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ORIGINAL RESEARCH PAPER

QUALITY PARAMETERS OF DAIRY WASTEWATER IN THE MUREŞ COUNTY, ROMANIA

Mihaela Tiţa[1], Roxana Tufeanu[1*], Ovidiu Tiţa[1], Dan Miricescu[2]

[1] "Lucian Blaga" University of Sibiu, Faculty of Agricultural Sciences, Food Industry and Environmental Protection, Victoriei Street, 10th, Sibiu, Romania
[2] "Lucian Blaga" University of Sibiu, "Hermann Oberth" Faculty of Engineering, Victoriei Street, 10th, Sibiu, Romania

*Corresponding author: elena.tufeanu@ulbsibiu.ro

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Abstract: The objective of this study was to investigate the main quality indicators of wastewater in a dairy factory located in Mureş County, with a water treatment plant built recently. The wastewater samples were tested for extractable matter, total suspended matter, fixed residue, biological oxygen demand, chemical oxygen demand, total suspended solids and *p*H values. The results indicated that pollution levels of wastewater samples tested were found high. This means that the method of treatment does not have the necessary effectiveness that can cause high load of effluent in NH_4^+, total suspended solids, Chemical Oxygen Demand - COD-Cr, Biochemical Oxygen Demand - BOD_5, *p*H for dairy wastewater from the production of cheese and butter. To maintain quality indicators of effluents discharged, in the limits established by the Romanian regulations in force, to avoid the environmental pollution, appropriate treatment method is required.

Keywords: *butter, cheeses, fresh dairy products, environment, pollution*

INTRODUCTION

Dairy industry is based on the processing of raw milk into various products such as yogurt, butter, cheese, ice cream by means of different processes: pasteurization, coagulation, filtration, etc. [1]. This industry is one of the main sources of industrial effluents [2, 3].
A typical dairy factory generates approximately 500 m^3 of waste effluent per day, whose organic load consists mainly in carbohydrates, proteins and fats derived from milk [4 – 6]. Wastewater is a result from the loading of natural water with materials and substances which modifies quality indicators.
Because dairy wastewaters contain high concentrations of organic matter, these effluents may cause serious problems on the local wastewater treatment systems [2, 7]. These wastewaters contain large quantities of milk constituents (casein, lactose) and washing water results from cleaning the tanks, pumps, transport lines, tank trucks etc. [3, 8].
For the treatment of wastewaters are various physicochemical techniques, such as: filtration, sedimentation, degasification, aeration, chlorination, ozonation, neutralization, coagulation, sorption etc. [9, 10].
Through NTPA 001/2002 are established the conditions to support industrial and urban wastewater discharge in order to ensure the protection and normal functioning of the receptors and to protect the environment from the harmful effects of accidental discharges of wastewater. NTPA provides quality indicators that should characterize wastewater and there of maximum limits (Table 1) [11].
In dairy wastewaters, the most important pollutant is the whey, because of the high organic load and the quantity generated. The amount of whey produced is in relation with the productivity of cheese and the type of milk processed. Carvalho *et al*. (2013) have made a comparison between the organic load of domestic wastewater [12] with organic load of cheese whey, and they concluded that is equivalent to the pollution load of one hundred times the volume of common domestic wastewaters [13].
Industrial wastewater includes also the washing waters results from the processing of butter (buttermilk). Usually, due to the content of lipids and mineral salts the first butter washing water is used in the feed.
The present research was carried out to determine the wastewater quality parameters from a dairy factory, in the spring period.

MATERIALS AND METHODS

In this study, physical and chemical parameters of wastewaters discharged from fresh dairy products (milk, yoghurt), cheese and butter production lines were analyzed for a month. The monitored dairy factory is placed in Mureș County with a water treatment plant built recently. All the analyses were performed in a specialized physico-chemical laboratory with analytical purity reagents.
Quality indicators of wastewater were determined in accordance with standardized methods presented in Table 1. The limit values for pollutants loading of industrial wastewater discharged into natural receivers according to Decision no. 352 of 21 April 2005 on amending and supplementing Government Decision no. 188/2002 approving

the rules on the conditions for discharge of wastewater into the aquatic environment are presented in Table 1.

Table 1. *Analysis methods for quality indicators of wastewater and the limit values for pollutants loading of industrial wastewater*

Indicators	m. u.	Limit value	Method of analysis
Extractable matter (EM)	$mg \cdot dm^{-3}$	20	SR 7587- 96
Total suspended solids (TSS)	$mg \cdot dm^{-3}$	60	SR EN 872 - 2005
Fixed residue	$mg \cdot dm^{-3}$	2000	STAS 9187 - 84
Chemical oxygen demand-method with potassium dichromate (COD-Cr)	$mg\ O_2 \cdot dm^{-3}$	125	SR ISO 6060 - 96
Biochemical oxygen demand in 5 days (BOD_5)	$mg\ O_2 \cdot dm^{-3}$	25	SR ISO 1899/2 - 02
NH_4^+	$mg \cdot dm^{-3}$	2.0 (3.0)	SR ISO 7150 - 1/2001
***p*H**	*p*H units	6.5 – 8.5	ISO 10523 - 97

Extractable matter

Soluble soaps and esters were hydrolyzed by acidification. The fatty acids with other extractable substances were extracted in petroleum ether. The residue after evaporation of the petroleum ether was weighed.

Total suspended solids (TSS)

Separation of the suspended matter by filtration was followed by bringing the residue to constant weight. Before analysis, the sample was vigorously shaken. Filtration was performed through filter paper for samples with a high content of suspended solids, and for samples with small content, through the crucible type G4 with asbestos layer. Centrifugation (Universal 320 R) was performed for samples that contain large amounts of colloidal materials.

Fixed residue

A measured volume of unfiltered water was evaporated on a water bath (Brookefield TC 502) and the residue was dried at 105 °C in a BINDER vacuum drying oven, VD series and was weighed.

Biochemical oxygen demand in 5 days (BOD_5)

The difference between the amount of oxygen presented in the sample initially and after 5 days of storage at standard conditions: temperature 20 °C and without of air and light, has been obtained.

Chemical oxygen demand (COD) - Method with potassium dichromate

Oxidizable substances from the water have been oxidized by potassium dichromate in sulphuric acid and warm medium, and the dichromate excess has been titrated with the Mohr salt (Iron(III) ammonia sulfate) in the presence of ferroin as indicator.

NH_4^+ determination

Spectrophotometric measurement of the blue compound formed by the reaction of ammonium with hypochlorite and salicylate ions in the presence of sodium nitroprusside was performed using VIS Spectrophotometer 4111RS Zuzi, at 650 nm. Hypochlorite ions are generated by the alkaline hydrolysis of the sodium salt of *N*, *N*-dichloro-1,3,5-triazine-2,4,6(1H, 3H, 5H)-trione. The reaction of chloramine with sodium salicylate takes place at *p*H 12.6 in the presence of sodium nitroprusside. Sodium citrate was added to mask the interference given by cations, particularly calcium and magnesium.

pH value

The *p*H value was monitored using a *p*H meter Hanna Instruments.

Determination of the *p*H is based on measuring the potential difference of an electrochemical cell. Reagents of recognized analytical quality were used: deionized water (Class 2, according to ISO 3696, conductivity < 0.1 $mS \cdot m^{-1}$); buffer solutions certified with an accuracy declared for the calibration of the *p*H meter; electrolyte filling solution recommended by the manufacturer; potassium chloride solution, *c*(KCl) = 3 $mol \cdot L^{-1}$.

RESULTS AND DISCUSSION

After performing the physicochemical analyses of the quality indicators for wastewater were obtained the following results (Tables 2 - 8). Quality indicators values of wastewater that exceed the limits allowed by law are highlighted in bold.

Table 2. *Values of the extractable matter for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	Extractable matter [$mg \cdot dm^{-3}$]				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	13.5	13.6	13.9	14	13.8
FDP	5	5.4	6	5.6	5.8
B	14	17.2	16	15.2	15.6

By analyzing the values obtained for extractable matter for wastewater we can observe that these are within the limits of the law in force, respectively 001/2002 NTPA.

Table 3. *Values of total suspended solids for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	Total suspended solids [$mg \cdot dm^{-3}$]				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	**84.5**	**83.5**	**90**	**88**	**84**
FDP	52	54	48	51	50
B	**65**	**66**	**62**	59	58

TSS is another important parameter used in defining the wastewater quality, which refers to all small particles suspended in water [14]. TSS should be less than or equal

60 mg·dm^{-3} for treated effluents discharged into natural receivers according to Romanian legislation. In this case the effluent from the production of cheese and butter exceeded the permissible limit of TSS due to more complex composition of wastewater: high quantities of fat, lactose, inorganic salts. Other studies have TSS value of 2137 mg·dm^{-3} [15], 222 mg·dm^{-3}, 136 mg·dm^{-3} [14] which are higher compared with the values obtained by us. Shakhatreh *et al*., have obtained in their research similar values to those obtained by us, for a dairy plant in Jordan, studied for 2008-2011 period: 46.5 mg·dm^{-3}; 41 mg·dm^{-3} [14].

Table 4. *Values of fixed residue for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	**Fixed residue [mg·dm^{-3}]**				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	255	266	261	260	262
FDP	122	130	132	128	129
B	305	312	319	311	313

The values obtained for fixed residue for wastewater are within the limits defined by Romanian law in force.

Table 5. *Values of COD-Cr for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	**COD-Cr [mg O_2·dm^{-3}]**				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	**598.5**	**593.6**	**603.3**	**608.6**	**602.5**
FDP	120.6	121.5	123.6	123	123.2
B	**611.2**	**609.6**	**609.8**	**607.8**	**610.8**

The major pollutant in wastewater is organic matter, which is measured traditionally as BOD and COD. The majority of the organic matter present in the sample is measured through chemical oxidation by dichromate. COD measurements are required for mass balances in wastewater treatment [16]. Significant variations in COD have been reported by various investigators of dairy wastewater: 193 - 459 mg O_2·dm^{-3} [14], 1900 - 2700 mg O_2·dm^{-3} [17], 1400 - 2500 mg O_2·dm^{-3} [18], 2500 - 3300 mg O_2·dm^{-3} [19]. According to the values obtained, COD-Cr for wastewater from the production of cheeses and butter exceed the limit because high organic load. As in the case of whey, buttermilk resulted from the production of butter comes with a higher quantity of organic constituents: carbohydrates, proteins and lipids.

Table 6. *Values of BOD_5 for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	**BOD_5 [mg O_2·dm^{-3}]**				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	**202.4**	**200.4**	**198.4**	**195**	**205.8**
FDP	20	22	20	21	23
B	**220.5**	**219.5**	**218**	**222**	**220**

BOD analysis has its origin in effluent control, and it is therefore one of the most useful determinations. The standard method for BOD analysis takes 5 days (BOD_5), but are other alternatives such as BOD_1, for speed, BOD_7, as in Sweden and Norway or BOD_{25} when is required measurement of all biodegradable material [20]. Researchers have been reported significant variations in BOD for dairy wastewater: 48 - 115 mg $O_2 \cdot dm^{-3}$; 110 - 496 mg $O_2 \cdot dm^{-3}$ [14], 9451 mg $O_2 \cdot dm^{-3}$ [15]; 1200 - 1800 mg O_2 dm^{-3} [17]. As in the case of COD, the wastewater resulted from the production of butter and cheese come with a higher organic matter content, which determine increased values for BOD_5 in comparison with effluents from fresh dairy products.

***Table 7**. Values of NH_4^+ for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	NH_4^+ [mg·dm^{-3}]				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	**9.9**	**11.56**	**7.12**	**13.56**	**10.64**
FDP	2	2	2.5	2	2.3
B	**9.28**	**9.29**	**9.27**	**9.28**	**9.28**

The influent in the production of cheese and butter comes with a high intake of NH_4^+ and the method of treatment is not effective, which causes high load of effluent in ammoniacal nitrogen, the values for this indicator exceeding the limits imposed by the regulations in force. A similar problem has been reported by Popa, who has studied wastewater quality in Mediaş. She found that the conventional method of sewage treatment plant applied in Mediaş city does not have the necessary effectiveness to obtain satisfactory purified water, particularly in terms of NH_4^+ (22 - 80 mg·dm^{-3}) [21].

***Table 8**. pH values for wastewater resulting from the production of fresh dairy products (FDP), cheeses (C) and butter (B)*

Products	***p*H**				
	03/02/2016	03/09/2016	03/16/2016	03/23/2016	03/30/2016
C	5.05	5.04	5.05	5.06	5.05
FDP	7.7	8.1	7.8	8	7.9
B	6.09	6.11	6.1	6.08	6.12

Dairy wastewater can present a fluctuation of *p*H values (3.0 - 10.0) due to many factors, among which is the cleaning process of production equipment by using alkaline and acidic agents. Analyzing the values obtained we can observe that *p*H of wastewater from the production of cheese and butter exceed the limit allowed by Romanian legislation. Investigators of dairy wastewater reported various values for *p*H: 6.5 - 7.4; 7.4 - 7.7; 7.5 - 10.2; average values resulted from the analysis of the wastewater samples from 3 dairy factory during the period, 2008-2011, in Jordan [21]; 7.2 - 8.8 [17]; 7.9 ± 1.2 for an Arab dairy factory [22]. *p*H has direct influence on wastewater treatability because dairy effluents contain fats, oil, suspended solids, phosphorus, heavy metals and the processes to remove these contaminants are dependent on the *p*H of the wastewater. So it is very important to maintain *p*H levels within the limits 6.5 - 8.5.

CONCLUSIONS

The conclusion that emerges from the data analysis is that the actual method of treatment applied to the wastewater treatment plant does not have the necessary effectiveness to achieve water treated, especially in terms of NH_4^+, total suspended solids, COD-Cr, BOD_5, *p*H for dairy wastewater from the production of cheese and butter. These parameters have values higher than limits set by the current regulations for pollutants loading of industrial and urban wastewater discharged into natural receivers.

In conclusion it may be stated that effluent treatment need to be done due to the following reasons: to avoid the environment pollution by discharging untreated wastewater; to meet the requirements established by the regulations in force and for the realization of our commitment to provide pollution free environment for the future generations.

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