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MICROFILTRATION OF DISTILLERY STILLAGE: INFLUENCE OF MEMBRANE PORE SIZE

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Stillage is one of the most polluted waste products of the food industry. Beside large volume, the stillage contains high amount of suspended solids, high values of chemical oxygen demand and biological oxygen demand, so it should not be discharged in the nature before previous purification. In this work, three ceramic membranes for microfiltration with different pore sizes were tested for stillage purification in order to find the most suitable membrane for the filtration process. Ceramic membranes with a nominal pore size of 200 nm, 450 nm and 800 nm were used for filtration. The influence of pore size on permeate flux and removal efficiency was investigated. A membrane with the pore size of 200 nm showed the best filtration performance so it was chosen for the microfiltration process.

KEY WORDS: Microfiltration, distillery stillage, wastewater

INTRODUCTION

Stillage (distillery wastewater) is the main waste product generated in the distilleries. Its pollution potential is one of the most serious problems today, so distillery industries are forced to develop new techniques for stillage purification and utilization. The amount and composition of stillage are variable and depend on the feedstocks used for bioethanol production, as well as various aspects of the production process.

It is characterized by a high content of organics and total solids, low pH and a very large volume, increasing together with the ethanol production. To produce 1L of ethanol, approximately 10 to 15 liters of distillery stillage are generated (1). Also, it has very high biological oxygen demand (BOD), chemical oxygen demand (COD) and a high BOD/COD ratio. The amounts of inorganic substances such as nitrogen, potassium, phosphates, calcium and sulfates are also very high (2). Distillery stillage contains some feedstock components and degraded yeast cells. Many of those components are characterized 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 (3).

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Compared to other distillery wastewaters (sugar-based stillage and stillage from cellulosic materials), the stillage from the fermentation of starch-based feedstocks contains more suspended solids due to the presence of grains remaining after fermentation. An important characteristic of stillage obtained from molasses-based feedstocks include color components. Phenolics from the feedstock, melanoidins from Millard reaction of sugars with proteins, caramels from overheated sugars and furfurals from acid hydrolyses can contribute to the color of the effluent (4). Chromium, copper, nickel and zinc were found at levels significantly above detection limits in some distillery effluents, especially in the stillages from cellulosic feedstocks. Some heavy metals are originating from feedstocks used for bioethanol production. The processing equipment used in the pretreatment of cellulosic feedstocks (acid hydrolysis) is often made of corrosion-resistant alloys. Heavy metals contained in these alloys may leach into the feedstock during the hydrolysis, resulting in detectable levels in the stillage(4). Also, corrosion of piping, reactors and heat exchangers may contribute to heavy metal content in the stillage.

Considering high pollution potential of distillery wastewater, it should not be disposed in the nature without previous treatment. Stillage disposal in the environment can be adverse. High COD and nutrient content may result in eutrofication of natural waters, colored compounds block out sunlight penetration in rivers and lakes, reducing photosynthetic activity and dissolved oxygen concentration. Disposal of distillery wastewater on land is also harmful, and can affect the vegetation and groundwater quality.

Different techniques for distillery stillage purification have been explored. Stillage is usually treated first with a screw decanter to remove solids (1). Also, centrifugation can be successfully used as a technique for solids separation (5). Further, stillage can be concentrated in the multi-effect evaporators with the co-production of condensate, which is lower in organics and almost devoid of inorganic salts. However, significant energy required to evaporate the stillage can negatively impact the energy balance of ethanol production (4). Coagulation and flocculation are also commonly used methods to remove particulates and organic matter from wastewaters. They are usually conducted by adding chemicals such as salts of aluminium and iron and polyelectrolytes. The limitations of coagulation and flocculation are: an increased salinity of the effluent, the storage and handling of corrosive chemicals, need for pre- and post-dosing adjustment of pH and sludge handling (6). Biological treatment processes such as anaerobic and aerobic digestion, as well as combination of these two methods have been successfully used for stillage treatment. Although the biological processes have several advantages such as the easy access and a large scale operation, the major drawbacks of these processes are high energy consumption, high labor costs, and large variations of the treatment efficiency with the change in feedstocks used for bioethanol production (1). However, it is hard and sometimes impossible to meet the environmental standards with aforementioned kinds of purification. Membrane separation techniques are widely used for distillery wastewater treatment, offering a possibility to improve the value of stillage and to meet environmental standards. The most commonly used membrane processes for wastewater purification are: microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

The current trend in the membrane market has shown significant improvements in technical efficiencies of membrane systems, which makes them a cost competitive alternative to conventional treatment systems. Permeate flux rate and throughput are critical

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measures of membrane performance and play important roles in determining the cost of membrane filtration system (7).

The aim of this study is to evaluate the application of microfiltration for stillage treatment, and to find the most suitable membrane for the filtration process.

EXPERIMENTAL

Experimental material

The experiments were performed using distillery stillage from the ethanol factory Reachem, Srbobran (Serbia), where it was obtained from starch feedstocks.

Microfiltration experiment

The experiments were carried out in a conventional cross-flow microfiltration (MF) unit (Figure 1).

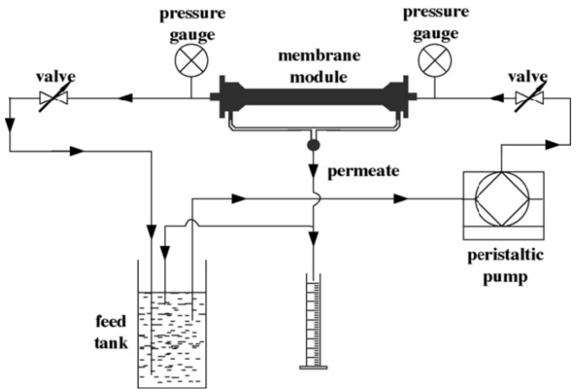

Figure 1. Schematic representation of the experimental setup for cross-flow microfiltration (8)

The feed was circulated by a peristaltic pump (ISMATEC, Switzerland), under the conditions of complete recirculation of the fluid. The feed suspension was concentrated to a volume concentration factor (VCF) of 1.88. The permeate was constantly drained away from the system, collected and analyzed. The transmembrane pressure difference was adjusted by the regulation valve. The inlet and outlet pressures of the membrane module were measured by two pressure gauges. The average of these two pressure values gave the value of transmembrane pressure (TMP) as the outside of the membrane is vented to the atmosphere. The experiments were performed under the TMP of 0.6 bar. The membrane module used was a MembraloxTM 1T1-70 module (SCT, Bazet, France). The single channel ceramic membranes used had nominal pore sizes of 200 nm, 450 nm and 800 nm (TAMI Deutschland) with the length of 250 mm and inner/external diameter of 6/10 mm. The useful membrane surface was 4.33×10^{-3} m^2. The membranes were cleaned according to the recommendation of the manufacturer after each experiment; the

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cleaning sequence was a classical acid-base one (alternate washing with 0.2% solution of NaOH and 0.2% solution of HNO_3, both with recirculation, and rinsing with distilled water). After that the water flux of the membranes was measured; the measurement provided the reference to assess the effectiveness of the membrane cleaning. The permeate flux was calculated from the time needed to collect 10 mL of permeate. All measurements were carried out in triplicate, and the results were averaged. All experiments were carried out at the room temperature (25ºC).

Analitical methods

Feed and permeate samples obtained after the microfiltration of stillage were analyzed for dry matter, ash, organic dry matter, suspended solids, BOD and COD using Standard Methods (9).

Dry matter content was determined by gravimetric method, drying the sample at 103-105ºC. Suspended solids were determined by centrifugation at 3000rpm during 10 minutes (centrifuge MLW T52.1); supernatant was poured off and the residue was determined by gravimetric method, drying at 103-105ºC. COD was determined by dichromate reflux method. BOD was measured using a VELP SCIENTIFICA BOD system according to the manufacturer manual. Total nitrogen was determined by Kjeldahl method (10)

RESULTS AND DISCUSSION

The stillage was analyzed immediately after its bringing from the factory. The results of the analyses are presented in Table 1.

Table 1. Results of the analyses of stillage and permeates obtained after microfiltration

Parameter	Stillage	Permeate from the membrane with pore size of:		
		200 nm	450 nm	800 nm
Dry matter (mg/L)	63700	50910	42590	40700
Ash (mg/L)	9640	15625	4340	4150
Organic dry matter (mg/L)	54060	35285	38250	36550
% of Organic dry matter (%DM)	85	69	90	90
Suspended solids (mg/L)	18340	-	-	-
Ash of suspended solids (mg/L)	1165	-	-	-
Organic dry matter of suspended solids (mg/L)	17175	-	-	-
% of Organic dry matter of suspended solids (mg/L)	94	-	-	-
COD (mgO_2/L)	102000	64500	64000	62600
BOD (mgO_2/L)	89000	48000	47750	46320
BOD/COD *100 (%)	87	74	74	74
Total Kjeldahl nitrogen (mg/L)	2866	1480	1420	1400

As can be seen, the stillage had high values of COD and BOD, as well as the values of dry matter and total nitrogen. About 29% of dry matter is in form of suspended solids. According to these results it was confirmed that the stillage is highly polluted. Further, the stillage was passed through the microfiltration membranes with different pore sizes, applying the same conditions for all membranes (TMP = 0.6bar, feed flow rate (Q) = 100 L/h, pH = 3 and t = 25ºC). The permeates were collected and also analyzed (Table 1). The filtration time for the membranes with pore sizes of 200, 450, 800 nm was 3 hours 36 minutes 28 seconds, 4 hours 11minutes 8 seconds, and 5 hours 14 minutes 18 seconds, respectively.

Based on the presented results, it can be said that the values of COD, BOD, total nitrogen and dry matter decreased compared to the initial values of the stillage. The removal efficiency of COD for the membranes of 200, 450, 800nm was 36.7%, 37.3% and 38.7%, respectively. The total Kjeldahl nitrogen content was lower by 48.4%, 50.5% and 51.2% respectively, whereas the BOD/COD ratio was the same for all permeates, which indicates that the same kind of organic matters that pass through examined membranes are biodegradable. Suspended solids were completely removed from the stillage. The ash content of the permeate obtained after filtration through the membrane with pore size of 200 nm was higher by about 60% compared to initial value in the stillage. Arora et al. (11) reported similar results obtained after the ultrafiltration of thin stillage. Their results showed that ash content of permeate was higher than in thin stillage. They concluded that this may be attributed to the solubility of mineral components in the stillage stream, which allowed them to pass through the membrane. However, ash content was reduced in permeates for the membranes with pore sizes of 450 nm and 800 nm, which can be explained by particles accumulation within pores of the membrane. The sizes and the shapes of particles in stillage are very variable and dependend of the feedstocks used for bioethanol production. Therefore, pores can be blocked with components of large molecular weights.

Considering the pore size of the membranes for microfiltration, it cannot be expected to remove all organic pollution from wastewater by their application, but it can be reduced considerably. That makes microfiltration suitable as a pretreatment for ultrafiltration or reverse osmosis (6).

The effect of the membrane pore size on the permeate flux is shown in Figure 2.

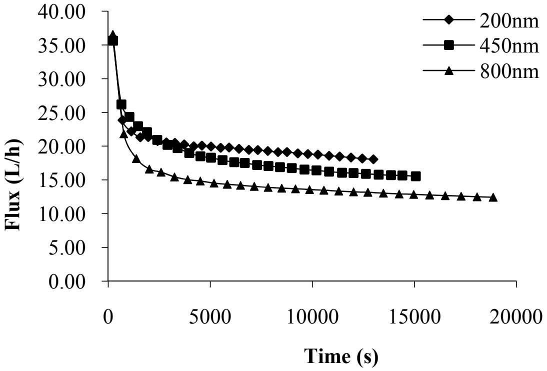

Figure 2. Time dependence of the permeate flux in the microfiltration of stillage

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Experimental results suggest that there is a fast initial flux decrease for all membranes, it takes place during the first ten minutes of filtration and does not decrease significantly later on. As can be seen from the figure, similar flux rate profiles were observed for all membranes. The membrane with pore size of 800 nm had the lowest value of permeate flux. The reason for this can be found in the fact that the membranes with a larger pore sizes may be blocked due to the presence of components with large molecular weights. Numerous examples show that membrane fouling is more severe with increasing pore size. There appears to be an optimum pore size, above which severe membrane fouling reduces the flux. Attia et al. (12,13), while processing skim milk on aluminium oxide MF membranes, found higher permeate fluxes with a 0.2 μm membrane than a 0.8 μm membrane. Stopka et al.(14) reported similar results obtained after the microfiltration of model yeast suspension and beer. Their study showed that the permeate flux for the membrane with a pore size of 500 nm was lower compared to that observed for the membrane with pore size of 200 nm. Arora et al. (11) presented results of ultrafiltration of thin stillage, using membranes with pore sizes of 10 and 100 kDa. The results showed that the membrane with larger pore size (100 kDa) had lower flux.

It is evident that the membrane with a pore size of 200 nm had the best performance, in terms of permeate flux. The values of the flux for the membranes of 450 nm and 800 nm were lower compared to the membrane of 200 nm for 13.8 % and 31.2 %, respectively. This can be explained by the foulants accumulation within the larger pores of the membrane, which leads to their clogging. In contrast, the difference in the removal efficiency of COD, BOD, total nitrogen, and dry matter (Table 1) for all membranes is insignificant.

CONCLUSIONS

Based on the obtained results it can be concluded that the membranes with the pore size of 450 and 800 nm had lower permeate flux than the membrane with pores of 200 nm. The difference in the permeate quality for all membranes is insignificant. The membrane with the pore size of 200 nm showed the best results in terms of duration of the filtration process. Hence, it was chosen for the microfiltration of investigated starch based distillery stillage. Eventually, it can be concluded that the selection of the membrane is very important for the successful implementation of the filtration process, both from the economic standpoint and the standpoint of environmental protection.

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REFERENCES

1. Lapišová, K., Vlček, R., Klozová, J., Rychtera, M. and Melzoch, K.: Separation techniques for distillery stillage treatment. Czech J. Food Sci. **24** (2006) 261-267.
2. Mohana, S., Acharya, B.K. and Madamwar, D.: Distillery spent wash: treatment technologies and potential applications. J. Hazard. Mater. **163** (2009) 12-25.

3. Krzywonos, M., Cibis, E., Miśkiewicz, T. and Ryznar-Luty, A.: Utilization and biodegradation of starch stillage (distillery wastewater). Electron. J. Biotechn. **12** (2009) 1-12.
4. Wilkie, A.C., Riedesel, K.J. and Owens, J.M.: Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass Bioenerg. **19** (2000) 63-102.
5. Vasić, V.M., Šćiban, M.B. and Prodanović, J.M.: The usage of membranes for distillery wastewater treatment, XV International Eco-Conference, Novi Sad, 21-24 September 2011, Proceedings: Environmental protection of urban and suburban settlements I, p. 281-286.
6. Ryan, D., Gadd, A., Kavanagh, J. and Barton, G.W.: Integrated biorefinery wastewater design. Chem. Eng. Res. Des. **87** (2009) 1261-1268.
7. Arora, A., Seth, A., Dien, B.S., Belyea, R.L., Singh, V., Tumbleson, M.E. and Rausch, K.D.: Microfiltration of thin stillage: Process simulation and economic analyses. Biomass Bioenerg. **35** (2011) 113-120.
8. Jokić, A., Zavarago, Z., Šereš, Z. and Tekić, M.: The effect of turbulence promoter on cross-flow microfiltration of yeast suspension: A response surface methodology approach. J. Membr. Sci. **350** (2010) 269-278.
9. APHA (American Public Health Association), Standard Methods for the Examination of water and wastewater, 20th ed., APHA, AWWA, WEF, Washington DC (1998).
10. MEBAK, Brautechnische Analysenmethoden, Bd. I, III Auflage (in German) (1997) 171-174.
11. Arora, A., Dien, B.S., Balyea, R.L., Wang, P., Singh, V., Thumbleson, M.E. and Rausch, K.D.: Ultrafiltration of thin stillage from conventional and e-mill dry grind processes. Appl. Biochem. Biotechnol. **164** (2011) 58-67.
12. Attia, H., Bennasar, M. and Tarodo de la Fuente B.: Study of the fouling of inorganic membranes by acidified milks using scanning electron microscopy and electrophoresis. I. Membrane with pore diameter 0.2 μm. J. Dairy Res. **58** (1991) 39-50.
13. Attia, H., Bennasar, M. and Tarodo de la Fuente B.: Study of the fouling of inorganic membranes by acidified milks using scanning electron microscopy and electrophoresis. II. Membrane with pore diameter 0.8 μm. J. Dairy Res. **58** (1991) 51-65.
14. Stopka, J., Schlosser, Š., Dömény, Z. and Šmogrovičov, D.: Flux decline in microfiltration of beer and related solutions of model foulants through ceramic membranes. Pol. J. Environ. Stud. **9** (2000) 65-69.

УТИЦАЈ ПРЕЧНИКА ПОРА НА МИКРОФИЛТРАЦИЈУ ЏИБРЕ

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Џибра представља један од најзагађенијих отпадних токова прехрамбене индустрије. Поред велике запремине, џибра садржи велику количину суспендованих чес-

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тица, има велику вредност хемијске потрошње кисеоника (ХПК) и биолошке потрошње кисеоника (БПК), па се не сме испуштати у околину без претходног пречишћавања. У циљу проналажења најпогодније мембране за процес филтрације џибре, испитане су три керамичке мембране за микрофилтрацију са различитим пречницима пора. За филтрацију су коришћене керамичке мембране са средњим пречником пора од 200 nm, 450 nm и 800 nm. Испитан је утицај пречника пора на флукс пермеата и ефикасност пречишћавања. Мембрана са пречником пора од 200 nm показала је најбоље перформансе, па је стога изабрана за процес микрофилтрације испитиване џибре.

Кључне речи: микрофилтрација, џибра, отпадна вода

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