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Effect of hydrophilic coating for membrane assisted air diffuser for *Chlorella vulgaris* cultivation

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Abstract

Microalgae cultivation has high potential in capturing atmospheric carbon dioxide (CO_2) but are limited by poor CO_2 mass transfer to the algae. Therefore, improving mass transfer by increasing total contact area of gas-liquid through minimizing bubble size formed is investigated. In this project, the effect of polyether block amide (PEBAX® 1657) coating (i.e. different concentration and coating cycle) on polyvinylidenefluoride (PVDF) membrane surface properties are investigated and their impact on algae cultivation are evaluated using *Chlorella vulgaris* for duration of 14 days. The presence of functional groups from PEBAX coating showed the success of coating process and membrane hydrophilicity is improved from 111.19 ± 0.10° to 40.57 ± 1.29° when PEBAX 2.0 wt% is used. Membrane porosity is reduced when PEBAX concentration and number of coating cycle increased. Concentration of biomass is the highest (1.107 g/L) when PVDF/PEBAX 2.0 wt% is used, likely because of small size of CO_2 bubbles delivered into culture medium.

Keywords: *Chlorella Vulgaris; Algae Cultivation; Membrane; Air Diffuser; Hydrophilic*

1. Introduction

Climate change is the biggest environmental challenge our generation has ever encountered. This phenomenon is in conjunction with increasing greenhouse gases (GHGs) emission to the atmosphere from both natural and anthropogenic origins. The intensified consumption of fossil fuels from vehicles and industrial activities is accounted for 71.8% of total CO_2 emissions in 2008 [1]. Concentration of CO_2 in atmosphere is estimated to be increased by 75 ppm during year 2000-2050 due to high demand of energy from fossil fuels [2]. Statistics on CO_2 emissions reported by scientist and researchers is at alarming state and the impact of it is more obvious nowadays with inconsistent extreme weather. Reducing CO_2 content in the atmosphere are critical to address to avoid irreversible climate change. Bioprocess is a promising technology for CO_2 capture because it is environmental and economically attractive which utilize CO_2 from atmosphere and producing oxygen through photosynthesis process. Studies have been done on the feasibility of using microalgae to efficiently absorb CO_2 from the atmosphere [2,3] and producing valuable biomass for the commercial and industrial purposes [4]. The efficiency of carbon capture using gas injection method for algae cultivation has been restricted by random bubble size formation that leads to high shear stress to algae cells [5]. This intense bubble diffusion later leads to cell death [1, 6]. Apart from that, high dissolved carbon dioxide (D_{CO2}) from the excessive CO_2 injection create a toxic environment for algae growth [1]. There is potential of CO_2 being released back into the atmosphere without being utilized by algae. Thus, an efficient approach to provide the CO_2 to the culture medium are crucial to ensure high removal CO_2 supplied. Membrane air diffuser, on the other hand, able to improve CO_2 capture by allowing good dispersion of CO_2 into culture medium with minimal loss to atmosphere. Polymeric membrane properties such as porosity and selectivity are the main drive in providing enough CO_2 supply into culture medium. However, performance of membrane in cultivating microalgae is still rarely explore due to some challenges in optimizing the CO_2 mass-transfer efficiency without affecting algae growth. The efficiency of CO_2 mass transfer depends on the size of bubbles produced, in a way that smaller bubbles provide high mass transfer coefficient due to high surface-contact area. Other than that, fouling effect reduces hydrophobic membrane integrity for long-term application [7]. Therefore, method to improve membrane air diffuser performance for C. Vulgaris cultivation will be proposed and evaluated based on the biomass concentration produced. In this study, microfiltration membrane (polyvinylidene fluoride, PVDF) is used as air diffuser on cultivation of C. Vulgaris. Surface properties of the membrane properties is controlled by hydrophilic coating (poly ether block co-polymer, PEBAX®) at different concentration and coating cycle. The effect of membrane properties on bubble formation and algae cultivation are evaluated.

2. Experimental

2.1. Materials

PVDF membrane of 0.45 µm pore size is purchased from Merck (Germany) acted as membrane air diffuser in C. Vulgaris cultivation system. PEBAX®1657 was purchased from Arkema Inc. and used as hydrophilic coating. Ethanol (EtOH) with 95% purity is supplied from HmBG Chemicals (Johor, Malaysia). C. Vulgaris strain and compost nutrients were obtained from Centre of Biofuel and Biochemical Research (CBBR)[8] of Universiti Teknologi PETRONAS.

2.2. *Methodology*

2.1.1. Preparing PEBAX solutions of different concentration

Different concentration of PEBAX solutions (0.5, 1.0, 1.5 and 2.0wt%) were prepared by mixing the pellets with solvents; EtOH and water at mass ratio of 70:30 in 100 ml Schott bottle. The mixture was heated and stirred at temperature of 75°C and 200 rpm until homogenous solution is observed. Stirrer temperature was set lower than boiling point of ethanol, which is 78.37°C, to prevent evaporation of ethanol solution which will affect the concentration of final solution. Magnetic bar was added in the Schott bottle to promote homogenous mixing of the solution.

2.1.2. Preparing PVDF/PEBAX membrane: Dip-coating method

The prepared PEBAX solution was then transferred into a 100 ml beaker for dip-coating process. PVDF membrane was immersed in the solution for 10 minutes and the beaker was covered with parafilm to prevent contaminations. The membrane must be fully dipped in the PEBAX solution to ensure a thorough coating layer is achieved. Coated membrane was then dried in oven for 30 minutes at 60°C. The process is repeated for different PEBAX concentrations and number of coating cycles. Precautions need to be taken throughout dip-coating process to ensure the membrane surface facing the culture medium is not being touched or destroyed.

2.1.3. Membrane characterization

FTIR analysis was carried out using Frontier 01 Perkin Elmer to identify the presence of functional groups in membrane. Images of membrane surface were obtained using Zeiss EVO Scanning Electron Miscroscope (Germany). Sample membranes were coated with gold using a sputter-coater before tested. Three-dimensional membrane surface image was recorded by using NanoNavi ESweep Scanning Probe Microscope (Japan). The image was generated by using tapping mode with a silicon-coated probe and were recorded over an area of 5µm x 5µm. Membrane contact angle was measured with Contact Angle System OCA. Membrane was adhered on sample platform and distilled water droplet was placed on it. Image of the droplet on the membrane was captured and contact angle is determined by the SCA 20 software. Measurements are taken from five different points to minimize the experimental error and average value is reported.

2.1.4. Chlorella vulgaris cultivation: Laboratory set-up & process condition

Prototype of membrane bubble column with five modules made of acrylic were built with the following dimensions; diameter of 8 cm, height from base 23 cm and volume of 1270 cm^3. The schematic diagram of the experimental setup used is shown in the Figure 1. Each module was filled with 800 ml tap water, 50 ml algae cell and 40 ml compost nutrients. Pumped air entered at the bottom of the chamber, pressurized and diffused through the membrane to supply CO_2 into the culture medium. Flow rate at the top of the module was fixed at 1 L/min to control the amount of bubble flow rate in the medium. Cultivation conditions for *C. Vulgaris* was carried out at room temperature 25°C in culture medium of pH range 4 to 6. The setup was illuminated by fluorescent light for 14 days. Daily observations on the culture medium condition was recorded throughout cultivation period for further discussions.

2.1.5. Determining biomass concentration

The efficiency of CO_2 capture is measured from the concentration of biomass produced by *C. Vulgaris*. Three samples of 10 ml algae suspension from each module were collected and transferred into aluminium dish. The empty aluminium dish was weighted beforehand. Samples were dried overnight at temperature of 80°C in drying oven. Mass of biomass produced was determined from the difference between dry weight (g) and empty aluminium dish weight

(g). Biomass concentration was calculated by dividing mass of biomass produced (g) over volume of sample collected (10 ml). The average biomass concentration was recorded and reported on daily basis for 14 days.

$$\text{Mass of biomass (g)} = \text{Dry weight (g)} - \text{Empty aluminium dish weight (g)} \quad \textbf{(1)}$$

$$\text{Biomass concentration (g/L)} = \frac{\text{Mass of biomass (g)}}{\text{Amount of sample taken (L)}} \quad \textbf{(2)}$$

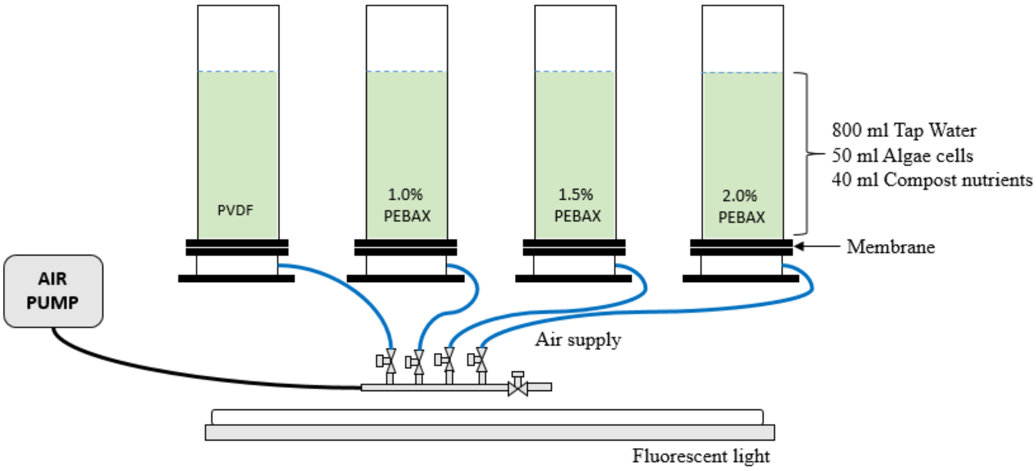

Figure 1: Schematic drawing of experiment setup

3. Results and discussion

3.1. Membrane characterization

Based on Figure 2(a), the presence of dual C-F stretching from PVDF is shown at 1207 and 1152 cm^{-1}. Bands located at 2915 and 2849 cm^{-1} are both corresponded to the CH_2 asymmetric and symmetric vibration of PVDF. The absorption peak appeared at 1469 cm^{-1} was attributed to CH_2 wagging vibrations. FTIR spectra for PVDF/PEBAX membranes shows peaks from both PVDF and PEBAX hence confirming the successful of the dip-coating process (Fig. 2). Strong bending vibration in the range of 1350–1470 cm^{-1} is detected from the CH_2 deformation of PVDF and PEBAX. The presence of C-O-C and N-H stretching from PEBAX ether segment and Nylon-6 are in the range of 1000-1320 cm^{-1} and 3250-3400 cm^{-1} respectively. There is some shift in the wavenumber for amide (O-C=O) segment from 1730 cm^{-1} in pure PEBAX to between 1640-1690 cm^{-1} upon introduction to PVDF membrane. Referring to Figure 2, as PEBAX concentration increased from 0.5wt% to 2.0 wt%, the intensity of N-H peak (3250-3400 cm^{-1}), O-C=O peak (1730 cm^{-1}) increases while CH_2 (2850-3000 cm^{-1}) diminished. The CH_2 stretching diminished as higher concentration of PEBAX is used due to disruption and formation of new hydrogen bonds between membranes [8]. The absorbance intensity of C-F bond attributed from PVDF is reduced which further confirms that higher coating concentration gives better surface coverage on the PVDF membrane. Based on Figure 3, the intensity of PEBAX-related functional group increases with increasing number of coating cycle. The amide and ether groups show high transmittance (%) when more coating layer is applied for PVDF/PEBAX 0.5wt% membrane. Water contact angle measured for pure PVDF is 111.19 ± 0.10°, slightly higher from contact angle reported by literatures which is at 92° [9]. Higher contact angle measured is attributed to the nanopatterns or shape of the PVDF surface which increased the surface contact area with a droplet and making it more hydrophobic. PEBAX coating has reduced membrane contact angle since presence of amide polar groups give good surface affinity to water and able to form hydrogen-bonds with water [10]. Hydrophilic characteristic of PVDF is more obvious when coated with PEBAX of higher concentration and increasing coating cycles. Higher PEBAX concentration has more polar groups as shown by FTIR analysis

(Figure 2) thus increases surface wettability of the membrane. Based on Figure 4, the lowest water contact angle is 40.57 ± 1.29° when PEBAX 2.0 wt% is used for coating. Number of coating cycle has significant effect on PVDF/PEBAX membrane contact angle as well. As number of PEBAX 2.0 wt% coating cycles increased, contact angle is increased, giving membrane less hydrophilic effect due to the low presence of polar groups. Effect of coating cycles on contact angle at PEBAX 0.5, 1.0 and 1.5 wt% did not showed the same trend due to effect of surface roughness. The rougher membrane surface, the less hydrophilic characteristic possessed by the membrane.

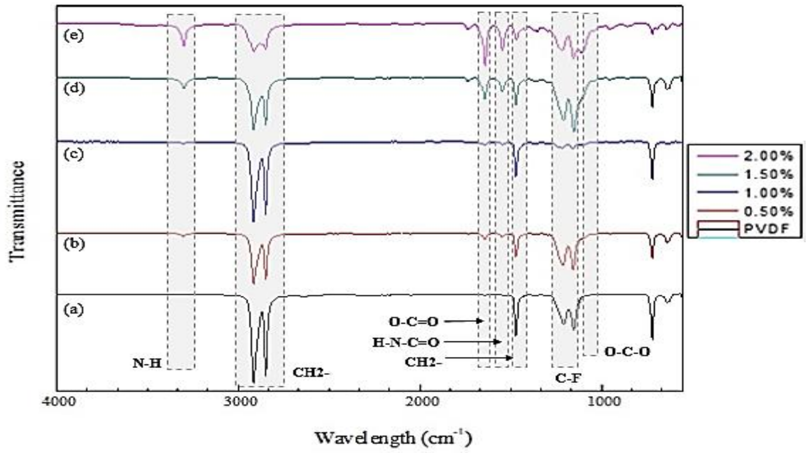

Figure 2: IR absorbance spectra for (a) uncoated PVDF; (b) PVDF/PEBAX 0.5 wt%; (c) PVDF/PEBAX 1.0 wt%; (d) PVDF/PEBAX 1.5 wt%; (e) PVDF/PEBAX 2.0 wt% at one coating cycle

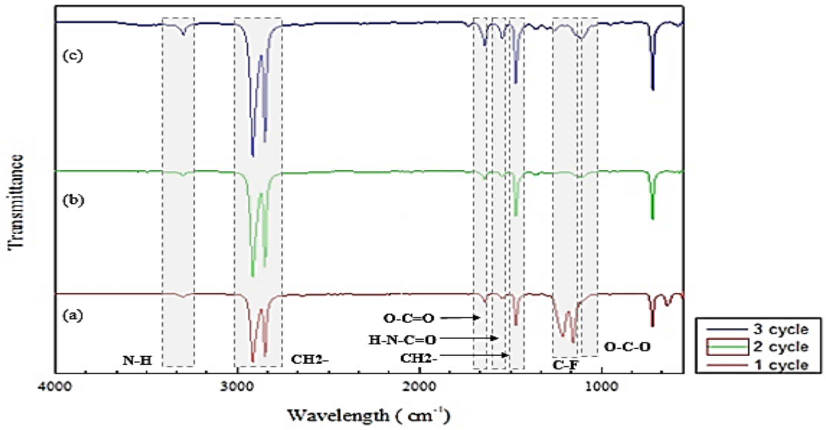

Figure 3: IR absorbance spectra for (a) one cycle; (b) two cycles; (c) three cycles at PEBAX 0.5 wt%

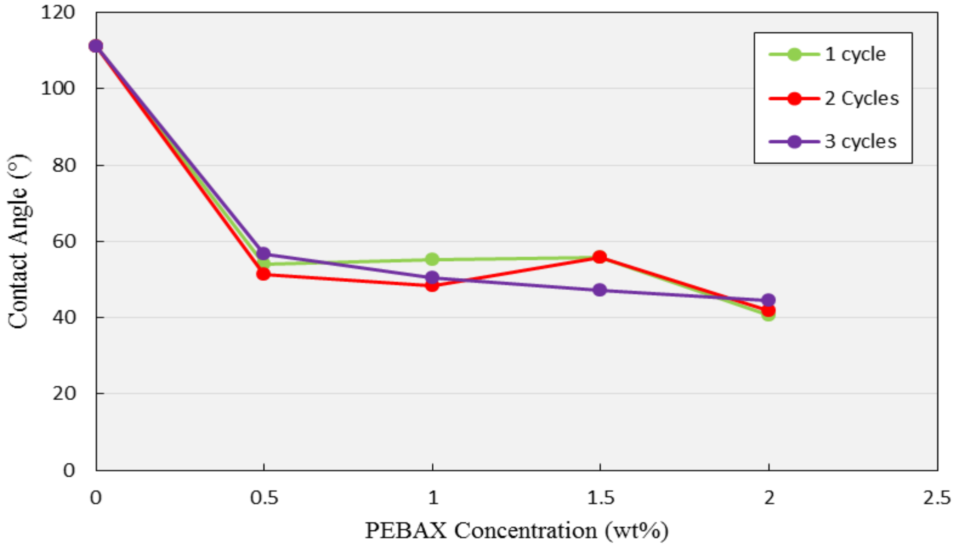

Figure 4: Water contact angle (°) for uncoated PVDF and PVDF/PEBAX at different concentration and coating cycles

3.2. Biomass production

Pure PVDF and PVDF/PEBAX membrane of different concentration at one coating cycle is used to investigate the effectiveness of membrane coating in supplying CO_2 for *C. Vulgaris* cultivation. The algae growth is superior that previously reported when using almost identical parameter was approximately only 0.6 g/L of *C. Vulgaris* concentration after 14 days of cultivation [11]. This is likely due to higher CO_2 mass transfer when using membrane as diffuser compares to typical air diffuser, thus significantly improve biomass productivity. Concentration of biomass produced in the first 24-hours of cultivation increases with concentration of PEBAX coating. Highest biomass concentration recorded was 1.1067 g/L by PVDF/PEBAX 2.0wt% that is 20% higher than PVDF followed by PVDF/PEBAX 1.5wt% and 1.0wt%. Small bubbles formed by PVDF/PEBAX 2.0wt% membrane has improved CO_2 utilization due to higher surface contact-area. Biomass concentration for PVDF and PVDF/PEBAX 1.5wt% was at peak on the last day of cultivation, 1.0503 and 1.0504 g/L respectively. PVDF/PEBAX 1.0wt% produced highest biomass concentration on day 12 at 1.0479 g/L before dropped drastically to zero. The inconsistent biomass concentration trend for *C. Vulgaris* cultivation is affected by size of bubbles formed and membrane fouling effect.

Table 1: Biomass concentration (g/L) of *C. Vulgaris* cultivation

Days	**PVDF**	**PEBAX 1.0 wt%**	**PEBAX 1.5 wt%**	**PEBAX 2.0 wt%**
1	0.9241	1.0688	0.9559	1.1067
2	0.8635	0.8126	0.7459	0.8871
3	0.6333	0.6821	0.7859	0.6367
4	0.8834	0.6412	0.6699	0.6379
5	0.8505	0.8203	0.7785	0.7840
6	0.7481	0.8184	0.6335	0.7212
7	0.8623	0.6069	0.8926	0.8260
8	0.9959	0.8925	0.6384	0.7506

Days	PVDF	PEBAX 1.0 wt%	PEBAX 1.5 wt%	PEBAX 2.0 wt%
9	0.6363	0.3501	0.4247	0.1053
10	0.7364	0.3505	0.7135	-
11	0.6966	0.3333	0.3527	-
12	1.0410	1.0479	1.0219	-
13	0.7149	0.3592	0.7154	-
14	1.053	0.0000	1.0504	-

Cultivation in PEBAX 2.0wt% module was stopped on day 10 due to leakage and small orifice was found upon inspection on PVDF/PEBAX 2.0wt% membrane. The orifice had caused sudden large bubbles formation in module and affected concentration of biomass produced. The effect can be seen from the drastic drop of biomass concentration on day 9. This happened probably because of the high capillary pressure for inlet air to overcome and as result membrane is punctured. Figure 6 shows biomass sediments accumulated on membrane surface observed in all module after few hours of cultivation. Low radial mixing inside bubble column could not uplift large biomass cells and settled at the bottom due to gravity. Highest amount of sediments was collected on PVDF/PEBAX 1.5 wt% surface since the membrane porosity is the lowest hence providing more non-active site for sediments to reside. The formation of bubbles on membrane surface was restricted and limited by biomass sediments. Lack of CO_2 supply for oxygen sweeping will lead to photooxidation in algae cell and reduces biomass viability [12,13]. Therefore, concentration of biomass started to drop since insufficient amount of CO_2 supplied into culture medium.

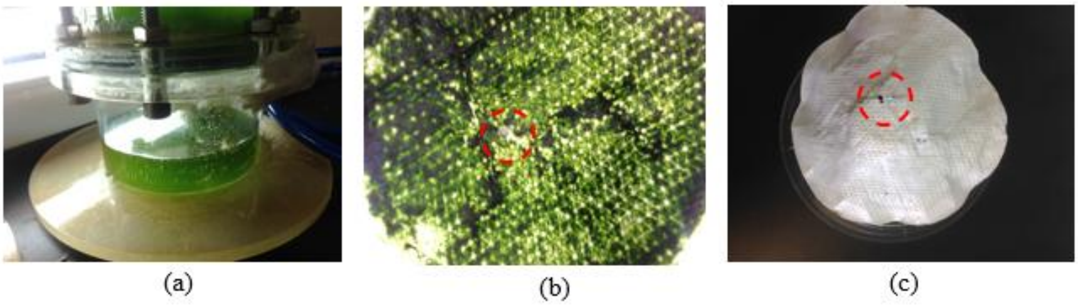

Figure 5: Observations on PEBAX 2.0 wt% module (a) culture liquid collected in air supply section; (b) orifice on membrane surface (active site); (c) orifice on membrane surface (back)

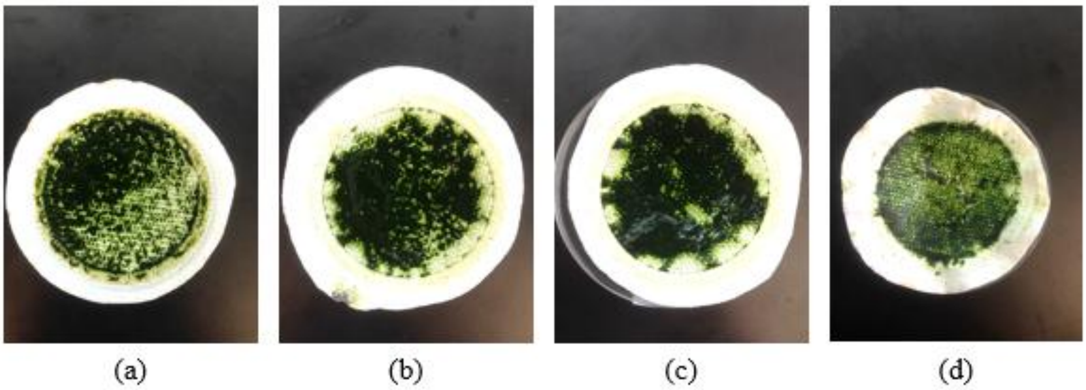

Figure 5: Biomass sediments on membrane surface (a) PVDF, (b) PVDF/PEBAX 1.0wt%, (c) PVDF/PEBAX 1.5wt% and (d) PVDF/PEBAX 2.0wt%

Table 2:Weight of biomass sediments on membrane surface

Module	Weight of biomass (g)
PVDF	0.08
PEBAX 1.0 wt%	0.10
PEBAX 1.5 wt%	0.23
PEBAX 2.0 wt%	0.05

4. Conclusion

This project has beneficial impact in mitigating climate change and promotes environmentally friendly and economical way of reducing CO_2 atmospheric concentration. Biomass produced from photosynthetic activity of microalgae making this project viable as a stepping stone going towards renewable source of energy. The implementation of membrane air diffuser has been carried out and showed a better carbon capture efficiency compared to conventional method. The highest biomass concentration recorded was 1.1067 g/L, that is 46% greater compared to typical air diffuser. The objectives of this project have been achieved since hydrophilic coating of PVDF membrane by using PEBAX is proven able to improve membrane surface properties and biomass production from cultivation of *C. Vulgaris*. Membrane surface wettability has been improved significantly when coated with PEBAX of higher concentration. The hydrophilic effect of modified membrane has significantly improved CO_2 diffusion into culture medium and provide a better mass-transfer efficiency. Conclusion can be withdrawn on the effect of surface roughness on surface wettability, in a way that membrane with rougher surface gives less hydrophilic effect. Nonetheless, cultivation of *C. Vulgaris* was inconsistent throughout 14 days period since CO_2 supply was restricted by sediments accumulated on membrane surface.

5. References

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