

Cleaning of Ceramic Ultrafiltration Membranes After Filtration of Hay Hydrolysate

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Abstract - Hydrolysis of the lignocellulosic biomass results in the release of high-value chemicals that during industrial processing can be recovered with membrane technologies. To maintain an effective performance of the membranes used in the technological processing of biomass, their regular cleaning is essential. Although several guidelines may be found for membrane cleaning in the cases of organic fouling, the data for cleaning membranes fouled by hydrolyzed lignocellulosic biomass is limited. Current research is aimed to evaluate physical (air backpulse) and common cheap chemical membrane cleaning methods. The results showed that air backpulse alone had a minor (9%) effect on the membrane cleaning. The alternation of NaOH (1 %) solution with the NaClO (200 mg/L of Free chlorine) was the most effective approach for membrane cleaning. The cleaning effectiveness was 95.1 % for 50 nm membrane and 89 % for 200 nm membrane, indicating that membranes used for hydrolyzed lignocellulosic biomass filtration can be effectively cleaned using affordable and accessible chemicals.

Keywords - ceramic membranes, cleaning, fouling, lignocellulosic biomass

I. INTRODUCTION

Lignocellulosic biomass is abundant on Earth with an annual global production of about 181.5 billion tonnes. Around 7 billion tonnes are used as fodder or for energetic and material purposes and about 3.5 billion tonnes are produced as agricultural residues without any further use [1]. At the same time, lignocellulosic raw materials and bio-based primary products can be converted into high-

value chemicals, e.g., biofuels, furfural, carbohydrates [2]. Traditionally, the conversion is one-way subsequent pre-treatment, hydrolysis, fermentation, and product extraction. To facilitate product concentration, purification, and resource recovery, the introduction of membranes in the process stream has been recognized and tested in the treatment of lignocellulosic biomass after enzymatic hydrolysis [3]. Despite the high potential of membrane technologies, their efficiency is highly dependent on the properties of the liquid to be treated and membrane material.

Ceramic ultrafiltration membranes in comparison to polymeric membranes possess several advantages, including toleration to high temperatures and harsh chemical conditions, and a lifespan of 10-20 years [4], [5]. Therefore, ceramic membranes are widely used in food production, pharmaceutical, bioenergy, and other industries. At the same time, membrane operation is cumbersome, especially when fouling is tackled, since it reduces membrane performance efficiency by flux decline (in constant transmembrane pressure (TMP) systems) or increases TMP in constant flux systems. To maintain the membrane performance at a satisfactory level, regular membrane cleaning should be performed [6]. Cleaning procedures are commonly divided into physical (non-reagent) and chemical. While every physical cleaning method has different parameters affecting efficiency, chemical cleaning depends on four basic parameters: flow, reagent concentration, temperature, and contact time [7]. In

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the food industry, where organic compounds are the main foulants, it is considered that the cleaning should be performed at the same temperature as the filtration [7], to avoid protein crosslinking and denaturation [8]. The selection of the most appropriate cleaning agent and its concentration is crucial to avoid unwanted chemical reactions, damage of the membrane, or worsen contamination. Similarly, as in the food industry, the same issues have also been observed in the treatment of hydrolyzed biomass, where the solution contains lignocellulosic residue, released carbohydrates, and proteins, if enzymatic hydrolysis is performed [3]. All of these tend to foul the membranes.

To remove the organic foulants, alkaline reagents are the most widespread, since alkalis dissolve organic compounds, saponificate fats, and oils, and hydrolyze proteins [9], [10]. Nevertheless, the longevity of the cleaning procedure should be carefully evaluated to perform effective cleaning from one side, and not to terminate the production process for too long on the other. Although, general guidelines can be found on the cleaning of membranes fouled with different types of contaminants, every case must be evaluated individually. There are detailed recommendations available for various fields of the food industry [7], however, cleaning protocols for membranes applied in the treatment of hydrolyzed lignocellulosic biomass have not been reported or the data is limited. Within this study, the selection of the most appropriate treatment protocol for cleaning of ceramic ultrafiltration membranes after the filtration of hay hydrolysate was performed. To mimic industrial production, a laboratory pilot scale membrane system was used for the studies. Permeate flux was selected as the representative parameter to characterize membrane fouling. The general acceptance, that the lower the flux, the bigger the fouling was used to estimate the efficiency of the cleaning procedure.

II. MATERIALS AND METHODS

A. Experimental Setup

Filtration experiments and cleaning procedures were performed in a pilot-scale system (JWCMP – C.2, Jiangsu Jiuwu Hitech Co, China) equipped with a 30L AISI 316 tank with a water jacket for temperature control. The filtration setup (Fig. 1) was designed for constant flux filtration experiments with an air backpulse option. The constant feed flow was supplied by pump 4 (Grundfoss, CM5-4 A-R-GE-AQQE F-A-A-N) and regulation valves 5 and 12. Air backpulse was driven by the air compressor 21, solenoid valves 15; 19; 20, and a programmable logic controller for permeate flow, air intake, and air exhaust time control. Two mechanical pressure meters (8, 11) were used for the pressure measurement in feed flow and retentate flow. Flow meters were used to measure the flow of permeate (16) and retentate (13). The temperature was recorded using an electronic thermometer (6).

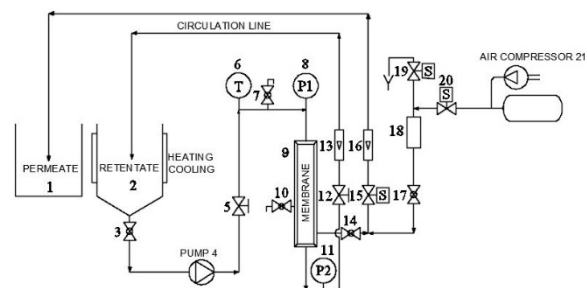


Fig. 1. Experimental filtration system with 30 L tank and 0.24 m² membrane filtration area.

B. Membranes

Two tubular ceramic membranes from Jiangsu Jiuwu Hitech Co (Jiangsu, China) with a pore size of 50 and 200 nm were used for filtration. Both membranes were made of TiO₂ filtering layer on α -alumina support with 19 parallel feed flow channels, an outer diameter of 25.4 mm, and a total length of 1016 mm. The inner diameter of the feed flow channels was 3.3 mm, the membrane area 0.24 m² and the porosity 35 %. The hydraulic resistance for 50 and 200 nm membranes was calculated from the deionized water flux to $4.8 \cdot 10^{-3}$ and $3.9 \cdot 10^{-3}$ bar m² hl⁻¹, respectively. The cross-flow velocity during filtration was 0.87 ms⁻¹.

C. Hydrolysate Preparation and Filtration

Dried hay from semi-natural grasslands was used as a source material for hydrolysate production. The biomass was milled (Retsch SM100, Haan, Germany) to obtain particle size ~ 1 mm. Then, the biomass (3% w/v in nanofiltered water) was thermally pre-treated/hydrolyzed (121°C, 1 bar for 5 minutes) in a 30 l AISI 316 reactor equipped with a mixer. Further, the hay solution was cooled to 30 °C and passed through the microfilter with a pore size of 1 μ m (Geyser, Russia) to remove major suspended solids able to block the ceramic membrane and the peristaltic pump. All tests were performed using 15 l of hydrolysed hay solution at 30°C that is the reported optimum concentration for biomass hydrolysis in the given reactor system [11].

Transmembrane pressure (TMP) was calculated according to (1) :

$$TMP = \frac{P_1 + P_2}{2} \quad (1)$$

where: – P₁ feed pressure, MPa; P₂ – retentate pressure, MPa;

After each filtration test, the membranes were cleaned using selected chemicals.

D. Biomass granulometric composition

To analyze biomass particle size and evaluate the efficiency of microfiltration, the granulometric composition of the biomass collected from the microfilter was determined with the vibration separator Controls D 407 (Newzeland) and different sieve sizes (<63, 63, 125, 250, 500, 1000).

E. Physical Membrane Cleaning

During air-water backpulse cleaning, the air was supplied by the compressor through valve 7 (Fig. 1). The air compressor pressure was set to 3 bar. The backpulsing was performed for 5 sec. every 5 mins. The air exhaust time was 8 mins.

F. Chemical Membrane Cleaning

The cleaning of membranes was performed according to the scheme in Table 1 at TMP of 0.5 bar and included 8 different test setups at a constant temperature regime. Before each chemical cleaning procedure, an initial rinse of the fouled membrane and the filtration system with deionized water at room temperature and a TMP of 0.5 bar was performed for 3 min. After the rinse, permeate flux (Q_b) with deionized water at 25°C and average TMP of 2.5 bar was measured. The second rinse (0.5 bar TMP) was performed with deionized water to remove chemical cleaning agents after the cleaning. Finally, permeate flux (Q_a) was measured with deionized water at temperature 25°C and TMP average 2.5 bar.

G. Cleaning Efficiency Calculations

Before every filtration experiment, the initial water flux of the clean membrane was measured using deionized water. The cleaning efficiency was evaluated as permeate flux recovery. The final flux recovery was based on the measurements of deionized water permeate flux through the cleaned membrane. Cleaning efficiency (%) was calculated according to (2)

$$F = \frac{Q_b - Q_a}{Q_b} \times 100 \quad (2)$$

where: Q_a – deionized water permeate flux after cleaning, l/h; Q_b – deionized water permeate flux before cleaning, l/h.

TABLE 1 TESTED CLEANING APPROACHES FOR 50 AND 200 NM CERAMIC MEMBRANES

Test	Membrane pore size, nm	Cleaning agents	Agent concentration, %	Cleaning time, min	Temperature, °C
1	50	HNO ₃	1	30	50
2	50	NaOH	1	30	60
3	50	backpulse	-	30	30
4	50	NaOCl	0.023	30	30
5	50	backpulse and NaOH	1	30 + 30	30 and 50
6	50	NaOH and NaOCl	1 and 0.02	30 + 30	50 and 30
7	200	NaOH and NaOCl	1 and 0.02	30 + 30	50 and 30
8	200	NaOCl and NaOH	0.02 and 1	30 + 30	30 and 50

III. RESULTS AND DISCUSSION

The initial permeability of the two membranes (50 nm and 200 nm) was determined before the experiments by linear regression of the deionized water flux (J) against the TMP (Fig.2).

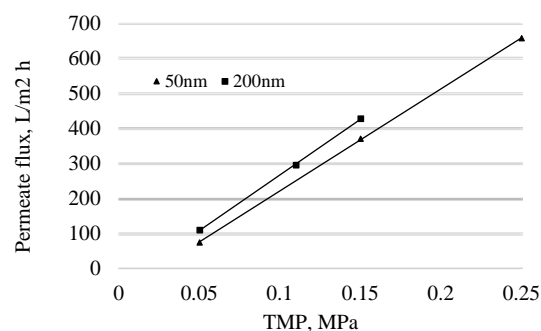


Fig. 2. Water flux against transmembrane pressure for the 50 nm (▲) and 200 nm (■) membranes at 25°C.

As expected, the permeate flux (J) of deionized water for clean membranes was higher for 200 nm membrane if compared to 50 nm membrane. The estimated maximal permeate flux in the pilot system was 1250 m² hl⁻¹ for 50 nm membrane and 1653 m² hl⁻¹ for 200 nm membrane.

A. Biomass and hydrolysate characterization

The estimated granulometric composition revealed that the particles are distributed within the whole range of used sieves. The highest fraction attributed to 125 and 250 μm sizes (Table 2). The fractions were acceptable for further filtration tests.

The estimated physical parameters of the hay hydrolysate (186 NTU turbidity, pH 5.1 – 5.5, conductivity 1850 μS/cm and zeta-potential of 17.5±4.5 mV) were representative of both thermally treated/hydrolyzed biomass and organic filtrates [12].

TABLE 2 GRANULOMETRIC COMPOSITION OF LIGNOCELLULOSIC BIOMASS

Sieve eye size, μm	Amount, %
1000	21,8
500	10,6
250	24,7
125	25,7
63	10,7
< 63	6,5

B. Permeate Flux

Two different stages concerning the permeate flux were distinguished in the thermally hydrolysed hay filtration process. In the first stage, permeate flux decreased significantly (from 28 hl⁻¹ to 10 hl⁻¹). This stage lasted approximately 15 minutes for both selected membranes. Then the permeate flux reached a steady-state and remained constant (Fig. 3). The calculated trendlines of the permeate flux decrease were similar when compared with

other studies utilizing 50 and 200 nm ceramic membranes [13], [14].

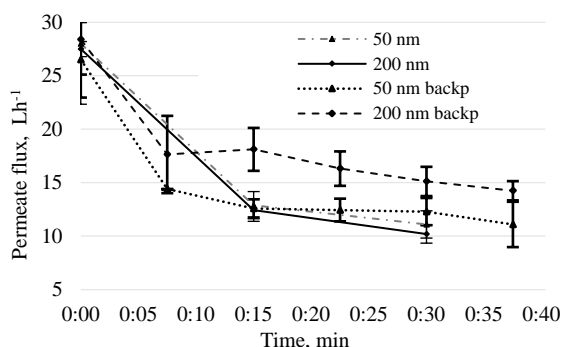


Fig. 3. The permeate flux of thermally hydrolyzed hay solution at 30°C with and without air backpulse for 50 nm and 200 nm ceramic membranes ($t=2.02$, $P=0.05$).

To enhance permeation flux, permeate or water can be used for membrane backwashing [15]. Alternatively, air backpulsing can be used [16]. In this study, backpulsing was used to enhance permeation during the hay hydrolysate filtration. The results showed a positive effect of air backpulsing only for a 200 nm membrane. And no effect for the 50 nm membrane. The 200 nm membrane air backpulsing could withstand permeate flux near 15 h^{-1} for 37 mins (until the full volume of thermally hydrolyzed hay was filtered) (Figure 3).

Similar results for the positive effect of air backpulsing for larger pore size membranes were obtained by [17] for synthetic leather industry wastewater and [18] for raw sugar cane juice filtration. The authors of both studies indicated no positive effect for 20 and 50 nm membranes. Thus, the results of the current study with lignocellulosic hydrolysate complement other findings where air backpulsing is useful for ceramic membranes of microfiltration range/or some loose ultrafiltration range (100-200 nm).

Furthermore, air backpulsing shortened the first phase of intensive flux decline from 15 minutes to 7 minutes. This phenomenon could be attributed to a small-size particle layer disruption and resuspension, leading to more intensive flux decline and faster stable phase onset.

C. Cleaning of Membranes

All of the thermally hydrolysed hay filtration experiments were followed by cleaning methods (Table 1). First, the efficiency of single-step cleaning methods (Test 1-4, Table 1) for a 50 nm membrane was evaluated (Fig. 4). Assessment of HNO_3 (1%) acid solution resulted in no positive effect on the membrane cleaning. This phenomenon may be attributed to the fact that the filtered solution of hydrolysed hay is of organic origin, whereas acids are effective for dissolving inorganic contaminants like metal oxides [8],[19]. The results were therefore excluded from the graphs. NaOH (1%) solution resulted in a 46.2% increase of permeate flux in 30 mins showing the best results obtained by single-step cleaning technique

(Fig.

4).

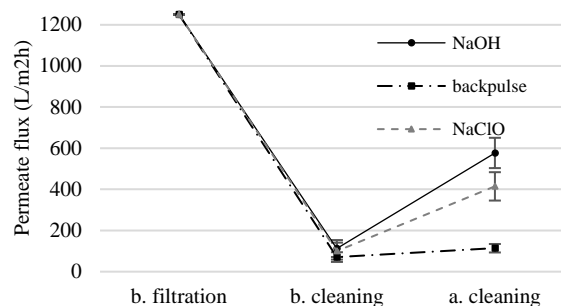


Fig. 4. The permeate flux for 50 nm membrane before filtration (“b. filtration”), after the filtration of thermally hydrolyzed hay solution (“b. cleaning”), and after the cleaning (“a. cleaning”).

The Zeta potential of the filtering solution was 17.5 ± 4.5 mV, meaning that the solution was in the unstable region, and particle aggregation and sedimentation could take place on the membrane surface [20]. In this case, it can be beneficial to raise the pH by adding alkali, promoting particle desorption from the membrane surface. The common concentrations of alkalis in these systems are in the range of 0.5 – 2% w/v [8].

Water + air backpulse showed minimal (9%) effect on the cleaning of 50 nm membrane, probably because residual hay particles present in the hydrolysate were much bigger in size than membrane pores. Furthermore, the size of air bubbles generated by the compressor was two orders of magnitude larger than the size of membrane pores, thus, air bubbles could not enter and clean the pores. Thus, air-based hydraulic cleaning techniques are unsuitable for microfiltration membranes [21], [22].

Application of NaOCl solution containing 200 mg/L of free chlorine (shock chlorination technique) resulted in 33.2% cleaning efficiency.

Since single-step cleaning approaches showed only modest results, two-step cleaning approaches were tested (Tests 5-6 in Table 1) to evaluate the potential use of apparently different chemicals in a single set-up.

The combination of air backpulse and NaOH resulted in 21% cleaning efficiency (Fig. 5),

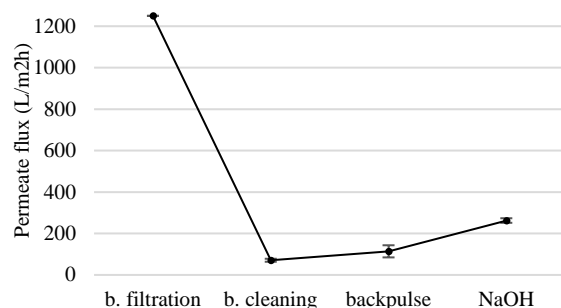


Fig. 5. The permeate flux for 50 nm membrane before filtration, after the filtration of thermally hydrolyzed hay solution, and after the cleaning with air-water backpulse and 1% NaOH solution. b.-before, a.-after.

which is low considering that in single-step cleaning approach with NaOH efficiency was 46.2%. Probably

backpulse disturbed debris layer presented in the pilot system walls, resulting in secondary contamination and decreased NaOH efficiency.

Subsequent use of NaOH and NaClO showed the best performance resulting in 95.1 % cleaning efficiency (Fig. 6).

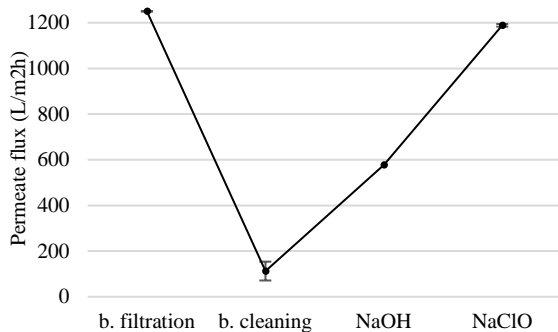


Fig. 6. The permeate flux for 50 nm membrane before filtration, after the filtration of thermally hydrolyzed hay solution, and after the sequencing cleaning with 1% NaOH solution and 0.023% NaClO solution. b.-before, a.-after.

Such consecutive use of alkali and active chlorine has been also shown to be effective for removing biofilms from pipe walls and killing *Bacillus* spores in a bulk [23]. After successful selection of the treatment approach, filtration of hydrolysed hay was validated for the 200 nm membrane. The results demonstrated 89 % efficiency for the consecutive use of NaOH and NaClO (Fig. 7), meaning that the method is equally effective for different size ultrafiltration membranes.

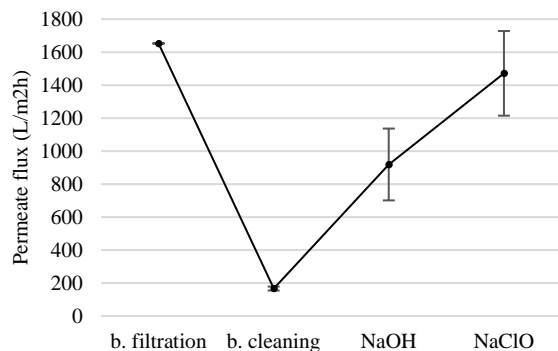


Fig. 7. The permeate flux for 200 nm membrane before filtration, after the filtration of thermally hydrolyzed hay solution, and after the sequencing cleaning with 1% NaOH solution 0.023% NaClO solution. b.-before, a.-after.

To demonstrate the efficiency of the selected step-wise treatment, NaOH and NaClO application was inverted. As expected, the two-step protocol resulted in a mere 46 % cleaning efficiency (Fig. 8), which was lower than using the opposite sequence of reagents.

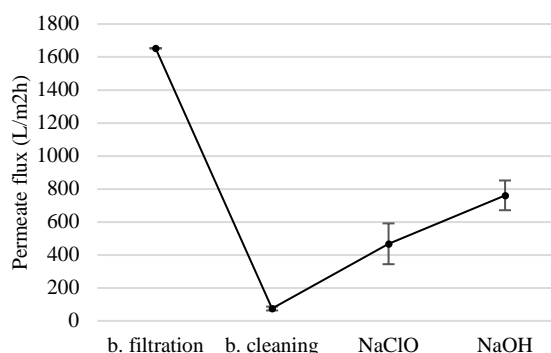


Fig. 8. The permeate flux for 200 nm membrane before filtration, after the filtration of thermally hydrolyzed hay solution, and after the sequencing cleaning with 0.023% NaClO solution and 1% NaOH solution. b.-before, a.-after.

This phenomenon may be attributed to the fact that NaOH loosens deposits on the membrane surface and disperse them, while NaClO promotes a gel layer on the membrane surface to decompose by oxidation and then fall off. The cleaning process is not as effective if active chlorine cannot penetrate the gel layer and effective reaction occurs only with loose particles. Thus, the sequence of the reagents is of big importance.

IV. CONCLUSIONS

Multiple physical and chemical methods have been tested to clean ceramic membranes after the filtration of hydrolyzed lignocellulosic biomass to extract fermentable carbohydrates. The results showed that single-step treatment does not provide efficient cleaning and result in less than 50 % cleaning efficiency. Alternation of NaOH (1 %) solution with the NaClO (0.023%) was the most effective approach for membrane cleaning resulting in 95.1 % for 50 nm membrane and 89 % cleaning efficiency for 200 nm membrane. Thus, membranes used industrial production of fermentable carbohydrates from hydrolyzed lignocellulosic biomass can be effectively and quickly cleaned with conventional inexpensive chemicals.

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