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DAIRY WASTEWATER UTILIZATION BY COMBINATION OF OXIDATION PRE-TREATMENT AND ULTRAFILTRATION

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Abstract

In this work the effects of oxidation pre-treatments (ozonation and Fenton reaction) on membrane filtration of dairy wastewater were investigated, together with the further utilization possibilities of residual wastes. The oxidation pre-treatments enhanced the membrane filtration efficiency, from which the short-term ozone treatment was found to be the most effective method both in terms of increasing the flux and the pollutant removal efficiency. After ozone pre-treatment the phosphate and ammonium content of the wastewater migrated to the permeate, while after Fenton pre-treatment the phosphate content remained in the concentrate, and the ammonium content in the permeate decreased. The concentrate was utilized as biogas resource and it was found that both pre-treatments increased the biogas production and its methane content as well. Based on our results it can be concluded that ozone pre-treatment combined with membrane separation have improved the efficiency of dairy wastewater treatment and may suit the requirements of circular economy.

Key words: biogas, dairy wastewater, membrane separation, ozone, pre-oxidation

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1. Introduction

The amount of wastewater discharged from the dairy industry has been continuously increasing, and it is considered to be the largest wastewater source in the food industry (Kushwaha et al., 2011; Slavov, 2017). These wastewaters contain high amounts of potentially water-polluting organic and inorganic compounds; they have high chemical oxygen demand (COD) and biological oxygen demand, moreover high nitrogen (N) and phosphate (P) content. Despite their severe polluting potential, these waters could be an inexpensive source of valuable compounds and nutrients, such as N and P. The wastewaters generated from milk processing can be originated from (1) the processing water (e.g. cooling waters or drying vapours, which are reusable because they are generally clean) and from (2) the cleaning and washing operations (Slavov, 2017). As a result of the latter, the components of milk appear in the wastewater (milk proteins, fats, carbohydrates/lactose, fats) as well as various sanitizing agents and detergents (USDA-SCS, 1992). Dairy wastewaters are predominantly treated either by mechanical (e.g. equalization), physicochemical (e.g. coagulation/flocculation), or biological methods (Demirel and Yenigun, 2004; Khani et al., 2020; Slavov, 2017). Coagulation-flocculation is a very cheap process; however, it requires a lot of chemicals which may decrease not only the organic, but the phosphorous content of the wastewater as well (Rao and Bhole, 2002). Dairy wastewaters contain a lot of

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N and P (Karadag et al., 2015), mainly in the form of amino groups (from milk proteins) and inorganic phosphates, respectively. The current wastewater treatment technologies used in the dairy industry not only cannot utilize them, but their presence in the wastewater may cause problems, in spite of that these compounds, in accordance with the requirements of circular economy, could be used as fertilizers after separating them from the wastewater (Cieślik et al., 2017; Huang et al., 2018). Recently there are several research aiming wastewater originated ammonia or phosphate adsorption by low-cost adsorbents prepared from agriculture waste (Karri et al., 2018). One of the problems with these methods, that the adsorbents are not selective enough, and the wastewaters contain several organic and inorganic compounds which can be adsorbed. Separating ammonia and/or phosphates from the colloidal particles, their adsorption would be more effective; for this the membrane separation would be an appropriate method. The scheme of the streams of raw materials and nutrients in case of present-day and a conceptual technology fitted to requirements of circular economy are presented in Fig. 1 a and b.

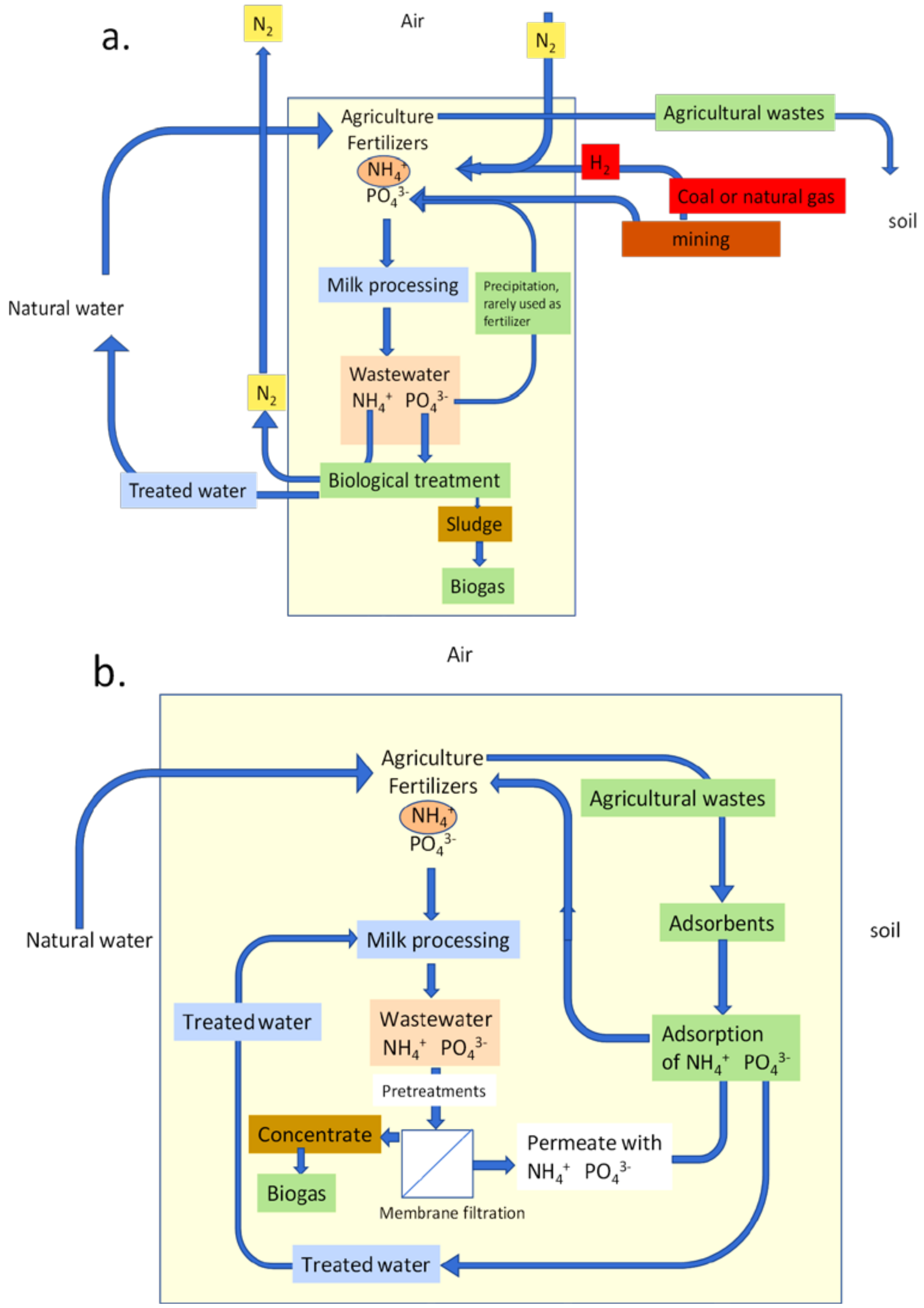


Fig. 1. Schematic representation of ammonia and phosphate streams in traditional milk and dairy wastewater processing (a), and a conceptual technology fitted to the requirements of circular economy (b)

Membrane filtration is widely used in the dairy industry to separate proteins from whey. Since membrane separation became cheaper, it would be a promising process to produce recyclable water from the dairy wastewater by eliminating milk proteins and lactose from it (Sarkar et al., 2006). However, membrane filtration also has drawbacks. The main disadvantage and limiting factor is flux decline caused by fouling and concentration polarization (Abdelkader et al., 2019). Fouling mitigation can be achieved by physical methods, such as stirring, ultrasonication or vibration (Koh et al., 2014) or by chemical and physicochemical processes which change the chemical characteristics of the particles by increasing their size (flocculation) (Van Geluwe et al., 2011) or by changing the characteristics of the membrane surface (Benavente et al., 2016) such as hydrophilicity, surface charge or zeta potential. By applying these processes, the irreversible binding of the particles to the surface can be mitigated.

The other drawback is that the concentrate needs further treatments, although by choosing the membranes correctly the purification efficiency can still be high. After successful filtration the concentrated dairy wastewaters do not contain any toxic materials or dangerous compounds, however, they still consist of high amounts of organic materials such as proteins, fats, lactose, etc. (Sarkar et al., 2016). The concentrated wastewater mixed with anaerobic sludge can be used for biogas production (Joshiba et al., 2019). Combination of membrane separation and advanced oxidation pre-treatments (that employ e.g., ozone, hydrogen peroxide, Fenton reaction, UV light or their combination) may be very advantageous, because ozone and hydroxyl radicals can induce changes in the particle size and surface charge, which can result in micro-flocculation (Cheng et al., 2011) or the oxidation of the fouling compounds (László et al., 2009; Zhu et al., 2008). Earlier experiments showed that pre-oxidation also can increase the biodegradability of food waste and may increase the production of biogas (Beszédes et al., 2009). Although ozonation is a well-known pre-treatment, some of its regarding key issues in this research field (i.e. its combination with membrane separation) are not clarified, such as optimal ozone dosage, micro flocculation caused by the presence of ozone, and possible toxic effects of the degradation products (Varga and Szigeti, 2016). Earlier works proved (Yi et al., 2009) that the addition of Fenton reagents may increase toxicity, however, this issue in the case of ozone has not been investigated.

Our goal was to investigate whether the combination of advanced oxidation processes and ultrafiltration could be an advantageous method to treat real dairy wastewaters, while focusing on minimal waste generation and further utilization possibilities, which may fit to the concept presented above (Fig. 1b). In the present study two advanced oxidation processes, namely ozone treatment and Fenton reaction were investigated as pre-treatment methods, since they have considerable coagulation-flocculation effect besides their high oxidation potential. Prior the ultrafiltration of real dairy wastewaters the oxidation processes were used as pre-treatments, and we investigated:

- their effect on the filtration mechanism, flux, and filtration resistances, and on the COD (protein and lactose) elimination efficiency,
- their effect on the utilization possibility of biogas production from the concentrate,
- and their effect on the quality of the permeate in terms of phosphate and ammonia content.

Although there are several research aiming utilizations of ammonia or phosphate from wastewaters, or using membrane separation to gain reusable clean waters, using advanced oxidation processes coupled with membrane filtration may be a new perspective in dairy wastewater treatment in terms of both nutrient and clean water recovery and waste utilization.

2. Experimental

The raw dairy wastewater was provided by Sole-Mizo Zrt., a dairy factory in Szeged, Hungary. The raw wastewater was characterised by COD, turbidity, conductivity, and pH (Table 1).

Table 1. Characteristics of the raw wastewater

	COD (mg/L)	*Turbidity (NTU)*	*pH*	*Conductivity (µS/cm)*
Untreated wastewater	~3200	~200–250	5.7–6.4	~1200–1400

During the ozone treatment experiments (Fig. 2) ozone-containing gas was bubbled (with 1 L/min flow rate for 5, 10, and 20 min) through a batch reactor containing 0.4 dm^3 wastewater. Ozone was produced from oxygen (Messer, 3.0) with an ozone generator (BMT 802X, Germany). After ozone treatment the remaining ozone was eliminated by bubbling nitrogen gas (Messer, 3.0) through the reactor for 30 min to avoid the membrane damage by residual ozone.

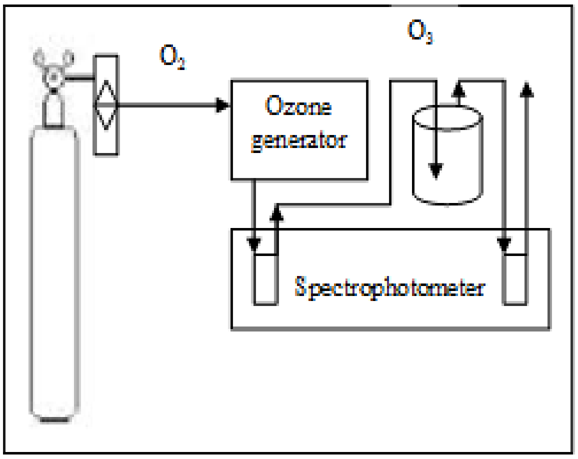


Fig. 2. Ozone pre-treatment setup

The amount of ozone was measured by a spectrophotometer (WPA Biowawe II+) before and after it entered the reactor, and the absorbed amount (in mg/dm^3) was calculated by the Beer-Lambert law (A = ε·l·c). The amount of absorbed ozone was 127.5, 210.0, and 360.0 mg/dm^3 after 5, 10, and 20 minutes, respectively.

The Fenton reaction experiments were conducted in a stirred batch reactor at pH 3, which was adjusted by 1 M H_2SO_4 (96%, Farmitalia Carlo ErbaSPA, Italy). 1.5 mmol/dm^3 $FeSO_4 \cdot 7H_2O$ (99%, VWR, EU) and H_2O_2 solution (30 wt.%, 99% purity, VWR) in 5:1 H_2O_2/Fe ratio were used during the experiments. The reaction was stopped by adding 1 M NaOH (99%, VWR, EU) solution to increase the pH to 7.

The ultrafiltration experiments were carried out in a stirred (350 rpm) ultrafiltration device (Millipore, SN:XFUF04701, USA) at 0.3 MP transmembrane pressure. Flat sheet polyether sulfone membranes (PES6 series, New Logic, USA) were used with 10 kDa molecular weight cut-off and 0.00173 m^2 effective membrane area during the experiments. The initial feed volume was 250 cm^3, and the volume reduction ratio was VRR=5. During experiments the temperature was 24±1°C.

For the COD measurements high and medium range (0–1500 and 0–15000 mg/L, respectively) photometric test kits (COD $K_2Cr_2O_7/H_2SO_4$ VARIO test tubes, Lovibond Tintometer) were used. Phosphate, ammonium, nitrite and nitrate content was determined with a Spectroquant® Nova 60 spectrophotometer (Merck Millipore), using Spectroquant® test kits (Merck).

Biogas production tests were performed in a batch reactor. Mesophilic conditions were applied (40 °C for 40 days) in an anaerobic laboratory digester equipped with a pressure measuring head (Oxitop Control AN12 measurement system, WTW Gmbh, Germany). The acclimated municipal wastewater sludge (Hódmezővásárhely Water Treatment Plant, Hungary) was added to the digester to reduce the lag phase of the anaerobic biological degradation. Afterwards, nitrogen gas was bubbled through the reactor to eliminate the residual oxygen, while pH 7.2 was set with 1 M NaOH and 1 M HCl (99%, VWR, EU) solution. All measurements were performed in triplicate.

The capacity of the digesters was 1000 mL, the volume of the mixed sample was 70 mL (50 mL from the retentate and 20 mL from the sludge), in accordance with our previous work and the pressure range of the equipment. e pressure values were automatically saved every 2 hours. The methane content was measured by an Agilent 6890 gas chromatograph equipped with a flame ionization detector, and a HP-PLOT Q PT (30 m × 0.53 mm × 40 μm) column. The split ratio was 9:1, the oven temperature was 80 °C (constant value), the flow rate was 4.5 mL/min, and the carrier gas was hydrogen (Messer, 5.0). Sample injection was carried out manually with a gas tight Hamilton 1710SL syringe equipped with a valve lock.

Daphnia tests were carried out based on the method of Tyagi et al. (2007).

After treatments, the COD elimination efficiencies were calculated by Eqs. (1-2):

$$R\%(oxidation) = 100 \cdot \frac{c_{raw} - c}{c_{raw}} \quad (1)$$

$$R\%(filtration) = 100 \cdot \frac{c - c_{perm}}{c_{perm}} \quad (2)$$

where: c is the COD after oxidation treatment, c_{raw} is the COD of raw wastewater; c_{perm} is the COD of permeate after filtration. The overall COD elimination efficiency was calculated as sum of R% (oxidation and R%(filtration).

In order to investigate the membrane fouling mechanisms, the resistances-in-series model was applied Eqs. (3-6). The membrane resistance was calculated as (Eq. 3):

$$R_M = \frac{\Delta p}{J_w \cdot \eta_w} \quad (3)$$

where: R_M is the membrane resistance (m^{-1}), Δp is the transmembrane pressure (MPa), J_W is the distilled water flux of the neat membrane and η_W is the water viscosity (Pa·s).

R_T is the total resistance (m^{-1}): (Eq. 4):

$$R_T = R_M + R_{irrev} + R_{rev} \quad (4)$$

where: R_{irrev} is the irreversible resistance (which cannot be eliminated by washing) and R_{rev} is the reversible resistance (m^{-1}; caused by the deposition of pollutants that can be washed from the membrane surface by rinsing).

The R_{irrev} was determined by (Eq. 5):

$$R_{irrev} = \frac{\Delta p}{J_{WA} \cdot \eta_W} - R_M \quad (5)$$

where: J_{WA} is the water flux after filtration and rinsing the membrane. Reversible resistance of the layer deposited on the membrane surface was calculated by (Eq. 6):

$$R_{rev} = \frac{\Delta p}{J_C \cdot \eta_{WW}} - R_{irrev} - R_M \quad (6)$$

where: J_c is the flux at the end of the filtration and η_{ww} is the viscosity of the wastewater (Pa·s).

3. Results and discussion

3.1. Effects of the pre-treatments on the filtration resistances

In the first series of the experiments the dairy wastewater samples were pre-treated with ozone for 5, 10, or 20 min or with Fenton reaction for 0, 30, or 90 min, then, the pre-treated samples were filtered. To get more information about the nature of the fouling, the filtration resistances were calculated and compared (Fig. 3). The filtration resistances were calculated based on the measured fluxes Eq. (2-5), and the results were compared to filtration resistances of untreated samples.

These experiments revealed that the filtration resistances (thus the fluxes) are not proportional to ozone treatment time; although the ozone pre-treatment decreased the resistances, the 10-minute-long ozone treatment resulted in the lowest filtration resistance and thus the highest flux. Comparing the change of reversible and irreversible resistances, it was found, that irreversible resistances (related to unwashable adsorption or pore fouling/blocking) were decreased by ozone treatment, possibly due to micro-flocculation effect of ozone (Jekel, 1983). This may cause formation of associates, which cannot clog the membrane pores; instead tend to form cake layer. As the ozonation is in progress, this effect results in larger associates (related to decreased resistances as these particles are swept off from the membrane surface). Further (20 min) ozonation oxidize the associate-forming molecules, changing their chemical structure (mainly by formation of carboxylic groups and finally oxalic acid); this may lead to formation of (e.g. Ca-oxalate) precipitates, which may enhance the cake formation, causing increased reversible resistance.

In case of Fenton reaction the precipitation of Fenton reagents and their adsorption to the membrane surface increases the irreversible resistances (causing decreased flux) (Fig. 3).

3.2. Effects of the pre-treatments on the purification efficiencies

After the filtrations were carried out, the purification efficiencies were measured and compared (Fig. 4). The pre-oxidation by itself could lower the COD of the wastewater but only slightly (6-12%), while most of the pollutants were eliminated by membrane filtration.

The highest purification efficiency was observed for the 10-minute-long pre-treatment (72%), and as the duration of the ozone treatment continued to increase, the purification efficiency decreased. For the Fenton reactions, the 0-minute-long Fenton reaction (i.e. practically without any oxidation) was the most effective (70%), which may be due to the coagulation-flocculation effect of the Fenton reagents. Nevertheless, ozone treatment and short-term Fenton reaction achieved the lowest (62.5%) COD-elimination-efficiency requirement (COD<1200 mg/L). Dairy wastewaters that were treated this way could be suitable to be further treated with municipal wastewater, or a second membrane filtration step (nanofiltration or reverse osmosis) could be used to produce recyclable water.

The short-term beneficial effect of the ozone pre-treatment can be explained as a result of micro-flocculation, causing emergence of associates, which can be retained by the membrane. In longer term, the oxidation process destroys these particles, the smaller compounds can easily pass through the membrane. The Fenton reaction has similar (coagulation/flocculation) effect as the coagulation/flocculation effect caused by the presence of the ferrous sulphate ($FeSO_4$) reagent, which was used to carry out the Fenton reaction, resulting in enhanced purification efficiency. However, if we increase the duration of the oxidation processes, then the larger particles can be degraded, but the smaller particles can pass through the membrane, and increase the COD in the permeate thus lowering the purification efficiency (Fig. 4). The smaller particles can also get into the membrane pores, increasing the irreversible resistances.

3.3. Utilizable compounds in the permeate: P and N

Dairy wastewaters usually contain different types of nutrients such as phosphates or ammonia. To reveal if these nutrients can be recovered, the phosphate and ammonia content of the permeate were investigated after long-term ozone (20 min) or Fenton (90 min) pre-treatments.

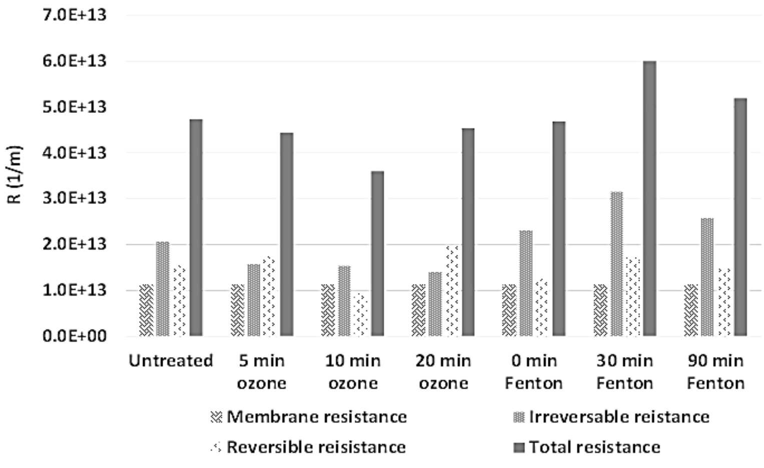
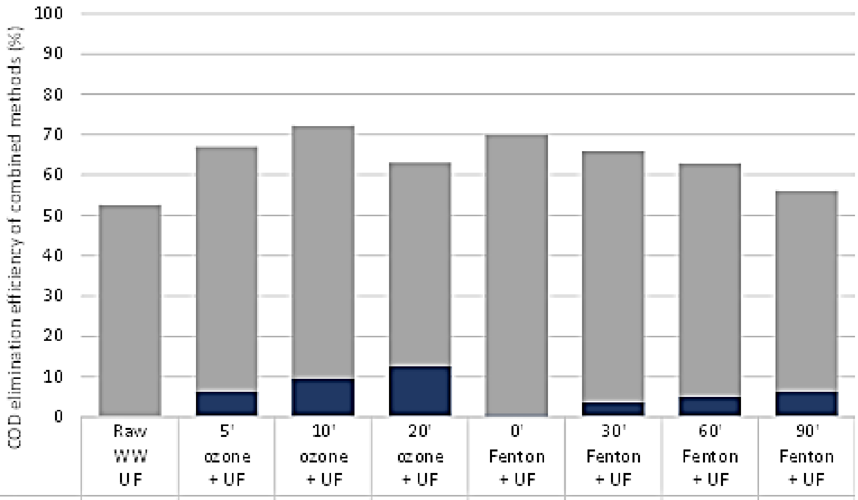


Fig. 3. Filtration resistances of the raw and pre-oxidized (ozone treated and Fenton treated real dairy wastewaters)



	Raw WW UF	5' ozone + UF	10' ozone + UF	20' ozone + UF	0' Fenton + UF	30' Fenton + UF	60' Fenton + UF	90' Fenton + UF
by membrane filtration after pre-treatment	52.55	60.79	62.86	50.60	69.38	62.21	57.89	49.85
by oxidation pre-treatment	0	6.25	9.375	12.5	0.625	3.75	5	6.25

Fig. 4. COD elimination efficiencies achieved by pre-oxidation and by ultrafiltration after pre-oxidation. The whole bars represent the COD elimination efficiencies of combined methods

It was found that the ozone pre-treatment did not significantly affect the phosphate content, while the Fenton pre-treatment decreased the phosphate content radically from 55.3 mg/L to 1 mg/L. Nitrate and nitrite contents of the permeates were also measured, but they were under 0.1 mg/L in every case.

As it was expected, in case of ozone treatment the phosphate ions remain dissolved and can permeate across the membrane, resulting the same phosphate concentration in concentrate and permeate. In case of Fenton reaction, the reaction system is completely different, as significant amount of Fe(III) ions presents, which can form insoluble precipitates or Fe(III)-phosphate complexes with phosphate ions (Lente et al., 2000; Senn et al., 2015). As in our system the Fe is in 3-fold excess to phosphate ions, phosphate ions can be precipitated and then retained by the membrane. The presence of precipitation also may cause the increased irreversible resistances during ultrafiltration of Fenton pre-treated samples (Fig. 3.).

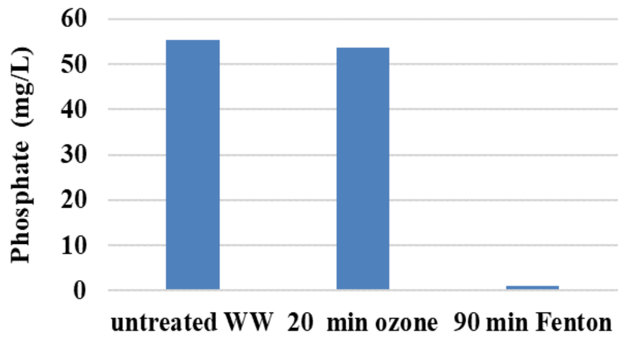
According to the literature, reactions of ozone with aliphatic amino-acids or proteins form nitrate, ammonium ions and other carbonyl and carboxylic by-products; the mechanism and the products depends on the type of reactive oxidation species – the hydroxyl radical pathway results ammonia, while ozone produces nitrate. In the present neutral pH it is unlikely that ammonia formed via OH-radicals; it is possibly formed from ozone via an electron-transfer reactions as proposed by de Vera et al. (2017). In case of Fenton reaction, the main reaction species are hydroxyl radicals, which should lead to ammonium formation. It is proved by the absent of nitrites and nitrates; on the other hand, the presenting colloidal precipitated particles (e.g. Fe(III)-phosphates, Fe-hydroxides, organic colloids etc.) may adsorb a part of the ammonium ions, resulting decreased ammonium concentration ion the permeate after the filtration.

After the filtrations were carried out, the toxicity of the purified wastewaters was also measured. There are only a few investigations in the literature about how the Fenton reaction affects the toxicity, while for ozone this has not been examined at all so far. The toxicity measurements were carried out by using Daphnia magna as test organism (Fig. 6). It was found that in the permeate of the untreated wastewater more than 50% of the subjects died after 48 hours. Generally, the Fenton pre-treatment increased the toxicity to a large extent, presumably as a result of adding the Fenton reagents to the wastewater. After this, however, the Fenton reaction decreased the toxicity, which then again increased over time. The ozone pre-treatment initially also decreased the toxicity, but then increased it over time, probably due to the appearance of the toxic oxidation by-products.

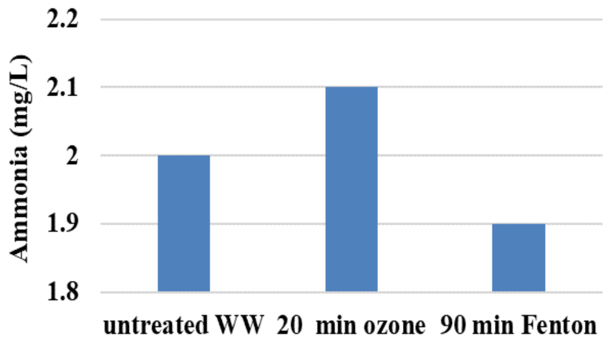
3.4. Utilizable compounds from the concentrate: biogas

After filtration, the concentrate still contains most of the organic content of the wastewater. Because of the high organic content and the lack of toxic materials, it is possible to use the as-treated wastewater for biogas production. To investigate the usability of the concentrate of the pre-treated samples for biogas production, it was mixed with anaerobic sewage sludge, which was used for biogas production before (Beszédes et al., 2009).

During a period of 40 days the pressure was measured in the biogas reactors at a constant temperature of 40 °C. As reference, the municipal sludge (70 cm^3) was used. The untreated concentrate, the ozone- and the Fenton-pre-treated mixture was also inoculated by mixing the samples with the anaerobic sludge (50 cm^3 sample + 20 cm^3 sludge).



(a)



(b)

Fig. 5. Phosphate (a) and ammonia (b) content in the permeate

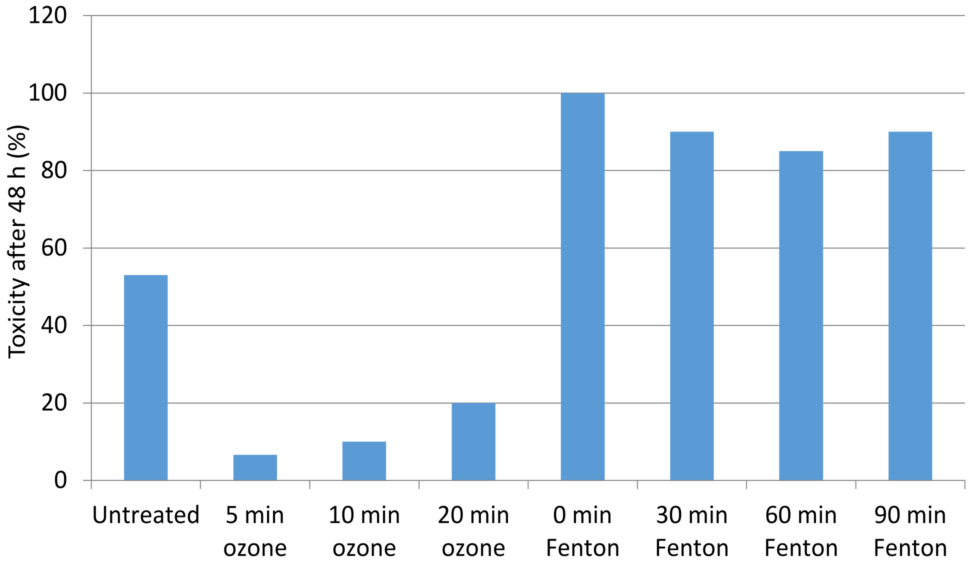


Fig. 6. Measured toxicity values of the purified wastewater

It was found (Fig. 7) that the ozone pre-treatment considerably increased the pressure in the biogas reactor, which means that biogas was constantly being produced during the 40 days. A plausible explanation could be that the oxidation pre-treatments may cause the degradation of the sludge cells, thus the organic matter becomes more accessible to the anaerobic microorganisms (Varga and Szigeti, 2016). The Fenton pre-treatment also increased the biogas production, but it resulted in only a slightly higher pressure compared to the untreated one.

To investigate the energetic usability of the concentrate of the pre-treated samples for biogas production, the methane content of the biogas was also followed (Fig. 8). Biogas can be used to produce energy if the methane content is high enough. It was found that the methane content was high even in the untreated samples, and the pre-treatments further increased it. In the untreated mixture 60% of the biogas was methane. This value increased to 70% after the ozone pre-treatment and to 68% after the Fenton reaction. Taking into consideration the amount of the biogas as well, the ozone pre-treatment was by far the most beneficial pre-treatment method in terms of biogas production, and the methane content was also high enough to use it for energetic purposes.

4. Conclusions

In this work ozonation and the Fenton reaction were used and compared as pre-treatments prior the membrane separation of real dairy wastewaters. Our goal was to investigate their application possibilities for the purification of real dairy wastewaters, and the usability of the biogas produced from the remaining concentrate. The short-term ozone pre-treatment decreased the fouling due to the microflocculation effect caused by the presence of ozone. Surprisingly the Fenton reaction decreased the fluxes and increased the filtration resistances, probably due the precipitated particles. It was also found that the 10-minute-long ozone pre-treatment was the most effective in decreasing the filtration resistances and resulted in the highest purification efficiency, which was more than 70%. This indicated that the COD of the permeate was under 1000 mg/L making it suitable to be treated together with municipal wastewaters.

However, further oxidation pre-treatments (20-min-long ozone and 90-min-long Fenton) were found to be inefficient, because as the large particles decomposed and passed through the membrane pores into the permeate, they resulted in higher COD and therefore lower purification efficiency.

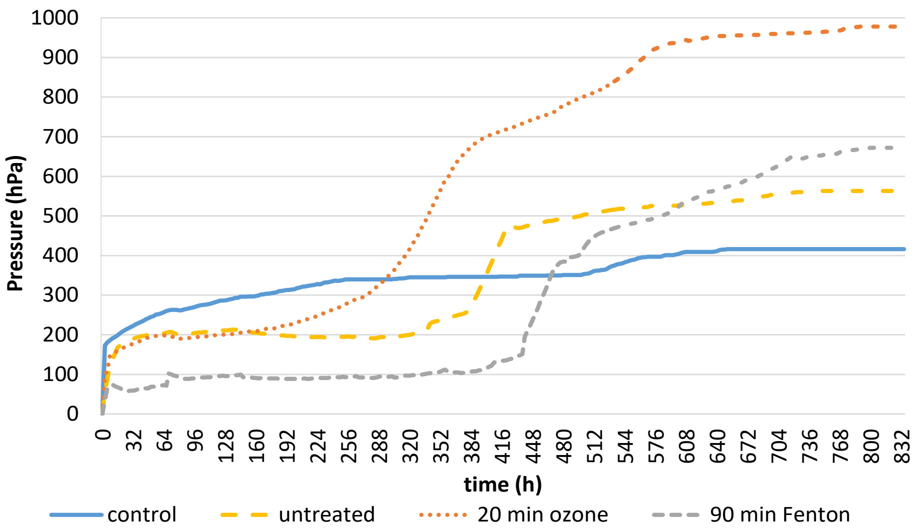


Fig. 7. Biogas production from the wastewater concentrate mixed with sludge

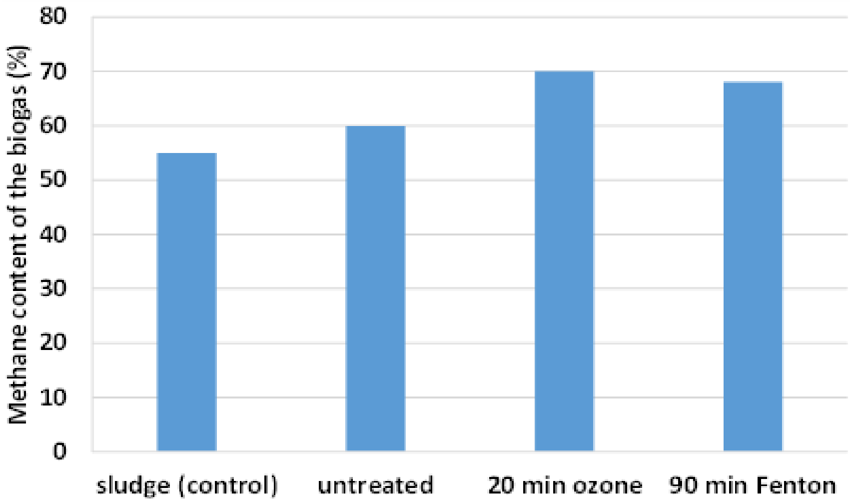


Fig. 8. Methane content of the biogas

Both pre-oxidation pre-treatments increased the biological degradability of the concentrate, and by mixing it with anaerobic sludge it was possible to produce biogas from the filtration leftover. By comparing the two pre-treatments, it was found that during the ozone treatments more biogas was produced, and higher methane content was observed in it (up to 70%), making it possible to use it for energetical purposes.

The nutritient content (phosphates and ammonia) of the wastewaters was also measured. It was found that by the addition of the Fenton reagents the phosphate content reduced greatly, and the ammonia content did not change significantly. In the case of the ozone pre-treatments none of the ammonia or phosphate content changed.

It is important to measure the toxicity during the application of pre-oxidation treatments, because as a result of them by-products can form, which can be toxic for the environment. Accordingly, the toxicity measurements revealed that the Fenton reagents by themselves significantly increased the toxicity of the permeate (from 52% up to 90-100%). At the same time, the ozone treatment reduced the toxicity (from 52% down to 6-20%), so the ozone-generated by-products were less toxic to the environment under our applied experimental conditions. Generally, it can be concluded that the ozone pre-treatment was more advantageous, and could be a promising method for dairy wastewater treatment.

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