Influence of confectionery wastewater pretreatment in vortex layer apparatus on its physical and chemical properties

E R Mikheeva[1,*], *I V* Katraeva[2], *Yu V* Litti[3], *A A* Kovalev[4] and *D A* Kovalev[4]

[1] Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Avenue, bldg 2, Nizhny Novgorod, Russia
[2] Nizhny Novgorod State University of Architecture and Civil Engineering, 65 Ilinskaya Str., Nizhny Novgorod, Russia
[3] Federal Research Centre “Fundamentals of Biotechnology” of the Russian Academy of Sciences, Leninsky prospect, 33, bldg 2, 119071 Moscow, Russia
[4] Federal Scientific Agroengineering Center VIM, 5, 1st Institutsky proezd, Moscow, Russia

Abstract. The paper studies the effect of pretreatment of highly concentrated wastewater from confectionery production in a vortex layer apparatus (VLA) on its physical and chemical properties, with the aim of its further use as a substrate for dark fermentation with the production of biohydrogen. Pretreatment in VLA resulted in a 2.6-fold increase in the iron content and 6.5% increase in soluble chemical oxygen demand after 3 minutes of exposure. After pretreatment in VLA, an increase in the content of acetic acid and a decrease in the contents of propionic, butyric and caproic acids were observed. An increase in the content of mono- and disaccharides was registered, and the effect of the VLA exposure time of confectionery wastewater on its physicochemical properties was studied. An increase in the concentration of iron and simple sugars in wastewater makes the use of VLA promising for improving the process of its subsequent dark fermentation.

1. Introduction

To speed up the process of anaerobic treatment of organic waste and increase the biogas yield, various methods of pretreatment (physical, chemical, physicochemical and biological) are used [1-4]. One of the most promising and energy-efficient methods is the use of vortex layer apparatus (VLA), in which a complex impact on the substrate takes place due to chaotically moving ferromagnetic bodies in a rotating magnetic field [5-6]. As a high-performance shredder, VLA has found applications in mineral processing, chemical, construction, food, cosmetic, and pharmaceutical industries [7-9]. The advantage of VLA is lower energy consumption for waste treatment in comparison, for example, with ultrasonic pretreatment. Grinding of the substrate is carried out by ferromagnetic cylindrical working bodies (ferromagnetic rods) placed in a tube made of non-magnetic material, in which a rotating magnetic field is created. Due to the high rotation speed of the field, the working bodies begin to move and collide, causing the dispersion of the processed material in the working space of the apparatus. Besides the impact of ferromagnetic particles, cavitation

* Corresponding author: biomikheeva@gmail.com

also contributes to the intensive dispersion of the material, which also occurs during the device operation. In the process of treatment in VLA, the sample is heated, which, on the one hand, contributes to its disinfection, and on the other hand, it allows heating it to the required temperature before feeding into the anaerobic reactor, eliminating the temperature shock of the anaerobic microbial community and contributing to its stable operation [5]. Previously, the authors showed a positive impact of pretreatment of various organic substrates in VLA on the process of anaerobic digestion, in particular, on the kinetics of methanogenesis, the degree of decomposition of organic matter, methane content in biogas, and waste decontamination [5, 6].

Currently, hydrogen is considered as an alternative clean gas fuel of the future, which will reduce dependence on fossil fuels and effectively initiate a new energy transition [10]. Among the biological methods of hydrogen production, dark fermentation (DF) of various organic wastes has several advantages, such as higher hydrogen productivity, versatility, and high speed of the process. Among various types of industrial wastewater, confectionery wastewater is rich in carbohydrates and is an ideal substrate for the production of hydrogen by anaerobic bacteria [11]. Several publications mention that sugar-rich wastewater, such as wastewater from molasses production, sugar beet and sugarcane processing, can produce high yields of hydrogen, up to 3.2 mol/mol of carbohydrates [12], and usually gives a relatively lower H_2 yield of about 1.9 mol/mol of glucose [13-16].

Compared to organic waste with high solids content (sewage sludge, food waste, lignocellulosic biomass, etc.), little attention has been paid to the pretreatment of wastewater to improve its subsequent DF. Hydrodynamic cavitation (HC) has recently been used as a pretreatment method to improve H_2 production from cheese whey. This system provided not only a sonication effect but also an increase in wastewater temperature. The HC treatment for 15 min resulted in a higher H_2 production yield (1.89 mol H_2/mol lactose) than other traditional pretreatment methods, such as heating and sonication [17]. The authors only mentioned an increase in the temperature of the pretreated cheese whey, and did not investigate which physicochemical properties of cheese whey were affected by HC pretreatment.

This work aimed to determine the effect of pretreatment in VLA on the physicochemical characteristics of wastewater from confectionery production, which can affect the improvement of the process of its subsequent dark fermentation.

2. Materials and methods

2.1. Wastewater

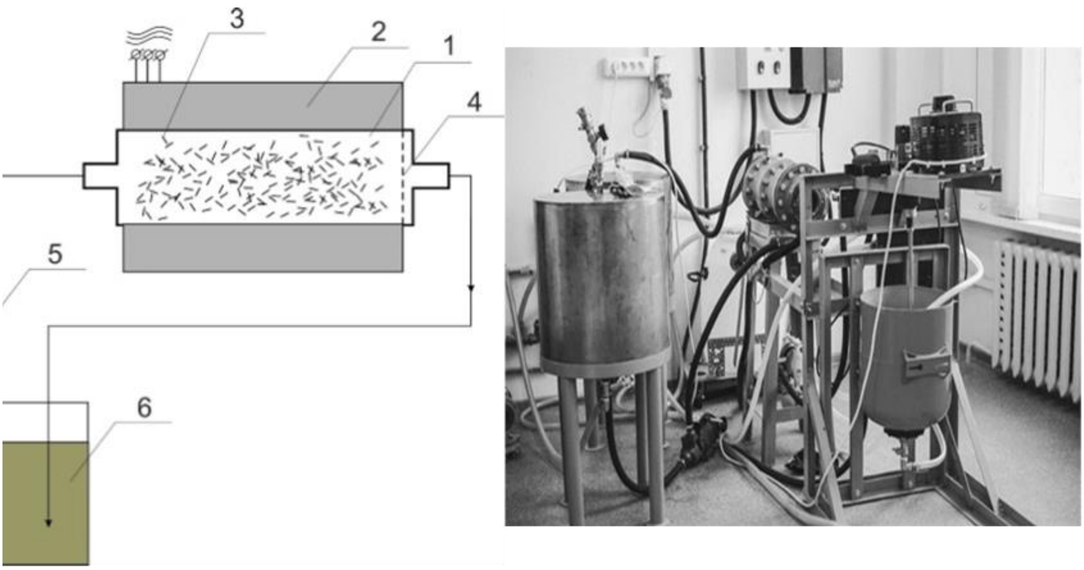
Highly concentrated wastewater of a confectionery plant producing confiture for the bakery industry was used as an object of research. Wastewater was passed through a sieve with a mesh size of 0.4 mm to remove large inclusions. The main characteristics of wastewater are shown in Table 1.

Table 1. The main characteristics of wastewater from confectionery plant.

Parameter	**Meas. unit**	**Value**
pH	-	6.34
TS	%	1.11
NVS	%TS	6.40
Fe	wt%	0.003
COD_{sol}	mg/l	12140
C	% TS	33
H	% TS	7.2
N	% TS	less than 0.3
S	% TS	less than 0.3
C/N	-	109.9/1
NH_4^+	mg/l	37.0
PO_4^{3-}	mg/l	2.31
Fats	mg/l	14.2
Fructose	wt%	0.085
Glucose	wt%	0.064
Sucrose	wt%	0.395

2.2. Vortex layer apparatus

The pretreatment of the substrate was carried out in the vortex layer apparatus (Regionmettrans, Russia) in a caprolon (nylon) flask with a working volume of 1.27 l in a flow-through mode (Figure 1).



(a) (b)

Fig. 1. Schematic diagram (a) and general view (b) of the vortex layer apparatus: 1 - chamber made of non-magnetic material; 2 - inductor that creates a rotating magnetic field; 3 - ferromagnetic particles; 4 - grid; 5 - pump; 6 - container with a substrate.

Ferromagnetic working bodies, i.e. steel needles with a diameter of 2.1 mm and a length of 19 mm, were used for processing wastewater of the confectionery production in VLA. The VLA power was 14 kW, the wastewater treatment time was 1 min and 3 min.

2.3. Analytical methods

The contents of total carbon, nitrogen, hydrogen, and sulfur were determined using the Vario EL cube elemental analyzer (Elementar, Germany). Volatile fatty acids (VFA) were determined using the GCMSQP2010 Ultra gas chromatography-mass spectrometer (Shimadzu, USA), the conditions and operating mode of which were described earlier [5]. The total solids (TS) content was determined after drying the samples to constant weight at 105°C. The nonvolatile solids (NVS) content was determined after burning a dry sample in a muffle furnace at 600°C. Soluble chemical oxygen demand (COD_{sol}) was determined by the dichromate method in a wastewater sample after it had been passed through a "Blue Ribbon" paper filter (JSC LenReaktiv, Russia) with a pore size of 5–8 μm. Redox potential (ORP) and pH were measured using the portable pH meter WTWpH 3110 SET (WTW, Germany). The fat content was determined gravimetrically after the extraction of fat with petroleum ether. The sugar content was determined by high-performance liquid chromatography (HPLC) at the LC-20 Prominence liquid chromatograph (Shimadzu, Japan) using a SUPELCOSILTMLC-NH2 column at 30°C and an infrared detector. The HPLC elution mode was low-pressure gradient, mobile phase included 68% of acetonitrile and 32% of ultrapure deionized water, with a mobile phase flow rate of 0.8 ml/min. The iron content was determined using the ProdigyHighDispersionICP atomic emission spectrometer with inductively coupled plasma (Teledyne Leeman Labs, USA). NH_4^+ and PO_4^{3-} were determined photometrically using Nessler's reagent and ammonium molybdate solution, respectively, on a B-1100 spectrophotometer (ECOVIEW, China). The measurements were carried out in duplicate.

3. Results

Analysis of iron content in the confectionery wastewater after treatment in VLA showed that its content significantly increased only after 3 minutes of exposure (Figure 2).

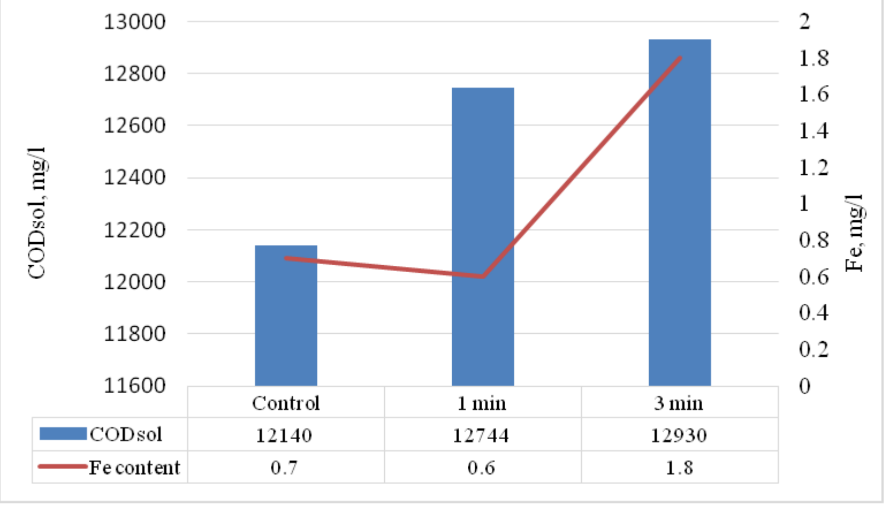


Fig. 2. Changes in COD_{sol} and iron content in confectionery wastewater after treatment in VLA.

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An increase in COD_{sol} was observed with increase in the duration of pretreatment (Figure 2). At the same time, pH changed towards insignificant acidification, and ORP decreased by 12.5-17.3% (Figure 3).

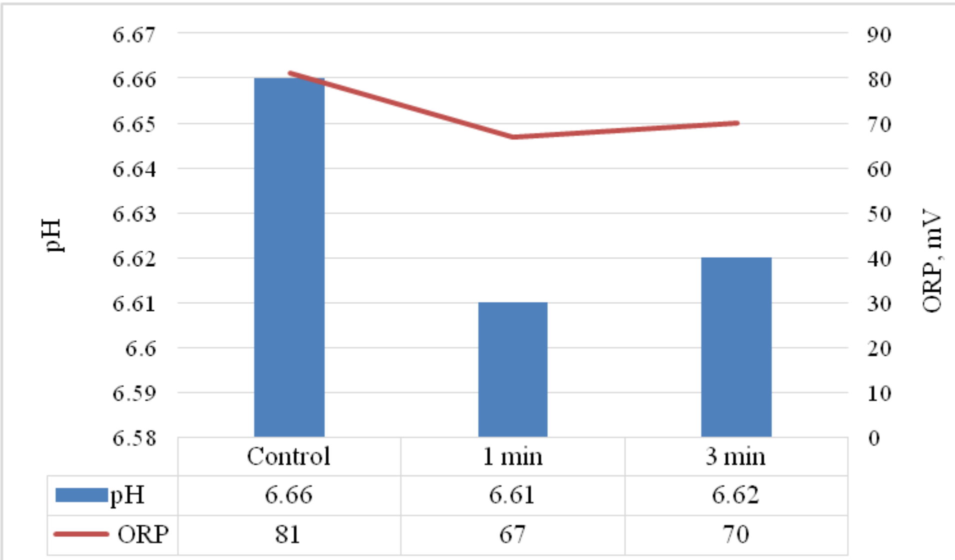


Fig. 3. Change in pH and ORP of confectionery wastewater after treatment in VLA.

The analysis of the sugar content showed that the treatment in VLA led to increase in the content of mono- and disaccharides (glucose, fructose and sucrose) (Figure 4), which may indicate the hydrolysis of polysaccharides contained in solid particles, as a result of treatment in VLA. The total sugar content in the filtered sample increased by 62% after 1 min of treatment, and by 22% after 3 min. However, it should be noted that the total sugar content decreases with increasing exposure time.

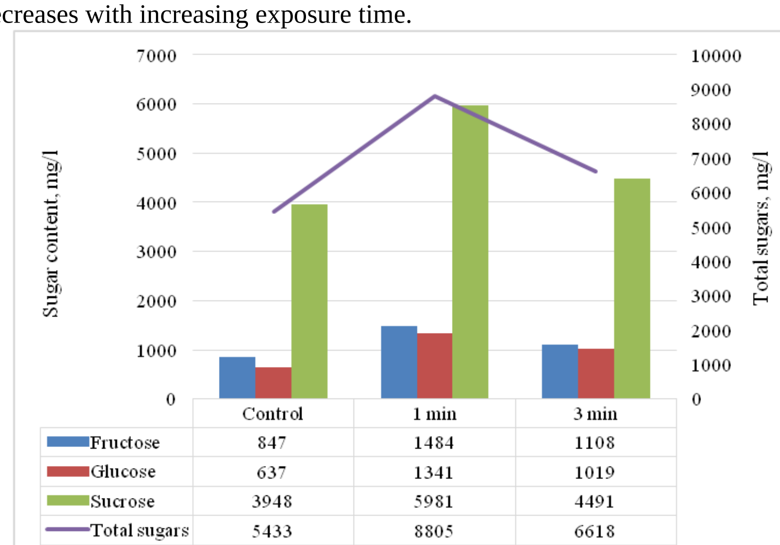
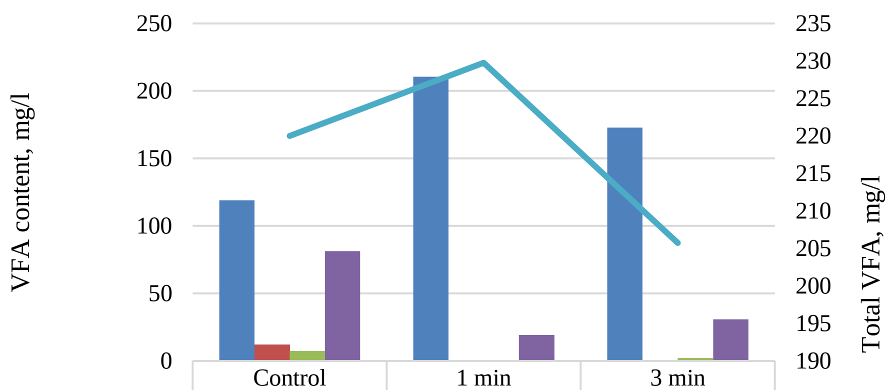


Fig. 4. Content of sugars in wastewater of confectionery production before and after treatment in VLA.

After pretreatment, an increase in acetic acid content was detected, while the total VFA content in the control sample and the samples after pretreatment remained practically unchanged (Fig. 5). Thus, there was a redistribution of the VFA content towards an increase in acetic acid and a decrease in the content of propionic, butyric and caproic acids. This was especially noticeable in the sample after 1 min of treatment in VLA. However, an increase in the retention time of wastewater in VLA contributed to a decrease in the content of acetic acid and the total VFA.



	Control	1 min	3 min
Acetate	119	211	173
Propionate	12	0	0
Butyrate	7	0	2
Caproat	81	19	31
Total VFA	220	230	206

Fig. 5. The content of volatile fatty acids in the confectionery wastewater after 1 and 3 min of pretreatment in VLA, and control - without pretreatment in VLA.

4. Discussion

Physicomechanical pretreatment of liquid waste (confectionery wastewater) in VLA contributed to an increase in COD_{sol} in wastewater by 5% after 1 min of treatment and by 6.5% after 3 min. The increase in COD_{sol} was probably caused by the dissolution of part of the solid particles under the influence of the destructive effect of VLA. The increase in COD_{sol} with increasing processing time was insignificant, so, from the point of view of energy efficiency, the pretreatment of wastewater in VLA for 1 min was sufficient.

The pretreatment increased the iron content by 2.6 times after 3 minutes of exposure. It has been shown that for DF, it is important to add metal ions, in particular iron, to the medium. Metal ions are part of enzymes, and they also take part in the processes of cell transport. Hydrogenase, a key enzyme involved in hydrogen production, contains a FeFe or NiFe bimetallic centre surrounded by FeS protein clusters [15-16]. Lee et al. [16] studied the effect of iron concentration on DF and found that the maximum hydrogen yield was 131.9 ml/g sucrose at an iron concentration of 800 mg $FeCl_2$/l, and the maximum specific rate of hydrogen production was 24 ml/g volatile suspended solids (VSS) per hour at adding 4000 mg $FeCl_2$/l to the medium. With the addition of nano-iron with zero valences, the highest specific yield of biohydrogen was 243 ml H_2/g glucose, which was 30% higher than in the control [18].

An increase in the content of acetic acid in wastewater after pretreatment in VLA and a decrease in the content of propionic, butyric and caproic acids were revealed. It is known that the accumulation of propionic acid has an inhibitory effect on the production of biohydrogen [19]. So, reducing the concentration of butyric and propionic acid in the dark fermentation reactor effluent can increase methane production during anaerobic digestion at the second stage of methanogenesis [19].

Consequently, the pretreatment of wastewater in the VLA will increase the methane yield at the stage of methanogenesis; the similar result was obtained by the authors during the anaerobic digestion of the organic fraction of municipal solid waste pretreated in the VLA [5].

The increase in the total sugar content was possibly associated with the destruction of polysaccharides (starch, pectin and other food additives). Ivetic et al. [20] reported that the hydrolysis of sugar beet was enhanced after sonication, the enhanced hydrolysis resulted in the increased production of reducing sugars. Kumar et al. [21] reported a 14% increase in reducing sugars after ultrasonic treatment of sugarcane bagasse. Xi et al. [22] reported a 29.5% increase in sugar production after acid hydrolysis of sugarcane bagasse using ultrasound. Eblaghi et al. [23] reported an increase in sugar production from 3.62 g/l (for untreated sugarcane bagasse) to 5.78 g/l for sonicated bagasse (35 kHz, 65 °C, 5 min). Bundhoo et al. [24] noted that the xylose yield increased from 22% for untreated fruits to 58% for the sonicated ones.

It should be noted that, in general, increasing the pretreatment time of wastewater in VLA did not give a clear correlation between the change in the physicochemical properties of the substrate and the energy consumption for treatment. Therefore, the determination of the optimal mode of wastewater treatment in VLA requires further research.

5. Conclusion

Studies have shown that pretreatment in VLA leads to changes in a number of physicochemical characteristics of not only solid waste [5] but also wastewater, which was experimentally established by the example of highly concentrated wastewater of confectionery production. Thus, pretreatment in VLA under certain operating conditions led to an increase in the content of soluble sugars, dissolved COD, and acetic acid. It was shown that due to the abrasion of iron needles in the pretreated substrate, the concentration of iron increased. An increase in the bioavailability of the substrate and the content of iron in it, which stimulates the activity of hydrogenases, makes pretreatment in VLA an attractive method for increasing the efficiency of the subsequent production of biohydrogen from food production wastewater during the dark fermentation process.

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References

1. S. Shanmugam, M. Sekar, R. Sivaramakrishnan, T. Raj, E.S. Ong, A.H. Rabbani et al, Int J Hydrogen Energy, 46(20), 11252–68 (2021).
2. B. Basak, S. Saha, P.K. Chatterjee, A. Ganguly, S. Woong Chang and B-H Jeon, Bioresour Technol, 299, 122592 (2020).
3. S. Lunprom, O. Phanduang, A. Salakkam, Q. Liao, T. Imai and A. Reungsang, Int J Hydrogen Energy, 44(6), 3339–46 (2019).
4. S. Kumari and D. Das, Bioresour Technol, 218, 1090–7 (2016)
5. E. Mikheeva, I. Katraeva, D. Vorozhtsov, Y. Litti and A. Nozhevnikova, Appl Biochem Microbiol, 56, 736–42 (2020)

6. Y. Litti, D. Kovalev, A. Kovalev, I. Katraeva, Y. Russkova and A. Nozhevnikova, In: Journal of Physics: Conference Series (2018)
7. M. Wołosiewicz-Głąb, D. Foszcz and S. Ogonowski, IFAC-PapersOnLine, 50, 14964–9 (2017).
8. M. Wołosiewicz-Głąb, S. Ogonowski and D. Foszcz, IFAC-PapersOnLine, 49(20), 67–71 (2016).
9. B. Khaydarov, D. Suvorov, A. Pazniak, E. Kolesnikov, V. Gorchakov, S. Mamulat et al, Mater Lett, 226, 13–8 (2018).
10. X-Y, Wu, Y. Luo, F. Hess, W. Lipiński, Front Energy Res, 9, 231 (2021)
11. M.K. Yogeswari, K. Dharmalingam, P. Mullai, J Environ Manage, 252, 109684 (2019).
12. J. Prakash, R. Sharma, S. Patel, I-W Kim, V. Kalia, PLoS One, 13, e0199059 (2018)
13. S. Wang, T. Zhang, H. Su, Renew Energy, 96, 1135–41 (2016)
14. L. Xiao, Z. Deng, KY Fung, LM Ng, Int J Hydrogen Energy, 38(32), 13907–13 (2013)
15. C. Zhao, A. Sharma, Q. Ma, Y. Zhu, D. Li, Z. Liu et al, Sci Total Environ, 758, 143658 (2021)
16. YJ Lee, T. Miyahara, T. Noike, Bioresour Technol, 80, 227–31 (2002)
17. YH Seo, Y-M, Yun Y-M, H. Lee, J-I Han, Fuel, 150, 202–7 (2015)
18. Sewwandi and R. Nitisoravut, Energy Reports, 6, 392–6 (2020)
19. C. Mamimin, P. Prasertsan, P. Kongjan, S. O-Thong, Electron J Biotechnol, 29, 78–85 (2017)
20. D. Ivetic, R. Omorjan, T. Djordjevic, M. Antov, Environ Prog Sustain Energy, 36 (2017)
21. G. Kumar, B. Sen, C-Y Lin, Bioresour Technol, 145 (2013)
22. Xi Y-L, Dai W-Y, Xu R, Zhang J-H, Chen K-Q, Jiang M, et al, Bioprocess Biosyst Eng, 36 (2013)
23. M. Eblaghi, M. Niakousari, M. Sarshar, G. Mesbahi, J Food Process Eng, 39, 273–82 (2016)
24. ZMA Bundhoo, R. Mohee R, Ultrason Sonochem, 40, 298–313 (2018)