METHODOLOGY FOR STABILIZING NATURAL AND TECHNOGENIC SYSTEM QUALITY

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Abstract. Certain methodology has been developed to study the destruction of organogenic waste containing biopolymer lignocellulose complexes, the composition of which is determined by the functioning of the natural soil-biotic ecosystem. Soils determine the stability of natural ecosystems. Soil quality is assessed by its fertility (humus content), which is regulated by the constant supply of biopolymers, the subsequent destruction and accumulation of intermediate substances in the soil-biotic complex, which are adsorbed on the mineral component of the soil with the formation of organomineral colloids or mineralized to biogenic nutrients or gaseous substances. The humified product was obtained using effective microorganisms, which are contained in the biologically active preparation "Tamir". The preparation contains a consortium of 86 beneficial soil microorganisms existing in symbiosis: lactic acid, nitrogen-fixing, photosynthetic, cellulose-destroying bacteria, unicellular microorganisms, microscopic fungi and cellulose-lignin waste: food waste, industrial (sawdust), agricultural (barley straw). The main stages of anaerobic bioconversion of cellulose-containing raw materials are: hydrolytic decomposition of biopolymers; growth of cells of effective microorganisms on hydrolysis products and the formation of humified soil. Waste bioconversion was carried out in mesophilic conditions (25-40 ºC) for three days. The main advantage of anaerobic enzymatic processing of cellulose-lignin waste from other utilization systems is the minimum energy consumption for the fermentation process and the production of additional energy in the form of biogas.

Keywords: Environmental safety, organogenic waste, humified product, bioconversion, biogas.

Introduction

The depletion of the world's oil and natural gas reserves is leading to an energy crisis. It is known that man-made carbon-containing waste products can be regarded as a potential renewable energy resource, while the accumulation of household and industrial waste exerts man-made pressure on the atmospheric air, surface water, and soil, reducing their quality. Wastes are distinguished - of organogenic nature: activated sludge, cellulose-containing or oily waste, domestic wastewater sludge; or synthetic: plastics, textiles and others. More than 75% of industrial and household wastes are toxic to the environment and humans. The greatest danger to human life is posed by large-tonnage man-made waste (hazard class II) of the petrochemical, chemical, mining, cellulose, wood processing industries with a long decomposition period. Synthetic polymer wastes belong to the fifth hazard class, however, an increase in the volume of consumption of synthetic polymer materials leads to the accumulation of non-biodegradable by biological agents of waste not typical to natural ecosystems, their storage at landfills, to the alienation of agricultural lands, soil and landscape degradation. The low degree of use of such wastes in Russia is associated with their heterogeneous chemical composition, unstable physicochemical properties, and significant energy costs for the destruction of polymer bonds. The largest share of polymeric household waste is made up of polyethylene terephthalate (PET) products used as containers for storing food. At present, in Russia, the volume of such waste exceeds 10 million tons per year [1; 2].

To obtain cheap and environmentally friendly renewable energy sources, improve the production efficiency and rational management of technological processes, an effective methodology for the disposal of synthetic and natural polymer waste has been developed using innovative tools for the disposal of carbon-containing waste to obtain useful products. The proposed methodology for assessing the stability of the quality and safety of natural and synthetic polymer systems is based on the principle of minimizing the technogenic risk, replacing natural raw materials (biopolymers) with synthetic analogs, as well as minimizing thermal and gaseous emissions [3; 4]. To achieve these goals, we used the tools of physical and chemical analysis, monitoring, modeling the rational use of natural energy resources, utilization of household and industrial waste.

Object and research methodology

When biopolymers are replaced by synthetic analogs, losses of their stability occur due to changes in the composition of low molecular weight components, changes in physicochemical, physical and

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mechanical properties. The study of phase equilibria of multicomponent systems containing low molecular weight toxic volatile amines and polar organic solvents using physical and chemical analysis tools made it possible to substantiate the hypothesis of minimizing volatile components and guarantee the quality and safety of materials based on them [5]. In the study of the problem of disposal of synthetic solid polymeric household waste, kinetic instruments of thermal destruction were used. Utilization of synthetic polymeric household waste was carried out using the example of polymeric PET bottles for storing Afanasy beer (dark brown) – PET_2 and Kashinskaya mineral water (transparent) – PET_1. The destruction of PET waste was carried out in the low-temperature range (280-400 ºC) in the presence of atmospheric oxygen at a heating rate of 10º min^{-1}, kinetic curves were plotted from the change in the concentration of carboxyl groups over time (Fig. 1). Analysis of the kinetic curves showed that in the temperature range 280-330 ºC there is no significant change in the acid number (about 4 mg $KOH \cdot g^{-1}$) within 40 minutes, that is, PET_1 does not degrade. At 340 ºC, the acid number of PET_2 in the range of 0 to 30 min increases to 10 mg $KOH \cdot g^{-1}$ (Fig. 1a), and at a temperature of 400 ºC within 30 minutes, the acid number increased by 30 ... 40 times. Mathematical processing of the kinetic curves indicates the first order of the reaction (Fig. 2 b). The obtained kinetic parameters were used to plot a graph in Arrhenius coordinates lnk – 1/T (Fig. 3), and the activation energy of the process of thermal destruction of PET_2 was calculated from the slope of the curve. The apparent value of the activation energy for thermal destruction of PET_1 -based wastes was 140 $kJ \cdot mol^{-1}$, and PET_2-based wastes – 187 $kJ \cdot mol^{-1}$.

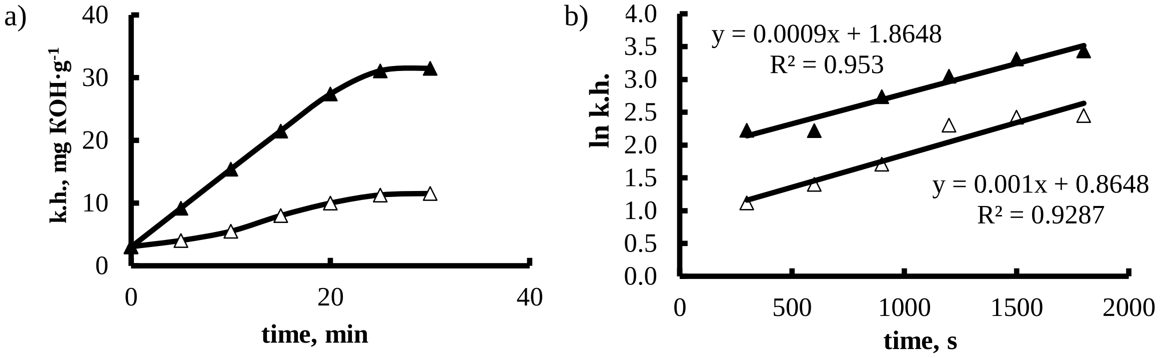

Fig. 1. **Change in the concentration of carboxyl groups (a) and ln k.h. (b) PET_2 versus time at △ – 340 ºC, ▲ – 400 ºC**

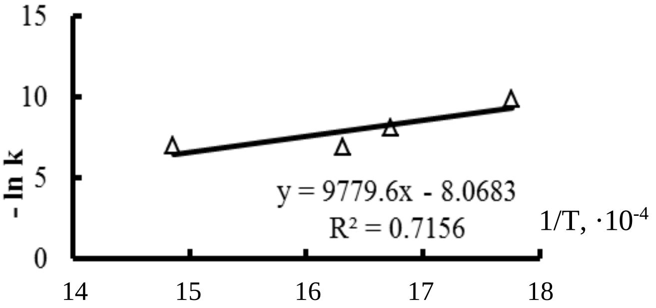

Fig. 2. **Change parameters of the process of thermal destruction of PET_2 in the temperature range 280-400 ºC in Arrhenius coordinates lnk - 1/T**

Analysis of the nature of the kinetic curves of the thermal destruction of waste based on PET_1 and PET_2 indicates a complex mechanism of the thermal destruction process. The obtained patterns can be explained on the basis of the basic provisions of the theory of random discontinuities [6]. At the initial stage, at temperatures close to the melting temperature of the polymer, the reaction rate of the formation of carboxyl groups is low and corresponds to the induction period, at which the break of physical bonds between macromolecules occurs. At a temperature of 400 º C, the weakest bonds in the main chain (─C─O─) are broken with the formation of free radicals and the acceleration of the depolymerization reaction by the chain mechanism with the formation of oligomers through the stage of an active intermediate complex and the formation of free carboxyl groups.

Kinetic studies of low-temperature destruction (280-400 ºC) substantiated the possibility of modifying bituminous compositions [7]. The introduction of the PET destruction product into bitumen made it possible to increase the performance characteristics of asphalt concrete mixtures: frost resistance and resistance to mechanical loads (shear deformation), adhesion to the mineral components of asphalt concrete mixtures and use of it as road building materials. The performance characteristics of bitumen compositions can be improved by using technical lignin as a functional modifying additive, which accelerates the course of physicochemical reactions with soot and bitumen with the formation of composite materials [8]. A hypothesis has been put forward about the combined use of technical lignin and PET processing products for the modification of bitumen compositions. The chemical nature of lignin will stabilize the PET degradation products and improve the efficiency of light and heat resistance of useful products made from these wastes. Unlike synthetic polymer waste, biopolymer organogenic waste (paper, cardboard, food or plant matter, activated sludge and others) synthesized by woody and herbaceous plants in natural ecosystems is subject to destruction for a long period of time. Man-made carbon-containing waste (industrial or agro-industrial) contains stable biopolymers containing cellulose and lignin. Modern technologies for the disposal of carbon-containing waste are based on thermochemical methods of conversion (pyrolysis) or biotechnological methods using microorganisms [9-11] to obtain efficient energy carriers (biogas). Utilization of carbon-containing waste based on the use of chemical instruments (hydrolysis) leads to the formation of a toxic by-product of technical lignin, which is stored at landfills and has a high reactivity when exposed to environmental factors. In this case, toxic substances are formed that are released into the atmospheric air or are concentrated in the surface layer of the soil, where their gradual deposition occurs, the chemical and physicochemical properties of the surface layer of soils change (compaction, change in the hydrological regime), violating their stability, decreasing soil fertility, which is renewed within 10 ... 100 thousand years, and the productivity of phytocenoses. Therefore, a methodology was developed for studying the destruction of organogenic waste containing biopolymer lignocellulose complexes, the composition of which is determined by the functioning of the natural soil-biotic ecosystem.

Research results

The priority in assessing the quality of natural and man-made systems is soil biotic monitoring tools, which make it possible to analyze the migration path of a hazardous substance in the system. Monitoring of the quality of surface water within the city of Tver showed that the water used for drinking water supply does not meet the sanitary and hygienic standards. The concentration of toxic substances increases along the length of the watercourse and remains in the control sections (10-15 km downstream) of the Volga River and in the mouths of tributaries of small rivers [12]. Investigations of the surface water quality of small rivers – Tmaka (sanitary protection zone of a mechanical plant and thermoelectric power station TPS-1) and the mouth of the Tvertsa river (Rechnoy Vokzal) within the city of Tver were carried out using chemical monitoring tools. The content of toxic ions of heavy metals (HM) of lead (Pb^{2+}), zinc (Zn^{2+}), copper (Cu^{2+}), nickel (Ni^{2+}), cobalt (Co^{2+}) in water does not exceed the MPC. The water quality does not meet the requirements of SanPiN 2.1.5.5980-00 in terms of such quality indicators as the content of total iron and chemical oxygen demand (COD) (Fig. 3 a), which are two to three times higher than the MPC. The presence of toxic HM ions in water can lead to their accumulation in the biomass of aquatic organisms and the death of the most sensitive species of biological environment. Therefore, studies of assessing the water quality were carried out using biomonitoring tools and using universal biotests – test plants typical for a given region, which allow an integral assessment of the quality of all natural environments [13].

When studying the effect of water quality on biomass growth, it was found that the biomass of barley roots and stalks is constant in control 1 (mineral soil component) and increases 2 times in control 2 (mineral + organic soil component) and decreases in the following order:

H_2O dist > H_2O (tap water) > H_2O (river water). Soils determine the stability of natural ecosystems. The quality of soils is assessed by the fertility (humus content), which is regulated by the constant supply of biopolymers, subsequent destruction and accumulation of intermediate substances in the soil-biotic complex, which are adsorbed on the mineral component of the soil with the formation of organomineral colloids, or mineralized to biogenic nutrients or gaseous substances. The use of biotests made it possible to assess the quality of technogenic soils and surface water in the small rivers Tvertsa and Tmaka in the city of Tver and to identify the most dangerous sources of pollution. Plant biotests were used in further studies to assess the quality of the bioconversion product of cellulose-containing waste using microbiocenosis of up to 80 species of soil effective microorganisms (EM) of lactic acid, nitrogen-fixing, photosynthetic, cellulose-destroying bacteria, unicellular microorganisms, microscopic fungi existing in the symbiosis of biologically active preparation “Tamir”, developed on the basis of the Japanese analogue “Waste Treatment”.

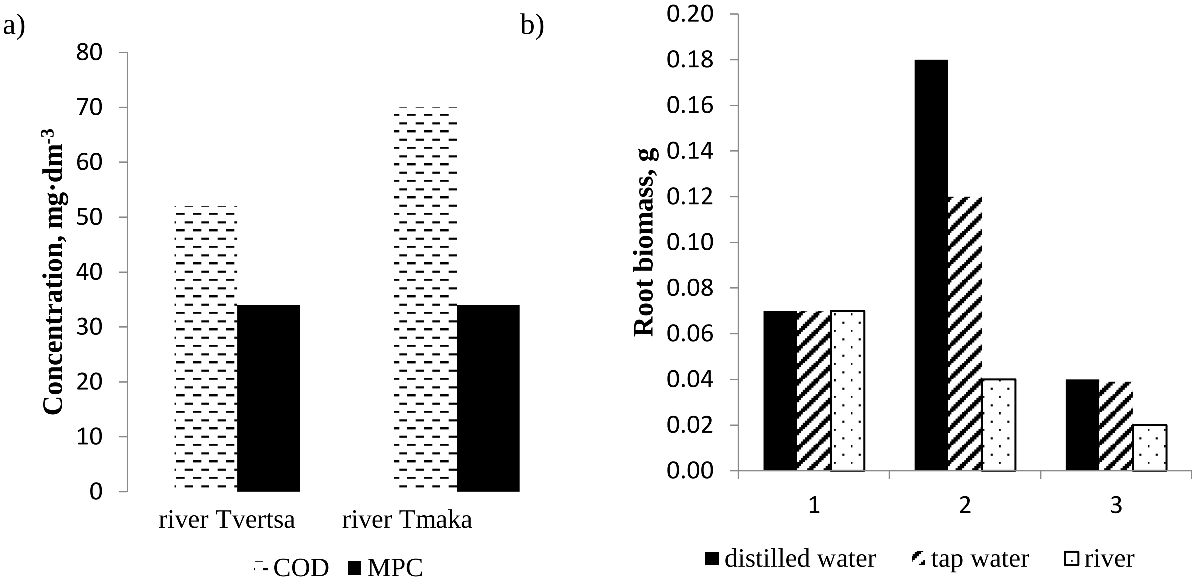

Fig. 3. **Change in water quality chemical oxygen consumption in the Tvertsa and Tmaka rivers (a) and root biomass test of barley plant (b):** 1 – control 1; 2 – control 2; 3 – zone 1

The humification of cellulose-containing wastes (CW) was carried out using the example of industrial (sawdust); household (dried after brewing tea leaves, cardboard); agro-industrial (barley straw) waste in a fermenter under anaerobic mesophilic conditions (temperature 30 ... 40 ºC) for 10 ... 30 days. The main advantage of anaerobic CW utilization from other destruction instruments is the minimum energy consumption for the fermentation process and the production of additional energy in the form of biogas (CH_4: CO_2) [14]. During fermentation, stable pH values were maintained. The range of changes in fermentation temperatures (20 ... 40 ºC) was chosen according to the condition of the process of bioconversion of solid CO: at temperatures below 20 ºC, the bioconversion process sharply slows down, at temperatures above 40 ºC, microorganisms of the working solution die and the bioconversion process stops. As a result of bioconversion of solid organic waste, humified soil and biogas were obtained [15]. To control the biogas consumption, the gasholder is installed on the scales. A sample of biogas was taken from the gasholder using a pump built into the GIAM gas analyzer. When sampling with a rotameter, the speed of biogas movement is measured, the sampling time is measured with a stopwatch, thus the biogas consumption was determined. The methane concentration in the biogas was determined with a GIAM gas analyzer, and then the amount of methane in the entire volume of biogas was calculated. The yield of biogas and methane in the identified zones increased over time (Fig. 4).

To assess the complex effect of bioconversion parameters and conduct a multifactorial experiment, an almost rotatable Box-Benkin plan of the second order was chosen, which minimizes the number of experiments while simultaneously varying the studied factors (Table 1). Coded parameters of variation are: X_1 is the temperature in the process of bioconversion; X_2 is the concentration of lignin in the central heating; X_3 is the concentration of Tamir in the EM suspension. For the optimization criterion Y_1, Y_2, the methane content in the biogas and the control content of carbon monoxide in the biogas are taken.

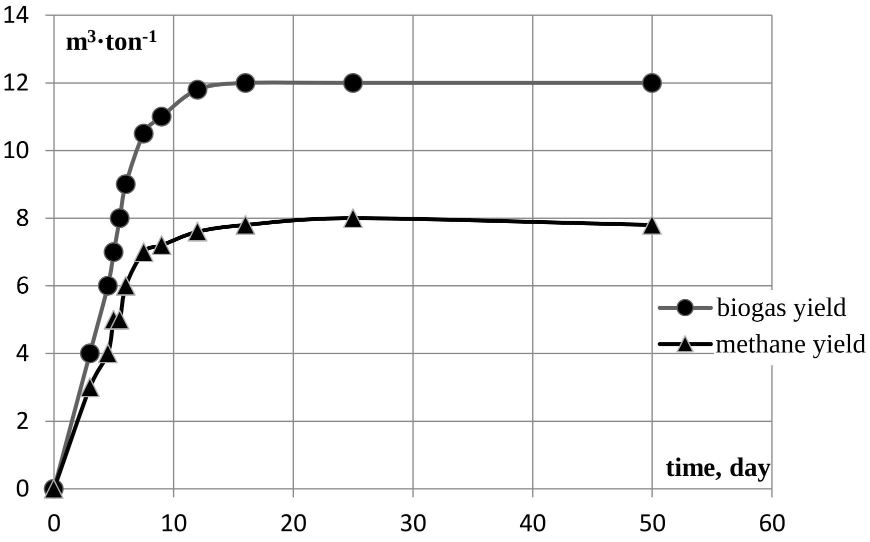

Fig. 4. Yield and composition of biogas depending on the time of fermentation at a temperature of 50 ºC

Table 1

Variation intervals of the variables of the three-factor experiment

Coded value of factors	***X*$_1$ temperature, ºC**	***X*$_2$ composition of central heating waste (*L*), %**	***X*$_1$ suspension composition EM (*T*), %**
Upper level (+)	20	5	0.1
Main level (0)	30	20	0.3
Lower level (-)	40	35	0.5

Discussion

Preliminary studies have established possible ranges of values of the main technological parameters: fermentation temperature 20-40 ºC; composition of the initial CO by the content of lignin (L) and cellulose (C): cardboard - 26% L + 48% C of the total composition or 35: 65; sawdust – 3% L + 63% C of the total composition or 5:95; drunk tea – 10% L + 50% C of the total composition or 20:80; composition of the working solution of effective microorganisms for the main component Tamir is 0.1-0.5 and the material balance of the technological process of solid waste bioconversion for a model biogas plant has been calculated. A model of a biogas plant for obtaining thermal or electrical energy from biogas can be represented by a diagram of two modules - a biogas production module – metantec and technological equipment and a cogeneration unit module with technological equipment (Fig. 5).

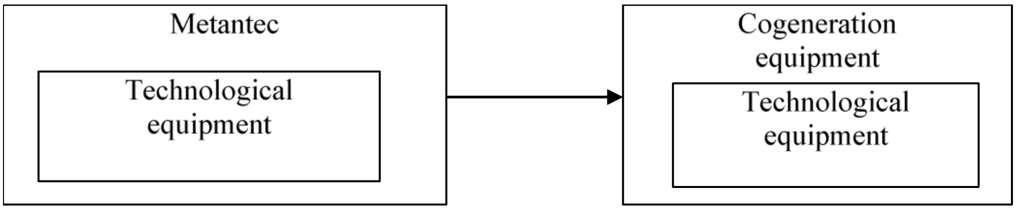

Fig. 5. **Diagram of a model biogas plant**

The effectiveness of the soil humifier was assessed by the increase in the yield of the test crops. When humified soil was added to the technogenic soil, the biometric indicators of the quality of the sod-podzolic soil improved: rooting accelerated, germination 2-5 times, the phytotoxicity coefficient in absolute value increased eight times, the yield of grain and forage crops – by 10-50%. The results obtained made it possible to formulate a hypothesis of stabilization of the quality of natural and technogenic soddy-podzolic soils by the product of bioconversion [16].

Conclusions

The developed methodology for the disposal of polymer solid industrial waste based on synthetic and natural polymers with the production of secondary raw materials allowed not only to solve environmental problems: minimization of industrial risks; regeneration of soils, but also to expand the raw material base to obtain an assortment of useful products used in the energetics and agro-industrial complex.

Biogas obtained from solid organic waste is recommended to be used as a renewable energy resource for cogeneration installations, which are equipment for combined production of electricity and heat. The advantage of small installations is reliability, inertia, the ability to generate the required amount of energy in the immediate vicinity of the consumer.

It is recommended to use humified soil for reclamation of technogenic soils.

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