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Membrane filtration for valorization of digestate from the anaerobic treatment of distillery stillage

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ABSTRACT

Currently, nutrient-rich digestates generated in anaerobic processing of distillery stillage are mainly used as fertilizers, which is a seasonal application. The objective of this study was to valorize the liquid phase of digestate with ultrafiltration (UF) membranes, depending on their cut-off and pressure. UF (150 kDa) resulted in the chemical oxygen demand (COD) rejection of 89%–93%, independently of the pressure (0.2–0.4 MPa). The pre-treatment with microfiltration (MF) and post-treatment with UF (5 kDa) increased the COD removal to 98%. The rejection of total nitrogen (TN) and total phosphorus (TP) reached 81 and 87%, respectively, in the 3-stage system (MF-UF150 kDa-UF5 kDa). Because permeates were particle-free and had low color and COD concentration, their quality was assessed in terms of suitability for algae production; low COD/N (below 0.7) may support the growth of autotrophic algae. The concentrations of phosphorus and microcomponents (iron and potassium) also indicated the potential of reusing these permeates for algae production. Nutrient-concentrated retentate (about 51 g COD, 13 g TN and 1.3 g TP from 10 L of the feed) can be used as fertilizers. The MF pre-treatment increased permeate flux in UF more than 10 times, which allows for energy saving and thus reduces the costs of digestate valorization.

Keywords: Distillery stillage; Digestate treatment; Membrane filtration; Ceramic membranes

1. Introduction

The management of digestate is one of the most crucial issues that affect the development and operation of biogas plants, including plants that use distillery residues as substrates. In the distillery industry, high volumes of residue (stillage) are produced, up to 15 m^3 per 1 m^3 of pure ethanol produced [1]. This residue is commonly used in methane fermentation for biogas production because of its composition (80,000–140,000 mg COD/L, 40,000–65,000 mg BOD/L, COD – chemical oxygen demand and BOD – biochemical oxygen demand) [2]. However, in addition to biogas, digestate is produced, which is considered to be waste. According to the principles of sustainable management, this nutrient-rich waste can be used as fertilizer or for improving compost quality [3]. However, the phosphorus present in digestate causes eutrophication of water, and the presence of nitrogen may cause nitrate leaching and ammonia emissions into the atmosphere. In addition, the use of digestate as fertilizer is seasonal, and the area near the biogas plant may not be sufficient for managing the entire volume of digestate, while digestate storage and transport increase the costs of plant operation. Another solution for managing this digestate is separating the liquid phase from the solid phase and then managing them separately [4]. This solution would facilitate storage and transport of the solid phase, which could then be used as fertilizer, dried and burnt, or used for recultivating degraded areas.

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However, managing the liquid phase of digestate is a more serious challenge because this fraction has a large volume and contains high concentrations of suspended solids, nitrogen and phosphorus [5]. If the liquid phase is improperly utilized, these pollutants will contaminate the surface and underground waters. Therefore, to reduce the volume of this fraction and concentrate the nutrients in a smaller volume, membrane techniques can be used [6,7]. For example, reverse osmosis (RO) was used to concentrate the effluent from an agricultural biogas plant and decreased the volume by about 25%, increasing the concentrations of total nitrogen (TN) and total phosphorus (TP) 4.2- and 4.4-fold, respectively [8].

In addition to the use of nutrients present in the liquid phase of digestate in agriculture, their use for the industrial cultivation of algae biomass, for example, for energy purposes [9–11] or as a source of bioactive compounds [12], may be a new direction in the utilization of digestate. The production of microalgae consumes water and nutrients, which is more than 20% of the total cultivation costs [13]. Therefore, utilization of the nutrient-rich liquid phase of digestate may reduce the cost of algae production [14].

To provide effluent that would be suitable for algae production, the liquid phase of digestate should not be turbid or contaminated with bacteria, and it should not contain high levels of nutrients [15]. The toxic effects of free ammonia on algae growth depend on the species of algae [15]; therefore, cultivation of algae-resistant to ammonia or dilution of the effluent may solve this problem. For removing turbidity and bacterial contamination, pressure membrane techniques can be used. Drosg et al. [3] used a sequential system (ultrafiltration (UF) and RO) for purifying the liquid phase of digestate. Those authors reported that to obtain permeate with a concentration of ammonium that made it suitable for release to the environment, 3-stage RO was necessary. Similarly, Schulze and Block [16] obtained the following permeate composition after 2-stage RO: 50–60 mg COD/L, 0 mg TS (total solids)/L, 300–320 mg NH_4–N/L, 320–340 mg TN/L and 53 mg TP/L. In addition, Brüß [17] obtained the following permeate composition after 3-stage RO: <5 mg COD/L, 0 mg TS/L, 0 mg NH_4–N/L, 3.5 mg TN/L and <0.05 mg TP/L. Although these studies indicate that RO membranes are most effective for concentrating digestate and separating nutrients, this technique requires much more energy for the operation of pumping systems than low-pressure membrane techniques. It has been reported that UF of digestate can produce permeate suitable for cultivation of *Chlorella* sp. and *Phaeodactylum tricornutum* [18]. With this permeate, both microalgae grew at rates similar to those obtained with the standard synthetic medium. These studies, however, focused on the treatment of digestates from the fermentation of organic wastes other than distillery residues. For this kind of waste, the literature on membrane treatment is very limited. For this reason, in the present study, the low-pressure membrane technique, that is, UF was used to purify the liquid phase of digestate from distillery stillage processing.

The main factor limiting the widespread use of membrane techniques is membrane fouling, which reduces the permeate stream, thus increasing the energy demand and necessitating frequent membrane washing. Fouling is particularly problematic during filtration of the digestate fraction because this fraction contains high concentrations of solids and organic compounds, which are the main causes of membrane fouling [19]. In addition, filtration fluxes are substantially different for digestates from different biogas plants. In the present study, therefore, ceramic membranes were used, which have a highly hydrophilic surface that makes them more resistant to fouling than more common polymer membranes [20]. Due to the possible increase in the use of ceramic membranes in the purification of liquids, it is necessary to provide experimental data documenting the degree of retention of pollutants as well as the susceptibility of ceramic membranes to fouling with compounds that are present in the liquid phase of digestate.

The objectives of the present study were to (i) determine the effect of UF membrane cut-off and transmembrane pressure (TMP) on the treatment of the liquid phase of digestate produced in anaerobic treatment of distillery stillage and on a nutrient balance, (ii) determine whether the permeates have an appropriate composition for microalgae cultivation, (iii) determine the effect of membrane cut-off and TMP on membrane susceptibility to fouling and the hydraulic parameters of permeation, and (iv) determine the effect of digestate pretreatment by microfiltration (MF) on the efficiency and capacity of UF.

2. Materials and methods

2.1. Characteristics of feed

The experiments were conducted with the use of the liquid phase of digestate produced during full-scale anaerobic treatment of distillery stillage. This liquid phase was separated from the solids with a mechanical screw separator. The composition of this feed was as follows: 6,749 ± 885 mg COD/L, 6,711 ± 146 mg TS/L, 1,958 ± 286 mg TN/L and 181 ± 27 mg TP/L. Total suspended solids (TSS) constituted about 75% of the TS.

2.2. Membrane filtration

The liquid phase of digestate was fed to the ceramic membrane installation containing the UF module (length of 300 mm, external diameter of 25 mm, 23 channels inside the membrane, a hydraulic diameter of each channel of 3.5 mm, filtration area of 0.1 m^2, specific area of 680 m^2/m^3, Inside CéRAM, Tami Industries, Germany). In the installation, cross-flow filtration was conducted with an initial feed flow velocity of 16–24 L/min at 21°C± 1°C. During filtration, permeate was taken out of the installation, whereas retentate was circulated back to the process tank. Therefore, this flow velocity was the velocity of both the feed and the retentate. More detailed description of the membranes and the membrane installation can be found in Zielińska and Galik [21].

Seven filtration series were conducted (Table 1). In series 1–3, UF was used with a membrane cut-off of 150 kDa (UF150) at TMPs of 0.2, 0.3 and 0.4 MPa, respectively. To determine the effect of feed pre-treatment on UF performance, in series 4–7, the digestate fraction after MF was the feed for UF. To produce this feed, the liquid phase of digestate was previously filtrated by an MF membrane

Table 1
Organization of the experiment

Series	Process	UF pressure (MPa)
1	UF150	0.2
2	UF150	0.3
3	UF150	0.4
4	MF0.45-UF150	0.2
5	MF0.45-UF150	0.3
6	MF0.45-UF150	0.4
7	MF0.45-UF150-UF5	0.4

with pore sizes of 0.45 μm (MF0.45) at a TMP of 0.3 MPa. Additionally, in series 7, a UF membrane with a cut-off of 5 kDa (UF5) was added as a third stage in the membrane system. In these 2- and 3-stage systems, the permeate from the previous stage was the feed for the next stage.

The installation was not equipped with automatic backwashing, and for this reason, it was operated in a batch mode. For permeation tests during the filtration cycles, the time necessary to obtain 50% permeate recovery was measured in duplicate. Then, the installation was washed in the following sequence: with 2% NaOH solution, with deionized water to obtain neutral pH, with 1% HNO_3 solution, and again with deionized water to obtain neutral pH. Washing was considered complete when 95%–97% of the initial permeation flux of deionized water was recovered.

2.3. Analytical methods and calculations

Feed, permeate and retentate samples were taken for the analysis. Organic compounds (COD), TN, TP, total iron and potassium were determined spectrophotometrically using cuvette tests in a DR 3900 Hach Lange spectrophotometer (Germany). Ammonium nitrogen, TS and TSS concentrations were determined according to Hermanowicz et al. [22]. The pH was measured with an HI 2210 pH meter (Hanna Instruments, USA). Color was measured with a Rayleigh VIS-7220G spectrophotometer (China).

Based on the results of the permeation tests and chemical analyses, the permeate flux (J_V), the permeate recovery (Y), the volumetric concentration factor, the total membrane resistance (R_m), the normalized flux (α) and the rejection coefficients (R) for pollutants were calculated as in Zielińska and Galik [21]. Based on the concentrations of COD, TN and TP in the feed, permeates and retentates, a nutrient balance was carried out.

For statistical analysis, STATISTICA 13.1 (StatSoft) was used, with $p \le 0.05$ defined as significant. After checking normality with the Shapiro–Wilk test and homogeneity of variance with Levene's test, analysis of variance followed by Tukey's HSD test was used to examine the differences between experimental series.

3. Results and discussion

3.1. Efficiency of pollutant removal in membrane filtration

Adding stages to the treatment process slightly improved the overall efficiency of COD removal. When the liquid phase of digestate was treated with UF alone, the COD rejection efficiency was 89%–93%, independently of the TMP (Fig. 1a). This result is similar to those reported by other authors who obtained about 85% [23] or 91.7% [24] of COD removal with UF of digestate from a biogas plant fed with organic waste. In the present study, after pre-treatment with the use of MF, the concentration of COD in the UF feed was 546 ± 20 mg/L, and the efficiency of COD removal in UF ranged from 33% at 0.2 MPa to 73% at 0.3 MPa. COD removal efficiency was substantially lower in UF after MF than in UF alone because in the first stage of the MF-UF system TSS were removed to levels below the limit of detection. In the permeate from MF, there were no suspended organic solids; therefore, in UF after MF, only dispersed colloids and high-molecular-weight (MW) organic compounds were removed. Total COD removal in this 2-stage system was slightly higher (94%–98%, independently of the TMP) than that in UF alone. The fact that MF pretreatment did not substantially increase total COD removal in the system indicates that organic compounds in the liquid phase of digestate were present mainly in the form of high MW compounds, which were effectively separated in UF with a cut-off of 150 kDa. The use of UF with a membrane cut-off of 5 kDa for the post-treatment of permeate from MF-UF150 improved the total removal of organic compounds to above 98%. In the UF permeates, the remaining COD could result from the presence of low-MW organic substances such as proteins, saccharides and humic substances [25].

In UF, independently of the TMP, the rejection of TS was 70%–77% (Fig. 1b). After MF pre-treatment, 25%–40% of TS were rejected in UF, which resulted in a total rejection of 82%–86%. Because TS include dissolved and undissolved compounds in wastewater, the total removal of TS in the 3-stage system that included a membrane with a cut-off of 5 kDa reached 90%. In addition to proteins, saccharides, and humic substances, the UF permeates contained salts, which was the reason for the remaining TS presence [25].

The efficiency of TN rejection in UF alone increased from 44% at 0.2 MPa to 58% at 0.4 MPa (Fig. 1c). In general, the increase in TMP accelerates water transport through the membrane, which could have lowered the concentration of TN in the permeate in highest TMP. However, this rule was not observed for COD and TS removal. In UF, TN removal was possible because organic nitrogen was retained by membrane as a component of the biomass. Additionally, some organic nitrogen could have been adsorbed on organic matter particles that were retained on the membrane. Similar results were obtained with MF pre-treatment, in which about 50% of TN was retained along with the retention of solids (data not shown). Therefore, because MF removed most suspended solids, the efficiency of UF in the second stage was substantially lower than that of UF alone. TN retention decreased from 41% to 7% as TMP was increased from 0.2 to 0.4 MPa. In total, 59 to 74% of TN was removed in the 2-stage system; however, the 2-stage system removed more TN than the 1-stage system only at TMPs of 0.2 and 0.3 MPa. With the 3-stage system, TN removal efficiency increased to above 81%.

Similar to TN removal, increasing TMP from 0.2 to 0.4 MPa in UF alone increased the efficiency of TP removal from 68% to 78% (Fig. 1d). A possible reason for phosphorus

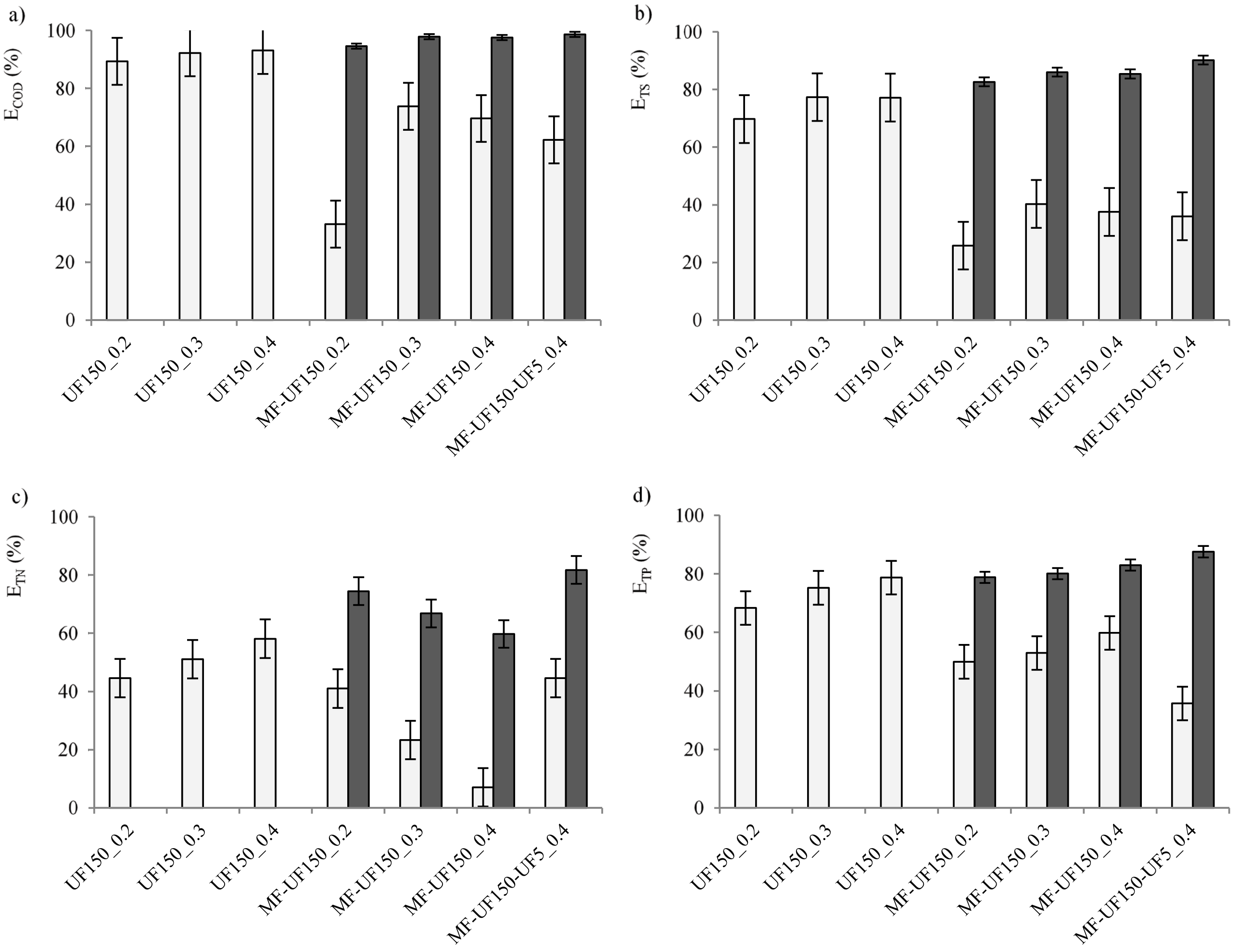

Fig. 1. Rejection efficiency of COD (a), TS (b), TN (c) and TP (d) in experimental series; light bars indicate rejection efficiency in the sole or last stage of the system, dark bars indicate cumulated rejection efficiency in 2- or 3-stage system.

rejection in UF was that phosphorus is essentially particulate as a result of its biological assimilation by microorganisms, and thus incorporated into the solid fraction. This solid fraction was then retained by UF. TP removal was higher in the 2-stage system, ranging from 78% at 0.2 MPa to 83% at 0.4 MPa. Finally, its removal equaled 87% in the 3-stage system.

3.2. Characteristics of permeates

Although there is an increasing trend of treating wastewater in a manner that produces effluent clean enough for use in different applications, the specific requirements given by the US Environmental Protection Agency [26] for so-called reused water concern only municipal wastewater. The requirements for other types of wastewater depend on the site-specific end-use. One such end-use could be the cultivation of microalgal biomass. This process currently plays a key role in the production of valuable organic compounds for energetic purposes, such as the production of biodiesel or biomethane [27]. From a practical point of view, it is important to achieve high productivity of algal biomass, its high quality and the lowest production costs. However, algae cultivation is expensive because it consumes large amounts of nutrients. Most microalgae cultivations (on a laboratory scale and in commercial production) are conducted using synthetic sources of nutrients; the cost of nutrient addition accounts for half the costs of cultivation [28]. To minimize these costs by increasing maximal specific growth rates and algal biomass productivity, the modifications of the medium composition and particularly the use of different waste effluents for nutrient reuse is an interesting approach and should be investigated. Therefore, the quality of the permeates produced in the present study (Table 2) was assessed in terms of their suitability as a cultivation medium in algae production.

Independently of membrane used and TMP, all permeates were particle-free and the turbidity was below the detection limit. The color was lowest in the permeates from MF-UF150 (about 0.526) and MF-UF150-UF5 (0.505 ± 0.020). These characteristics provide the major evidence that the permeates could be used for algae production, as they

Table 2
Characteristics of permeates from single- and multi-stage membrane systems

Process	COD (mg/L)	TS (mg/L)	TN (mg/L)	TP (mg/L)	Color (–)	Fe (mg/L)	K (mg/L)
UF150_0.2	719 ± 35	2,029 ± 101	1,085 ± 54	57 ± 5	0.798 ± 0.04	5.2 ± 0.3	1,795 ± 88
UF150_0.3	523 ± 26	1,519 ± 75	958 ± 47	45 ± 3	0.781 ± 0.03	2.2 ± 0.1	1,988 ± 92
UF150_0.4	468 ± 23	1,531 ± 76	820 ± 40	39 ± 3	0.639 ± 0.03	1.6 ± 0.1	790 ± 33
MF0.45-UF150_0.2	365 ± 18	1,164 ± 58	500 ± 25	38 ± 3	0.549 ± 0.03	0.4 ± 0.04	1,190 ± 62
MF0.45-UF150_0.3	143 ± 7	937 ± 46	650 ± 31	36 ± 2	0.513 ± 0.02	0.4 ± 0.03	958 ± 54
MF0.45-UF150_0.4	166 ± 8	980 ± 49	788 ± 39	31 ± 2	0.516 ± 0.02	0.5 ± 0.05	660 ± 28
MF0.45-UF150-UF5_0.4	91 ± 8	657 ± 32	358 ± 17	23 ± 2	0.505 ± 0.02	0.6 ± 0.03	210 ± 12

would not block sunlight, which is a key condition for algal growth.

After filtration of the liquid phase of digestate in UF alone, the COD concentrations in permeates were 468–719 mg/L. With the 2-stage system, the COD concentrations decreased to below 150 mg/L. With the 3-stage system, the concentrations were the lowest, about 91 mg/L, which even fulfilled effluent requirements of wastewater treatment plants of size up to 14,999 people equivalent. These organic compounds can be used by microalgae as a source of carbon and/or energy, as indicated by the fact that, depending on the species and cultivation of microalgae, the carbon content in the biomass is between 17.5% and 65.0% of dry weight [29]. The amount of organic compounds available for algal growth determines strongly the growth conditions (autotrophic or mixotrophic) and affect the final utilization of harvested algae. For example, in the growth medium for *Platymonas subcordiformis* cultivated for further hydrogen production, organic compounds were present in the concentration of about 55 mg/L and were increased to about 11 g/L by addition of glucose [30]. This increase in COD availability did not influence biomass production but it significantly increased biogas production.

In the permeates, the lowest TN concentrations were recorded after the 2-stage (500–788 mg/L) and 3-stage treatments (358 ± 17 mg/L). Nitrogen is an essential component of organic structures such as nucleic acids, amino acids and pigments like chlorophylls, and nitrogen content in microalgal biomass ranges from 1% to 14% of dry weight [29]. In the present study, UF did not affect the concentration of ammonium; ammonium nitrogen accounted for 38%–55% of TN in the permeates and the rest was organic nitrogen. The optimum amount of nitrogen in the cultivation medium is specific for the particular groups of algae and should be defined experimentally. In different digestates used as the growth media, an increase in the initial concentration of ammonium from 40 to 160 mg/L significantly reduced the growth of *Scenedesmus* sp. [31]. According to Collos and Harrison [15], ammonium was tolerated by *Chlorophyceae*, *Cyanophyceae*, *Prymnesiophyceae*, *Diatomophyceae*, *Raphidophyceae*, and *Dinophyceae* at concentrations of 39,000; 13,000; 2,300; 3,600; 2,500; and 1,200 μM, respectively. NH_3 is particularly toxic when the pH is above 9, but in those conditions, the toxic effect was due to the ammonium ion, not ammonia. In the present study, the pH of all permeates was 8.5 ± 0.3, which means that, without any pH adjustment, ammonium would be available for assimilation by microalgae cells, and not present in toxic form of ammonia. In addition, the pH of permeates obtained in the present study indicates alkaline conditions, which are favorable for the growth of some microalgae, like, for example, *Spirulina* sp. [32].

For the efficiency of algal biomass production, not so much the individual concentrations of organics and nitrogen are important, but the proportion between them. Barros et al. [33] reported that the C/N ratio consumed is an important parameter to control the growth of *Chlorella vulgaris* and should be compensated by the C/N ratio in the growth medium. The authors indicated the average C/N ratio consumed as 7.47. They postulated a careful control of this parameter because it can affect the shift of the algal metabolism from the production of proteins to the accumulation of lipids and starch. In the present study, the COD/N ratio in the permeates were much lower (up to 0.7); however, it does not eliminate using these permeates as feed medium, but it may affect the selection of some species. For cultivation of *Chlorella* sp. aimed at biogas production, anaerobically digested effluents of dairy wastewater, municipal wastewater sludge, maize silage and swine slurry, and of cattle manure were used as waste sources of the medium [34]. After dilution of these wastes with deionized water, the medium contained about 197 mg TN/L, 14 mg TP/L and COD/N of 1.5–7.0. The composition of the medium significantly affected the C/N ratio in obtained algal biomass, which subsequently affected the biogas yield. The highest C/N ratio in the biomass and methane production was observed when *Chlorella* sp. was cultivated with anaerobically digested effluent of municipal wastewater sludge in which the COD/N ratio was the lowest, 1.5. These almost autotrophic conditions favored mainly the growth of algae, whereas at higher COD/N ratios heterotrophic bacteria developed more intensively.

Phosphorus is a crucial element in maintaining high production rates of microalgae, because their growth requires phosphorus for building membrane phospholipids and nucleic acids; its content in biomass ranges from 0.05% to 3.3% [29]. The major form in which algae acquire phosphorus is inorganic phosphate, $H_2PO_4^-$ or HPO_4^{2-} [35]. In the present study, the concentrations of TP in the permeates decreased as the pressure was increased and additional purification stages were introduced. In the permeate of the 3-stage system, the TP was present in concentrations of 23 ± 2 mg/L, which means that it could be useful as a substrate for the growth of valuable organisms. This option should be particularly considered because phosphorus reserves are non-renewable and may be depleted in the future [36]. However, the study on the effect of TP concentration on the growth of particular microalgae should be conducted to avoid disturbances in growth because of phosphorus limitations. In different digestates used as the growth media for the cultivation of *Scenedesmus* sp., TP was present in concentrations of 4.3–20.3 mg/L and was reported to be a limiting factor for the growth of this organism [31]. Thus, phosphorus supplementation should be sometimes considered when using digestate as the medium.

In addition to organic compounds and nutrients, algae also require elements like iron and potassium for effective growth. Microalgae require iron for enzymatic processes, such as oxygen metabolism and synthesis of DNA, RNA and chlorophyll [37], but iron is needed in trace amounts and present only as an impurity in the growth medium may fulfill the requirements [32]. Potassium is a cofactor for many enzymes, involved in protein synthesis and osmotic regulation, required for photosynthesis and respiration [32,38]; potassium content in microalgae biomass ranges between 1.2% and 1.5% [29]. In the present study, during the purification of the liquid phase of digestate in UF alone, the iron concentrations in the permeates were 1.6–5.2 mg/L, whereas in the 2-stage and 3-stage systems, they were about 0.5 mg/L. Potassium concentrations in the permeates ranged from 1,988 ± 92 mg/L in UF alone to 210 ± 12 mg/L in the 3-stage system. Raoof et al. [32] confirmed the necessity of using these elements in the growth medium for producing a protein-rich culture of *Spirulina*; they used K_2HPO_4 (0.5 g/L), K_2SO_4 (1 g/L), $FeSO_4{\cdot}7H_2O$ (0.01 g/L) and obtained 0.345 mg proteins/mL. Dudek et al. [30] used about 0.2 mg Fe/L for the successful cultivation of *Platymonas subcordiformis* (algae with the ability to produce hydrogen) for the purpose of biogas production.

3.3. Nutrient balance; characteristics of retentates and suggestions for their use

In Table 3, the nutrient balance was given, calculated for a portion of the feed of 10 L that was subjected to membrane filtration. For estimation of this balance, average values for each technological system at all used TMPs were calculated. To quantify the accuracy of the balance, a proportion between outlets (permeate + retentate) and inlets (feed) was calculated. This proportion was 0.76–0.79 for COD, 0.79–0.84 for TN and 0.80–0.83 for TP. The proportions have not amounted to 1, which indicates that some amounts of COD, TN and TP from the feed were not found in retentates and the loadings in the retentates were smaller than it should have been expected from the balance. This inconsistency resulted from the fact that some amounts of pollutants adsorbed on the membrane surface or in its pores. It was 21%–25% of COD, 20%–22% of TN and 19%–21% of TP. This indicates that simple size exclusion was supported by the adsorption of pollutants by the membrane. The percent of adsorption was not influenced by the TMP.

Apart from offering the advantage of producing reusable permeate, in the investigated systems, concentrated nutrient-rich retentate was produced as an end-product, in which high concentrations of nutrients were achieved in a volume twice less than the volume of the unprocessed liquid phase of digestate. The cumulated pollutant loadings in the retentates were 48.5–53.0 g COD, 11.8–14.0 g TN and 1.3 g TP per cycle of filtration of 10 L of the feed. Studies that investigate retentate utilization are scarce. Retentate management can involve its recirculation to a biogas plant where it serves as a substrate for fermentation. This is an especially attractive option because, although the residual organic matter in the digestate is difficult to biodegrade, the high pressure of the membrane process disrupts the particles, increasing their biodegradability. Additionally, the nutrient-rich retentate can be used as fertilizer; in this case, the nitrogen and phosphorus mass introduced into the soil must be controlled [39]. In addition, retentate can be thermochemically transformed; thermal drying decreases retentate volume and dried retentate can be used as an organic fertilizer or biofuel [40]. Pyrolysis allows obtaining solid char, pyrolytic oil, and gas (containing H_2, CH_4, CO, CO_2 and N_2); produced pyrolytic oil can substitute diesel fuel due to very similar properties and heating value [41]. In addition, literature gives examples of the recovery of struvite [42] or nitrogen compounds [43] from retentates.

3.4. Hydraulic capacity of membrane systems

The changes in permeate flow (J_V) over time that were determined based on permeation tests are depicted in Fig. 2, and the average values of J_V are given in Table 4. Changes in J_V over time indicate a gradual decrease in the permeate flux as a result of progressive blockage of membranes by impurities. In most cases after the start of filtration in the present study, the permeation rate dropped sharply, after which membrane permeability remained at a constant level. After 50% of permeate was recovered, the permeation test was completed and the membranes were washed. In UF alone (Fig. 2a), the initial J_V was about 37 L/(m^2 h), independently of the TMP. At 0.2 MPa, the decrease in permeate flow due to fouling was highest; under these conditions, 50% of permeate was recovered after 2.5 h of

Table 3
Balance of COD, TN and TP in the membrane systems

Process	COD (g/10 L)			TN (g/10 L)			TP (g/10 L)		
	Feed	Permeate	Retentate	Feed	Permeate	Retentate	Feed	Permeate	Retentate
UF150	67.5	2.8	48.5	19.6	4.8	11.8	1.8	0.2	1.3
MF0.45-UF150	67.5	1.0	51.2	19.6	2.9	13.2	1.8	0.2	1.3
MF0.45-UF150-UF5	67.5	0.4	53.0	19.6	1.6	14.0	1.8	0.1	1.3

filtration. An increase in pressure is one method of improving flux; hence, at higher TMPs, the time for 50% permeate recovery was shortened to 1.4–1.7 h. Waeger et al. [23] observed UF permeate fluxes between 20 and 50 L/(m^2 h) for digestate from an organic waste biogas plant (TMP of 0.1 MPa). In the present study, UF alone gave the fluxes between 24.7 and 36.5 L/(m^2 h), at TMPs of 0.2–0.4 MPa. Similar values of the flux at much higher TMPs could have resulted from the fact of different feedstock for digestate production and operational mode of the membrane installation. In the study of Waeger et al. [23], permeate was totally recirculated to the system, whereas in the present study, permeate was yielded from the system and the digestate circulating in the installation became continuously concentrated.

Table 4
Average values of parameters that characterize membrane performance and capacity

Process	J_V (L/(m^2 h))	α (–)	R_m ((MPa s)/m)
UF150_0.2	24.7	0.027	29,149
UF150_0.3	31.2	0.023	34,615
UF150_0.4	36.5	0.020	39,452
MF-UF150_0.2	242.7	0.270	2,966
MF-UF150_0.3	328.0	0.243	3,292
MF-UF150_0.4	442.0	0.246	3,257
MF-UF150-UF5_0.4	71.3	0.223	20,196

To minimize organic fouling, UF requires high cross-flow velocities, high TMP, thus high operating cost. Therefore, the use of MF as a pre-treatment was an effective solution. This resulted in much higher permeate flux in UF, which equals energy savings and decreases the overall cost of the valorization of distillery stillage. With a permeate yield of 50%, an average UF permeate flux of about 330 L/(m^2 h) could be achieved (Table 4). In MF, most of the solids had been retained. As a result, the initial J_V in UF ranged from 367 L/(m^2 h) to as high as 514 L/(m^2 h) at 0.4 MPa (Fig. 2b). Compared to UF alone, the initial J_V in UF as the second stage was 10 times higher at 0.2 MPa, 11.5 times higher at 0.3 MPa, and 13.5 times higher at 0.4 MPa. As in the experiments with UF alone, the decline in permeate flow was substantially higher at 0.2 MPa, and as a result, 50% of permeate was recovered in 0.7 h. At both 0.3 and 0.4 MPa in the 2-stage systems, 50% of permeate was recovered after 0.2 h. These 2-stage membrane systems were the most effective in terms of membrane capacity. In UF at 5 kDa as a third step in the membrane system, the initial J_V was 128 L/(m^2 h), and 50% permeate recovery was achieved after 2.75 h (Fig. 2c). Unexpectedly, the initial J_V in the final stage of the 3-stage system was lower than that in the 2-stage system, indicating that compounds present in permeate after UF 150 kDa blocked the membrane with a cut-off of 5 kDa.

Apart from a decrease of permeate flow in time, the ratio between permeate flow and deionized water

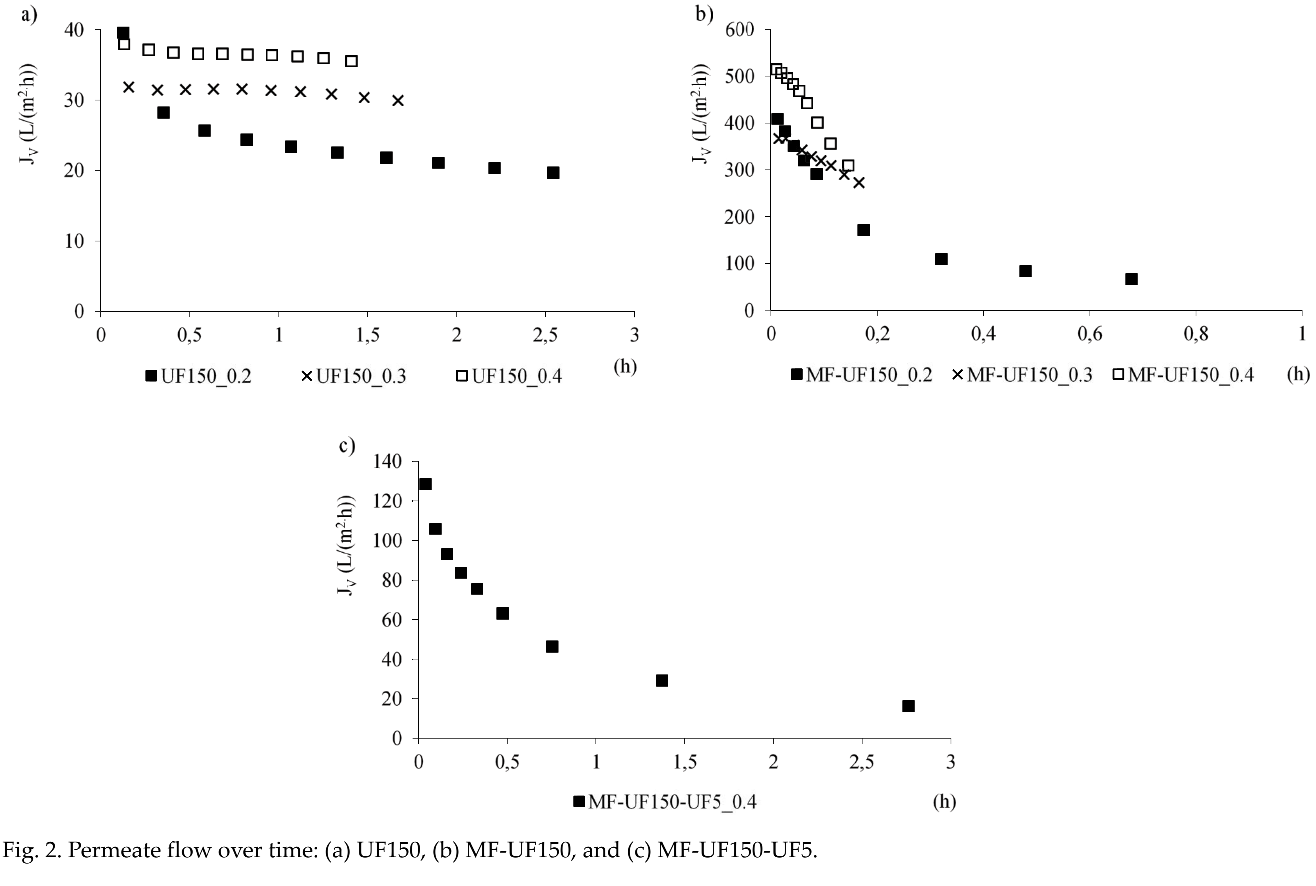

Fig. 2. Permeate flow over time: (a) UF150, (b) MF-UF150, and (c) MF-UF150-UF5.

flow (α) when reaches values below 1 is another indicator of membrane fouling. Significantly lowest values of α in UF alone confirms the highest susceptibility of this membrane in a 1-stage system to fouling (Table 4). In addition, the values of R_m were the highest under these conditions. Although membrane blocking is caused mainly by colloids and soluble organic molecules of sizes 0.45–0.026 µm [44], fouling is reported to be connected rather with the ratio between pore size of the membrane and sizes of particles in the feed. In this case, when feed particles were bigger than membrane pores, these particles were retained on the membrane surface. Although the membrane capacity was the lowest in UF alone, the blocking of this membrane positively affected the permeate quality. Blocking with impurities causes a decrease in the nominal diameter of membrane pores; a new effective diameter leads to the retention of molecules smaller than would appear from the limit cut-off of the membrane [45]. In UF alone, the rejection of COD was as high as 89%–93%. In UF in a 2-stage system, the lowest fouling susceptibility was observed, as can be visible by the highest α and also the lowest R_m. This not intense fouling resulted in the fact that this 2-stage system only slightly improved total COD removal to 94%–98%.

4. Conclusions

The results contribute to the development of methods of valorization of the liquid phase of digestate after anaerobic processing of distillery stillage with the use of low-pressure membrane filtration. The membrane installation produced permeates that may be discharged or reused for algae cultivation due to lack of turbidity, low color and appropriate COD/N ratio and concentration of microcomponents, and nutrient-rich retentates that may be used as fertilizer. Although the use of MF for digestate pre-treatment only slightly increased the efficiency of rejection, it increased UF permeate flux more than 10 times, thus saving energy and substantially improving the economy of the process.

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