Evaluation of denitration of nitrocellulose by microbiological treatment for industrial waste effluents using calorimetry analysis

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Abstract

The problem of utilization of the compounds present in the effluents of the production of cellulose nitrates (NC) is very important and complicated, and its decision is inextricably related to the environment. The process of heat release in the samples of nitrocellulose subjected to biological processing of different types was studied. Biological processing was conducted by incubation with sulfate-reducing bacteria *Desulfovibrio desulfuricans* BKMB-1388, microscopic fungi *Fusarium solani* BKM F-819, and their mixed culture. The studies were carried out on the native NC (13.38% nitrogen) and the NC processed (NC_{proc}) using ultraviolet radiation and ozone (UV + ozone). It has been shown that the pre-treatment of the NC by UV + ozone significantly increases the degree of decomposition of the NC during its subsequent biodegradation assisted by symbiotic microorganisms of *D. desulfuricans* and *F. solani*. A substantial result was achieved on the fifth day of NC_{proc} incubation, which is promising from the viewpoint of practical applications.

Keywords Nitrocellulose · Biological degradation · *Fusarium solani* · *Desulfovibrio desulfuricans* · Calorimetry

Introduction

High-energy capacity materials such as aromatic compounds, nitroesters, and nitroamines are components of polymeric composite materials. Large amounts of effluents with wastes containing environmentally hazardous substances are formed in the process of industrial production of such polymers. The problem of their utilization is important and complicated, and its decision is inextricably related to health of the present and future generations of people. The development of methods and techniques aimed at accelerating the decomposition of the compounds present in the effluents of the production of cellulose nitrates (NC) will allow one to solve environmental problems associated with the accumulation of large quantities of flammable, explosive, and poorly degradable materials in

the sediment ponds and to reduce the negative impact on the environment.

The volumes of NC production in the world are very considerable. It is known [1] that Germany produced 26,050 tons of gunpowder within the period from January to March 1945. The scientific base of special chemistry in the USA is concentrated in the state enterprises, such as Livermore, Argonne, and Los Alamos National laboratories and the research center at the China Lake. Twenty-six plants producing gun powders, solid propellants, and explosives were placed in the 1980s in these cities [2].

Investigations in this area are aimed at searching for the possibility of prolonged and safe storage of NC [3] and eliminating the main drawbacks of NC. These are low density, high fragility, and low combustion temperature. The modification of the NC precursor was used in [4]. Microcrystalline cellulose nitrate was successfully prepared from Alfa grass (a cheap and easily renewable source) and showed a high potential for the use as a component of propellants. It is also proposed [5] to prepare a nanometallic fuel based on NC modified by nanoborane. The introduction of nanoborane by electrospinning into nitrocellulose fibers induces a faster and intensive combustion.

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However, NC also finds other spheres of application. Nitrated cellulose with a low nitrogen content (lower than 12.5%) is used as coatings, varnishes, and paintings and in microelectronics. Nitrated cellulose with a high nitrogen content (higher than 12.5%) is used as the major component of many propellants, fireworks, explosives, and gas generators.

Nitrated cellulose was used [6, 7] as an additive to improve thermal characteristics and mechanical properties of propellants. The use of the polymer based on glycidyl azide with the same purpose showed [8] that the initial decomposition temperature was 5.67 °C higher than that of purely spherical NC powders, which is very important for safety characteristics.

The most promising and environmentally friendly are biological methods for the disposal of industrial effluents as well as the wastes accumulated in the sediment ponds [9, 10]. However, it is known that the cellulose and its nitrated derivatives are characterized by high resistance to biological degradation [11]. Nevertheless, works in this direction are persistently continued. There is an evidence for the partial destruction of the NC with the use of fungi [12–14] and bacteria [15–17] or when processes are conducted in anaerobic bioreactors [18]. The preliminary chemical or physicochemical treatment is used to obtain substances that are easily assimilated by microorganisms [19].

Cellulose nitrate is a basis for the production of gun powders, which are explosives that decompose to release a significant quantity of energy within a short time period. Therefore, the characteristics of the thermal decomposition of NC are among the most important parameters for the establishment of the mechanism and rate of decomposition. Thus, they provide a clear representation about the maximum possible comparative stability of this highly explosive substance.

Multiple methods, primarily, the determination of nitrogen, nitrates, and nitrites, are used in laboratory research as well as in monitoring the technological process of NC degradation. One of the most important and highly informative indicators is the heat release rate and the total heat of decomposition of the NC isolated from the solution after microbial degradation. The results of calorimetric studies allow one to examine the full thermodynamic characteristic of the phenomenon under study and to draw exacter conclusions and predictions. It is typical that the thermodynamic approach is being more widely used in biology as a precise method for the investigation of processes in living organisms. The parameters of heat release characterize the degree of denitration of NC.

Thermogravimetric analysis is efficiently used in all numerous studies [1–8]. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of NC raw

materials and mixtures used in the production of pyrotechnical firecrackers, guns, and other units were monitored under different conditions and in various processes of mixing in air [20]. It was found by TG and DSC that the temperature of the environment used for drying the initial mixture, the high relative moisture content, and granulation did not induce self-ignition.

Microencapsulation of ammonium azide particles with fibrous NC was carried out both in solvent and without solvent [21]. X-ray diffractometry, scanning electron microscopy, infrared spectroscopy, TG, and DSC were used to characterize the structure, morphology, and thermal stability of these particles. The results of the study [21] showed that the efficiency of the proposed thermogravimetric method is more informative than that of a sequence of other complicated methods.

The thermal characteristics of the propellant before designing the industrial setup for the combustion of propellants with expired storage term were also determined by TG in argon [22].

The listed above and other industrial productions for the synthesis and use of NC give large volumes of wastewater. Therefore, wastewater decontamination and the possibility of repeated use in the technological cycle are important tasks of the modern ecological chemistry. Various microorganisms or active silt from purification plants (being a secondary power source) is used for the solution of this complicated problem [23].

The microbiological NC degradation with the sulfate-reducing bacteria *Desulfovibrio desulfuricans* [19] and filamentous fungus *Fusarium solani* [24, 25] has been studied, and the influence of the preliminary NC treatment on the process when UV-irradiation and ozone are used has been considered.

In this work, the possibility of using UV radiation combined with ozone and the mixed culture of the fungus *Fusarium solani* BKMF-819 and sulfate-reducing bacteria *Desulfovibrio desulfuricans* BKMB-1388 on the NC in the wastewater treatment in the industrial production and detoxification in the sediment ponds was evaluated. For comparison of the whole body of such a vast amount of data and for choosing the most efficient microbiological treatment conditions, the evaluation method was applied to one of the characteristic parameters, namely the heat of thermal decomposition of NC samples isolated from the solution after the microbiological treatment, since it is known that the heat of NC thermal decomposition increases with an increase in the nitrogen content in the sample.

The aim of this work is to evaluate the degree of microbiological degradation of NC under the influence of different types of microorganisms. The heat of thermal decomposition of selected NC samples is used as a parameter of the degradation process. We also intended to

choose which of the variants of microbial degradation of NC would be most suitable for the industrial use.

Experimental

Materials and methods

The following reagents and solvents manufactured by Sigma (USA), BioRad (USA), and Reakhim (Russia) were used: KCl, NH_4Cl , $\text{CaCl}_2 \times 2\text{H}_2\text{O}$, K_2HPO_4 , $\text{MgCl}_2 \times 6\text{H}_2\text{O}$, NaNO_3 , Na lactate, Na salicylate, NaOH, glucose, tetrahydrofuran (THF), and acetone. They were used for the preparation of nutrient culture media and buffer systems and in the physicochemical studies. The NC samples (trade mark M/1 26 432-01) with a nitrogen content of 13.38% (mass of an elementary unit of a macromolecule is 284.4, degree of polymerization is 1140, molecular weight is 324,216) according to GOST R 50461-92 provided by the Kazan Gunpowder Plant were used.

Treatment of NC by ultraviolet light and ozone

Ultraviolet irradiation and ozonation (UV + ozone) were used for the pretreatment of NC taken in an initial concentration of 10 g L^{-1} . The photochemical reaction was carried out in a round-bottom quartz reactor with an inner diameter of 10.0 cm and a volume of 500 mL. The reactor was installed at a distance of 4 cm from the radiation source. The arc mercury discharge lamp with the lumino-phore of the high-pressure 400 W DRL-400 lamp (trade-mark E 40) manufactured at the OAO Lisma (Russia) was used for irradiation. The wavelength range was 250–600 nm, and the luminous flux in the UV range was 24,000 lm.

The ozonator manufactured at the IPCP RAS with the volume rate of the oxygen purge $Q_{\text{O}_2} \approx 350 \text{ cm}^3 \text{ min}^{-1} = 21 \text{ L h}^{-1}$ was used as a source of ozone. At the 2.5% content of ozone in oxygen, the ozonator capacity was about $0.5 \text{ L O}_3/\text{h} = 1.125 \text{ g O}_3/\text{h}$. The native NC solution was purged with ozone through a capillary.

The samples of 10 mL of the mixture were taken at an interval of 1, 3, 7, 12, and 27 h from the onset of experiment to determine the pH of the reaction solution and the nitrogen content in the NC.

Microorganisms

The mycelial fungus *Fusarium solani* BKMF-819 and sulfate-reducing bacteria *Desulfovibrio desulfuricans* (strain BKM B-1388) obtained from the All-Russia Collection of Microorganisms (G.K. Skryabin Institute of

Biochemistry and Physiology of Microorganisms, Russian Academy of Sciences) were used.

Bacteria biomass increasing

For increasing the biomass, the strain of *D. desulfuricans* BKMB-1388 was cultivated on the medium enriched with Na lactate (50 mM) and Na sulfate (10 mM) with the formation of sulfide (9.8 mM) on the fifth day of cultivation. The sowing was performed in the Hungate vials and incubated at 30 °C. The biomass of the bacteria was cultured anaerobically in medical bottles 250 mL in volume with the working volume of the medium of the sulfate reducer (DSV) equal to 100 mL. The absorbance of the culture fluid (at the wavelength $\lambda = 600 \text{ nm}$) in 7 days of the incubation was 0.34–0.35, which corresponded to $(6.5\text{--}8.5) \times 10^8$ cells in 1 mL of the cultivation medium.

Medium for sulfate reducer growth

The medium for sulfate reducer growth was prepared from solutions 1, 2, and 3. Solution 1: KH_2PO_4 0.5 g, NH_4Cl 1.0 g, Na_2SO_4 1.0 g, $\text{CaCl}_2 \times 2\text{H}_2\text{O}$ 0.1 g, $\text{MgSO}_4 \times 7\text{H}_2\text{O}$ 2.0 g, Na DL-lactate 2.0 g, yeast extract 1.0 g, resazurin 1.0 mg, Wolin vitamin 10 mL, trace (micro) elements SL-10 1 mL, and distilled water 980.0 mL. Solution 2: $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ 0.5 g and distilled water 10 mL. Solution 3: Na thioglycolate 0.1 g, ascorbic acid 0.1 g, and distilled water 10 mL. The solution of microelements contained (mg L^{-1}): $\text{FeCl}_3 \times 4\text{H}_2\text{O}$ 1500, ZnCl_2 70.0, $\text{MnCl}_2 \times 4\text{H}_2\text{O}$ 100.0, H_3BO_3 6.0, $\text{CoCl}_2 \times 6\text{H}_2\text{O}$ 190.0, $\text{CuCl}_2 \times 2\text{H}_2\text{O}$ 2.0, $\text{NiCl}_2 \times 6\text{H}_2\text{O}$ 24.0, $\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$ 36.0, and 10.0 mL HCl (25%, 7.7 M). The solution of Wolin vitamins contained (mg L^{-1}): biotin 2.0, folic acid 2.0, pyridoxine-HCl 10.0, thiamine-HCl 5.0, riboflavin 5.0, nicotinic acid 5.0, DL-calcium pantothenate 5.0, vitamin B12 0.1, *p*-aminobenzoic acid 5.0, and lipoic acid 5.0.

To prepare the medium, the ingredients of each solution were dissolved in an appropriate amount of water. Solution 1 was boiled for about 1 min and then cooled to room temperature purging 100% N_2 . Then, solutions 2 and 3 were added to bring the pH to 7.8 with NaOH, and the mixture was dispensed aerobically under 100% N_2 in tubes or vials. During the preparation, the medium was continuously stirred, keeping the gray precipitate suspended. Sterilization was conducted in the autoclave for 15 min at 121 °C.

Medium for experiments on NC microbiological degradation

For the preparation of the culture nutrient medium to study the NC biodegradation, the following reagents were used: KCl 5.0 g, NH_4Cl 10 g, $\text{CaCl}_2 \times 2\text{H}_2\text{O}$ 1 g, K_2HPO_4 10 g, $\text{MgCl}_2 \times 6\text{H}_2\text{O}$ 20 g, yeast extract 10 g, Na lactate 60 mL, and glucose 20 g. The components were dissolved in distilled water (2 l). The resulting concentrate of the culture nutrient medium before the experiment was diluted in a ratio of 1:4 with distilled water.

The necessary quantity of bacteria for the cultivation was quickly injected with a syringe into a laboratory reactor and stirred. Before sowing, the pH was 6.5–7.0. The incubation temperature of the bacteria was maintained throughout the experiment at 28–29 °C.

Growth of culture of fungus *F. solani*

For experiments, *F. solani* BKM F-819 was grown in tubes with the beveled maltose agar at 24–25 °C. The sowing of the fungi in the reactor was carried out by flushing with distilled water. Two vials with the grown cultures of the fungi were used for one sample. The temperature of the incubation of the fungi was maintained throughout the experiment at approximately 27–29 °C.

Microbiological destruction of the NC with bacteria cultures

D. desulfuricans bacteria are conditionally aerobic and, therefore, for the best result they should be used under anaerobic conditions. The experiments on the study of NC biological degradation were carried out in a laboratory glass reactor with a volume of 3 L under the natural sunlight without air blowing. Such experimental conditions were used with the aim of establishing the degree of possible biotransformation under the conditions extremely favorable for the bacteria. Each reactor contained 500 mL of the nutrient medium and 50 mL of the cultivated bacteria. In the first series of the experiments, the reactor was loaded with 10 g L⁻¹ of the native NC. In the second series, the reactor contained 10 g L⁻¹ of NC, which was pretreated for 27 h by UV radiation and ozone (NC_{proc}). The samples for analysis were taken on the 5th, 16th, and 38th day from the onset of experiment in a volume of 50 mL after mechanical stirring.

Microbiological destruction of the NC with fungi cultures

The experiments on the study of NC biological degradation were carried out in a laboratory glass reactor with a volume of 3 L under the natural sunlight without air blowing. Each reactor contained 500 mL of the nutrient medium seeded with *F. solani* BKM F-819. In the first series of the experiments, the reactor was loaded with 10 g L⁻¹ of the native NC. In the second series, the reactor contained 10 g L⁻¹ of NC, which was pretreated for 27 h by UV radiation and ozone (NC_{proc}). The samples for analysis were taken on the 5th, 16th, and 38th day from the onset of the experiment in a volume of 50 mL after mechanical stirring.

Destruction of NC with a mixed culture of bacteria and fungi

The experiments on the study of the biological destruction of the NC at the simultaneous impact of the fungus *F. solani* and bacteria *D. desulfuricans* were conducted in a laboratory glass reactor with a volume of 3 l containing 500 mL of the medium and inoculated with *F. solani* BKM F-819 (3 × 2 tubes with the beveled agar) and *D. desulfuricans* BKMB-1388 (50 mL of the culture containing 6.5–8.5 10⁸ cells mL⁻¹) under the natural sunlight without air blowing. The NC was added in the both reactors at a concentration of 10 g L⁻¹. In the first series of the experiments, the reactors were loaded with the native NC. In the second series, the reactors contained the NC_{proc}, which was pretreated by UV radiation and ozone. The samples for analysis were taken on the 5th, 16th, and 38th day from the onset of the experiment in a volume of 50 mL after mechanical stirring. The temperature was maintained at 25–27 °C during bacteria and fungi incubation.

The variants considered for the microbiological treatment of the NC are presented in Table 1.

Isolation of the NC from the solution

The samples (50 mL) were regularly taken from each laboratory reactor. The precipitate from the culture fluid containing the bacterial cells, insoluble salts, and particles of NC was separated by centrifugation at 7000 rpm for 20 min in an Optima L-90 K ultracentrifuge (Beckman, USA). Then, the precipitate was washed twice with distilled water and dried to a constant weight at 105 °C. The dry residue was treated with acetone (50 mL) and left to stay for 2 h at 40 °C to attain the complete dissolution of the NC in acetone. The bacterial cells and insoluble salts from the solution in acetone were separated by repeated

Table 1 Variants for the study of the microbiological degradation of the NC

Sample	Variants of microbiological processing
K1	NC native (control 1)
NC _{proc} – K2	NC + (UV + ozone) for 27 h (control 2)
No. 1	NC + bacteria <i>Desulfovibrio desulfuricans</i>
No. 2	NC _{proc} + bacteria <i>Desulfovibrio desulfuricans</i>
No. 3	NC + fungi <i>Fusarium solani</i>
No. 4	NC _{proc} + fungi <i>Fusarium solani</i>
No. 5	NC + bacteria <i>Desulfovibrio desulfuricans</i> + fungi <i>Fusarium solani</i>
No. 6	NC _{proc} + bacteria <i>Desulfovibrio desulfuricans</i> + fungi <i>Fusarium solani</i>

centrifugation at 7000 rpm for 15 min, and then, the solution was poured into round porcelain cups and evaporated to 50% volume at 40 °C. Then, an ethanol–water (1:2) mixture was added dropwise to the precipitate of the NC. The NC isolated was dried to a constant weight in an oven at 40 °C.

Characterization

Quantification of the NC

The amount of the NC isolated as described above was determined by the gravimetric method. It was found in the blank experiment that the total mass loss of the NC in the course of dissolution and centrifugation can reach 6%. The parameter **W** (%) corresponding to a decrease in the NC content in the isolated solutions was calculated using these data by the equation

$$W\% = 100\% - (W_{\text{isolated}} + 6)\% \quad (1)$$

Determination of nitrogen in the NC

The contents of C, H, N, and S were determined in the fully dried samples of the NC (0.01 g) using a Vario MICRO cube CHNS/O elemental analyzer (Elementar GmbH, Germany). No sulfur was detected in all the analyzed samples.

Determination of nitrate and nitrite

The contents of nitrate and nitrite ions in the solution of the culture fluid were determined by the photometric method on a KFK-2MP photocolormeter (Technocom, Russia). Nitrate ions were determined by measuring the absorbance at the wavelength $\lambda = 400$ nm of a yellow-colored complex formed by the reaction of nitrate ions with salicylic acid in a cuvette 2 cm thick (modified Lurie method [26]). Nitrite ions were determined by measuring the absorbance at the wavelength $\lambda = 540$ nm of a red-violet azo dye (diaz compound) in a cuvette 5 cm thick. The azo dye is

formed in the presence of α -naphthylamine and sulfanilic acid (modified Lurie method [26]). The content of ions was calculated by the previously obtained calibration curves. The working solutions containing $13.8 \mu\text{g cm}^{-3}$ of nitrate and $10.4 \mu\text{g cm}^{-3}$ of nitrite were used, respectively, to plot the curves. Some solutions of the samples were turbid and, hence, they were filtered through a paper filter (“blue ribbon”) before measuring.

Determination of the heat release rate and the heat of thermal decomposition of the selected NC samples

The study of the heat release kinetics in the thermal decomposition of the utilization products of the NC was performed with a DAC-1–2 automated differential microcalorimeter [27] at 139.8 °C in a glass pre-evacuated sealed ampule with an internal volume of about 2 cm³. This microcalorimeter is designed and manufactured at the Institute of Problems of Chemical Physics RAS. The instrument can operate under isothermal conditions over a wide range of temperatures from ambient up to 400 °C and can measure the heat release rate in the range from 10^{-5} to 1 W. The ampule had no cold parts, which allowed one to keep all the decomposition products in the reaction zone. The sample weight of the substance under study was 10 mg, unless otherwise indicated.

The rate curves were straightened in the coordinates of the first-order autocatalytic reaction $d\eta/dt/(1 - \eta)$ on η [28], which showed that the process can be described by Eq. (2) until the reaction conversion reached about 0.4 (Fig. 1), except for the initial section.

$$\frac{d\eta}{dt} = k_1 \cdot (1 - \eta) + k_2 \cdot (1 - \eta) \cdot \eta. \quad (2)$$

Here, $\eta = \frac{\int_0^t \frac{dQ}{dt} dt}{\int_0^\infty \frac{dQ}{dt} dt}$ is the depth of thermal decomposition of the NC; $\frac{d\eta}{dt} = \frac{1}{Q_0} \left(\frac{dQ}{dt} \right)$, $1/h$ is the reaction rate of thermal decomposition of the NC; $\frac{dQ}{dt}$, cal h^{−1} g^{−1} is the heat

Fig. 1 Dependence of $\frac{d\eta}{dt(1-\eta)}$ on η for the thermal decomposition of the native NC

release rate; $\int_0^t \frac{dQ}{dt} \cdot dt = Q$, cal g⁻¹ is the current heat of the

process; $\int_0^\infty \frac{dQ}{dt} \cdot dt = Q_0$, cal g⁻¹ is the full heat of the

process, and k_1 , 1/h and k_2 , 1/h are the rate constants of the catalytic and non-catalytic steps of the reaction.

The current heat process (Q) was calculated by the numerical integration of the curve of the heat release rate from zero to the current time, and the full heat (Q_0) was calculated by the integration of the curve from zero to the infinite time value.

Results and discussion

Degree of biological degradation of the NC

The data on the change in the nitrogen content in the NC and the contents of nitrate and nitrite ions in the culture fluid solution during incubation are given in Table 2. In the aqueous solution of the control sample (K1), the nitrite ions were not detected, whereas the content of nitrate ions was 5.94–6.24 μg mL⁻¹.

Before conducting experiments on biological degradation, a portion of the native NC was subjected to the UV + ozone treatment for 27 h [24].

This NC_{proc} was the initial in the parallel series of the experiments. In the solution of the control sample (K2) NC_{proc}, no nitrate ions were detected, whereas in the solution of NC_{proc} after 27 h of the UV + ozone treatment, the content of nitrite ions was 1.46 μg mL⁻¹.

Nitrates are present in the solutions of all the samples in significant quantities, while the content of nitrite ions is negligible (Table 2). It is most likely that these microorganisms consume the nitrite-containing compounds. The highest number of nitrate and nitrite ions was determined in the experiment with the treated NC_{proc}. It is probably that the pretreatment allows the fungi to penetrate deeper into the polymer globule and, hence, the process of degradation of the NC proceeds more efficiently, in particular, by the cleavage of the NO₂ groups [29].

Also, a decrease in the nitrogen content is observed with an increase in the incubation time of the NC with the microorganisms (Table 2). The lowest nitrogen content in the samples was recorded after the incubation with

Table 2 Change in the contents of elements in the NC and nitrate and nitrite ions in the solutions during the incubation time with the microorganism

Sample	Content/%									Content/μg mL ⁻¹					
	C			H			N			NO ₃ ⁻			NO ₂ ⁻		
	Time/day			Time/day			Time/day			Time/day			Time/day		
	5	16	38	5	16	38	5	16	38	5	16	38	5	16	38
K1							13.38			5.94–6.24					
K2	25.15			3.38			11.67						1.46		
No. 1	31.72	25.97	25.99	3.97	2.89	3.11	11.57	11.72	10.77	5.80	3.23	5.55	*n/d	n/d	0.52
No. 2	32.05	30.61	29.40	4.83	3.83	3.79	11.17	10.92	10.58	13.00	9.01	5.06	n/d	n/d	0.20
No. 3	30.19	25.14	26.34	3.83	2.69	3.23	11.76	10.61	10.51	11.40	5.15	2.78	3.34	0.52	0.22
No. 4	28.56	27.95	26.30	3.85	3.59	2.97	11.80	10.39	10.15	12.20	8.64	2.67	3.38	0.49	0.26
No. 5	30.23	26.26	26.68	3.84	2.94	3.26	11.57	10.92	10.28	5.70	3.08	3.03	n/d	n/d	0.25
No. 6	31.35	28.69	27.38	4.03	3.33	3.48	11.07	10.70	10.03	23.60	9.14	6.26	n/d	n/d	0.21

The designation of the samples is listed in Table 1. *n/d means “not detected”

microorganisms for the period from 16 to 38 days and varied from 10.03 to 10.77%.

In general, it is remarkable that the NC_{proc} pretreated by ultraviolet radiation and ozone is degradable to a greater extent than the non-treated one. For example, in sample 1 after 38 days of incubation with bacteria *D. desulfuricans* the content of N is 10.77%, whereas in sample 2 the content of N is 10.58%.

The measurements taken over a period of 5 days demonstrate no significant benefits of the UV + ozone pretreatment. After 16 and up to 38 days of the incubation, there is a clear picture that the nitrogen content in the NC_{proc} is lower than that in the non-pretreated NC samples.

The data in Table 2 show that during the period from 16 to 38 days, a change in the general trend to the degradation of the NC is observed, namely the biodegradation rate by microorganisms decreases. The observation of all samples was continued up to 65 days. The tendency to decreasing the biodegradation rate established to the 38th day naturally increased. A decrease in the biodegradation rate of the samples with *D. desulfuricans* with incubation time indicates that the bacteria lose the activity. The reasons can be the acidification of the reaction solution or the total consumption of the nutrient medium necessary for the life of bacteria. Therefore, the incubation period up to 38 days is the most technologically justified (without additional fertilizing of microorganisms).

After 38 days, the lowest degree of degradation of the NC was shown by the samples incubated with one culture of bacteria as in the case of the NC (sample 1, [N] = 10.77%) and in the case of NC_{proc} (sample 2, [N] = 10.58%).

After 38 days of the incubation, the minimum amount of nitrogen was detected in sample 6 and was equal to 10.03%. Thus, the maximum level of degradation was achieved in a series of experiments with the NC_{proc} when the mixed culture of bacteria and fungi was used and was equal to 25.04%. A slightly lower level of degradation is shown by sample 4 of the N_{proc}, which was incubated with one culture of fungi *F. solani* for 38 days. In this case, the N content is 10.15% and the degree of degradation of the NC is 23.39%.

Figure 2 shows that, according to the weighing data, a decrease in the NC content in solution (W%) exceeds the degree of decomposition of the NC, which was determined from the decrease in the nitrogen content in the samples. This difference indicates that the microorganisms perform two different processes, namely the elimination of nitro groups and the breakage of the bonds of the hydrocarbon skeleton and the evolution of the low-molecular fragments.

The total amount of nitrates and nitrites determined within 38 days of incubation with *F. solani* (23.41 $\mu\text{g mL}^{-1}$ for sample 3 and 28.03 $\mu\text{g mL}^{-1}$ for

Fig. 2 Change in parameter **W** (%) corresponding to the amount of the NC isolated from solutions in different variants of microbiological processing after 38 days of the treatment according to weighing the samples. Variants of microbiological processing: (1) sample No. 1; (2) sample No. 2; (3) sample No. 3; (4) sample No. 4; (5) sample No. 5; and (6) sample No. 6

sample 4) is higher than that after incubation with *D. desulfuricans* (15.1 $\mu\text{g mL}^{-1}$ for sample 1 and 27.27 $\mu\text{g mL}^{-1}$ for sample 2). This can be explained by the fact that *D. desulfuricans* utilizes nitrates and nitrites as electron acceptors reducing them to N_2 , which is characteristic of many types of this sulfate-reducing bacteria [30].

As it is given in Table 2, the amount of the NC itself decreases with NC incubation on microorganisms. The data presented take into account the “blank experiment,” i.e., minus 6.0% that are lost when the NC is isolated from the solution with acetone. For incubation with fungi *F. solani* (samples 3 and 4), the NC degrades to a higher extent than that for incubation with bacteria *D. desulfuricans*. Evidently, the microorganisms decrease the nitrogen content in the studied samples and also substantially transform the NC itself. So, hydrogen sulfide, which is a natural product of metabolism of sulfate-reducing bacteria *D. desulfuricans*, hydrolyzes NC. It is known that *F. solani* is a denitrifying fungus that produces exohydrolase enzymes hydrolyzing nitroester bonds of this polymer. In addition, many fungi including *F. solani* have cellulolytic activity, i.e., can decompose esters. However, the efficiency of hydrolysis of nitroester bonds is low under aerobic conditions without the preliminary physicochemical treatment [18]. This is observed in our experiments: In samples 2, 4, and 6, NC_{proc} is taken, since much more NC_{proc} is removed than in the variant with the non-processed NC.

Thus, the functions of microorganisms are diverse. They hydrolyze nitroester bonds resulting in a decrease in the degree of nitration of the polymer and destruct the carbon chain at the β -1,4-glycoside bond to form nitrooligosaccharides of various lengths [31, 32]. As a result, the overall

losses of the NC (Fig. 2) increase to 39.85% (for NC) and 45.03% (for NC_{proc}) under the combined action of bacteria and fungi. However, the preliminary processing (UV + ozone) favors a deeper penetration of microorganisms into the polymer globule and increases the degree of degradation of the NC.

The results obtained make it possible to build a sequence of the efficiency of the microorganisms used for the biological degradation of the NC: bacteria *D. desulfuricans* < fungi *F. solani* < bacteria *D. desulfuricans* + fungi *F. solani*.

The scatter of the data on the changes in the contents of nitrogen, nitrate ions, and nitrite ions in the NC solutions indicates that the microorganisms assimilate the NC with different rates. For isolation from the reaction solution with acetone, mainly non-damaged macromolecules are extracted, whereas destroyed pieces of the NC can remain in the reaction solution.

To answer the question about the degree of degradation of the NC, the degradation was monitored using another parameter characterizing the process, namely the heat of thermal decomposition of the extracted and isolated samples of the NC after biodegradation.

Thermal decomposition kinetics of the NC after different microbiological treatment options

Treatment by ultraviolet light and ozone

Calorimetric measurements make it possible to establish the amount of released heat and the heat release rate for specific experimental conditions. The data obtained indirectly indicate the degree of degradation of the NC. The calorimetric parameters of the native NC sample were

Fig. 3 Dependences of the heat release rate on time during the thermal decomposition of the NC samples at 139.8 °C. (1) Native NC (control 1); (2) NC_{proc} (control 2)

compared with those obtained for the NC samples studied after preliminary biological processing under different conditions.

The dependences of the heat release rate on time during the thermal decomposition are shown in Fig. 3.

It can be seen from the dependences presented (Fig. 1) that the thermal decomposition of the samples studied proceeds according to the law of autocatalytic reaction with the degree of acceleration (ratio of the maximum rate to the initial one) about 6.

As shown in Fig. 3, there is a slight increase in the initial rate of thermal decomposition of the irradiated NC_{proc} (control 2). This leads to a decrease in the time of achievement of the maximum rate [27, 33]. The full heat release of the native NC is about 1110 cal/g_{NC} on the average. The heat of NC_{proc} decomposition is slightly lower and equal to 1010 cal/g_{NC}. This value can serve as an indirect indication of the fact that the UV + ozone treatment of the NC leads to the separation of the nitro groups. The further confirmation of this fact is a strong decrease in the pH in the UV treatment according to [19].

A small increase in the initial rate of the thermal decomposition of the irradiated NC is probably due to changes in the supramolecular structure of the NC in the NC irradiation process [19]. In turn, the increase in the initial rate leads to the shortening of the time of achievement of the maximum rate in the NC_{proc} decomposition reaction [27]. As a result of the separation of nitro groups [19, 24], there is a decrease in the total heat of thermal decomposition of the NC_{proc}.

Incubation with *D. desulfuricans* bacteria, fungi *F. solani*, and mixed cultures

The recovery of the ONO₂ groups in the NC is a key reaction reducing its toxicity and paving the way for further deep transformations. Conventionally, aerobic bacteria *D. desulfuricans* form a specialized group of microbes that use sulfate (SO₄²⁻) as the final electron acceptor during respiration. The sulfate-reducing bacteria are able to recover nitroxy groups to ammonium by the dissimilation mechanism [34]. Therefore, it was proposed [15] to use the strain of the genus *Desulfovibrio* as the primary link in the microbial consortium for initiating the NC degradation process under the conditions of plant effluents, since the latter contain significant amounts of sulfates [15].

For the biological treatment of effluents of the pulp industry, microorganisms need to grow rapidly, predominate competitively in the environment, and degrade in low and high molecular weight derivatives of lignin. In particular, it is shown [35] that cellulolyticus (*S. rolfii* ATCC 24459) and the denitrifying fungus (*F. solani* IFO 31093) can aerobically decompose NC in a liquid medium.

However, it should be remembered that the degradation of NC is influenced by many factors that can limit its utilization.

On this basis, the options of the biological degradation of the NC by incubation on the bacteria *D. desulfuricans* (sample 1, Table 1) and the fungus *F. solani* (sample 3), as well as at their combined action (sample 5), were reviewed. In parallel, their effect on the NC_{proc} (samples 2, 4, and 6) was tested. For the isolated NC and NC_{proc}, the rate and thermal effect of their thermal decomposition were studied with the purpose to reveal the conversion of their microbiological processing.

Figure 4 presents the dependences obtained for the maximum heat release rate during the thermal decomposition of the NC for the samples incubated with microorganisms over a period of 38 days. It was established experimentally that the decomposition proceeds via the law of the autocatalytic reaction for both the native NC and the NC subjected to microbiological processing in all the variants.

Figure 4 shows that the heat release rate during the decomposition of samples 1 and 2 pre-incubated with bacteria *D. desulfuricans* differs from that for the decomposition of the native NC to the lowest extent. The incubation with the culture of the fungus *F. solani* results in a significantly higher effect, and the thermal decomposition rate of samples 3 and 4 significantly decreases as compared with the control. Finally, under the combined action of the bacteria and fungi the thermal decomposition rate decreases even more strongly (NC_{proc}, sample 6).

The initial heat release rate $(dQ/dt)t = 0$ is 14–15 cal h⁻¹ g⁻¹ on the average, and its deviation in the

increase direction is observed for microbiological treatment options 2, 4, and 6 for incubation for 38 days. The maximum heat release rate $(dQ/dt)_{\max}$ is about 60 cal h⁻¹ g⁻¹ on the average. The heat release rates for sample 1 are higher.

The time of achievement of the maximum heat release rate $t_{\max}$ in the decomposition of the NC after microbiological processing for 38 days for sample 2 is minimum being 13.2 h (Fig. 5). This time is maximum for sample 3 and equal to 17.9 h. For the control samples, the time is 20.8 and 14.0 h for K1 and K2, respectively. For all the treatment options, $t_{\max}$ for 38 days of the incubation is shorter than that for 16-day processing. The shortest time for the achievement of the maximum heat release rate in NC decomposition after microbiological processing for 38 days is observed for sample 2. This is probably due to the highest initial rate of decomposition.

Figure 6 shows the dependence of the total heat (Q_{tot} , cal g⁻¹) released in the thermal decomposition of the isolated NC on the incubation time in different variants of the biological treatment. It is seen that the UV + ozone pre-treatment leads to the situation that NC_{proc}, in general, has a lower heat of thermal decomposition than the native one.

Figure 6 shows that for the entire set of microbial variants for NC processing, the incubation of samples 3 and 6 with the microorganisms for 38 days leads to a lower heat of thermal decomposition (Q_{tot}) and, hence, to a smaller content of nitrogen in the NC dissolved in acetone.

The conducted calorimetric measurements clearly demonstrate serious changes that occur with an NC molecule during incubation on the microorganisms. The change in the character of heat release, namely a decrease in the total released heat and a considerable decrease in the heat

Fig. 4 Change in the maximum of the heat release rate during the thermal decomposition of the NC samples at 139.8 °C on the time of the preceding treatment (0–38 days) at different variants of microbiological processing: K1 is native NC and K2 is NC_{proc}; (1) sample No. 1; (2) sample No. 2; (3) sample No. 3; (4) sample No. 4; (5) sample No. 5; and (6) sample No. 6

Fig. 5 Change in the time of achievement of the maximum heat release rate during the thermal decomposition of the NC samples at different variants of microbiological processing: K1 is native NC and K2 is NC_{proc}; (1) sample No. 1; (2) sample No. 2; (3) sample No. 3; (4) sample No. 4; (5) sample No. 5; and (6) sample No. 6

Fig. 6 Change in the total heat (Q_{tot} , cal g⁻¹) released in the thermal decomposition of the selected samples of the NC at 139.8 °C depending on the incubation time in various options of the biological treatment: (1) sample No. 1; (2) sample No. 2; (3) sample No. 3; (4) sample No. 4; (5) sample No. 5; and (6) sample No. 6

release rate, proves that the NC undergoes microbiological transformation into the stationary phase of microorganism growth. Nitrates and cellobiose are formed due to the action of enzymes and metabolites of the used fungi and bacteria. As a result, the parameters inherent in the NC as an explosive decrease significantly. Undoubtedly, the products of NC transformation have some intrinsic heat of decomposition, and it is difficult to isolate and estimate quantitatively their contribution. However, according to the available literature data [36], the amount of released heat in cal (Q_{tot}) corresponds rather exactly to the nitrogen content in the NC. Evidently, the data of the calorimetric measurements confirm the qualitative pattern of activity of the studied microorganisms toward the NC:

bacteria *D. desulfuricans* < fungi *F. solani* < bacteria *D. desulfuricans* + fungi *F. solani*.

In this report, it has been shown for the first time that the preliminary treatment with UV + ozone favors the subsequent biological degradation of the NC. An attempt to use the physical treatment of this kind was made earlier. An attempt to use this type of physical treatment was made in [37]. However, there is a basic distinction between our work and [24]. We treated the NC with UV radiation, while the authors [24] first treated the wastewater containing NC with alkali (alkaline hydrolysis occurred) and only then subjected the alkali-treated NC with UV radiation.

The screening of the microorganisms to nitroesterase activity revealed active producers of exohydrolase enzymes hydrolyzing nitroester bonds of xenobiotic among various taxonomic groups of pro- and eukaryotes: *Pseudomonas fluorescens* [17], *Escherichia coli*, *Bacillus circulans*, *Rhodococcus rubropertinctus*, and in culture

mixture *Desulfovibrio desulfuricans* [15, 16]. The biodegradation of NC was conducted [18] by incubation in a culture mixture with the methanogenically enriched culture. In 11 days of incubation, the content of N (% and equal weight amount) decreased from 13.3 to 10.1%. Under the conditions where bacteria were additionally fed with lactate, the decrease in the NC within 60 days was more than 25%.

It is shown [38] that the bacteria *Desulfovibrio desulfuricans* ATCC 27774 can grow in the presence of an almost atmospheric content of oxygen. Since the wastewaters of the NC production contain significant amounts of sulfates, the bacteria *Desulfovibrio* are very interesting from the viewpoint of their possible practical use. For NC with a nitrogen content of 11.8% [15], the decrease in the NC within 60 days of incubation was 28.1% and the nitrogen content decreased by 2–6%.

The decrease in the NC amount from 12.65 to 15.59% obtained in this work with a decrease in the nitrogen content by 3% in samples 1 and 2 for 38 days of incubation for *D. desulfuricans* without the addition of the nutrient medium can be considered consistent with the available literature data.

The fungi cultures, including *Fusarium solani*, are most efficient from the viewpoint of biodegradation of NC [34, 39]. The degree of degradation of the NC equal to 23.6% (initially [N] = 13.17%) and losses of 0.3% N within 7 days of incubation on *F. solani* with the addition of starch as a cosubstrate were obtained [39]. The maximum degree of degradation was 24.8% during the incubation time shorter than 7 days on fungi of other types: *Acremonium persicinum* ATCC 60921, *Basidiomycetes* sp. NRRL 6464, *Bjerkandera adusta* ESF 620, *Cyathus stercoreus* NRRL 6473, *Irpex lacteus* Z 212, *Phanerochaete chrysosporium* ATCC 32629, *Trametes versicolor* ESF 491, and *Trichoderma pseudokoningii* FTK 228 [39]. The further increase in the degree of degradation of the NC is achieved for increasing the incubation time in the presence of nutrient medium for microorganism growth, for example, 43% within 28 days (initially [NC] = 13.4% N, carboxymethylcellulose as a cosubstrate) for incubation on *Chaetomium elatum* [40].

Thus, a decrease in the NC content by 34% (sample 4) obtained in this work with a decrease in the nitrogen content by 3% can be considered as a serious achievement.

The attempts to create a symbiosis of microorganisms for the maximum efficient degradation of NC are known. For the combined incubation on *F. solani* and *Sclerotium rolfsii* ATCC 24459, the 31% NC degradation was achieved [35] within 3 days (initially [N] = 13.17%, starch as cosubstrate).

It was also attempted to create a symbiosis of microorganisms: bacteria and fungi. It is seen from the

obtained data that we failed to obtain the symbiosis: There is no significant increase in the degree of degradation of the NC with a simultaneous decrease in the nitrogen content in the variant of combined incubation on the bacteria and fungi compared with the incubation by fungus *F. solani* only. However, the achieved degree of degradation, namely a decrease in the NC amount to 39.85% and 45.03% in experiments on the native NC and NC_{proc} (experiments 5 and 6, respectively), can be considered substantial.

Conclusions

The oxidation of nitrocellulose (NC) containing 13.38% nitrogen has been investigated. The process of heat release in the samples of nitrocellulose subjected to biological processing of different types was studied. Biological processing was conducted by incubation with sulfate-reducing bacteria *Desulfovibrio desulfuricans* BKM B-1388, microscopic fungi *Fusarium solani* BKM F-819, and their mixed culture. It has been shown that the pretreatment of NC by UV + ozone significantly increases the degree of degradation of the NC during its subsequent biodegradation assisted by symbiotic microorganisms of *D. desulfuricans* and *F. solani*. The present work provides the following results.

The complete NC degradation was not achieved within the studied terms of incubation (from 5 to 38 days).

The use of the NC pretreated with UV + ozone significantly favors a decrease in the NC content after incubation with all considered biological substrates.

The most substantial results of NC degradation were achieved for the destruction of the NC with the mycelial fungus *F. solani* (samples No. 3 and No. 4).

The denitration of the NC by the combined action of the studied microorganisms (bacteria *D. desulfuricans*, mycelial fungus *F. solani*) was obtained on the NC pretreated with UV + ozone (sample No. 6).

The heat release kinetics in the thermal decomposition of the NC samples isolated after incubation on the microorganisms was studied. The degree of degradation of the NC was estimated by a comparison of the heats of decomposition and a decrease in the amounts of NC and nitrogen. These data made it possible to construct the sequence of efficiency of the microorganisms used for the biological oxidation of NC: bacteria *D. desulfuricans* < fungi *F. solani* < bacteria *D. desulfuricans* + fungi *F. solani*.

Substantial parameters were achieved within the incubation period of NC_{proc} on the combined culture of bacteria and fungi for the first 5 days, which is promising from the viewpoint of practical use.

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