IMPROVING THE QUALITY OF CELLULOSE FOR USE IN DISPOSABLE SANITARY AND HYGIENE PRODUCTS

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Under modern conditions the creation of materials for sanitary hygiene and medical products based on cellulose is of paramount importance. Development and improvement in this area has become particularly relevant in the context of viral epidemics, including the COVID 19 pandemic. The production of disposable non-woven materials for sanitary and medical purposes has imposed a number of specific requirements on cellulosic raw materials used for their production including the content of impurities. The content of organochlorine compounds in the pulp is determined mainly by the bleaching technology. With the new bleaching technology, which includes ozonation and treatment with hydrogen peroxide, it is possible to minimize this content. An improved method for determination of the total chlorine and organically bound chlorine contents in cellulosic materials was developed on the basis of ISO 11480:2017. The method essentially involves the absorption of gaseous chlorine formed during the combustion process by an electrolyte and measurement of the amount of chloride ions by microcoulometric titration with determination of their mass in a recording device. The method is highly reliable and makes it possible to determine concentrations in the range of 1-1000 mg/kg.

Cellulose is one of the most widely used natural polymers used as the starting material for the production of polymeric compositions in pharmaceutics, cosmetics, and other fields. One of the most important stages in cellulose production for chemical treatment is bleaching. The quality of the finished product is determined by a well-organized sequence of bleaching stages. The correct choice of bleaching agent and the order in which it is used has a significant effect on the operating costs and profitability of an enterprise. The aim of bleaching is to remove noncellulose components and to give the pulp specific physicochemical characteristics, which is particularly important in the production of cellulose for chemical treatment.

The bleaching technology involves a complex multistage process including treatment of the unbleached pulp with chemical and biological reagents. During selection of the order in which the bleaching agents are used the chemical stability of the final product, the safety of the production process, the transportation and storage of the reagents and finished products, the production economics, the availability of raw materials and energy, the geographical location and infrastructure, the balance of chemicals at the pulp plant, and the environmental friendliness of production process are all taken into account.

In contemporary world practice the use of molecular chlorine and hypochlorite as bleaching agents has been reduced to a minimum. The alternatives include chlorine dioxide and oxygen-containing compounds: ozone, hydrogen peroxide, and oxygen. The physicochemical processes that occur during bleaching of the pulp can be controlled by varying the selective and nonselective chemical reagents. The key quality characteristics of the final product are achieved in this way: whiteness, viscosity, and the content of alpha cellulose. Selective reagents chlorine, chlorine hypochlorite, chlorine dioxide, and ozone, which enter into chemical reactions with the chromophoric groups of lignin and decolorize them, are used to obtain the necessary degree of whiteness. The advantage of bleaching with chlorine dioxide is its selective effect on lignin with maximum retention of the structure of the cellulose fiber. Chlorine dioxide oxidizes the aldehyde groups to carboxyl groups, thereby stabilizing the whiteness. The less toxic hydrogen peroxide has similar characteristics.
Cellulose for chemical processing, including the production of sanitary, hygiene, and other medical products, must have high purity and molecular homogeneity [1]. This is achieved by isolating the difficultly reached part of the hemicellulose and lignin. The content of alpha cellulose is increased by hot or cold refining. The economic feasibility of treating cellulose with a highly concentrated alkali solution at low temperatures is dictated by the required content of “pure” cellulose.

The standard solution for establishing the order of the bleaching process is to use chlorine dioxide in the first and last bleaching stages. Today technical and economic advances have made it possible to achieve high quality bleached cellulose pulp by replacing chlorine dioxide with other oxidizing agents: ozone, oxygen, hydrogen peroxide.

Sodium hydroxide, oxygen, and hydrogen peroxide, which soften the structure of the cellulose cells and facilitate release of the remaining noncellulose components, are used for the production of high-purity cellulose.

There are three bleaching methods: ECF, ECF-light, and TCF. Molecular chlorine is not used in the industrial ECF process, but chlorine dioxide, which forms toxic organochlorine compounds and contaminates the waste water, is used as an alternative. For this reason this type of bleaching is considered the most ecological.

In the ECF-light process ozone, hydrogen peroxide, and oxygen are used as alternatives for the chlorine-containing bleaching reagents. Chlorine dioxide is also used in bleaching but only on a smaller scale. This method is economically and energetically profitable and does not cause much damage to the environment due to the much smaller amount of organochlorine compounds in the waste water.

TCF is a completely chlorine-free bleaching method that eliminates the use of chlorine dioxide. Bleaching is done with ozone, oxygen, and hydrogen peroxide and other ecologically safe reagents. The technology does not harm the environment. This type of bleaching is, however, quite energy intensive. Larger amounts of water, electricity, and steam are used in order to ensure the output of high-quality pulp, and the process is inefficient and expensive.

The best bleaching method is therefore the ECF-light method.

The authors have developed an industrial method based on the ECF light technology [2, 3]. It includes ozonation, bleaching with chlorine dioxide, washing from oxidation products of lignin, hemicellulose, and reagents, oxidative alkanization and intermediate washing, bleaching with hydrogen peroxide, and treatment with acid. The introduction of ozonation and hydrogen peroxide treatment into the bleaching system is dictated by the need to reduce the consumption of chlorine dioxide. By including the ozonation step it is possible to obtain high-grade cellulose for chemical processes. The environmental friendliness of the bleaching process is improved as a result of the formation of smaller amounts of organochlorine compounds. In addition to ozonation the proposed ECF-light method also includes bleaching with chlorine dioxide. This is marked by the ability to oxidize the lignin and destroy the dyes highly selectively while hardly destroying the cellulose at all.

Due to the use of nontoxic chemicals by the developed method it is possible to reduce the sodium hydroxide and chlorine dioxide consumption compared with information from BAT documentation and also to reduce the amount of organochlorine compounds discharged with the waste water.

An important advantage of the developed bleaching method is the possibility of producing cellulose with a minimal content of harmful impurities, including chlorine.

If the feedstock for the manufacture of sanitary and hygiene products contains chlorine compounds they can dissolve in bodily fluids such as perspiration and pass through the skin, disrupting the epidermis and having a negative impact on human health. The maximum chlorine content of cellulose is not clearly defined in the regulatory documents. It is indicated only that in the TCF chlorine-free bleaching method it is less than 30 mg/kg of cellulose pulp, while in the ECF method without the use of molecular chlorine it is 120-200 mg/kg. The modern consumer prefers bleached pulp with a small content of chlorine compounds [4-6].

The regulatory requirements for raw materials in the production of sanitary, hygiene, and medical products in the countries of the world differ; they are subject to mandatory enforcement or control by the manufacturers, depending on the country.

In the United States the requirements for bleached cellulose pulp manufacturers are regulated by the medical regulation of the FDA (Food and Drug Administration). This department controls the quality of food products, medicines, cosmetics, tobacco products, and certain other categories of goods and also monitors compliance with legislation and standards in this area. The FDA is responsible for maintaining public health by regulating and overseeing the safety of food, tobacco products, dietary supplements, drugs (both prescription and over-the-counter), vaccines, medical devices, and veterinary
drugs. The tasks of the agency include monitoring compliance with the legislative standards in the region of maintaining the quality of food products, medicines, and cosmetics. The FDA regulation has no legal force and is regarded as a guideline or recommendation for production control. According to the FDA recommendations, before being sent to market bleached cellulose pulp for sanitary hygiene products is tested voluntarily and is provided with clinical data in terms of health risk in accordance with ISO 10993 (GOST ISO 10993-1–2011, medical products. Evaluation of the biological action of medical products. Part 1. Evaluation and research). This applies primarily to new compositions that differ from those sold previously. According to the FDA, the requirements for sanitary hygiene products are regulated, in particular, by federal registration codes 21 (CFR 884.5425 and CFR 884.5435).

In the EU sanitary hygiene products are subject to less stringent rules for consumer products. However, EDANA (European Disposables and Nonwovens Association) and the global organization IDNA (Nonwovens Manufacturers Association) pay special attention to the requirements for materials for sanitary hygiene products.

In Russia there are currently no strict restrictive standards for the chlorine content of industrial cellulose pulp, but given that a significant part of the pulp is exported controls to reduce it are being introduced.

Under modern conditions the creation of materials for sanitary hygiene and medical products based on cellulose is of paramount importance. The need for development and improvement in this area has become important in the context of viral epidemics such as the COVID 19 pandemic.

The bleaching systems that exist in Russian plants do not, in general, provide the level of organically bound chlorine required by international standards while achieving high quality in the bleached cellulose pulp.

To comply with international standards it is necessary to modernize the bleaching systems currently operating at Russian plants to include ECF light schemes with an increased proportion of oxygen-containing bleaching agents, such as oxygen, hydrogen peroxide, and ozone. Other reagents are not effective enough: they are too complicated for introduction into production or are expensive to use. Moreover, systematic assessment of the content of chlorine compounds in the products is required [7].

The principal method of determining the content of chlorine compounds in cellulose is pyrolysis. An improved method based on ISO 11480:2017 has been developed for determination of the total content of chlorine (TC) and organically bound chlorine (OBC) in cellulose materials. Essentially the method involves the absorption of the gaseous chlorine formed during combustion of the analyzed sample by an electrolyte and measurement of the amount of chlorine ions by microcoulometric titration and determination of their mass with a recording device. The method is highly reliable and accurate for measurement of concentrations in the range of 1-1000 mg/kg.

The figure shows the dynamics of changes in the chlorine content of the cellulose pulp for one of the bleaching methods used at Russian plants. According to the given sequence of bleaching stages of the ECF method, delignification is carried out in two stages: oxygen-alkali refining (OAR) and bleaching with chlorine dioxide (D0). The OAR stage is characterized by high delignification efficiency, which makes it possible to use a small amount of chlorine dioxide in bleaching. After the D0 stage the concentration of organochlorine compounds in the cellulose pulp increases slightly, but
then the level of TC and OBC does not exceed 250 mg/kg throughout the entire bleaching process and reaches minimum values at the end of the process.

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