Sludge-lignin of the Baikal Pulp and Paper Mill as a Substrate for Generating Electric Energy in MFC

G. O. Zhdanova[1][a], D. I. Stom[1,2,3][b], S. V. Alferov[4][c], N. Yu. Yudina[4][d],
A. B. Kupchinsky[2][e] and T. S. Lozovaya[3]

[1]Irkutsk State University, Irkutsk, Russia
[2]Baikal Museum of the SB RAS, Listvyanka, Russia
[3]Irkutsk National Research Technical University, Irkutsk, Russia
[4]Tula State University, Tula, Russia

Keywords: Electric current generation, biofuel cells, biotechnology, lignin sludge, Baikal pulp and paper mill.

Abstract: We studied the performance of microbial fuel cells (MFCs) based on 1) strain Cl. acetobutylicum VKPM-4786; 2) a complex commercial biological product for cesspools and septic tanks "Doctor Robik 109". Lignin sludge from the Baikal Pulp and Paper Mill was a substrate for microorganisms in the MFC. Strain Cl. acetobutylicum VKPM-4786 was distinguished by a higher efficiency in the MFC from the tested bioagents. The voltage generated by this bacterium upon the addition of 2.0 g/l of sludge-lignin reached 402 mV in 123 h, and the current strength was 742 μA. The microbiological preparation "Doctor Robik 109K" generated a voltage of up to 387 mV (for 117 h) in the MFC with the addition of 1 g/l of lignin sludge. The current strength reached 400 μA. The generated values were significantly lower when lower (0.1 g/l) and higher concentrations of lignin sludge (2 and 5 g/l) were introduced into the MFC.

1 INTRODUCTION

The problem of global depletion of fossil resources encourages the search for cheap and renewable energy sources. Such a resource can be waste from the pulp and paper industry, as well as agricultural and industrial waste. According to general calculations, up to 300 million tons of cellulose-containing industrial (hydrolyzed lignin), agricultural (straw, stems, cake, fruit pits, nutshells and others) and even up to 50 million tons of household organic waste (paper, cardboard) (Gromova 2012). On the one hand, they act as pollutants, and on the other hand, they are potential sources of raw materials. Cellulose-containing waste decomposes under natural conditions for a rather long period of time.

One of the largest pollutants in the Angara region is the waste from the enterprises of the sulphate-pulp industry (Nikonorov et al. 2012). The problem with the waste of the Baikal Pulp and Paper Mill, located right on the shore of Lake Baikal, is also very acute at the present time. This business is currently closed. However, its sludge reservoirs are filled with gigantic volumes (6.2 million m^3) of toxic waste. On the territory of the Baikal Pulp and Paper Mill, a huge mass of lignin sludge poses a special danger. Due to the increased seismicity and climatic features of the region, the sludge-lignin accumulated in the maps can at any time get into the open Baikal. A promising method for the disposal of various organ-containing wastes with simultaneous generation of electricity is microbial fuel cells (MFCs) (Varanasi et al. 2015).

The purpose of this work was to study the possibility of using lignin sludge from the Baikal Pulp and Paper Mill as a substrate in MFC.

[a] http://orcid.org/0000-0002-8355-9517
[b] http://orcid.org/0000-0001-9496-2961
[c] http://orcid.org/0000-0002-5217-7815
[d] https://orcid.org/0000-0002-4054-9642
[e] https://orcid.org/0000-0001-8884-8636

Zhdanova, G., Stom, D., Alferov, S., Yudina, N., Kupchinsky, A. and Lozovaya, T.
Sludge-lignin of the Baikal Pulp and Paper Mill as a Substrate for Generating Electric Energy in MFC.
DOI: 10.5220/0011571100003524
In *Proceedings of the 1st International Conference on Methods, Models, Technologies for Sustainable Development (MMTGE 2022) - Agroclimatic Projects and Carbon Neutrality*, pages 316-321
ISBN: 978-989-758-608-8

2 MATERIALS AND METHODS

2.1 Microbial Fuel Cell (MFC)

The generation of current by microorganisms using sludge-lignin was studied in two-chamber MFCs, the design of which is described in (Stom et al. 2017) (Fig. 1).

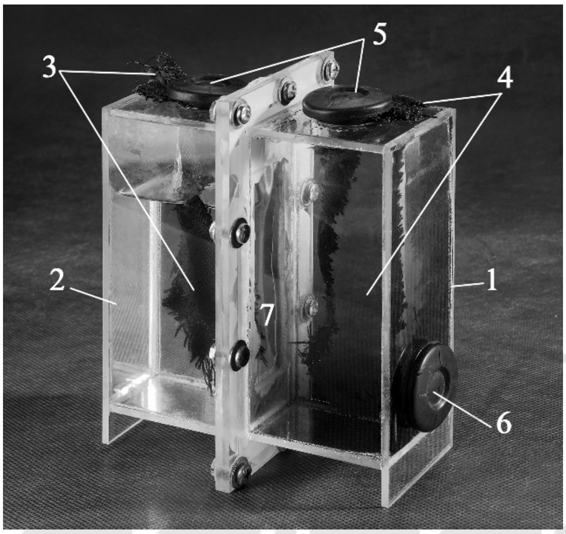

Figure 1: Microbial fuel cell (1 – anode chamber; 2 – cathode chamber; 3 – cathode electrode; 4 – anode electrode; 5 – rubber covers of the anode and cathode chambers; 6 – rubber plug for introducing components and sampling)

The carbon cloth URAL T-22R A (OAO Svetlogorskkhimvolokno, Republic of Belarus) served as electrodes in the MFC. For the manufacture of electrodes, the fabric was cut into strips 15 × 4 cm in size. The main working medium in the MFC was model waste water (MWW) of the following composition (g/l): Na_2CO_3 - 0.05; KH_2PO_4 - 0.03; $CaCl_2$ - 0.01; $MgSO_4 \times 7H_2O$ - 0.01. The preliminary sterilization of the medium was carried out by autoclaving at 1 atm for 45 min.

The lignin sludge from the Baikal Pulp and Paper Mill served as a substrate for microorganisms. This waste is a jelly-like product. Its main component is insoluble substances formed at the stages of chemical and biological wastewater treatment of enterprises producing bleached pulp using the sulphate method. Great difficulties with its disposal are caused by high humidity (more than 90%). Lignin sludge samples were taken from the map of sludge collector No. 2 of the Baikal Pulp and Paper Mill of the Irkutsk Region (Baikalsk). Waste was introduced into the MFC at concentrations of 0.1; 1.0; 2.0; 5.0 g/l.

2.2 Microorganisms

The following microorganisms acted as bioagents in MFC:

1) Complex commercial microbiological preparation "Doctor Robik 109K" (manufactured by LLC "VIPECO", Russia, Moscow). Designed for cesspools and septic tanks. Contains a mixture of microorganisms of the genus *Bacillus*. Before adding the drug to the MFC, it was added in an amount of 2 g to 100 ml of saline. solution and placed on a magnetic stirrer for 15 minutes. Thanks to this operation, bacterial cells and spores were separated from the carrier (sawdust) on which they were adsorbed. The resulting suspension of bacteria was introduced into the MFC (3 ml per cell).

2) *Clostridium acetobutylicum* VKPM-4786 strain. Taken from the All-Russian Collection of Industrial Microorganisms (Federal State Unitary Enterprise GosNIIgenetika, Ministry of Education and Science of Russia BRC VKPM). The strain was cultivated in a liquid nutrient medium of the following composition (g/l): KH_2PO_4 – 0.7; K_2HPO_4 - 0.7; $MgSO_4 \times 7H_2O$ - 0.1; $MnSO_4 \times H2O$ - 0.02; $FeSO_4 \times 7H_2O$ - 0.015; NaCl - 0.01; ammonium acetate - 3.0; yeast extract - 1.0; peptone - 1.0; cysteine - 0.5; glucose - 20.0. To preserve the culture and maintain anaerobic conditions, a small amount of sterile vaseline oil was added to the test tubes on the surface of the nutrient medium inoculated with microorganisms. Incubation was carried out at a temperature of 35-37°C. A 5-day culture of *Cl. acetobutylicum* VKPM-4786 was used to add to the MFC. 3 ml of culture liquid were added to the MFC anolyte.

2.3 Generation of Electricity in MFC

Before starting operation, the MFC chambers were sterilized with a 3% hydrogen peroxide solution. Then they were washed with distilled water and kept under an ultraviolet lamp for 15 min. The anode compartment of the MFC was filled with pre-sterilized model waste water. The test substrate was also placed here. Model waste water was also poured into the cathode chamber, but without the addition of an organic substrate. At the same time, the anode chamber was completely filled to expel air from the chamber, and the liquid level in the cathode chamber was left 1.5–2.0 cm below the chamber cover to aerate the catholyte. Working electrodes made of URAL T-22R A carbon cloth were placed in both compartments of the MFC. The introduction of microorganisms into the anolyte was carried out with

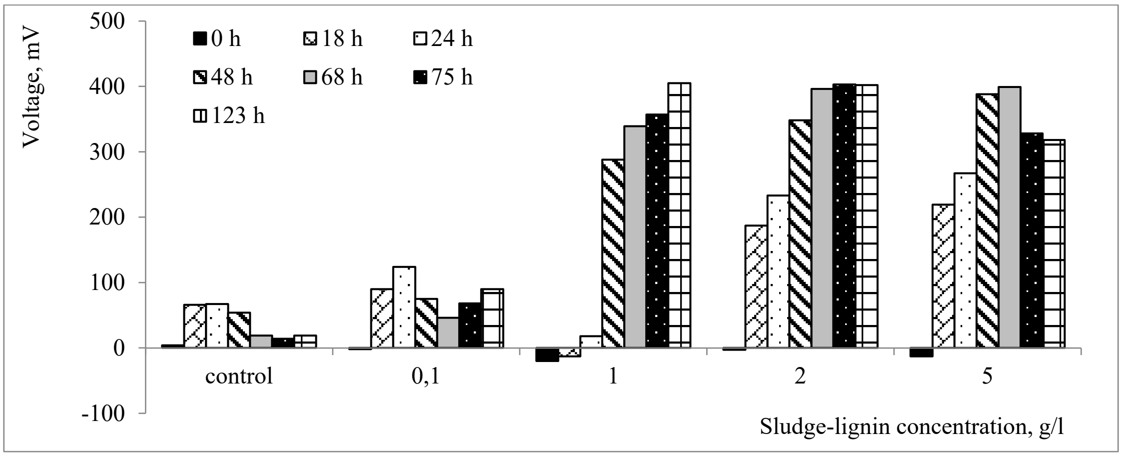

Figure 2: Dynamics of voltage (measured in open circuit mode), generated in the MFC by strain *Cl. acetobutylicum* VKPM-4786 (medium - model wastewater, substrate - sludge-lignin from the Baikal Pulp and Paper Mill (0.1; 1.0; 2.0; 5.0 g/l), electrodes – carbon cloth).

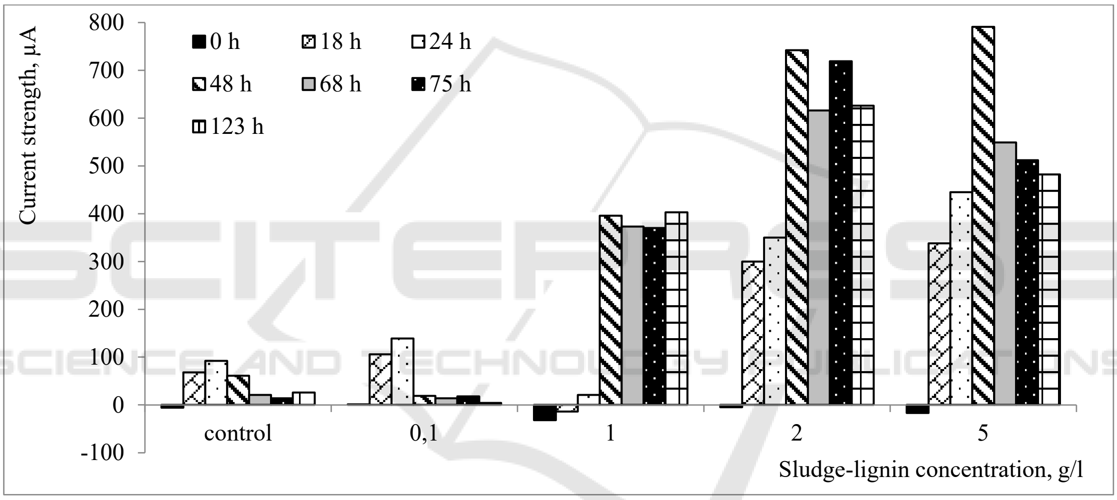

Figure 3: Dynamics of the current strength (measured in the short circuit mode), generated in the MFC by strain Cl. acetobutylicum VKPM-4786 (medium – model waste water, substrate – sludge-lignin from the Baikal Pulp and Paper Mill (0.1; 1.0; 2.0; 5.0 g/l), electrodes – carbon cloth).

a sterile syringe through a special rubber plug in the side of the chamber. The ability of microorganisms to generate an electric current in the MFC when using the tested substrates was evaluated by increasing the electrical parameters of the MFC. Voltage was measured in open circuit mode, current strength was measured in short circuit mode, using a Fluke 17B digital multimeter. The duration of the experiments was up to 120 h, depending on the kinetics of the MFC readings.

2.4 Statistical Processing of Results

All experiments were carried out in at least 3 independent experiments with 3-5 parallel measurements in each. For statistical processing of the obtained data, the Microsoft Excel software package was used. Conclusions are made with the probability of an error-free forecast $P \geq 0.95$. Significance of differences was determined using Student's t-test.

3 RESULTS AND DISCUSSION

The experiments revealed a fairly good electrogenic activity of Cl. acetobutylicum VKPM - 4786 when using lignin sludge from the Baikal PPM as a substrate. At the same time, the values of electrical parameters increased with an increase in the

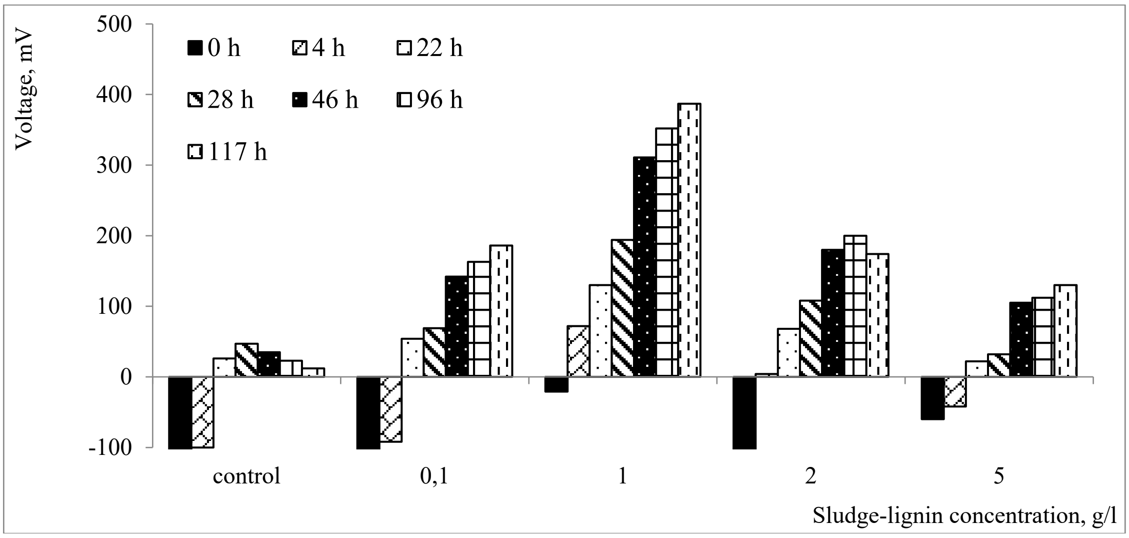

Figure 4: Dynamics of voltage (measured in open circuit mode) generated in the MFC by the biological product "Doctor Robik 109K" (environment – model wastewater, substrate – lignin sludge from the Baikal Pulp and Paper Mill (0.1; 1.0; 2.0; 5.0 g/l), electrodes – carbon cloth.

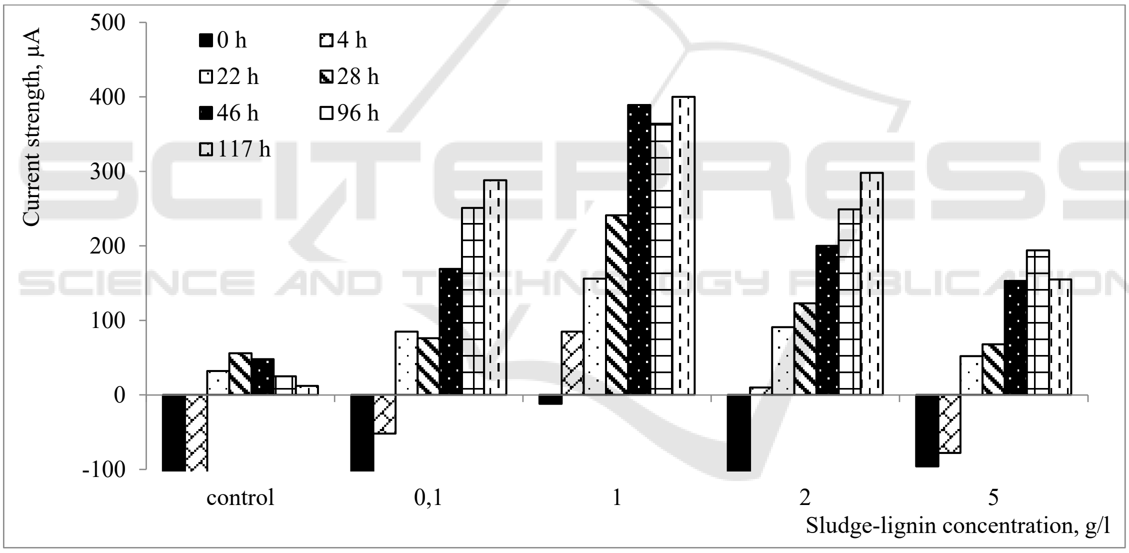

Figure 5: Dynamics of the current strength (measured in the short circuit mode) generated in the MFC by the biological product "Doctor Robik 109K" (medium – model wastewater, substrate – lignin sludge from the Baikal Pulp and Paper Mill (0.1; 1.0; 2.0; 5.0 g/l), electrodes – carbon cloth).

concentration of this waste in the anolyte. So, in the MFC with the addition of 0.1 g/l of sludge-lignin, for 123 hours of the experiment, the values of voltage and current only slightly exceeded the control ones (in the experiment – up to 124 mV and 139 µA, in the control – up to 67 mV and 92 µA, respectively). But an increase in the content of the substrate to 1 g/l led to a significant increase in indicators. In this case, the voltage generated by Clostridium increased to 405 mV, and the current increased to 403 µA. When 2.0 g/l of the tested waste was added to the MFC, these indicators reached 402 mV and 742 µA, in the presence of 5.0 g/l - 400 mV and 791 µA, respectively (Fig. 2, 3).

The ability to generate current in MFCs, in which the lignin sludge from the Baikal Pulp and Paper Mill acted as a substrate, was also noted in the commercial microbiological complex biological preparation “Doctor Robik 109K. However, the efficiency of these bioagents was significantly lower than that of Cl. acetobutylicum.

Thus, the microbiological preparation "Doctor Robik 109K" in MFC with the addition of 1 g/l of sludge-lignin during 117 hours of the experiment generated a voltage of up to 387 mV, a current of 400 µA. When lower (0.1 g/l) and higher concentrations of lignin sludge (2 and 5 g/l) were introduced into the MFC, the generated indicators were significantly lower (Fig. 4, 5).

Waste incineration is used in the world to dispose of waste from the pulp and paper industry; pyrolysis; direct liquefaction; oxidation with moist air; gasification, including plasma; composting (Zainith et al. 2019); production of ethyl alcohol, lactic acid; animal feed production; sludge granulation; anaerobic digestion (Mandeep et al. 2020; Bakraoui et al. 2019). Waste can also become a raw material for the production of coal, fibreboard, cement and cement products, concrete, ceramic material, drywall, sorbents, fillers, as well as nanocomposites and additives in the road surface (Larionova 2017; Jaria et al. 2017; Simão et al. 2018).

This retreat presents a big problem in the Baikal region (Tkachev, Dagaev 2021). The negative features of the Baikal pulp and paper mill lignin sludge are the formation in its deeper layers of a large amount of toxic and foul-smelling gases: hydrogen sulfide and methyl mercaptan, the presence of organochlorine compounds, as well as the formation of explosive methane gas (Solovyanov 2017). A number of different physicochemical and biotechnological approaches have been proposed for the disposal of lignin sludge from the Baikal Pulp and Paper Mill: drying in centrifuges and filter presses followed by incineration (Fedyaeva et al. 2020), backfilling of maps with lignin sludge with construction debris, dehydration by layer-by-layer freezing (Stom et al. 2018), use in the manufacture of building materials (Bogdanov et al. 2017), composting (Patent No. 2159756 RU), as a coagulant in wastewater treatment (Patent No. 2136599 RF), for obtaining organomineral fertilizers (Patent No. 2086521 RU) and soils (Bogdanov et al. 2021; patent No. 2086521 RU), filling cards with ash pulp from thermal power plants (Patent 2 526 983 RU), filling and monolithic sludge (Samarin et al. 2020; Kondratiev et al. 2017). However, despite the large number of proposed approaches, the problem of eliminating waste from the Baikal Pulp and Paper Mill is still not resolved.

The data obtained in this work demonstrate the possibility of utilizing lignin sludge from the Baikal Pulp and Paper Mill in MFC with simultaneous generation of electric current. The generation of electricity in an MFC by adding pulp and paper waste has been previously demonstrated by other authors (Takeuchi et al. 2017; Cheng et al. 2012; Sugano et al. 2010; Javed et al. 2017). This approach can be promising both as one of the stages of processing lignin sludge from the Baikal Pulp and Paper Mill, and as an independent technological solution.

4 CONCLUSIONS

The possibility of using lignin sludge from the Baikal Pulp and Paper Mill as a substrate in microbial processes for generating electrical energy, on which the MFC technology is based, has been demonstrated. The scale of accumulation of this waste in the maps of the sludge collectors of the now defunct enterprise, their danger to the environment, especially in connection with the territorial proximity to the unique protected natural object - Lake Baikal, force us to look for ways to effectively dispose of these wastes. Great prospects for these purposes are seen in biological technologies, which can make it possible to convert waste into useful products - fertilizers, fertile soil, etc. MFC can also act as one of the stages of such a biotechnology for processing waste from the Baikal Pulp and Paper Mill.

Of the tested strains and consortiums of microorganisms, the *Cl. acetobutylicum* VKPM-4786. Positive results were also obtained when using the complex commercial biopreparation for cesspools and septic tanks "Doctor Robik 109" as a bioagent, however, the current generation processes by this microbial consortium were less effective than when using *Cl. acetobutylicum*.

ACKNOWLEDGEMENTS

The work was financially supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of the state task in the field of scientific activity (project no. FEWG-2021-0013).

REFERENCES

Gromova, N. Yu., 2012. Theoretical aspects of the bioconversion of cellulose-containing waste. *Proceedings of the International Academy of Agricultural Education.* 15(1). pp. 8-12.

Nikonorov, A. M., Matveev, A. A., Reznikov, S. A. et al., 2012. Results of multiyear studies on the dynamics of pollution of lake Baikal by polycyclic aromatic hydrocarbons in the area waste water discharge from the Baikal Pulp and Paper. *Plant Dokl. Earth Sc*. 443. pp. 361–364.

Varanasi, J. L., et al., 2015. Improvement of energy recovery from cellobiose by thermophillic dark fermentative hydrogen production followed by microbial fuel cell. *International journal of hydrogen energy.* I(II). pp. 1–11.

Stom, D. I., Zhdanova, G. O., Kashevskii, A. V., 2017. New designs of biofuel cells and testing of their work. *IOP Conference Series: Materials Science and Engineering.* 262. 012219.

Zainith, S., Chowdhary, P., Bharagava, R. N., 2019. *Recent Advances in Physico-chemical and Biological Techniques for the Management of Pulp and Paper Mill Waste.* Bharagava R., Chowdhary P. (eds). Emerging and Eco-Friendly Approaches for Waste Management. Springer, Singapore.

Mandeep, G. K. G., Pratyoosh, Sh., 2020. Insights into the resources generation from pulp and paper industry wastes: Challenges, perspectives and innovations. *Bioresource Technology.* 297. 122496.

Bakraoui, M., Karouach, F., Ouhammou, B. et al., 2019. Kinetics study of the methane production from experimental recycled pulp and paper sludge by CSTR technology. *J Mater Cycles Waste Manag.* 21, pp. 1426–1436.

Larionova, N. A., 2017. *The Use of Industrial Waste as a Secondary Mineral Raw Materials for the Production of Building Materials with Desired Properties*. Moscow: GeoInfo.

Jaria, G., Silva, C. P., Ferreira, C. I. A., Otero, M., Calisto, V., 2017. Sludge from paper mill effluent treatment as raw material to produce carbon adsorbents: An alternative waste management strategy. *Journal of Environmental Management.* 188. pp. 203–211.

Simão, L., Hotza, D., Raupp-Pereira, F., Labrincha, J. A., Montedo, O. R. K., 2018. Wastes from pulp and paper mills - a review of generation and recycling alternatives. *Cerâmica,* 64 (371).

Tkachev, V., Dagaev, Y., 2021. Requiem for Baikal as a warning. *E3S Web Conf*., 284, 01012.

Solov'yanov, A. A., 2017. Past (accumulated) environmental damage: problems and solutions, 10. Waste of the Baikal Pulp and Paper Mill. *Ecological Bulletin of Russia, Publisher: Bulletin "Ekologicheskiy Vestnik Rossii".* 2. pp. 19–27.

Fedyaeva., O. N., Vostrikov, A. A., Artamonov, D. O. et al., 2020. Combustion of Sludge-Lignin in Water-Oxygen Mixture. *J. Engin. Thermophys*. 29. pp. 26–41.

Stom, D. I., Zhdanova, G. O., Potekhin, S. A., Balayan, A. E., Saksonov, M. N., Butyrin, M. V., Kondratiev, V. V., Ivanov, N. A., Spirin, V. I., Kizeev, D. A., 2018. Assessment of the possibility of using the method of sludge-lignin dehydration of the Baikal Pulp and Paper Mill by the freeze-thaw method. *International Journal of Engineering & Technology*. 7 (2.23). pp. 114–118.

Bogdanov, A., Shatrova, A., Kachor, O., 2017. Use of the Accumulated Waste of the Pulp and Paper Industry as a Component Raw Material for the Production of Cements. *Ecology and Industry of Russia.* 21(11). pp. 15-19.

Grishin, V. K., Method for composting sewage sludge Patent No. 2159756 RU Publ. 11/27/2000.

Leonov, S. B. et al., Wastewater treatment method Patent No. 2136599 RU Publ. 09/10/1999.

Suturin, A. N. et al., Method for obtaining organomineral fertilizer Patent No. 2086521 RU, Publ. 08/10/1997.

Bogdanov, A. V., Shatrova, A. S., Darmaeva, L. B., Shkrabo, A. I., 2021. The use of pulp and paper industry waste as soil for recultivation of disturbed lands. *IOP Conf. Ser.: Earth Environ. Sci*. 677. 052005.

Suturin, A. N., Goncharov, A. I., Minaev, V. V., Kulikova, N. N., Dambinov, Yu., A Method for reclamation of sludge accumulators of enterprises for the production of bleached sulfate pulp Patent 2 526 983 RU dated 11/14/2012.

Samarin, E., Kravchenko, N., Zerkal, O., Chernov, M. and Rodkina, I., 2020. Grouting of Waste of the Baikal Pulp and Paper Mill to Reduce the Technogenic Impact to the Baikal Lake Ecosystem. *Journal of Geoscience and Environment Protection.* 8. pp. 112–118.

Kondratyev, V. V., Gorovoy, V. O., Stom, D. I., Ivanov, N. A., Balayan, A. E., 2017. Development of technology of neutralization and binding sludge-lignin in cards sludge collectors of the Baikal pulp and paper mill. *17th International Multidisciplinary Scientific Geoconference SGEM 2017 (conference proceedings).* 17(52). pp. 257–264.

Takeuchi, Y., Khawdas, W., Aso, Y., Ohara, H., 2017. Microbial fuel cells using Cellulomonas spp. with cellulose as fuel. *Journal of Bioscience and Bioengineering.* 123(3). pp. 358-363.

Cheng, H., Qian, Q., Wang, X., Yu, P., Mao, L., 2012. Electricity generation from carboxymethyl cellulose biomass: A new application of enzymatic biofuel cells, *Electrochimica Acta,* 82, pp. 203-207.

Sugano, Y., Vestergaard, M., Yoshikawa, H., Saito, M. and Tamiya, E., 2010. Direct Electrochemical Oxidation of Cellulose: A Cellulose-Based Fuel Cell System. *Electroanalysis.* 22. pp. 1688-1694.

Javed, M. M., Nisar, M. A., Muneer, B. and Ahmad, M. U., 2017. Bioelectricity from Vegetable Waste Extract by Designing a U-shaped Microbial Fuel Cell. *Pakistan J. Zool*. 49(2). pp. 711–716.