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STUDY OF THE ANAEROBIC PROCESS OF INDUSTRIAL WATER PURIFICATION IN COMBINATION WITH SORPTION METHODS

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Abstract. The issues of rational use of natural resources, ecological safety and environmental protection are extremely urgent and require immediate human influence on the optimization of technological processes, reducing the impact on the ecosystem. The implementation of food industry technology is accompanied by the formation of a significant amount of wastewater, into which about a third of processed raw materials go, and the concentration of polluting components in them is 10...100 times higher than in household water. The choice of wastewater treatment methods depends on their composition, prospects for further use, the economic feasibility of applying the methods, and the payback rate of the equipment. Therefore, the modern direction of the development of scientific research and wastewater treatment technology consists in the development of fundamentally new methods of deep wastewater treatment and the study of the possibility of using sorbents of natural and artificial origin.

Keywords: sorbents, activated sludge, food industry, BSC, HSC, wastewater, methanogenesis.

1. Introduction

1.1. Statement of the problem in a general form and its connection with important scientific or practical tasks

Environmental protection occupies one of the most important places in the activity of any enterprise. Our future and present depend on the quality of the environment, so environmental issues increasingly attract people's attention. Industrial enterprises are one of the main polluters and sources of environmental problems (Stryzhak, 2020)

Contamination of surface water with organic substances from food production effluents is a significant environmental hazard. These substances, falling into reservoirs, cause the development of decay processes, infection with pathogenic bacteria, water bloom, negatively affect fauna and flora (Malyovaniy et al., 2008; Dyachok et al., 2008; Sakhnevich et al., 2008)

In recent decades, the pollution of water bodies all over the planet has become catastrophic. Enterprises of the processing industry play a significant role in the pollution of the hydrosphere. As a result, surface water sources are becoming more and more polluted, the use of water from them for industrial, thermal energy, domestic and other needs necessitates increasingly complex and expensive cleaning (Petrushka et al. 2003, Leskiv et al. 2003, Plakhtiy et al. 2003).

Recently, more and more attention has been paid to the need to take into account environmental factors and consequences caused by food enterprises with their activities. And this is especially acutely felt by enterprises manufacturing food products, because their products directly depend on the quality of raw materials, which are affected by environmental factors. The activities of such enterprises also have a negative impact on the environment (Stryzhak, 2020).

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The main environmental consequences of the work of these enterprises include:

– significant energy consumption per unit of production. The specific energy consumption depends to a certain extent on the condition of the equipment and its efficiency, the range of products, the condition of the technical equipment and on the workload of the production facilities of the enterprise. Energy consumption affects the cost of products, which is the reason for finding ways to reduce it;

– high consumption of water resources per unit of production;

–generation of polluted wastewater. Due to the inefficiency of the existing treatment facilities, these enterprises discharge insufficiently treated wastewater;

– accumulation of waste from packaging materials;

– generation of emissions at the stage of transportation and production (Stryzhak, 2020).

Pollution that enters the environment as a result of the activities of dairy companies poses a danger to people and the biosphere as a whole. That is why the problem of disposal of waste from the food industry is one of the priorities.

All natural sorbents (bentonite, glauconite, zeolite) can be used to clean industrial wastewater.

Effective natural minerals for water purification can be zeolites, glauconites, bentonites, ionic resin and biodestructive sorbent Ecolan M, which, thanks to their porous structure, can absorb aggressive and toxic compounds. The choice of a specific adsorbent for wastewater treatment is determined by the adsorption capacity of the adsorbent and based on specific initial conditions, namely: the degree of pollution of the wastewater, its volume, the location of the treatment facility, as well as the necessary technology for the regeneration or disposal of spent sorbents.

1.2. Analysis of recent research and publications

The food industry in Ukraine is developing dynamically and is the most widespread. Wastewater is the most dangerous of all the wastes of enterprises. Wastewater (WW) is characterized by high concentrations of organic pollutants, which include components of raw materials, and soluble and sparingly soluble organic compounds are also included in wastewater. Mostly, all effluents are discharged into sewage systems without preliminary treatment, this leads to significant losses to city sewage treatment plants, because the concentration of pollutants exceeds the permissible norms by several times, so the need for the construction of local sewage treatment plants at milk processing enterprises is not in doubt (Havryshko et al., 2020; Popovych et al., 2020).

Problems of the food industry are widely studied by Ukrainian scientists. In particular, in the works of V. M. Lytovchenko, L. A. Kozachenko, Yu. Yu. Cheban, I.V. Fedulova, T. L. Keranchuk, and V. M. Tsikhanouska the problems of industrial enterprises, the product market of Ukraine and this sector of industry in general are highlighted.

The signing and ratification of the Association Agreement between Ukraine and the EU contributed to the development of the legal and institutional framework for water quality and water resources management in Ukraine. At the same time, there was an urgent need to harmonize national legislation in accordance with European and international legal systems. The strategy focuses on the creation of an effective integrated legislative framework and contains a list of necessary regulatory innovations. In Ukraine, the concepts of environmental security are provided and implemented by the Laws of Ukraine: "On the protection of the natural environment" [, "On the Basic principles (strategy) of the state environmental policy of Ukraine for the period until 2030", "On the foundations of national security of Ukraine".

The aim of the work is investigate the process of methanogenesis in anaerobic conditions and the use of the Ekolan-M sorbent for the purification of industrial waters of food enterprises.

2. Theoretical part

The production of food products is accompanied by the formation of liquid, gaseous and solid wastes that pollute the hydrosphere, atmosphere and soils. But the main problem of the ecology of food production is the problem of water used directly in the technology of the main product, for washing equipment and other purposes. Most of this water is discharged from the process and into the environment in the form of contaminated effluents. Their main feature is a high content of dissolved organic substances (Havryshko et al., 2020; Popovych et al., 2020). The characteristics of wastewater from food industry enterprises are given in Table 1.1 (Ovcharenko et al., 2019, Larintseva et al., 2019; Ogurtsov et al., 2019).

Table 1

Composition of wastewater from various food industries

Production	pH	Total result, mg/l	COD, mg O_2/l	BOD_5, mg O_2/l
Sugar production	6–9	1200–2600	4900	1400–3600
Yeast production	6.8	1900	1800	1500
Breweries	6.9	2650	2000–6000	1500–4000
Distilleries (barda)	4	32 000– 45 000	20 000– 48 000	15 500–29 900
Production of low-alcohol drinks	6	–	1760	1200
Starch processing (potato) plants	7.2	600–4700	100–2520	300–1300
Diary enterprises	6.5–9	350–600	1200–3000	500–2000
Cheese factories	3.55	400–750	51200	40 000
Fruit and vegetable production	4	20–1800	440–2690	350–2175
Meat processing industries	6.5–7.5	410–12 000	1800– 12 500	650–5100
Confectionery (average flow) enterprises	4.5–9.9	1220–1790	6060	2190
Production of ice cream	6–11	8000	6000	4000

The implementation of food technologies is accompanied by the formation of a significant number of HC discharges, which include about a third of processed raw materials, and the concentration of polluting components in them is 10... 100 times higher than in household waste.

Wastewater from food industries is a complex polydisperse system and contains various types of pollution: fat, milk, scales, wool, blood, salts, sand, lint, insoluble mineral impurities, detergents, etc. This complicates the operation of sewage networks, pumping stations and sewage treatment plants. Wastewater from food industries is diverse both in its component composition and in the concentration of pollutants and with a complex physico-chemical system (Havryshko et al., 2020; Popovych et al. 2020).

The issue of the effectiveness of monitoring the state of water resources is acute. First, it concerns the pollution monitoring methodology. For example, today there is no systematic information on the diffuse pollution of water bodies. Secondly, control over the implementation and observance of technological standards both at treatment plants and at enterprises in general. Therefore, monitoring is the main tool for the implementation of national water policy, and monitoring programs should become an integral part of river basin management plans.

Therefore, the study of the qualitative composition of industrial waters of the food industry is important and necessary.

3. Results and Discussion

3.1. Materials and methods

The qualitative composition of wastewater (WW) of the sewage treatment systems of the food industry operating enterprises was determined on certified equipment in the Wastewater Treatment Laboratory of the Department of Ecology and Sustainable Environmental Management (determination of BOD, COD, pH, suspended solids and ammonium nitrogen), and in the certified laboratory of the ENERGOMONTAZHVENTILATISIA Design Architectural Technical Scientific Production Private Enterprise (chlorides, sulfates, nitrites and nitrates, phosphates and common iron were determined).

We have previously published an analysis of the results of research into the quality indicators of wastewater at food industry enterprises in the scientific article “Experimental research of industrial water parameters of canning plant and bakery. Analysis of treatment technologies” (Havryshko et al., 2021; Popovych et al., 2021).

Fig. 1. Study of biological oxygen consumption

Fig. 2. A sample of the studied activated sludge to filtering

Fig. 3. A sample of the studied activated sludge after filtering

The study of chemical oxygen consumption was determined according to standard methods.

COD before purification = 2500 mg/l - this is a typical value for the food industry.

COD:

2500-100 % = 85 %

2500 * 15 % = 375 mg/l

After the application of activated sludge, COD decreased by 85 %.

We determined the study of biological oxygen consumption according to standard methods.

BOD before purification = 3500 mg/l - this is a typical value for the food industry.

BOD:

3500-100 %=90 %

3500*10 %=350mg/l

After the application of activated sludge, BOD decreased by 90 %.

After the application of activated sludge, COD decreased by 85 %.

The color of the sludge changed from green, which was introduced into the system, to gray, which absorbed pollutants.

At the time of the research, the age of the sludge was 15–20 days, to increase the capacity of wastewater treatment, the age of the sludge will be up to 50 days. After all, the older the sludge, the better it cleans.

It is important to analyze and compare the composition of activated sludge elements. For experimental research, the first filtering was carried out from December 9 to 13, the next from December 13 to 15, 2021 (Fig. 1)

After filtering, the filtered sediment (activated sludge) was weighed on an electronic laboratory balance (AXISAD1000)

The next stage was drying of the filtered sediments using a Radwag MA 110.X2.A infrared moisture meter with a touch screen. Drying temperature: 50-160°C. .Quality: II according to DSTU EN 45501. The elemental composition of the samples was studied on the X-ray fluorescence analyzer EXPERT 3L.

3.2. The sorbent used in the research

Ekolan M belongs to the class of biodestructive sorbents. The composition of the drug includes active natural strains of oil-destroying bacteria Acinetobactercalcoaceticus, Gordoniarubropertinctusi Rhodococcuserythropolis, immobilized on an oil-absorbing sorbent (charcoal) and mineral components.

Ekolan-M has a number of advantages in comparison with the most well-known in Ukraine preparations for cleaning contaminated oil and oil products. Specially selected highly effective compositions of strains of microorganisms, which have a high ability to synthesize surface-active substances, allow the drug to ensure the destruction of both soluble and water-insoluble components of oil. Microorganisms of the drug are able to develop and destroy hydrocarbons in a wide range of mineralization of the environment (0.05-7.0 %), temperature (+10 ... +37 degrees C) and pH (4.5-9.0). They absorb a wide range of hydrocarbons (crude oil, mineral and vegetable oils, diesel and aviation fuel, gasoline, kerosene and other petroleum products), the final products of their decomposition, which are ecologically neutral compounds that do not have a negative impact on ecosystems.

After the end of the biomass cleaning process of the introduced and multiplied microorganisms in the polluted environment, the drug dies and turns into organic substances that ensure the interaction of the development of natural microflora and the restoration of the ecosystem.

Ekolan-M is ecologically harmless, made from vegetable raw materials, does not contain pathogenic microflora and meets all the requirements of the current sanitary legislation of Ukraine, which confirms the conclusion of the State Sanitary and Epidemiological Examination No. 05.03.02-07/36786 06 of the Minister of Health (Popovych et. al., 2022; Havryshko et. al., 2022).

Fig. 4. General appearance

According to the results of X-ray fluorescence analysis of the mass fraction (%) of the main chemical elements using the EXPERT 3L x-ray fluorescence analyzer, it was established that the most pronounced element in the composition of the biodestructive sorbent Ekolan M is Calcium (Ca), the content of which is 93.035 %. The composition also includes such elements as Silicon (Si), Sulfur (S), Potassium (K), Titanium (Ti), Vanadium (V) and Iron (Fe).

To study the structure of the sorbents, X-ray structural (X-ray phase) analysis (XSA) of the investigated sorbents was used, which is based on the identification of crystal lattices and includes qualitative phase analysis, determination of their periods, interplanar distances and analysis of microvoltages in the samples, registration of ionization excited radiation. For implementation, a DRON-4-07 general-purpose X-ray diffractometer is used (Fig. 5–6).

Table. 2

The results of the study of the elemental composition of Ekolan M, on the EXPERT 3L X-ray fluorescence analyzer

№	Element	Mass fraction, %	Measurement error, %
1.	Silicon (Si)	0.866	±0.103
2.	Sulfur (S)	2.300	±0.087
3.	Potassium (K)	2.983	±0.025
4.	Calcium (Ca)	93.035	±0.146
5.	Titanium (Ti)	0.400	±0.057
6.	Vanadium (V)	0.125	±0.041
7.	Iron (Fe)	0.292	±0.014

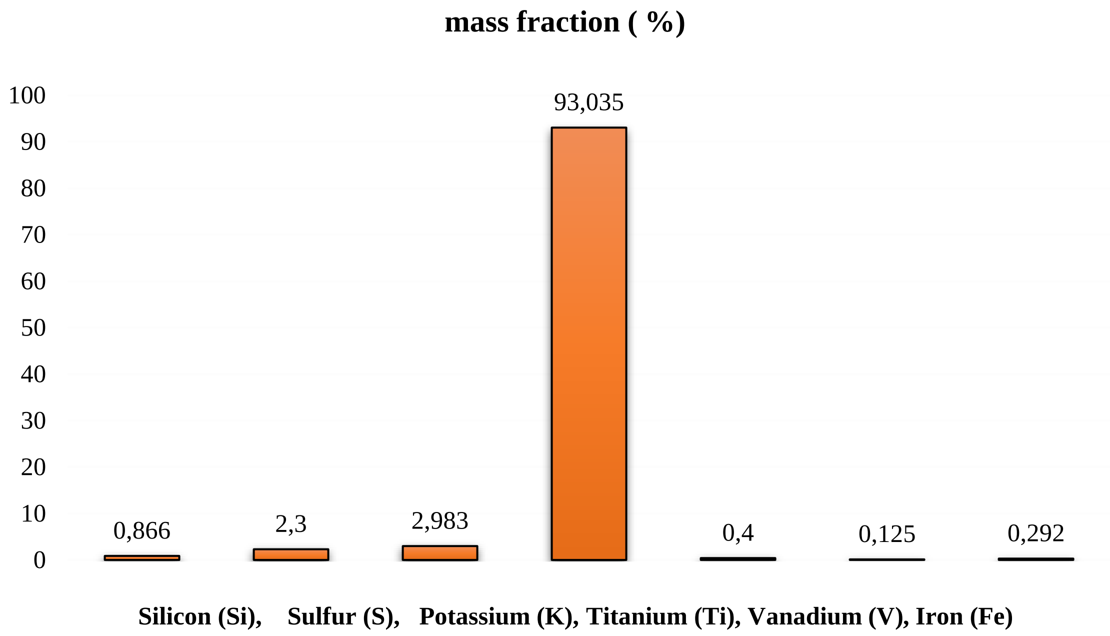

Fig. 5. Mass fraction (%) of the main chemical elements using the EXPERT 3L

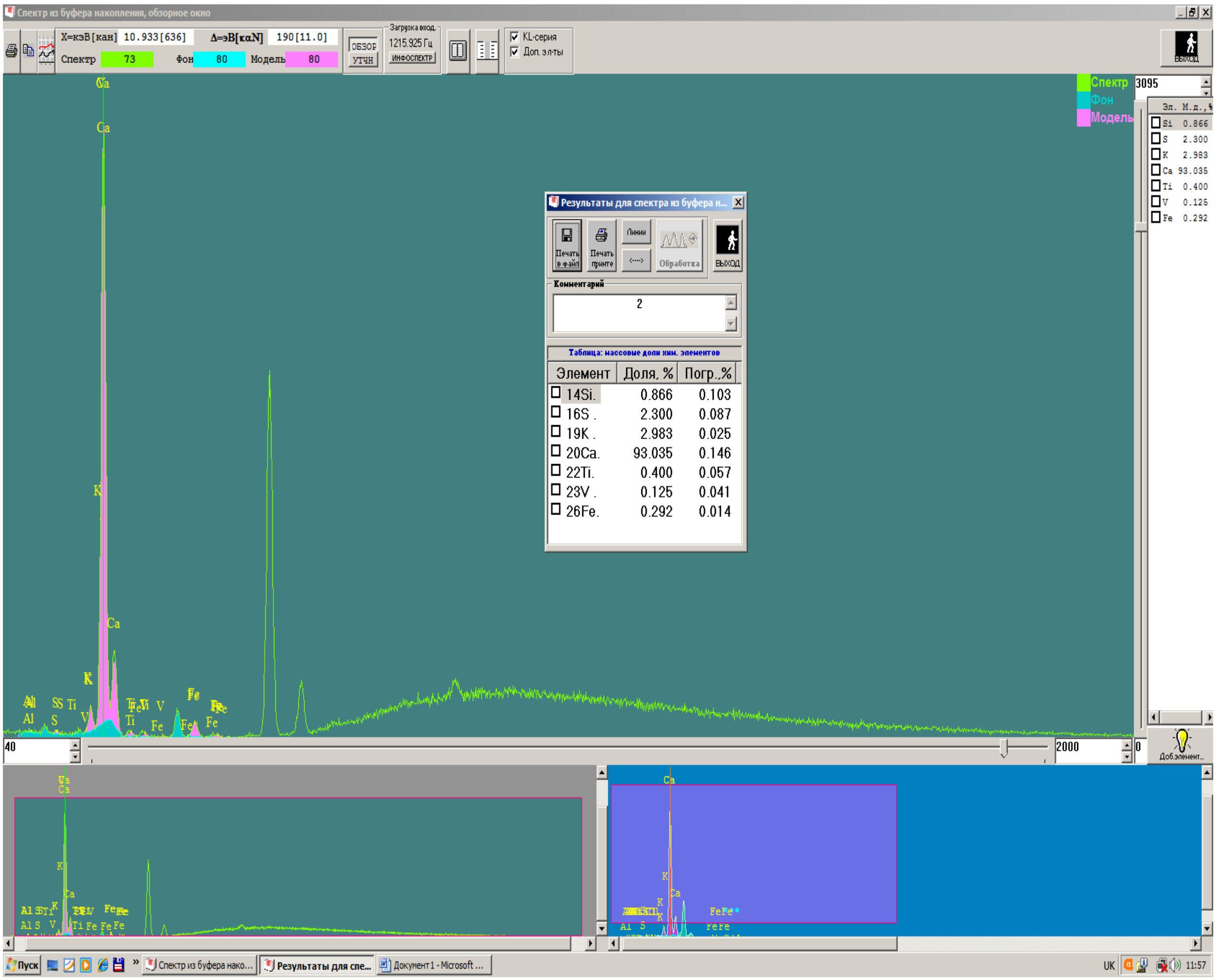

Fig. 6. Ecolan results on EXPERT 3L X-ray fluorescence analyzer

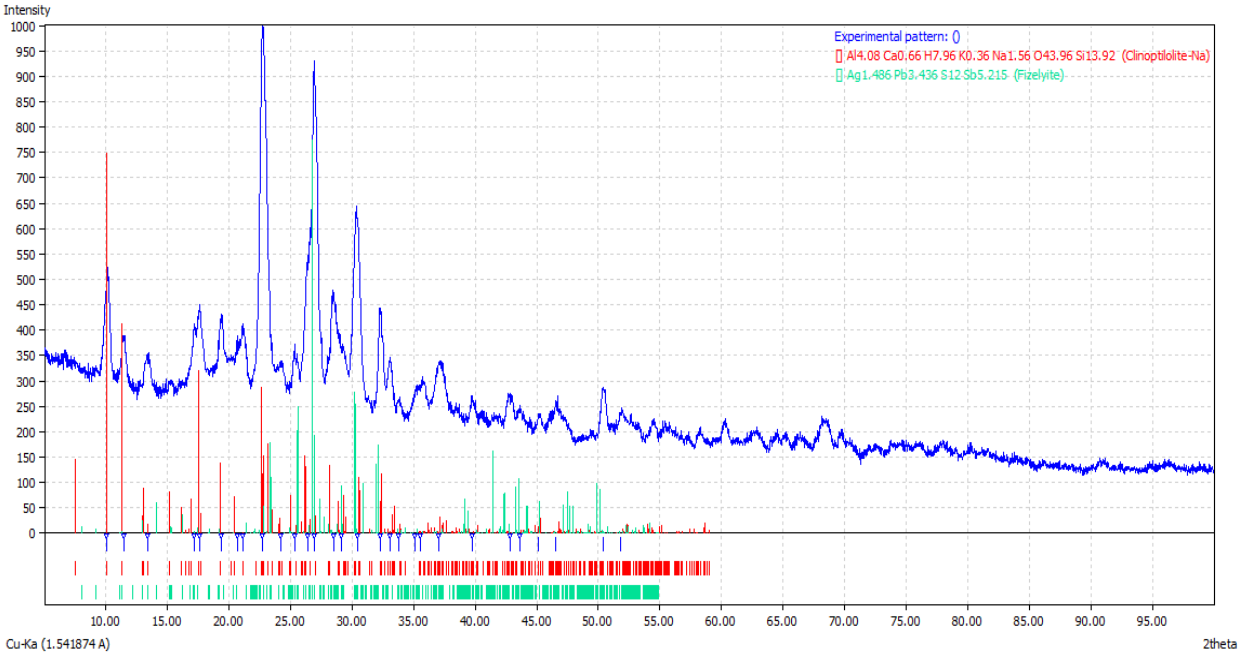

Fig. 7. Diffractogram of the sorbent (Ecolan M)

According to the analysis of diffraction patterns, the structure of the studied sorbents can be identified as follows:

Ekolan M sorbents (Fig.7.) do not have long-range order in the arrangement of particles (atoms, molecules, ions) and do not form crystal lattices, but short-range order exists in such substances. Thus, they can be classified as amorphous substances. Examples of amorphous substances are glass, plastic, resin, rosin, amber, and plastic sulfur.

3.3. Analysis of research results

According to the results of X-ray fluorescence analysis of the mass fraction (%) of the main chemical elements using the X-ray fluorescence analyzer EXPERT 3L, it was established that in the composition of activated sludge sediments in both samples, in percentage terms, such elements as Iron (Fe), Calcium (Ca) are also present, and other elements but they are not so clearly expressed. Also, the decrease in the percentage content of iron compounds in the second sample indicates that redox reactions took place.

Anaerobic sludge must be adapted to the spectrum of wastewater pollution and contain all the necessary groups of microorganisms to ensure methanogenesis. The problem can be solved by introducing activated sludge from similar operating sewage treatment plants of other enterprises, or by working up the mass of activated sludge in the laboratory. In the process of biological treatment with activated sludge, microorganisms are mixed with wastewater and distributed throughout the volume of the aeration tank during the aeration process. Microorganisms come into contact with biodegradable materials in wastewater and consume them for food. The process of biological treatment with aerobic activated sludge is very effective under appropriate conditions. During this process, 85-95 % of solid particles are removed and BOD is reduced by about the same amount. The main process that occurs under anaerobic conditions and is used to decompose and remove organic pollutants and wastes is methanogenesis. The entire organic substrate undergoes anoxic oxidation and anaerobic fermentation: natural polymers (cellulose and proteins), organic alcohols, carbohydrates, fats, bases and acids, hydrocarbons, etc. (Kuznetsov, 2012). The process of methanogenesis is being studied. The most important factors affecting the development and viability of activated sludge: temperature, availability of nutrients, content of dissolved oxygen in the sludge mixture, pH value, presence of toxins.

Anaerobic cleaning takes place without access to air. It is mainly used for neutralization of solid sediments formed during mechanical, physico-chemical and biological treatment of wastewater.

Fermentation of sewage sludge takes place by the method of methane fermentation.

After the discovery of the ANAMMOX process, ANAMMOX bacteria were successfully implemented in full in wastewater treatment systems for the effective removal of nitrogenous compounds. Currently, ANAMMOX is used at mesophilic temperatures on wastewater containing high concentrations of ammonium. The initial discovery of the ANAMMOX process took place in various treatment facilities [85], ranging from wastewater treatment plants with high nitrogen loads and low concentrations of dissolved oxygen to municipal sewage treatment plants.

Advantages of ANAMMOX technology

• High efficiency of denitrification;

• Reduction of CO_2 emissions up to 90 %;

• Reduction of the installation area (up to 50 %);

• Low energy consumption: saving up to 60 %;

• No need for methanol;

• The installation does not require constant maintenance;

• Reducing the amount of excess sludge;

• Effective decomposition of ammonia and stable operation of the installation.

It was necessary to select sorbents for immobilization. Rational use of natural sorbents.

Effective natural minerals for water purification can be zeolites, glauconites, bentonites, ionic resin and biodestructive sorbent Ecolan M, which, thanks to their porous structure, are able to absorb aggressive and toxic compounds. Zeolite, due to the peculiarities of its crystal structure, is a three-dimensional "sieve" that also has high adsorption and ion exchange properties. Therefore, it is possible to use natural zeolite and bentonite and glauconite for the treatment of wastewater from the food industry, in particular, sugar factories, which is an actual problem.

The efficiency of adsorption cleaning reaches 80...95 % and depends on the chemical nature of the adsorbent, the size of the adsorption surface and its availability, on the chemical structure of the substance and the form of its presence in the environment.

The adsorption method is effective for wastewater treatment, but the widespread use of carbon sorbents is not economically promising, due to the high cost of both the activated carbon itself and the subsequent stages of its regeneration. Natural sorbents of non-carbon origin, which include zeolites, are increasingly used in chemical, food and environmental protection technologies due to their sufficiently high selectivity and adsorption capacity, relatively low cost and availability.

The advantage of the sorption method is that, with the correct selection of sorbents, wastewater can be purified from many impurities almost completely. With the help of sorbents, pollutants can be extracted from water at any concentration, when other cleaning methods are ineffective. This method allows you to avoid costs associated with the regeneration of sorbents, since the used sorbents in combination with biological treatment are removed together with excess activated sludge for further treatment. Sorbet in a mixture with activated sludge significantly improves the moisture yield of the sediment, and during fermentation in methane tanks, the yield of biogas increases (Stuzhuk, 2017).

4. Conclusion

Treatment of wastewater containing a high content of organics, suspended solids, nutrients, oil and grease should be carried out using combined treatment technology.

Based on the obtained values and taking into account experimental facts, it was established that wastewater from food industry enterprises is highly concentrated in the content of organic impurities, suspended substances, may have a content of biogenic elements and a pH value that are unfavorable for biological purification. showed that the wastewater of the vast majority of food industry enterprises can be purified by biological methods.

Therefore, currently, sewage treatment plants combining the use of modern methods of biological purification, anaerobic (methane fermentation) and aerobic methods and the use of sorbents in the purification scheme allow not only to purify wastewater, but also to obtain high-quality fertilizers and electricity from burning biogas.

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