply of raw materials, low cost and the absence of an environmentally harmful tree felling process. Therefore, since the end of the last century, the production of cellulose materials by processing annual plants has become an urgent issue. In addition, agricultural waste is a source of raw material for cellulose fibers. Currently, the secondary use of this type of raw material is not carried out in full. In particular, the husk of sunflower seeds (sunflower husk), which is simultaneously related to annual plant residues and is a residue of the oil extraction process, is of interest in obtaining micro- and nanocellulose material.

Sunflower seed husk (SFH) is a by-product (14% of the total seed weight) formed during the preparation of sunflower seeds for oil production. SFH - cylindrical, 20-70 mm long and 6-8 mm in diameter, with a density of up to 1.2 thousand kg per cubic meter. m and humidity up to 8%. According to some reports, the amount of cellulose in SFH is 31-42.4% by weight. Sunflower cultivation is a steadily developing leading branch of the oilseed industry in Kazakhstan. Increasing the processing of sunflower seeds increases the waste from oil refineries. At the oil extraction plant, about 14-25 kg of husks are produced from 100 kg of sunflower seeds, which is about ¼ of the raw material. Due to its high cellulose fiber content, SFH is not suitable for use as animal feed because it is difficult to digest in animal stomachs. In this regard, at present, SFH is mainly used only as a fuel. Due to the lack of research on the chemical composition and properties of SFH and off-the-shelf technology, cellulose-rich SFH is simply incinerated. .Therefore, the study of SFH as a raw material for the production of cellulose and nanocellulose materials is an urgent issue.

There are a number of studies on obtaining nanocellulose from agricultural waste, in particular from annual plants growing in Kazakhstan, weed hemp, rice husks, wheat and straw, as well as cotton waste were considered. A review of the literature shows that there are no studies on the production of nanocellulose materials from SFH. There is only one known method for obtaining nanocellulose from SFH, performed by Chinese scientists. During the study, microcrystalline cellulose (MCC) was obtained by pre-alkalinization with SFH and bleaching with sodium hypochlorite. At the next stage, MCC was transferred to nanocellulose by sulfuric acid hydrolysis. However, this method allows you to increase the amount of man-made liquid waste. Therefore, it is very important to conduct a systematic study of the processing of agricultural waste according to the principle of "green" technology, in particular, the production of nanocellulose from SFH.

Research goal. Obtaining microcrystalline cellulose (MCC) from the biomass of annual plants, in particular from the husk of sunflower seeds, by the method of organosolvent oxidation under "mild" conditions and studying the possibility of converting MCC into nanocrystalline cellulose, followed by obtaining a composite material.

In order to achieve this goal, the following objectives have been set:

1. Development of a "soft" method for obtaining MCC from cannabis weed lat. Cannabis Ruderalis Janisch (CbR) and sunflower seed husks (SFH) by the method of organosolvent oxidation and determination of physicochemical and quality parameters of obtained MCC;
2. Determination of the cycle of reuse of the delignifying agent - peroxyacetic acid (PAA), under "soft" conditions of the organo-solvent oxidation method;
3. Studying the possibility of obtaining nanocrystalline cellulose (NCC) by mechanical activation from MCC, obtained under "soft" conditions of the organo-solvent oxidation method (on the example of CbR);
4. Obtaining MCC under "soft" conditions by the organo-solvent oxidation method with transfer to NCC by acid hydrolysis and studying their physicochemical properties;
5. Studying the Possibility of Obtaining Film Material from NCC.

Research object: obtaining of MCC and NCC materials from annual plants, incl. weed hemp and sunflower seed husks.

Scientific and technical level of research and metrological support of research work. The studies used classical and modern methods of physical and chemical research.

The development of a “soft” method for obtaining MCC by the organo-solvent oxidation method, the study of physicochemical and qualitative characteristics, the determination of particle size, charge, chemical and crystal structure, surface morphology and thermal characteristics of MCC and NCC, were carried out in the laboratory of Nazarbayev University, the laboratory of engineering profile of the Kazakh National Research Technical University named after K.I. Satpayev, at the National Laboratory of Nanotechnology of the Kazakh National University named after al-Farabi and the National Scientific Shared Laboratories of the Sarsen Amanzholov East Kazakhstan University.

Moisture was determined using ASTM D1348-94 (2008), α-cellulose content ASTM D1103-60 (1977), residual lignin ISO/DIS 21436 and hemicellulose content according to ASTM D5896 (ASTM D5896) and ASTM 965. Ash content microcrystalline cellulose (SiO_2) was determined by firing in a muffle furnace (SNOL8.2/1100 l Lithuania) and by using the gravimetric method. The particle size and zeta potential of MCC and NCC were determined on a Zetasizer NanoZS 90 (Malvern, UK). Optical absorption was studied using a UV spectrophotometer (PE-5400UF, Russia), chemical structure on an IR spectrometer (FTIR FT-801 Simex, Russia), crystal structure in an X-ray diffractometer (X´PertPRO Malvern Panalytical Empyrean, Netherlands), morphology surfaces using a scanning electron microscope (Quanta 200i 3D FEITM, Netherlands) and thermal stability using a differential thermogravimetric analyzer (LabSysevo Setaram, France).

Scientific novelty.

1. By improving the method of organosolvent oxidation, MCC was obtained for the first time in a “soft” way from annual plant material, in particular from hemp weed (CbR) and sunflower husk (SFH). It has been established that with a 2-fold decrease in the concentration of glacial acetic acid and hydrogen peroxide used to obtain peroxyacetic acid by organo-solvent oxidation, the yield of MCC from CbR and SFH is 50.6% and 47.8%, respectively. In the "soft" conditions of the organo-solvent oxidation method, the optimal ratio of raw materials and delignifying agent is 1:14 g/ml for CbR and 1:20 g/ml for SFH. With the specified optimal ratio, the possibility of reuse of the delignifying agent, peroxyacetic acid, was determined;
2. The possibility of obtaining NCC by mechanical processing of MCC obtained from the stems of hemp weed under “soft” conditions was studied. As a result, the crystal structure of MCC changes according to a certain pattern depending on the speed and time of mechanical processing, namely, with an increase in activation time for every 0.5 hour and a mechanical processing speed of 50 rpm, the size of cellulose crystallites decreases by 4.4 %. It has been established that the mode of complete transition to amorphous cellulose during pre-treatment is 400 rpm and 2 hours;
3. Received NCC by sulfuric acid hydrolysis from MCC (SFH), obtained under "soft" conditions by the method of organo-solvent oxidation. The optimal ratio of MCC and sulfuric acid was established -1:10 g/ml, respectively;
4. The possibility of obtaining a film material from NCC, the optical conductivity of which is - 50%, was studied.

Basic provisions for defense:

1 "Soft" way to obtain MCC by improving the organo-solvent method of oxidation of annual plants by reducing the concentration of glacial acetic acid and hydrogen peroxide by 2 times, used in the production of peroxyacetic acid - a delignifying agent;

2 The optimal ratios of raw materials and delignifying agent in the preparation of MCC by the organo-solvent method under "soft" conditions, which are 1:14 and 1:20 g/ml for CbR and SFH, respectively. With the secondary use of peroxyacetic acid as a delignifying agent, the yield of CbR and SFH is 46.3 and 44.2%, respectively;

3 During mechanical processing of MCC obtained from hemp stems under “soft” conditions, with an increase in the mechanical processing speed by 50 rpm every 0.5 hour, the size of cellulose crystals decreases by 4.4%, and the mode of complete transition to amorphized cellulose is 400 rpm and 2 hours;

4 The optimal ratio of MCC and sulfuric acid (conc. 60%) when obtaining NCC by sulfuric acid hydrolysis for SFH is 1:10 g/ml, respectively;

The optical conductivity of the film obtained from cellulose nanocrystals is 50%.

Personal contribution of a doctoral student. In the course of the study, the applicant independently searched and analyzed literature data, conducted experimental work in accordance with the goals and objectives set. Performed the synthesis of MCC from CbR and SFH under “soft” conditions by the method of organo-solvent oxidation, and also obtained NCC from MCC by sulfuric acid hydrolysis.

Scientific and practical significance of the work. The practical significance of the development of a “soft method for obtaining cellulosic materials from annual plants and agricultural waste is very high. Since this method does not require additional pulp bleaching and it is possible to use a delignifying agent in several cycles. And also this method has a low technogenic impact on the environment, is highly environmentally friendly and one-stage. At the same time, the film material based on cellulose nanocrystals is relatively biodegradable; therefore, it is widely used in agriculture as a “conditioner” for soils, in the food industry, pharmaceuticals and medicine. The data obtained as part of the dissertation can be used as additional material when passing the courses "Chemical Technology" and "High-molecular Compounds".

Relationship of work with research programs. The thesis work was carried out in accordance with the plans of the research work of the National Scientific Shared Laboratory of the Sarsen Amanzholov East Kazakhstan University and performed within the framework of grant funding for the scientific and (or) scientific and technical project AP09260644 " Development of an effective encapsulating composition of a multifunctional purpose in order to increase the yield of legume crops".

Approbation of work. The main results of the dissertation were presented and discussed at the following conferences:

1. Satpaev readings-2018 "Innovative solutions to traditional problems: engineering and technology" (April 2018, Almaty);

2. International scientific and practical conference for students, undergraduates, doctoral students and young scientists "Science and youth: problems, searches, solutions" (April 10, 2019, Almaty);

3. 8th IUPAC International Symposium on Macro-Molecular Complexes (MMC-18) (June 10-13, 2019, Moscow, Russia);

4. X-International Beremzhanovsky Congress "Chemistry and Chemical Technology" (October 24-25, 2019, Almaty);

5. International scientific and practical conference dedicated to the memory of the scientist-teacher, candidate of chemical sciences, associate professor Kuanyshbaev Tolybek Dosaevich (1952-1998) "Actual problems of natural science and natural science education" (November 7-8, 2019, Kyzylorda);

6. 84th scientific and technical conference dedicated to the 90th anniversary of BSTU and the Day of Belarusian Science (February 3-14, 2020, Minsk, Belarus);

Publications. As a result of the study, 10 scientific papers were published, including:

1 articles in scientific publications recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (KOKSON):

1. Journal "Bulletin of the National Nuclear Center of the Republic of Kazakhstan";

2 articles in journals indexed in Web of science and Scopus databases:

1. Journal "Oxidation Communications" - CiteScore - 0.9, percentile - 28% Q4 IF=0.5;

2. Journal "Cellulose" - CiteScore-6.6, percentile-88% Q1 IF=5.044.

2 articles and 4abstract reports were published in the materials of the International and Republican Conference.