Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749178

51 (2013) 3325–3334
April

Taylor & Francis
Taylor & Francis Group

Application of membrane processes for distillery wastewater purification—a review

Jelena M. Prodanović*, Vesna M. Vasić

Faculty of Technology, University of Novi Sad, Blvd. Cara Lazara 1, 21000 Novi Sad, Republic of Serbia
Tel. +381 21 485 3813; Fax: +381 21 450 413; email: jejap@uns.ac.rs

Received 1 December 2011; Accepted 10 September 2012

ABSTRACT

Worldwide environment regulatory authorities are becoming more and more stringent in setting norms for discharge of wastewaters from industries. Distillery wastewaters are highly polluted and their pollution potential is one of the most critical environmental issues of today. For these reasons, distillery industries are forced to look for more effective technologies for wastewater treatment. In recent years, membrane processes have been widely used for various applications, especially for wastewater treatment. The usage of membrane technologies is reflected in high removal efficiency, optimal costs and simple handling with devices. This review presents these membrane processes in the sense of their application on distillery wastewater purification.

Keywords: Membrane filtration; Bioethanol; Distillery spent wash; Wastewater treatment

1. Introduction

Under the influence of several factors, such as the increasing demand for limited non-renewable energy resources, fast exhausting of reserves of these resources, the rising oil prices and concern about greenhouse gasses, the interest in biofuels has been increasing worldwide in recent decades. Bioethanol is the most employed liquid biofuel and as a clean and renewable combustible, it is considered as a good alternative for oil replacement [1–4].

Currently, the conventional feedstocks for bioethanol production are sugar-based (mainly sugarcane, sugar beet and sweet sorghum) and starch-based feedstocks (mainly wheat, corn and cassava) [5,6]. Some intermediate products from sugar production can be used for fermentative bioethanol production, and these are: extraction juice, thin juice and thick juice. However, the relatively high market price of sugar limits a direct conversion of these juices to ethanol. Instead, ethanol is often produced from molasses, a by-product of sugar production from sugar beet and sugarcane (remains after concentration and precipitation of sugar from juice). In recent years, in addition to these feedstocks based on sugar and starch, a lot of effort has been invested worldwide in the investigations of lignocellulosic biomass (woody material [7], straws [8,9], agricultural waste [10] and crop residues [11]) as a raw material for bioethanol production. A disadvantage of this type of feedstock is the fact that it requires a pretreatment in order to reduce cellulose crystallinity and improve the digestibility of the biomass, so that the fermentable sugars can be released from polysaccharides present in lignocellulosic materials (cellulose and hemicellulose) in the

---

*Corresponding author.

step of hydrolysis. For the pretreatment, several physical, physico-chemical, chemical and biological processes have been developed [6].

After fermentation, ethanol is isolated from the fermented mash by distillation. The liquid residue of the fermented mash is termed spent wash, distillery wastewater or stillage. The production and characteristics of spent wash are dependent on raw materials used and the bioethanol production technology. Distillery effluent is approximately 8–20 times greater than the volume of the ethanol produced. Distillery wastewaters are highly polluted—they have very high biological oxygen demand (BOD), chemical oxygen demand (COD) and high BOD/COD ratio. They also contain high amounts of inorganic substances such as potassium (sugar-based stillages), phosphates, nitrogen, calcium and sulphates [12,13].

As can be seen from the paper of Krzywonos et al. [14], starch-based stillages have high organic matter content, so they should not be discharged directly to the sewage system or into a watercourse or soil. The COD of starch-based stillages ranges from 12.1 g O_2/L to 122.3 g O_2/L [14]. They contain total and phosphate phosphorus, as well as the large amounts of total nitrogen (TN) that can be explained by the high protein proportion in the feedstock from which the stillage comes [15].

Distillery stillage from starch-based feedstock contains many components characterised by a high nutritive value—they contain vitamins (with large amounts of those classified as group B), proteins rich in exogenous amino acids and mineral components (Table 1) [14]. Thus, it could be a benefit if these components are isolated during the process of stillage purification.

Table 1
Group B vitamins (mg/kg dm) in potato stillage and rye stillage, and mineral compounds (g/kg dm) in barley and wheat stillage [14]

Vitamins of group B	Potato stillage	Rye stillage
Vitamin B_1	7.8	15
Vitamin B_2	18.6	14.4
Vitamin B_6	18.8	4.0
Vitamin B_{12}	0.0088	0.118
Biotin	0.014	0.56
Nicotinic acid	212	54.9
Pantotenic acid	71.2	60.0
Folic acid	0.78	2.4
Mineral compounds	Barley stillage	Wheat stillage
Ca	5.3	4.2
P	11.3	12.1
Mg	5.4	5.9
K	0.0016	0.0016
Mn	0.0522	0.1101
Na	0.0006	0.0002
Fe	0.4932	0.4191
Cu	0.0054	0.0057

Upon comparing the proportions of particular mineral compounds in barley and wheat stillage, it can be seen that barley stillage contains more calcium, iron and sodium than wheat-based stillage. Chemical composition of dry matter content of stillage from starch-based feedstock is given in Table 2. As can be seen from this table, starch-based stillages can be considered valuable fodder. Unprocessed warm stillage has the highest feeding value, but it cannot be stored over a longer period of time because of its tendency towards souring and mould growth [14]. This fact presents a problem since the animals should be fed shortly after the stillage is produced. Also, the utilisation of unprocessed stillage as an animal feed is cost-effective only if the distillery is integrated in the animal farm or the farm is in the close proximity of the distillery, since the transport of the stillage over long distances is expensive because of the high water content. Above-mentioned facts lead to the conclusion that stillage must be processed. Another method of utilizing stillage is recirculation of liquid part of the stillage, which also requires previous stillage processing in order to separate solids and to decrease or, if possible, remove compounds that inhibit the activity of the yeast cells.

A summary of stillage characterisation for beet molasses, cane juice, cane molasses and cellulosic feedstocks is given in Table 3, and characteristics of stillages obtained after bioethanol production on different substrates (sugar beet extraction juice, thin juice, thick juice and molasses) are presented in Table 4.

Based on presented data (Table 3), it is obvious that beet and cane molasses wastewaters exhibit the highest levels of COD, BOD, COD/BOD ratio, phosphorous, potassium and sulphates, while cane juice wastewater demonstrates the lowest levels of COD and BOD. The explanation is that evaporation of cane and beet juice and sugar crystallisation increases the content of non-fermentable organics which remain in molasses and in the stillage after fermentation. High levels of sulphates are a result of sulfiting process applied in sugar production. Data shown in Table 4, obtained from Prodanović et al. [16] for different stillages, are similar to that from Table 3. Organic load of beet molasses wastewater is very high, with COD of 126,170 mg O_2/L and COD/BOD of 5.3. TN content is also very high (several times higher than in other stillages).

The main low molecular weight organics of distillery wastewaters are lactic and acetic acid, glycerol,

Table 2
Chemical composition of dry matter content for starch stillage of choice (%) [14]

Stillage	Dry matter	Crude protein	Fat	Crude fibre	Sugars	Starch	Ash
Grain sorghum	5.8	1.7	nd	1.51	2.6	1.01	3.77
Barley	5.97	2.21	0.76	2.35	2.14	0.04	0.58
Maize	6.2	1.3	1.3	0.1[a]	2.8	0.5	0.8
Maize	3.7	1.44	nd	1.81	0.97	0.56	0.27
Maize	7.5	2.3	nd	nd	0.5	nd	2.1
Potato	6.0	1.45	0.05	0.7	3.1	nd	0.7
Wheat	8.4	3.8	1.14	2.86	2.67	0.185	0.7
Wheat	12	3.8	2.3	0.12	6	nd	0.156

Notes: nd—no data available.

[a] Acid detergent fibre.

Table 3
The summary of stillage characterisation for beet molasses, cane juice, cane molasses and cellulosic feedstocks [15]

Feedstock		COD (g/L)	BOD (g/L)	COD/ BOD	N (total) (mg/L)	P (total) (mg/L)	K (mg/L)	Total S (as SO_4) (mg/L)	pH
Beet molasses	Average	91.1	44.9	1.95	3,569	163	10,030	3,716	5.35
	SD	38.9	21.7	0.21	2,694	66	6,322	2,015	1.02
	n	5	3	3	5	3	2	4	4
Cane juice	Average	30.4	16.7	1.96	628	130	1,952	1,356	4.04
	SD	8.2	3.4	0.35	316	110	1,151	1,396	0.49
	n	6	5	4	6	6	5	5	7
Cane molasses	Average	84.9	39.0	2.49	1,229	187	5,124	3,478	4.46
	SD	30.6	10.8	0.57	639	350	3,102	2,517	0.35
	n	22	19	16	20	17	12	16	25
Cellulosics feedstock	Average	61.3	27.6	2.49	2,787	28	39	651	5.35
	SD	40.0	15.2	0.54	4,554	30	nd	122	0.53
	n	15	11	10	8	5	1	6	7

Notes: nd—no data; SD—standard deviation; *n*—number of literature values used.

Table 4
Results of analysis of wastewaters obtained after bioethanol production on different substrates [16]

	EJW[a]	TNJW[b]	TKJW[c]	MW[d]
Total solids (mg/L)	34,543	28,258	32,132	109,078
Fixed solids (mg/L)	5,052	3,994	4,140	26,946
Volatile solids (mg/L)	29,491	24,264	27,992	82,132
% of organic dry matter	85.37	85.86	87.11	75.30
TN (mg/L)	1,326	1,015	983	5,675
Settleable matter (ml/L)	31.7	8.5	2.1	nd*
COD (mg O_2/L)	66,850	60,730	96,960	126,170
BOD_5 (mg O_2/L)	41,000	12,000	26,700	23,800
$(BOD_5/COD) \times 100$ (%)	61.33	19.76	27.54	18.86
Permanganate demand (mg $KMnO_4$/L)	53,190	37,800	51,510	92,900
pH	4.23	4.40	4.24	5.40
SS (mg/L)	12,550	8,698	9,215	10,164

*Not determined.

[a] EJW—sugar beet extraction juice wastewater.

[b] TNJW—sugar beet thin juice wastewater.

[c] TKJW—sugar beet thick juice wastewater.

[d] MW—sugar beet molasses wastewater.

ethanol, lactose, glucose, arabinitol, ribitol and trace amounts of amino acids [15]. Heavy metals (chromium, copper, nickel and zinc) can be detected in distillery wastewaters, too [15].

Compared to other distillery wastewaters, molasses spent wash is more polluted and its treatment is more complicated, since it contains dark brown polymers called melanoidins (formed in Maillard reaction of sugars with proteins), which are hardly degraded in conventional treatment processes. They are toxic to aquatic organisms [17] and many micro-organisms [15,18]. Other components that contribute to the colour of the effluent are phenolics (tannic and humic acids), caramels from overheated sugars and furfurals from acid hydrolysis [19]. The highly coloured compounds of the distillery wastewater block out sunlight penetration in rivers, lakes or lagoons, hence decreasing both photosynthetic activity and dissolved oxygen concentration and affecting aquatic life. High organic load and high nutrients content of the effluent lead to eutrophication of natural waters [18]. The unpleasant odour of effluent is a result of organics such as skatole, indole and other sulphur compounds [12]. Spent wash also leads to significant levels of soil pollution and acidification (because of low pH of wastewaters) in the cases of inappropriate land disposal [12] and affects the groundwater quality.

Different biological and physico-chemical treatment processes have been explored for the treatment of distillery wastewaters. This review aims to present an overview of the membrane technologies employed for distillery wastewater treatment.

2. Membrane processes

Considering the above-presented composition complexity of distillery wastewaters, special care must be put in their treatment. Membrane processes are being used in various technologies, especially for water and wastewaters purification. The paper will review membrane opportunities for distillery wastewaters treatment.

A conventional stillage treatment consists of pretreatment in terms of suspended solids (SS) removal followed by anaerobic and aerobic treatment. The biological treatment process has some advantages such as an easy access and a large-scale operation. However, the main disadvantages of this treatment are high-energy consumption and large variations of the process efficiency with the change in feedstocks used for ethanol production—as it was presented in the work of Vasić et al. [20], the composition of stillages obtained from two batches (where different feedstocks based on starch were used for ethanol production) varied significantly. Even if the stillage comes from the same feedstocks, it differs considerably in its chemical properties; that should be attributed to the fact that the COD is influenced not only by the feedstock but by the technology of alcohol production and the method of feedstock and stillage storage as well [14]. Also, it is difficult and sometimes impossible to achieve standards from effluent discharge regulations with this kind of treatment. Membrane technologies offer a possibility to improve the quality of treated water and to meet the environmental standards.

Contrary to another conventional treatment of wastewaters by coagulation with alum, when difficulties with sludge treatment or discharge appear (because of the alum present in the sludge), a retentate obtained after membranes application can be used (after additional analyses) as an addition to fertilizers or feed, for biogas production, or it can be disposed into nature without any adverse effects. Besides, distillery wastewaters contain high amount of dead yeast cells, as well as yeast metabolites (amino acids, vitamins and proteins), which have high nutritive value and can be recycled by use of membranes. Many investigations reported usefulness of membrane separation techniques for distillery wastewater treatment.

Arora et al. [21] reported study for ultrafiltration (UF) of thin stillage obtained from conventional and E-Mill dry-grind processes (enzymatic dry-grind process). The objectives of this work were to compare filtration characteristics of two stillages, evaluate solids separation and composition of permeates obtained after UF. Two regenerated cellulose membranes (YM10 and YM100) with pore sizes of 10 and 100 kDa and effective membrane area of 41.8 cm^2 were used for filtration. Filtrations were performed with each membrane using five replicates. Results were expressed as yield means and standard deviations. In order to compare yield means of conventional and E-Mill processes for both membranes, an analysis of variance procedure was performed. Composition of thin stillage and membrane filtered streams for two UF membranes are presented in Table 5.

Presented results showed that there were no differences detected in composition of permeate streams between YM10 and YM100 membranes. Total solids content of retentate streams obtained from conventional thin stillage fractionation were higher (27.6–27.8%) compared to E-Mill process (22.2–23.4%). Permeate flux rates were higher for YM10 membrane than for YM100 membrane. Results presented in this work showed that the removal efficiency was the same for membranes with different pore sizes. On the other hand, permeate flux was higher for the membrane with smaller pore size. These results are unex-

Table 5
Composition of thin stillages and membrane filtered streams for YM10 and YM100 membranes (mean ± standard deviation) [21]

Parameter	Composition	Conventional		E-Mill	
		YM10	YM100	YM10	YM100
Total solids (%)	Initial material	5.2 ± 0.6ax	5.2 ± 0.7ax	4.9 ± 0.3ax	4.9 ± 0.3ax
	Permeate	2.1 ± 0.2ay	2.3 ± 0.2ay	2.3 ± 0.3ay	2.4 ± 0.3ay
	Retentate	27.8 ± 2.6az	27.6 ± 1.8az	23.4 ± 3.5abz	22.20 ± 1.5bz
Protein (%db)	Initial material	33.3 ± 2.8ax	33.3 ± 2.8ax	39.5 ± 0.6bx	39.5 ± 0.6bx
	Permeate	15.5 ± 2.3ay	15.6 ± 3.1ay	22.8 ± 2.6by	31.1 ± 2.4by
	Retentate	38.1 ± 4.2abz	36.9 ± 2.3ax	45.2 ± 2.6bz	42.7 ± 2.9bx
Fat (%db)	Initial material	9.7 ± 1.6ax	9.7 ± 1.6ax	3.1 ± 0.8bx	3.1 ± 0.8bx
	Permeate	ND	ND	ND	ND
	Retentate (measured)	21.5 ± 2.5ay	21.3 ± 1.2ay	5.1 ± 2.0bx	4.36 ± 1.4bx
	Retentate (calculated)	17.5 ± 2.5ay[a]	16.3 ± 1.2ay[a]		
Ash (%db)	Initial material	6.3 ± 0.7ax	6.3 ± 0.7ax	6.7 ± 1.1ax	6.7 ± 1.2ax
	Permeate[a]	14.4 ± 1.2ay	14.4 ± 1.2ay	12.6 ± 0.9ay	12.6 ± 0.9ay
	Retentate	1.7 ± 0.4az	1.8 ± 0.3az	2.6 ± 0.6az	2.6 ± 0.6az
NDF (%db)	Initial material	15.7 ± 2.5ax	15.7 ± 2.5ax	15.3 ± 2.2ax	15.3 ± 2.2ax
	Permeate	ND	ND	ND	ND
	Retentate	39.8 ± 3.7ay	41.8 ± 6.5ay	35.7 ± 4.5ay	40.8 ± 12.2ay

Notes: Means in same row (abc) and composition stream differ ($p < 0.05$). Means in same column (xyz) and same composition stream differ ($p < 0.05$).

NDF—neutral detergent fibre.

ND—insufficient material to conduct analyses.

[a] Data calculated from mass balance based on composition of initial total solids and solid contents of retentates.

pected and can be explained by accumulation of particles and foulants inside larger pores of the membrane. Therefore, pores can be clogged with components of large molecular weights. Our unpublished work showed similar results for microfiltration (MF) of stillage with membranes of different pore sizes (200, 450 and 800 nm), where the membrane with pore size of 800 nm had the lowest permeate flux, while the removal efficiency was similar for all membranes.

Considering a pore size of membranes for MF and UF, it cannot be expected to remove all organic pollution from wastewater, just to reduce it. Various combinations of membrane processes may result in higher efficiency of distillery wastewater purification. Murthy and Chaudhari [22] evaluated the distillery wastewater purification with combined use of UF and reverse osmosis (RO) processes. The experiments were carried out at the pressure range of 2–10 atm (2.03–10.13 bar). In the first stage, UF experiments are carried out for concentration of effluent by removing SS. Experimental results showed that the removal of SS and COD was high, with percentage rejection of 95.5 and 63%, respectively. Also, the removal efficiencies of BOD, colour and potassium were satisfactory. The reduction of total dissolved solids (TDS) was marginal. In the second stage, permeate obtained from UF unit was used as a feed for RO experiments. Percentage rejections of TDS, BOD, colour, chlorides, sulphates and potassium were 97.9, 97.9, 93.2, 99.8, 99.7 and 94.65%, respectively.

Nataray et al. [23] reported results for TDS removal from distillery wastewater by its purification with combined use of nanofiltration (NF) and RO hybrid processes. Their analyses showed that, at the optimal pressure range of 30–50 bar, TDS in permeate were reduced from 51,500 to 9,050 mg/L, conductivity from 346 to 15.06 mS/cm and chloride concentration from 4,900 to 2,650 mg/L.

Separation of potato stillage by using combinations of three-channel ceramic membranes with the pore diameter ranging from 0.2 μm to 300 kDa was considered by Lapišova et al. [24]. The separation unit was fitted with one membrane module and trials were carried out in batch mode (after the usage of one membrane, it was replaced with the next one). At first, the separation processes were carried out in five-, three- and two-step membrane arrangements in order to experience and confirm the course of the separation process. Since two membrane arrangement proved more convenient, due to the operational costs reduction at the same separation efficiency, it was applied in the next experiments. The best results were achieved with 0.2 μm MF membrane supplemented with 50 kDa membrane—removal efficiency was more than 50% for all analites (solids, COD, nitrogen and reducing components).

Many researchers used the combination of membranes with other separation processes for stillage purification. Madaeni and Mansourpanah [25] used various RO membranes for treatment of biologically treated wastewater from alcohol production plant. The polyethylene terephtalate, polysulfone and polyamide RO membrane were used. The polyethylene terephtalate (Polyvinyl Derivative (PVD)—from Hydraunatics) membrane showed outstanding performance with 100% COD removal. Also, other membranes showed a high degree of COD removal.

Rai et al. [26] investigated tertiary treatment of aerobically treated wastewater by using NF membranes. Results showed that the method can be successfully used for the separation of contamination in the wastewater. The membrane used in the experiment was composite polyamide membrane in spiral-wounded module. The separation of organic and inorganic compounds was quite high, with COD and TDS reduction in the range of 96–99.5% and 85–95%, respectively. The separation of inorganic compounds was found to be in the range of 25–90%.

Application of membrane and natural coagulants for stillage treatment was evaluated by Vasić et al. [27]. In this work, natural coagulants extracted from common bean were added in stillage in order to increase the efficiency of MF. After MF COD reduction was 35%, while after the combined use of natural coagulants and MF COD reduction, compared to initial value, was 50%. Although the efficiency of stillage purification got higher with addition of natural coagulants, the question is whether and how costs of the process increased.

Research of Ryan et al. [28] considers viable disposal and options for tertiary treatment of distillery stillage. Among the various processes (chemical flocculation, electrocoagulation, evaporation, membranes, etc.) that can be used for tertiary treatment of stillage, membrane technologies are one of the most suitable for meeting the effluent discharge standards. All four classes of membranes (MF, UF, NF and RO) can be used for distillery wastewaters treatment, while NF and RO appear to be the most promising methods for stillage purification with ability to produce high-quality water. Also, the study shows how the secondary and tertiary treatment stages can be energy integrated via power from the anaerobic digester, which is important from the economic point of view.

In the work of Vasić et al. [20], efficiency of use of MF membranes for distillery wastewater purification was compared with efficiency of conventional technique for wastewater treatment—centrifugation. Obtained results showed that about 85% of both, COD and TN were removed from stillage by use of MF membrane with pore size of 200 nm, while 88% of COD and only 20% of TN were removed by centrifugation at 3,000 rpm for 10 min. Also, it was concluded in the same work that significantly lower energy consumption would be required for filtration than for centrifugation, since low pressures were applied for MF.

In recent years, composite membranes prepared by surface modification of ceramic supports using a thin polymer coating have resulted in improved barrier performances in terms of flux and selectivity over the nascent membrane modules [29]. Nataraj et al. [29] developed a novel method to reduce the pore size of microporous ceramic tubular membranes by coating their inner surfaces using cellulose acetate (CA) solution forming a thin coating of ~35 μm. The original ceramic membrane pore size was reduced from 1.2 ± 0.1 μm to 10–20 nm. Three tubular membrane configurations (hollow 1-channel, 7-channel array and 19-channel array) were used for CA coating trials and further testing for the treatment of effluents collected from various industrial sources (distillery wastes, paper and pulp wastes and sugar industry wastes). The main objective of this work was to examine and compare the efficiency of the coated membranes in the treatment of model contaminated water and various industrial effluents with higher organic contents. Hollow tubular modules have shown the most significant rejections for TDS and conductivity as well as flux that decreased by about 2–3-fold compared to nascent ceramic module. For distillery spent wash, flux was nearly 10 times smaller than that of pure water, tap water and sugar industry wastewater. The characteristics of composite membranes make them less susceptible to membrane fouling and provide a great potential for wastewater purification.

Other membrane processes, such as membrane bioreactors (MBRs), have been introduced a long time ago and since then they have increasingly been used for wastewater treatment. There are many published works about application, characteristics and efficiency of MBR, but only a few of them study the possibility of MBR application for stillage purification. In the work of Satyawali and Balakrishnan [30], the operation of a laboratory scale MBR (Fig. 1) for distillery wastewater purification was investigated. The aim of this research was to investigate continuous operation of MBR, with focus on COD removal and biomass

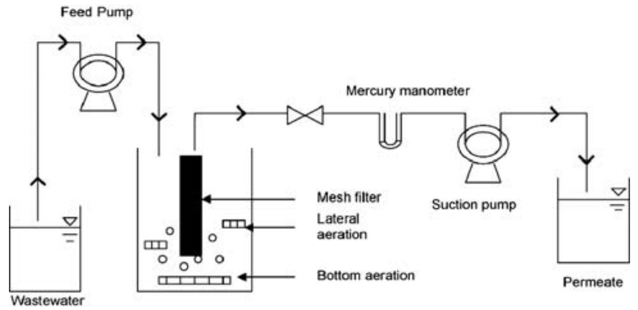

Fig. 1. Schematic diagram of continuous reactor [30].

growth in the reactor. Nylon mesh filter with a pore size of 30 μm was used for the experiment. Anaerobically treated effluent was collected from molasses-based distillery and used as a feed. Municipal activated sludge was used as an inoculum, which was acclimatised in a fed-batch reactor before starting continuous operation. Results showed that removal of COD ranged from 23 to 41%, with a maximum at a COD loading rate of 3.4 kg COD/m^3 d. SS retention was 87% at a mixed liquor suspended solids (MLSS) of 10–12 g/L (MLSS concentration represents the biomass concentration in the reactor). Also, it was found that the system could operate up to two weeks without significant flux decrease.

Zhang et al. [31] reported aerobic treatment of simulated distillery wastewater (Table 6) using metallic membrane bioreactor.

In this study, a flat stainless-steel membrane with a 0.2 μm pore size was used in aerobic MBR. The experiment was carried out at temperatures of 30–45°C (in 5°C gradients) in terms of short-term activities for about 10 days at each temperature. According to obtained results, it was found that at a given conditions mean COD and mean TN removal efficiencies were 94.7 and 84.4%, respectively. Also, it was determined that although soluble COD (S_{COD}) and soluble TN (S_{TN}) in the supernatant increased with temperature, permeate quality was uniform which indicates that the metallic membrane had an excellent retention ability for soluble organic compounds and SS.

Table 6
Feed and operating conditions [31]

Item	Value
Feed COD (mg/L)	700–1,500
Feed TN (mg/L)	7–21
Feed pH	4–5
Effective volume (L)	17
Effective filter area (m^2)	0.12
Aeration rate (m^3/h)	0.5
Dissolved oxygen in descending region (mg O_2/L)	2–4
MLSS (SS) (mg/L)	3,000–8,000
Hydraulic retention time (h)	10–30
COD-volume load rate (kg COD/m^3 d)	0.6–2.8
COD-sludge load rate (kg COD/kg VSS d)	0.2–1.2

After the alcohol production, stillage may be concentrated by evaporation in order to reduce its volume. The condensates which are formed during this concentration process represent a large volume of water (320,000 t/y for an average distillery producing 45,000 t/y alcohol) [32], which could be reused as dilution water in the fermentation step. However, condensates contain volatile organic compounds which are inhibitors of fermentation process. Also, it cannot be discharged without previous treatment because of its high organic compounds content. Hence, the water recovering from effluent streams is a major challenge for many process plants, as it would lead to simultaneous reduction of the volume of effluents rejected and the fresh water consumption [33]. There are some published works on membrane application for the condensate purification [32–34], with focus on removing compounds that inhibit yeast growth and metabolism. Also, there is the possibility of water recycling after direct treatment of stillage by membranes, but the lack of works that investigate presence and distribution of inhibiting compounds in permeates is apparent.

In a recent study, Arora et al. [35] evaluated nutrient recovery and the permeate streams for potential water recycling (based on organic acid contents), using MF and UF membranes. They filtered thin corn stillage through various membranes in two phases. In the phase I, thin stillage was filtered through one of the next membranes—stainless steel MF membrane with 0.1 μm pore size, and regenerated cellulosic UF membranes YM1, YM10 and YM100 with 1, 10 and 100 kDa molecular weight cut-off, respectively. In phase II, permeates obtained from MF runs were filtered using YM100, YM10 and YM1 membranes. Results of retentates analyses from various membranes (after phase I) showed that total solids in retentate were similar among MF and UF membranes. Also, protein contents of MF, YM 100 and YM 10 membrane streams were similar. Ash contents were reduced by more than 50% in retentates of all membranes. This can be explained by the solubility of mineral compounds in the stillage stream, which allows them to pass through the membranes. The highest protein recovery was achieved in YM 1 retentate compared to other membranes. Lactic acid and glycerol concentrations of thin stillage and permeate were similar. This indicates that permeates obtained after MF, UF and MF + UF would require additional treatment in order to affect the amount of water recycling within the plant.

Although the above-mentioned results proved very good in terms of selectivity and efficiency of purification, there are some limitations for the use of membranes. Fouling, which forms on the surface of membranes, can be considered the main disadvantage of these techniques, which leads to reduction of efficiency of filtration (decline of flux, loss of product quality, shortening lifetime of the membranes). The understanding of fouling formation on the membrane surface is complicated due to the fact that the stillage is a mixture of many different components with very variable sizes and shapes of particles. This phenomenon causes problems in obtaining an economical flux. To overcome this problem, many researchers reported studies about membrane fouling [36–38] in an attempt to find a solution for reduction of its impact on membranes. The most efficient solution is the usage of appropriate pretreatment that would eliminate most of the foulants from feed solution [39–41] or controlling the hydrodynamic conditions of the feed using turbulent promoters [42]. Also, cleaning of membranes is a very important part of the process that should provide regeneration of membranes and high flux recovery. Cleaning efficiency, energy consumption and amounts of water and chemicals required for cleaning process are dependent on fouling. Cleaning process requires the use of various chemicals (NaOH, H_2O_2, EDTA, HNO_3, bleach) whose amounts need to be optimised for minimising the environmental impact [24].

The pressure driven membrane processes, especially RO, are very effective in meeting strict effluent discharged standards. However, besides fouling, the main "drawback" of this kind of purification and recovery is extremely high operating pressures, which can affect investment and operational costs of the process (price of the pumps for achieving required pressures and electricity consumption for the pump). Therefore, the main task for distilleries is to find the most suitable membrane system which will ensure optimal permeate flux rate, maximal solute rejection and minimal costs. For this reasons, it is necessary to optimise the filtration process for distillery stillage treatment, as it was presented in the work of Arora et al. [43].

Design optimisation and operation of a continuous MF system for the corn dry-grind process was considered in this work. The objectives of the study were to simulate a multistage MF system, optimise area requirement and number of stages required for a multistage system to achieve minimum costs and evaluate the design under varying final concentration factors (CF) and input flow rates (F_F). Two CF values (8 and 15) and three input stream flow rates 450,000, 550,000 and 760,000 gal/day (1.54×10^6, 2.1×10^6 and 2.89×10^6 L/day) were chosen for analyses. The system includes an N stage membrane module system where each membrane unit is connected in series, and retentate collected from one membrane is an input stream for the next membrane, etc. (Fig. 2). A tubular stainless steel MF module with 0.1 μm pore size and area of 0.28 m^2 was used for MF experiment. Five stage membrane system was found to be optimum for CF = 15, with area requirement of 655 m^2 for minimum cost. Also, it was found that input feed flow rate had the greatest effect on the total capital costs of the system. Increase in the input stream flow rate from 450,000 to 760,000 gal/day (1.54×10^6–2.89×10^6 L/day) increased total capital costs by 47%. Compared to a single stage system, an optimal system had a reduction of 50% in operating costs.

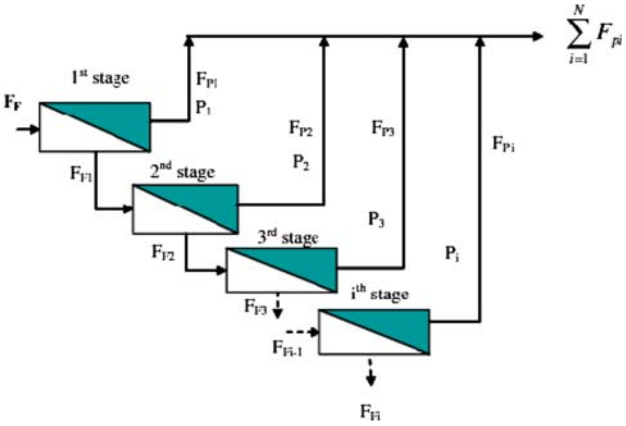

Fig. 2. Multistage system for thin stillage filtration [43].

Considering composition complexity of stillage and required quality of treated water, the selection of the membrane is very important for the successful implementation of the filtration process from both, the economic standpoint and the standpoint of environmental protection.

3. Conclusions

- Although a conventional biological treatment of stillage has some advantages, it is difficult and sometime even impossible to meet standards from effluent discharge regulations with this kind of treatment. Thus, the alternative treatment methods should be researched.

- As it was presented through this review, membrane separation processes are promising techniques for distillery stillage purification. Advantages of these processes are: high efficiency; a retentate obtained after membranes application can be used as an addition to fertilizers or feed, for biogas production, or it can be disposed in the nature without any adverse influence; the high nutritive value compounds can be recycled from stillage by use of membranes; and some percentage of water can be recycled from stillage to fermentation process, leading on the one hand to decrease of effluent volume and on the other hand to decrease of water consumption. The main drawback of membrane processes in stillage purification is membrane fouling which can be controlled by appropriate pretreatment of stillage.
- Among membrane processes, RO processes are the most effective with a high percentage of COD and other analytes removal. The drawback of this kind of purification is extremely high operating pressures, which affect costs of the process. MF and UF membranes operate at lower pressures but they cannot remove all organic pollution from wastewater.
- Also, combinations of membrane techniques may result in high efficiency for distillery wastewater treatment. All four classes of membrane processes (MF, UF, NF and RO) can be utilized in various combinations. MF and UF can be used successfully in preventing fouling for RO and NF processes.
- Combination of membranes with other separation processes, such as biological treatment processes, evaporation, coagulation and flocculation, can increase efficiency of stillage purification.
- Likewise, there are studies about membrane application for purification of condensate obtained after concentration of stillage (in terms of yeast inhibitor removal), but presence and distribution of inhibiting compounds in permeate, obtained after membrane filtration, are not sufficiently explored considering the importance of water recycling during the production of bioethanol.
- Other membrane processes such as MBR are also used for wastewater purification. Although there are many published works about application of MBR for wastewater treatment only a few of them discussed their application for stillage purification.
- Due to expansion of bioethanol production in the world and more stringent regulations on environmental protection and discharge of wastewaters into nature, it is necessary to develop techniques that will enable maximum efficiency in terms of wastewaters reuse. Application of membrane processes for recycling of valuable matters from stillage as well as utilisation of retentate as animal feed, for biogas production and cultivation of some micro-organisms are crucial from an economic standpoint. Hence, it can be concluded that stillage purification and utilisation remains a considerable challenge for distilleries all over the world.

Acknowledgements

This research was supported by the grant number TR 31002 from the Ministry of Education and Science of the Republic of Serbia.

References

[1] F.W. Bai, W.A. Anderson, M. Moo-Young, Ethanol fermentation technologies from sugar and starch feedstocks, Biotechnol. Adv. 26 (2008) 89–105.

[2] A. Singh, D. Pant, N.E. Korres, A.S. Nizami, S. Prasad, J.D. Murphy, Key issues in life cycle assessment of ethanol production from lignocellulosic biomass: Challenges and perspectives, Bioresour. Technol. 101 (2010) 5003–5012.

[3] S. Prasad, A. Singh, H.C. Joshi, Ethanol as an alternative fuel from agricultural, industrial and urban residues, Resour. Conserv. Recycl. 50 (2007) 1–39.

[4] J. Johnson, News of the week: New world for biofuels, Chem. Eng. News 86 (2008) 10.

[5] P.S. Nigam, A. Singh, Production of liquid biofuels from renewable resources, Prog. Energy Combust. 37 (2011) 52–68.

[6] Ó.J. Sánchez, C.A. Cardona, Trends in biotechnological production of fuel ethanol from different feedstocks, Bioresour. Technol. 99 (2008) 5270–5295.

[7] M. Ballesteros, J.M. Oliva, M.J. Negro, P. Manzanares, I. Ballesteros, Ethanol from lignocellulosic materials by a simultaneous saccharification and fermentation process (SFS) with *Kluyveromyces marxianus* CECT 10875, Process Biochem. 39 (2004) 1843–1848.

[8] C.F. Huang, T.H. Lin, G.L. Guo, W.S. Hwang, Enhanced ethanol production by fermentation of rice straw hydrolysate without toxification using a newly adapted strain of *Pichia stipitis*, Bioresour. Technol. 100 (2009) 3914–3920.

[9] J.P.A. Silva, S.I. Mussatto, I.C. Roberto, The influence of initial xylose concentration, agitation, and aeration on ethanol production by *Pichia stipitis* from rice straw hemicellulosic hydrolysate, Appl. Biochem. Biotechnol. 162 (2010) 1306–1315.

[10] Y. Lin, S. Tanaka, Ethanol fermentation from biomass resources: Current state and prospects, Appl. Microbiol. Biotechnol. 69 (2006) 627–642.

[11] B. Hahn-Hägerdal, M. Galbe, M.F. Gorwa-Grauslund, G. Lidén, G. Zacchi, Bio-ethanol—the fuel of tomorrow from the residues of today, Trends Biotechnol. 24 (2006) 549–556.

[12] S. Mohana, B.K. Acharya, D. Madamwar, Distillery spent wash: Treatment technologies and potential applications, J. Hazard. Mater. 163 (2009) 12–25.

[13] Y. Satyawali, M. Balakrishnan, Wastewater treatment in molasses-based alcohol distilleries for COD and color removal: A review, J. Environ. Manage. 86 (2008) 481–497.

[14] M. Krzywonos, E. Cibis, T. Miśkiewicz, A. Ryznar-Luty, Utilization and biodegradation of starch stillage (distillery wastewater), Electron. J. Biotechn. 12 (2009) 1–12.

[15] A.C. Wilkie, K.J. Riedesel, J.M. Owens, Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks, Biomass Bioenerg. 19 (2000) 63–102.

[16] J.M. Prodanović, M.B. Šćiban, M.G. Antov, J.M. Dodić, Comparing the use of common bean extracted natural coagulants with centrifugation in the treatment of distillery wastewaters, Rom. Biotechnol. Lett. 16 (2011) 6638–6646.

[17] D.D. Kitts, C.H. Wu, H.F. Stich, W.D. Powrie, Effects of glucose-glycine maillard reaction products on bacterial and mammalian cells mutagenesis, J. Agric. Food Chem. 41 (1993) 2353–2358.

[18] V. Kumar, L. Wati, F. Fitzgibbon, P. Nigan, I.M. Banat, D. Singh, R. Marchant, Bioremediation and decolorization of anaerobically digested distillery spent wash, Biotechnol. Lett. 19 (1997) 311–313.

[19] M.J. Kort, in: G.G. De Birch, K.J. Parker (Eds.), Colour in the Sugar industry, Science and Technology, Applied Science, London, 1979, pp. 97–130.

[20] V.M. Vasić, M.B. Šćiban, J.M. Prodanović, The usage of membranes for distillery wastewater treatment, in: XV International Eco-Conference, Proceedings: Environmental Protection of Urban and Suburban Settlements I, Novi Sad, Serbia, 21–24 September 2011, pp. 281–286.

[21] A. Arora, B.S. Dien, R.L. Belyea, P. Wang, V. Singh, M.E. Tumbleson, K.D. Rausch, Ultrafiltration of thin stillage from conventional and e-mill dry grind processes, Appl. Biochem. Biotechnol. 164 (2011) 58–67.

[22] Z.V.P. Murthy, L.B. Chaudhari, Treatment of distillery spent wash by combined UF and RO processes, Glob. Nest J. 11 (2009) 235–240.

[23] S.K. Nataray, K.M. Hosamani, T.M. Aminabhavi, Distillery wastewater treatment by the membrane based nanofiltration and reverse osmosis processes, Water Res. 40 (2006) 2349–2356.

[24] K. Lapišová, R. Vlček, J. Klozová, M. Rychtera, K. Melzoch, Separation techniques for distillery stillage treatment, Czech J. Food Sci. 24 (2006) 261–267.

[25] S.S. Madaeni, Y. Mansourpanah, Screening membranes for COD removal from dilute wastewater, Desalination 197 (2006) 23–32.

[26] U.K. Rai, M. Muthukrishnan, B.K. Guha, Tertiary treatment of distillery wastewater by nanofiltration, Desalination 230 (2008) 70–78.

[27] V.M. Vasić, J.M. Prodanović, D.V. Kukić, M.B. Šćiban, M.G. Antov, D.Ž. Ivetić, Application of membrane and natural coagulants for stillage purification, Desalin. Water. Treat. (2012). DOI: 10.1080/19443994.2012.714525.

[28] D. Ryan, A. Gadd, J. Kavanagh, G.W. Barton, Integrated biorefinery wastewater design, Chem. Eng. Res. Des. 87 (2009) 1261–1268.

[29] S.K. Nataraj, S. Roy, M.B. Patil, M.N. Nadagouda, W.E. Rudzinski, T.M. Aminabhavi, Cellulose acetate-coated α-alumina ceramic composite tubular membranes for wastewater treatment, Desalination 281 (2011) 348–353.

[30] Y. Satyawali, M. Balakrishnan, Treatment of distillery effluent in a membrane bioreactor (MBR) equipped with mesh filter, Sep. Purif. Technol. 63 (2008) 278–286.

[31] S. Zhang, F. Yang, Y. Liu, X. Zhang, Y. Yamada, K. Furukama, Performance of a metallic membrane bioreactor treating simulated distillery wastewater at temperatures of 30 to 45˚C, Desalination 194 (2006) 146–155.

[32] E.M. Couallier, B.S. Ruiz, M.L. Lameloise, M. Decloux, Usefulness of reverse osmosis in the treatment of condensates arising from the concentration of distillery vinasses, Desalination 196 (2006) 306–317.

[33] C. Sagne, C. Fargues, B. Broyart, M.L. Lameloise, M. Decloux, Modeling permeation of volatile organic molecules through reverse osmosis spiral-wound membranes, J. Membr. Sci. 330 (2009) 40–50.

[34] C. Sagne, C. Fargues, R. Lewandowski, M.L. Lameloise, M. Gavach, M. Decloux, A pilot scale study of reverse osmosis for the purification of condensate arising from distillery stillage concentration plant, Chem. Eng. Process. 49 (2010) 331–339.

[35] A. Arora, B.S. Dien, R.L. Belyea, V. Singh, M.E. Tumbleson, K.D. Rausch, Nutrient recovery from the dry grind process using sequential micro and ultrafiltration of thin stillage, Bioresour. Technol. 101 (2010) 3859–3863.

[36] L. Puro, J. Tanninen, M. Nyström, Analyses of organic foulants in membranes fouled by pulp and paper mill effluent using solid–liquid extraction, Desalination 143 (2002) 1–9.

[37] W.S. Ang, A. Tiraferri, K.L. Chen, M. Elimelech, Fouling and cleaning of RO membranes fouled by mixtures of organic foulants simulating wastewater effluent, J. Membr. Sci. 376 (2011) 196–206.

[38] M.F.A. Goosen, S.S. Sablani, H. Al-Hinani, S. Al-Obeidani, R. Al-Belushi, D. Jackson, Fouling of reverse osmosis and ultrafiltration membranes: A critical review, Sep. Sci. Technol. 39 (2004) 2261–2298.

[39] B. Van Der Bruggen, J.H. Kim, F.A. Di Giano, J. Geens, C. Vandecasteele, Influence of MF pretreatment on NF performance for aqueous solutions containing particles and an organic foulant, Sep. Purif. Technol. 36 (2004) 203–213.

[40] A.I. Schäfer, A.G. Fare, T.D. Waite, Cost factors and chemical pretreatment effects in membrane filtration of waters containing natural organic matter, Water Res. 35 (2001) 1509–1517.

[41] Y. Soffer, R.B. Aim, A. Adin, Membrane for water reuse: Effect of pre-coagulation on fouling and selectivity, Water Sci. Technol. 42 (2000) 367–372.

[42] A. Jokić, Z. Zavargo, Z. Šereš, M. Tekić, The effect of turbulence promoter on cross-flow microfiltration of yeast suspension: A response surface methodology approach, J. Membr. Sci. 350 (2010) 269–278.

[43] A. Arora, A. Seth, B.S. Dien, R.L. Belyea, V. Singh, M.E. Tumbleson, K.D. Rausch, Microfiltration of thin stillage: Process simulation and economic analyses, Biomass Bioenerg. 35 (2011) 113–120.