Qualitative composition and local pretreatment of dairy wastewaters

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Abstract. On the territory of the Tyumen region there are a number of enterprises that discharge wastewater without pretreatment into water bodies and disturb their ecological condition. For example, one of the dairy industry plants produces 500 m³/day of industrial wastewater, which cannot be discharged even into the domestic sewage system due to its pollution density and aggressiveness. Thus, it is necessary to study wastewater quality and the mode of its inflow for local waste treatment plants’ designing. This article presents the results of the wastewater composition study on such indicators as pH, biochemical oxygen demand, chemical oxygen demand, suspended solids, fats, nitrogen, phosphate and other types of pollution. According to the obtained data, the conclusions were drawn about the wastewater composition inconstancy, associated with peculiarities of dairy production technology. In addition, the drains are characterized by a high variation of pH medium, which decreases sharply when the whey or acid solutions are discharged into the sewage production system after equipment washing. Based on these results, a scheme for organization of a dairy plant water disposal system is proposed, including local pretreatment of wastewater before its dumping into domestic sewage network.

1. Introduction
Modern industrial society is developing rapidly, increasing the amount of manufactured products every year and improving the product development technologies for production cost reduction. At the same time, plants harm the environment with chemicals, exhaust gases and conversion products. Industrial enterprises discharge effluents without any treatment into water bodies and damage the environment, causing water bodies’ deterioration and having a negative impact on public health.

In recent decades the environment pollution, including water pollution, has become global throughout the world and also in the Russian Federation. The work of large and small industrial enterprises leads to the pollution of water bodies with heavy metals, phenols, radioisotopes, detergents, dyes and other specific matters.

Dairy industry plants are not the exception. Industrial wastewater of dairy industry plants has a specific composition with high amount of organic matters and low pH, which do not allow to dump such wastewater into domestic sewage system without any pretreatment. Because of the absence of local treatment facilities, some plants remove industrial effluents to containment ponds that are often permeable constructions. These containment ponds create negative environmental situation due to objectionable odor and groundwater seepage. Stable hydrologic connection between containment ponds and the nearest water bodies leads to water qualitative composition change, oxygen decrease,
flora and fauna destruction. In this case water bodies do not correspond to the requirements of water use. In connection with the constant deterioration of water quality in rivers and lakes of Russia, and in Tyumen region in particular, it becomes necessary to improve wastewater treatment quality at such plants through the construction or reconstruction of local treatment facilities.

World scientific community pays much attention to the modernization of dairy industry plants’ wastewater treatment technologies.

Traditional technological schemes of wastewater treatment include mechanical treatment on drum filters and screens, sewage regulator (for fats removal and effluents neutralization), physicochemical treatment by means of air flotation (with or without reagent) and biological treatment in aerotanks [1-3]. However, these technologies are accompanied by high electric power consumption, formation of large amount of hard-to-treat sludge, operation complexity of aerobic biological treatment facilities.

The technologies of anaerobic digestion in UASB-reactors, ASBR-reactors and different anaerobic digesters (covered lagoon and complex-mix digesters) have become widespread abroad [4-7]. Besides, milk fat enzymatic pretreatment during the anaerobic digestion with methane production was studied [8]. The ferments produced by Candida rugosa were the most effective ones and the maximum methane production was achieved during the anaerobic digestion.

Mahvi A. et al. [9] describes sequencing batch reactor SBR as another variant of biological treatment. It consists of number of reactors, where wastewater passes through five stages: reactor filling, aeration, sedimentation, sewage disposal, sludge removal. Following advantages of SBR are given in his works:

- some stages can be achieved in a single reactor;
- common wall construction for rectangular reactors;
- operating flexibility and control.

A large number of scientists conduct the researches on the possible use of membrane technologies (nanofiltration, ultrafiltration, reversed osmosis membranes) for valuable products’ separating (proteins, lactose) [3, 10-16]. At the same time, not only one-stage filtration, but two-stage ultra- and nanofiltration of dairy wastes were studied. In this case, proteins and lipids are retained by first stage of ultrafiltration, while lactose and inorganic salts are retained by nanofiltration membranes [12]. Besides, the possibility of membrane bioreactor (MBR) and nanofiltration membrane usage was examined [16] for wastewater reusing. In MBR, organic impurities are retained, while the dissolved salts are retained on nano-membranes. Various materials were considered as membranes, including polymeric ones (sulfonated polyetheretherketone, polyvinyl dene fluoride, polyethersulfone, etc.), as well as bentonite [17].

Many researchers suggest methods of electrical and magnetic wastewater treatment (electrochemical oxidation, electrocoagulation) with different electrodes (aluminum electrodes, dimensionally stable anodes) [18-19].

However, these technologies have not yet become widespread in the Russian Federation.

Besides, special attention is paid to curd and cheese whey and its reuse, which prevents the discharge of this valuable protein product into sewage system.

The most widely used method of whey treatment is lactose enzymatic hydrolysis with a formation of glucose and galactose. During the hydrolysis process, β-galactosidase can be used as enzymes, and various catalysts, such as sulfuric acid, Amberlyst 70, zirconium phosphate, can be used also [20-21].

A number of scientists [22-24] suggest using membrane technologies for whey treatment (ultrafiltration, nanofiltration) combined with coagulation, flocculation, heat and ultrasound pretreatment. Aluminum sulfate, ferrous sulfate, polyacrylamide can be used as coagulants and flocculants.

Probiotic agents can also be useful in the treatment technologies of wastewater, containing high amounts of the organic matter. Nowadays this technology is only being studied [25].

Thus, the purpose of this research is to study the composition of dairy industry plant’s wastewater, which is formed at different stages of the technological process, as well as to suggest a possible scheme of effluents treatment and removal. To achieve this goal, a number of tasks were set:
wastewater sampling at various points of enterprise operation (different technological processes which are carried out at the dairy plant); analysis of the main quality indicators of selected samples; selection of the appropriate wastewater treatment technological scheme.

2. Methods

The research has been carried out at the laboratory of the Department of Water Supply and Sanitation (Industrial University of Tyumen, with the use of standard techniques and real wastewater of a dairy industry plant in the Tyumen Region (Russia).

The initial wastewater is a mixture of fecal and industrial wastes, which are collected in an impounding reservoir, from which they are periodically removed by sewage truck. In order to obtain full qualitative analysis of wastewater, the samples were taken in different days and after changes of technological processes (equipment washing):

- Sample 1 is taken from the impounding reservoir prior to shift;
- Sample 2 is taken from the impounding reservoir after equipment washing with alkaline solution;
- Sample 3 is taken from the impounding reservoir after equipment washing with acid solution;
- Sample 4 is taken from the impounding reservoir after equipment washing with acid solution prior to shift.

The time and place of samples’ taking were pointed on the bottles with wastewater.

In addition to determining the wastewater mixture quality from the entire enterprise, a wastewater composition, which was formed at each separate production line, have been studied: after alkaline and acid equipment washing, pack washing, truck tank washing with rinse water after butter production, and the analysis of curd and cheese whey has been done.

The quality of wastewater was estimated according to the specific indices for this water: pH, concentration of suspended solids, ammonium $\text{NH}_4^+$, nitrates $\text{NO}_3^-$, nitrites $\text{NO}_2^-$, phosphates $\text{PO}_4^{3-}$, total iron, total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD$_5$), fats and oil products.

The pH measurement was made with the use of pH-meter pH-150MI with standard electrode. To measure COD, a photometrical method was used. Vials with the sample, potassium dichromate, sulfuric acid and silver sulphate were heated during two hours at 150°C in the thermoreactor "TERMION" and then COD was defined with fluid analyzer "FLUORAT-02".

The concentrations of $\text{NH}_4^+$, $\text{NO}_3^-$, $\text{NO}_2^-$, $\text{PO}_4^{3-}$ were measured by the system of capillary electrophoresis "Kapel-150M". BOD$_5$ was determined by manometric method with the help of the BOD-system Lovibond® OxiDirect, in special bottles for incubation. The samples were held in this system during five days (20°C) and then BOD was measured by BOD-sensor.

Total iron was measured photometrically. To eliminate the interfering influence of organic matter, the original water was added with sulfuric (2 cm$^3$) and nitric (5 cm$^3$) acid, boiled to white smoke and then diluted with distilled water. Then, after boiling with hydrochloric acid (0.2 cm$^3$), and addition of ammonium chloride, salycil-sulphonic acid and ammonia (1 cm$^3$) the concentration of total iron was determined by spectrophotometer PE-5400VI.

The amount of fats was measured gravimetrically by petroleum benzene extraction with sodium chloride. The extraction was carried out for three times. Then extract was dried by calcined sodium sulphate, washed with petroleum benzene and mixed. Aliquot sample was put into the weighing bottle, heated at water bath and in drying oven. After that, the amount of fats was identified.

The concentration of oil products was determined by fluorimetric method, by hexane extraction of oil products from the wastewater sample with the use of "FLUORAT-02".

3. Results and Discussions

The results of laboratory research, on the determination of wastewater qualitative indices, taken from impounding reservoir, are shown in Table 1.
Table 1. The results of wastewater laboratory measurements, taken from impounding reservoir.

| Qualitative indices | Wastewater samples, taken from sewage truck after effluent pumping from impounding reservoir |
|---------------------|------------------------------------------------------------------------------------------------|
|                     | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
| **pH**              | 5.72     | 5.16     | 4.72     | 6.17     |
| Suspended solids, mg/dm³ | 662.6   | 1143    | 9947    | 729.5    |
| COD, mgO/dm³         | 2777     | 5020    | 7860    | 3113     |
| BOD₅, mgO/dm³        | 1204     | 1932    | 3626    | 626      |
| TDS, mg/dm³          | 2050     | 2268    | 2341    | 1033.5   |
| Total iron, mg/dm³   | 0.2      | 1.12    | 0.82    | 2.53     |
| NH₄⁺, mg/dm³         | 20.9     | 12.69   | 5.7     | 13.51    |
| NO₂⁻, mg/dm³         | 4.0      | 0.4     | 4       | 0.2      |
| NO₃⁻, mg/dm³         | 15.16    | 52.45   | 75.56   | 4.04     |
| PO₄³⁻, mg/dm³        | 90.65    | 147.25  | 675.9   | 63.05    |
| Fats, mg/dm³         | 25       | 66      | 825     | 22       |
| Oil products, mg/dm³ | 2.4      | 4.5     | 6.67    | 18.1     |

According to obtained results, the incoming wastewater has volatile character and high degree of pollution concentration irregularity. The wastewater pH can vary from acid to neutral; the concentration of suspended solids can increase tenfold. High amount of organic matters, which is determined by COD and BOD₅, as well as high concentration of fats can change from 2.5 to 6 times. Besides, the wastewater mixture is characterized by elevated concentration of nitrates, ammonium and phosphates, which indicate the curd and cheese whey in the effluent. Since the processes of sewage treatment, as well as the state of pipelines and structures are greatly influenced by the reaction of the medium (pH), pH measurements have been made at different periods of the plant operation. The pH values on different days of plant operation and at different technological processes are presented in Figures 1-2.

![Figure 1](image-url)  
Figure 1. The pH change of wastewater mixture (industrial and domestic wastewaters), taken at the beginning of week.
According to Figures 1-2, wastewater pH can vary in a wide range, that is why, it is necessary to neutralize effluents before their treatment.

The research results on the quality of wastewater, which is taken from separate technological flows, are shown in Table 2.

**Table 2.** The results of wastewater quality research for separate technological flows.

| Qualitative indices                  | CIP cleaning with alkaline solution | Curd whey | Cheese whey | Equipmen t washing | Tank truck washing | Pack washing | Churn (after first rinse) |
|-------------------------------------|------------------------------------|-----------|-------------|--------------------|--------------------|--------------|--------------------------|
| pH                                  | 11.85                              | 5.30      | 5.56        | 4.46               | 7.24               | 4.77         | 8.72                     |
| Suspended Solids, mg/dm³            | 95.5                               | 383.5     | 29646       | 528                | 35.5               | 2306         | not measured             |
| TDS, mg/dm³                         | 1793                               | 10063     | 68092       | 1.415              | 621                | 16833        | measured due to inability to filter the sample |
| Total iron, mg/dm³                  | 0.097                              | 0.78      | 0.2         | 0.1                | 0.9                | 0.1          | 0.1                      |
| NO₃⁻, mg/dm³                        | 6.46                               | 3.4       | 31.5        | 8.7                | 2.09               | 27.6         | 27.6                     |
| NO₂⁻, mg/dm³                        | 97.16                              | 26.14     | 42.72       | 56.84              | 26.36              | 51.88        |                          |
| PO₄³⁻, mg/dm³                       | 2.63                               | 442.45    | 551.75      | 144.15             | 3.45               | 18.83        |                          |
| COD, mg/dm³                         | 457                                | 10493     | 119200      | 3175               | 458                | 20417        | 14900                    |
| BOD₅, mg/dm³                        | 355                                | 3312      | 67500       | 1493               | 325                | 11100        | 1715                     |
| Fats, mg/dm³                        | 650                                | 2340      | 1639        | 870                | 20                 | 699          | 5897                     |
| Oil products, mg/dm³                | -                                  | -         | -           | -                  | 7.07               | 0.68         |                          |

In addition, after equipment CIP washing with acid solution, the wastewater pH was 1.22.

According to Table 2, all wastes have indices, that differ from each other dramatically. For example, the amount of organic matters (COD, BOD₅) in various effluents can differ approximately...
200-300 times (from whey to CIP washing with alkaline solution), while concentration of suspended solids can differ 800 times (whey and tank truck washing). Generally, the highest contamination concentrations are peculiar to different kinds of whey, while the lowest ones – to wastewaters from tank truck washing.

So, the pollution concentrations of dairy industrial wastewaters are tenfold and sometimes hundredfold higher than maximum allowable concentrations for discharge. Also, these wastewaters do not correspond to regulatory requirements for dumping into domestic sewage system. Therefore, a combined removal of these effluents without pretreatment of separate ones, as well as discharge into the domestic sewage system or water body is impossible. Curd and cheese whey should be utilized separately from other effluents or should be reused.

Based on the obtained data, the variant of wastewater treatment is suggested (Figure 3).

Figure 3. The possible variant of dairy industry plant wastewater treatment: 1 – oil remover, 2 – grease-removal tank, 3 – local waste treatment facilities, 4 – domestic sewage system.

According to Table 2 and Figure 3, the wastewaters after tank truck washing, can be dumped into domestic sewage system after petroleum product removal in the oil remover (1). The whey, as a source of valuable products, should be reused separately. Acid and alkaline effluents, which are formed during acid and alkaline equipment washing, are sent to mutual neutralization that can be carried out, for instance, in settling tanks. Then neutralized effluents, together with effluents from pack washing and butter production, are sent to grease-removal tank (2) and further to local waste treatment facilities (3) for organic matters’, nitrates’, ammonium’s, phosphates’ removal. After treatment, the effluents should have qualitative indices which correspond to regulatory requirements for dumping into domestic sewage system (4).

4. Conclusions
According to conducted research on industrial dairy wastewater quality, following conclusions can be made:

- wastewaters, formed during technological process, have volley character and are notable for high concentration of organic contaminations, fats, nitrates, ammonium and phosphates;
- wastewater pH value can change during the day and during the week, and can vary from strongly acidic to strongly alkaline environment depending on the type of equipment washing and discharge into the total whey flow;
- dairy effluents are not subjected to dumping neither into water body nor into domestic sewage system. The following organization of dairy industry plant water disposal system is suggested: the effluents after tank truck washing can be discharged into domestic sewage system after the oil removal; acid and alkaline effluents should be neutralized mutually for pH equalization; the most fat-containing flows should be treated in a grease-removal tank; effluents from pack washing and butter production equipment washing should be sent to local waste treatment facilities after grease-removal tank, and then can be discharged into domestic sewage system;
- secondary products (cheese and curd whey), containing valuable proteins are subjected to reuse with the purpose of food additives’ receiving.
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