Dairy Wastewater Treatment Using Membrane Bioreactor

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Abstract. The paper presents the results of scientific researches in the field of biomembrane treatment of dairy products industry enterprises wastewater. Practical experiments confirmed the possibility of reducing the inhibition degree of the process of biological treatment of dairy products industry wastewater, which has been physically and chemically purified, by increasing the concentration of active sludge. This effect can be achieved while using membrane bioreactor technology (MBR). The experiments also showed that if dairy plants wastewater is pre-treated with coagulants and flocculants, specific speed of biocontamination oxidation decreases in 1.2-2.3 times at BOD₅ = 250 mg/l in comparison with the initial wastewater. It happens because of substrate inhibition rate of biochemical reactions. The identified dependencies show that it is advisable to exclude the stage of reagent flotation before the biological treatment of dairy products industry wastewater. It can reduce costs of using a large number of expensive reagents and simplify the technological scheme. During the experiments dairy plants wastewater was taken as a model. Later, the researchers used real wastewater and confirmed the main kinetic constants and coefficients for calculations of biological purification plants. These results are as follows: temperature constant χ, grad¹, for aerobic heterotrophic conversion – 0.079-0.091, for nitrification – 0.096; for denitrification – 0.13. Coefficients of inhibition by active sludge Φ metabolic products amounted to (l/g): for organic substances oxidation by BOD₅ – 0.39-0.54; for nitrification – 0.19, for denitrification – 0.22; active reaction of the environment corresponding to the highest rate of oxidation of organic substances pH_opt – 6.9 at pH-constant 150. The maximum specific speed of organic substances oxidation r_{max} is 82.5-101.1 mg/(g × h), the Michaelis constant K_{m} is 15 mg/l. The maximum specific speed of nitrification r_{max} is 1.49 mg/(g × h), the Michaelis constant K_{m} is 0.12 mg/l, the constant of inhibition a is 43. The maximum specific speed of denitrification r_{max} is 10.8 mg/(g × h), the Michaelis constant K_{m} is 3.5 mg/l. The calculated values of kinetic coefficients and constants make it possible to calculate membrane bioreactors of sewage treatment plants of dairy industry to the specified degree of purification. The estimated annual economic effect for "Pestravskiy" diary plant of the Samara region equaled 4 mln. rub/year (at 2017 values).

1. Relevance, scientific importance of the issue
Wastewater from dairy products industry is characterized by a high concentration of contaminants. Existing sewage treatment facilities generally do not answer to the existing specifications, which significantly disrupts the operation of municipal biological treatment facilities and causes environmental pollution. Practical experience of membrane bioreactors (MBR) use at enterprises of...
various industrial branches at repeated increase of active biomass concentration and with complete retention of microorganisms in bioreactors together with excluding desilting and filtration stages, proves economic efficiency of this technology application at the enterprises of dairy industry.

2. Main part
The researchers based their analysis on existing enterprises of the dairy industry data on wastewater composition and developed a new classification by type of products, by modes of washing of technological equipment and pipelines and by methods of whey processing [1]. The developed classification made it possible to introduce qualitative composition of the wastewater model for carrying out practical experiments. It goes as follows: $\text{BOD}_{\text{full}} = 480-960 \text{ mg/l}$, nitrogen ammonium $= 24-96 \text{ mg/l}$, nitrogen nitrate $= 0-40 \text{ mg/l}$, phosphorus phosphates $= 4.8-9.6 \text{ mg/l}$. Concentrations of nitrogen compounds were taken in a wider range than used in the existing enterprises in order to describe the processes of nitrification and denitrification.

Fundamental regularities of enzymatic kinetics [2-4] were used for processing the results of biological treatment of dairy products industry wastewater as well as for describing and analyzing biological processes.

The experiments in contact conditions were conducted to study oxidation kinetics of organic substances in wastewater, in the presence of components that differ in their ability to bio-oxidation, as well as to study kinetics of processes in membrane bioreactors operating with high doses of sludge [2-4].

The experiments in dynamic conditions were performed on the pilot MBR installation (see Figure 1), which consisted of a receiving chamber with a capacity of 200 L, equipped with a paddle mixer, an anoxic area of 9 l, an aerobic area of 70 l, a compressor, feed pumps for source wastewater, permeate drainage, recirculation of the sludge mixture from the aerobic area to the denitrifier. There was a flat-frame membrane element made by the SINAP company with an area of 0.25 m$^2$ and a size of pores 0.1 microns located in the aerobic area.

Pilot installation studies were being conducted for four months. Table 1 presents the range of changes in the qualitative composition of the model runoff and purified water during the experiments.

The obtained results made it possible to 1.7 times increase in the bioreactor oxidizing power while increasing the concentration of active sludge from 3 to 9 g/l, which is possible only with the use of MBR technology (see Figure 2).

In the course of pilot MBR installation experiments and kinetic experiments in contact conditions, carried out on the model of dairy plants wastewater, the following inhibition coefficients of active sludge metabolic products were determined (l/g): for organic substances oxidation by $\text{BOD}_{\text{full}}$ – 0.39, for nitrification – 0.19, for denitrification – 0.22 (see Figure 3); temperature constants values of the Vant Hoff’s equation $\chi$ grad’to aerobic heterotrophic conversion – 0.091, for nitrification – 0.096 and for denitrification – 0.13 (see Figure 4).
Table 1. Quality composition of the source water and permeate during the experiment.

| Characteristic                        | Source Water | Permeate |
|---------------------------------------|--------------|----------|
|                                       | Minimum      | Maximum  | Minimum | Maximum | Average |
| BOD_{full}, mg/l                      | 480          | 1060     | 738     | 1       | 35      | 7.4     |
| Nitrogen ammonium, mg/l               | 15.9         | 96       | 58.9    | <0.05   | 4       | 0.5     |
| Nitrogen nitrate, mg/l                | <0.05        | 11.4     | 3.3     | <0.05   | 20.1    | 7.2     |
| Sludge dose, g/l                      | 0.8          | 14       | 6.1     | -       | -       | -       |
| Sludge Index, ml/g                    | 33           | 151      | 87      | -       | -       | -       |

Figure 2. Dependence of the bioreactor oxidizing power on the dose of active sludge.

Figure 3. Determination of $\phi$ coefficient by the grapho-analytical method for organic substances oxidation by BOD_{full} (right line 1), denitrification (right line 2) and nitrification (right line 3).

Figure 4. Dependence of oxidation specific speed on BOD_{full} on temperature.

Figure 5. Kinetics of organic substances oxidation by BOD_{full}. 
The research conducted in the range of 5.5-8 pH made it possible to find the dependence of the oxidation rate of organic substances on pH. It is determined that pH_{opt} for dairy plants wastewater is 6.9 at pH-constant of 150.

Figures 5-7 show kinetic dependences for organic substances oxidation, nitrification and denitrification in MBR experimentally defined at a temperature of 25°C and pH of 6.9, reduced to a dose of sludge 8 g/l.

In order to confirm the data obtained on the model drainage, the researchers carried out the analysis of wastewater composition and local purification methods. The also undertook experimental studies of biological purification on real wastewater of four dairy industry plants.

Local treatment of these plants wastewater is represented by the structures of mechanical and physico-chemical treatment on pressure-tight flotation units. Various types of coagulants and flocculants [5-9] are used on wastewater treatment facilities of these plans. All plants use aluminium-based coagulants. Biocontamination concentration in purified water of these plants was 490-2450 mg/l (by COD), BOD_{full} was 300-940 mg/l, exceeding the permissible values for discharge in the municipal sewage networks. At the same time, the concentration of phosphates in some periods decreased to 0.07-0.5 mg/l, which is not enough for subsequent biological purification.

The study of the influence of physico-chemical wastewater treatment on the speed of biochemical processes was carried out in contact conditions. It was found that the kinetics of biocontamination oxidation of the initial wastewater from the plants in Pestravka and Nikolskoye villages was described by the the Michaelis-Menten equation without inhibition (see Figure 8, Curves 2a and 3a). For Chekmagushevsky dairy plant and "Ulyanovskkurort" dairy products manufactory it was the equation with substrate inhibition (Curves 1a and 4a), starting with 300 and 70 mg/l respectively. At the same time, biological oxidation of wastewater contamination after reagent flotation at all plants took place according to the mechanism of substrate inhibition (Curves 1b-4b), that is it was observed at three plants at BOD_{full} over 120 mg/l and at BOD_{full} 40 mg/l at "Ulyanovskkurort" dairy products manufactory.

The graphs in Figure 8 show a significant decrease in the specific speed of biochemical processes after wastewater treatment with coagulants and flocculants. The value of the inhibition constant α was 6.2-49.4 (the degree of inhibition increases with the decrease of α). The received direct dependence of the inhibition constant α from concentration of active sludge indicates the possibility of toxic effect reduction by increase of a dose of active sludge in the structure. It all means that it is technologically efficient to use aeration constructions working with high doses of active sludge, e.g. membrane bioreactors, for biological purification of this particular type of wastewater. The contact experiments confirmed the necessity of local biological purification at dairy industry plants before they enter municipal sewage treatment plants, since the discharge of the treated wastewater after its preliminary physico-chemical treatment can cause disruption of the process on these structures.
Dependence of the specific speed of oxidation on the organic substances concentration in the wastewater of plants in Pestravka (1), Chekmagush (2), Nikolskoye (3) villages and "Ulyanovskkurort" dairy products manufactory(4), up to (1a-4a) and after reagent flotation (1b-4b).

The researches on the pilot MBR installation, conducted during the four months from July to October 2016 on the wastewater of "Pestravskiy" dairy plant, confirmed that biomembrane treatment with nitro-denitrification can be successfully applied while purifying dairy industry plants wastewater.

According to the results of the pilot installation work, the maximum rate of biocontamination oxidation \( \rho_{\text{max}}' \) is 101.1 mg/(g·h) at 25°C and pH_{opt} = 6.9. Specific speed at a dose of sludge 3 g/l \( \rho_{\text{max}} \) is 40 mg/(g·h), the Michaelis constant \( K_m \) is 15 mg/l, the coefficient of inhibition by products of metabolism \( \varphi \) – 0.54 l/g, the temperature constant \( \chi \) for aerobic heterotrophic conversion – 0.079 grad^{-1}, allowing to calculate both membrane bioreactors and traditional biological treatment structures of dairy plants wastewater. The obtained kinetic dependencies and constants were close to those defined on the wastewater model, which confirms the possibility of using kinetic coefficients and constants obtained during experiments conducted on the model solution (Figure 9).

Figure 9. Kinetics of organic substances oxidation at the concentration of sludge 8 g/l.
Technical and economic comparison is performed for three designs of new construction of wastewater treatment facilities for "Pestravskiy" diary plant conditions. The first design is connected with reagent flotation and biological purification in MBR; the second option involves biological purification in MBR; the third one is biological purification in aerotanks which are nitro-denitrifiicators with secondary clarifiers and effluent filter [10, 11]. In the calculation the average daily wastewater consumption of 500 m$^3$/day is taken into account. Source water composition, mg/l: BOD$_{full}$ – 1000; nitrogen ammonium – 20; nitrogen nitrate – 20; suspended materials – up to 500. The quality of the purified drainage corresponds to the MAC for fishery water bodies. The calculation includes structures for dehydration of precipitation up to 80% humidity. Averaging structures, mechanical purification, neutralization and decontamination are the same for all options and have not been taken into account. Kinetic constants and the described methodology were used for the calculation of biological purification facilities. The techno-economic comparison was performed using the life cycle cost methodology. (Lifecylecost, LCC). The lifecycle cost analysis shows that Option 1 provides the largest amount of LCC: Option 2 (with biomembrane purification) is the technology with the lowest LCC. The amount of funding here, with account of investment during construction and twenty-five years of operation, is 100.8 million rubles less than costs of Option 1. The estimated annual economic effect equaled 4 mln. rub/year (at 2017 values). The third option, which involves the traditional scheme of biological purification with secondary clarifiers and granular effluent filter, took the intermediate position. The capital cost of this design was 9.2 mln rub. more than the second.

3. Conclusions
The research yielded the following conclusions:
1. Practical experiments confirmed the possibility of reducing the inhibition degree of the process of biological treatment of dairy products industry wastewater, which has been physically and chemically purified, by increasing the concentration of active sludge. This effect can be achieved while using membrane bioreactor technology (MBR).
2. The experiments also showed that if dairy plants wastewater is pre-treated with coagulants and flocculants, specific speed of biocontamination oxidation significantly decreases in comparison with the initial wastewater. It happens because of substrate inhibition rate of biochemical reactions. The value of reduction at different plants, with different types and doses of reagents was 1.2-2.3 times with substrate concentration of 250 mg/l according to BOD$_{full}$. The identified dependencies show that it is advisable to exclude the stage of reagent flotation before the biological treatment of dairy products industry wastewater. It can reduce costs of using a large number of expensive reagents and simplify the technological scheme.
3. During the experiments dairy plants wastewater was taken as a model. Later, the researchers used real wastewater and confirmed the main kinetic constants and coefficients for calculations of biological purification plants. These results are as follows: temperature constant $\chi$, grad$^{1}$, for aerobic heterotrophic conversion $=- 0.079$-0.091, for nitrification $=- 0.096$; for denitrification $=- 0.13$. Coefficients of inhibition by active sludge $\phi$ metabolic products amounted to ($/g$): for organic substances oxidation by BOD$_{full}$ $=- 0.39$-0.54; for nitrification $=- 0.19$, for denitrification $=- 0.22$; active reaction of the environment corresponding to the highest rate of oxidation of organic substances pH$_{opt}=- 6.9$ at pH-constant 150. The maximum specific rate of organic substances oxidation $r'_{max}$ is $82.5$-$101.1$ mg/(g × h), the Michaelis constant $K_m = 15$ mg/l. The maximum specific speed of nitrification $r'_{max}$ is 1.49 mg/(g × h), the Michaelis constant $K_m = 0.12$ mg/l, the constant of inhibition $a$ is 43. The maximum specific speed of denitrification $r'_{max}$ is 10.8 mg/(g × h), the Michaelis constant $K_m = 3.5$ mg/l. The calculated values of kinetic coefficients and constants make it possible to calculate membrane bioreactors of sewage treatment plants of dairy industry to the specified degree of purification.
4. The estimated annual economic effect for "Pestravskiy" diary plant of the Samara region equaled 4 mln. rub/year (at 2017 values).
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