Fabrication technique of composite chitosan/alginate membrane module for greywater treatment

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Abstract. A novel chitosan/alginate composite membrane is proposed for the application of greywater treatment. In particular, the effect of stirring speed of mixing chitosan and alginate solution was investigated in this study. The study revealed that 150CSAL and 210CSAL membranes swell significantly compared to CS membrane due to the porous structure of composite membrane. The FTIR spectra revealed that the mixing speed has no influence in terms of molecular interaction between CS and AL due to fixed CS and AL concentrations used in this study. On the other hand, the complexation of AL with CS made outstanding improvement to the dense structure of CS where 180CSAL membrane has UP water flux as high as 90 L/m2h at 2 bar. All membranes have the capability to remove the pollutants present in GW and the COD removal was further improved up to 7% using CSAL membranes. In addition, increasing mixing speed improved the pathogen removal efficiency compared to CS membrane. The treated GW met the non-potable GW reuse standard for turbidity<5 NTU and TSS<20 mg/L. To summarize, the proposed fabrication technique on CSAL membrane showed improved characteristics to CS membrane and has significant performance on GW treatment.

Keywords: Alginate, Chitosan, Greywater, Composite Membrane, Polyelectrolyte Complex

1. Introduction

Availability of freshwater resources over the years has been decreasing due to explosion of population growth rate, industrialization, and urbanization. United Nation (UN) predicted that over a third of global population to face water scarcity by 2025 due to factors as identified by several researchers[1]. Thus, escalating demand for freshwater supply will be at peak and exacerbate the situation in near future. Over the decades, Malaysia was reported to consume freshwater up to 226 L/person/day and 67% of freshwater consumption catered for domestic usage[2,3]. The reported figure is alarming for a developing country like Malaysia as the available evidence pertaining to high freshwater consumption usually concentrated in the developed countries[4]. In contrast, other south-east Asian countries such as Thailand, Singapore, Nepal and Vietnam reported to consume lower freshwater for domestic usage ranging from 72-155 L/person/day [5–7]. Under such circumstances, Malaysia and other countries with high freshwater consumption should place an immense priority on freshwater management. Henceforth, greywater (GW) recycling and management has been receiving tremendous attention recently as
alternative source of water for non-potable applications. This approach has been well practiced in many developed countries such as Australia, Germany, Japan and United States of America[8–10].

GW is defined as wastewater originate from laundry, kitchen sink, bathroom, handbasin and shower. Generally, GW considered as low strength wastewater due to exclusion of blackwater that typically treated in a sewage treatment plant. With appropriate treatment, 30-50% of freshwater consumption can be minimized through GW recycling[11,12]. Even though biological, physical and chemical treatment technologies well explored GW treatment, the biological treatments such as membrane bioreactors (MBR) are much favoured due to their high pollutant removal efficiency[13,14]. Li et al. [15]claimed that physical treatment as the main treatment is inadequate for GW treatment. However, a contemporary studies have highlighted that efficacy of physical treatment such as membrane filtration to have better performance on GW treatment [16–18]. Commonly synthetic polymers are mostly explored for GW treatment through filtration process. This approach regarded as less feasible due to biodegradability issue with synthetic polymer and reliance on fossil fuel for polymer synthesis[19–21]. Thus, tailoring a path to much eco-friendly and green approach regarded as a sustainable approach where the use of biopolymer as a replacement for synthetic polymer provides much greener outputs.

Chitosan (CS) and alginate (AL) are examples of biopolymer that have been well explored in different applications. The primary reason of such exploration is due to formation of polyelectrolyte complex (PEC) between positively charged CS and negatively charged AL [22–24]. It is difficult for CS and AL to stand alone as a membrane due to hydrophilicity of AL and dense structure to CS that complicates filtration process [25–27]. However, interaction of CS and AL reduces the hydrophilicity of AL and forms insoluble PEC membrane [25,26]. Several challenges were highlighted from fabrication of composite chitosan/alginate (CSAL) membrane. The reaction between protonated amino groups of CS and carboxylic groups AL occurs instantaneously and forms insoluble heterogenous coacervates [26–28]. This problem is much apparent if high molecular weight CS used as it has longer polymer chain. Numerous studies reported to add acetone as part of CS solvent which helps to restrict complete PEC formation and maintain CS is less extended conformation [26–28]. However, complete PEC interaction of CSAL always preferred, as it will provide desirable mechanical strength and problem with alginate leaching can be avoided. Another method to avoid complete coacervate of CSAL formation are dropwise addition of CS to AL and mixed under vigorous condition and addition of crosslinker such as calcium chloride. Upon casting, the solution allowed to dry under vacuum condition to have bubble free membrane[29,30]. Molieres et al.[31] studied the influence of homogenization technique on CS and AL using different types of homogenizers. Ultra-turrax homogenizer was operated at 1000 rpm while Stephen homogenizer operate under vacuum condition at 500 rpm. Another study presented ultrasonication as a mode for CS dispersion but depolymerization occurs at different sonication intensity [32].

This study presents a simple yet cost effective method for solution casting technique of composite CSAL membrane without the need for acetone, crosslinkers, vacuum drying condition and dispersion through ultrasonication. The primary objective of this study was to investigate the applicability of proposed fabrication technique of composite CSAL membrane without addition of crosslinker and acetone as additional solvent. Correspondingly, the influence of mixing speed on membrane characteristic and GW filtration efficiency were investigated. The concentration of CS (1wt%) and AL (0.5wt%) were fixed while the mixing speed were varied systematically.

2. Materials and Methods

2.1 Materials
Powdered chitosan (high molecular weight, $M_w>310kDa$, deacetylated chitin, Iceland) and sodium alginate (China) were obtained from Sigma Aldrich. Meanwhile, polyethylene glycol 6000 (PEG-6000, $M_w=6000$ Da, Russia) and glacial acetic acid (AR grade, Germany) were purchased from Merck. Sodium
hydroxide (AR grade, pellet) was purchased from R&M chemicals. Selective nutrient agar (*Brillance E.Coli/Caliform, CM-1046, England) were purchased from Oxoid. All chemicals were used as received without additional purifications.

2.2 Fabrication of Composite CSAL
1 wt% of PEG-6000 were dissolve in 2 vol% of acetic acid. In the same solution 1 wt% of CS were added. On a separate solution, 0.5 wt% of PEG-6000 and 0.5 wt% AL were dissolve in similar order in ultrapure (UP) water. Both solutions, 1 wt% CS and 0.5 wt% AL were stirred separately using mechanical stirrer (CAT, R50D) at 800 rpm for 4 hours until homogenous solutions obtained and left to degas overnight. Upon degas, 1 wt% CS was added in dropwise manner using syringe into 0.5 wt% AL at volume ratio of 3 CS:1 AL and stirred at 150 rpm for 3 h. After mixing, 25 mL were withdrawn from the solution and casted on petri dish. The cast solution on petri dish was placed on flat surface for approximately 15 minutes for an even surface to be obtained. After that, the solution was left in oven to dry at 60℃ for 24 h. Upon 24 h drying and successful membrane formation, the membrane was treated with 2 wt% sodium hydroxide (NaOH) for 15 min. The membrane then washed multiple time with UP water to remove excess solvent and NaOH. Finally, the membrane was subjected to hot water bath at 80℃ to wash out PEG-6000 in the membrane and generate a porous structure. The overall process was repeated with different CSAL mixing speed of 180 and 210 rpm and stored in wet state prior to usage. Table 1 present the abbreviation of membrane with respect to the preparation condition.

| CS:PEG (wt%:wt%) | AL:PEG (wt%:wt%) | Mixing speed (rpm) | Membrane name |
|------------------|-------------------|-------------------|---------------|
| 1:1              | 0                 | 800               | CS            |
| 0                | 0.5:0.5           | 800               | AL            |
| 1:1              | 0.5:0.5           | 150               | 150CSAL       |
| 1:1              | 0.5:0.5           | 180               | 180CSAL       |
| 1:1              | 0.5:0.5           | 210               | 210CSAL       |

2.3 Membrane Characterization
2.3.1 Fourier Transform Infrared (FTIR) Spectroscopy
The presence of different functional groups of CS and AL were detected through FTIR (PerkinElmer, Spectrum 100). In addition, the changes in molecular structure of CS and AL upon formation of PEC also captured through FTIR analysis. Transmittance wavelength range was set at 450 cm⁻¹ to 4000 cm⁻¹ with 16 overlapping scans.

2.3.2 Swelling Ratio
Swelling ratio was performed to study the water uptake ability of the membrane as well as the degrees of crosslinking between CS and AL. To perform this study, the membranes were cut into 1 cm (width) x 1 cm (length) and immersed in UP water at room temperature. Then, the membranes were removed and wiped with filter paper to remove excess water on the membrane surface. Thereafter, the membranes were weighed at different time intervals of 1, 5, 10, 15, 20, 25, 30, 60, 90, 120 and 150 min. The study was repeated five times to obtain average swelling ratio which calculated using Eq. (1).

\[
\text{Swelling ratio} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100% \\
\text{Eq. (1)}
\]

Where,
\[W_{\text{wet}}\] is the wet membrane weight and \[W_{\text{dry}}\] is the dry membrane weight.
2.3.3 Porosity
The membrane porosity was measure based on dry-wet weight method, where the membranes were cut into 1 cm (width) x 1 cm (length) and immersed in UP water at room temperature and left for 30 minutes. The study was repeated for five times and the porosity was calculated based on Eq. (2).

\[
\text{Porosity (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_w A \delta} \times 100\% \tag{2}
\]

Where,
\( W_{\text{wet}} \) is the wet membrane weight (g), \( W_{\text{dry}} \) is the dry membrane weight (g), \( \rho_w \) is the density of UP water (g/cm\(^3\)), \( A \) is the membrane wet state area (m\(^2\)) and \( \delta \) is the membrane wet state thickness (cm)

2.3.4 Water Flux
A dead-end filtration unit as presented in Fig.1 was used to study the water flux of the membrane at various operating pressure ranging from 1 to 4 bar. A clean membrane was placed on the filtration unit and loaded with 0.2 L of UP water. The permeate was collected at various pressure and the duration was fixed at 30 min. Based on the collected permeate, the water flux was calculated using Eq. (3) and the experiment repeated for fives to obtain the average results.

\[
\text{Flux}, J \left( \frac{L}{m^2 h} \right) = \frac{V_{\text{permeate}}}{A \times t} \tag{3}
\]

Where,
\( V_{\text{permeate}} \) is the volume of permeate collected, \( t \) is the filtration duration and \( A \) is the effective area of the membrane.

![Fig. 1. Dead-end filtration unit](image)

2.4 Greywater Filtration Performance
Bathroom GW which was always collected on the day of filtration process was used in this study. The source of GW collection was maintained at single source to ensure the consistency of pollutant present in the GW. The characteristic of raw GW is as presented on Table 2.

| Parameters         | Unit       | Average | Standard Deviation |
|--------------------|------------|---------|--------------------|
|                     |            |         |                    |
pH | n.a | 6.58 | 0.18  
Turbidity | NTU | 216.27 | 63.27  
TSS | mg/L | 247.53 | 190.79  
COD | mg/L | 518.93 | 102.95  
Other organism | cfu/100mL | 1.21×10⁵ | 1.93×10⁵  

TSS: Total suspended solids, COD: Chemical oxygen demand

The GW filtration was studied using the same setup in Fig.1. The filtration efficiency was monitored through removal of turbidity, total suspended solids (TSS), chemical oxygen demand (COD) and pathogens. Turbidity and pH were recorded using turbidimeter and pH meter, respectively. TSS and COD was measured using Merck photometer method while spread plate technique (selective nutrient agar) was used to enumerate the presence of pathogen in raw and treated GW. All these parameters were measured on both raw and treated GW and the pollutants removal efficiency were calculated based on Eq. (4):

\[
\text{Removal percentage} = \frac{C_o - C_f}{C_o} \times 100\%
\]

\text{Eq. (4)}

Where,

\(C_o\) in the feed concentration and \(C_f\) is the permeate pollutants concentration.

3. Results and discussion

3.1 Membrane characterization

3.1.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR analysis revealed the evidence of PEC interaction between CS and AL in Fig 2. Based on the Fig 2(i), multiple intense peaks were identified for AL spectra. This is due to the presence of PEG in AL that cause multiple intense peaks. In general, asymmetric and symmetric vibrations of carboxylate anions were detected at 1599 cm⁻¹, 10467 cm⁻¹ and 1101 cm⁻¹[33]. In addition, broad band of 3341 cm⁻¹ correspond to O-H group were detected.

Fig. 2. FTIR spectra of membranes (i) Alginate (ii) CS and CSAL at different mixing speed
As for Fig. 2 (ii), CS membrane present with broaden O-H and N-H stretching peak at 3357 cm\(^{-1}\) (3000-3500 cm\(^{-1}\)). On the other hand, peaks corresponding to amide I (1600-1670 cm\(^{-1}\)) and amide II (1550-1640 cm\(^{-1}\)) were detected at 1638 cm\(^{-1}\) and 1560 cm\(^{-1}\) respectively. In addition, C-O and amino groups (1000-1300 cm\(^{-1}\)) of CS were detected at 1027 cm\(^{-1}\) and 1120 cm\(^{-1}\) respectively[34]. Despite addition of PEG-6000 into CS solution, the multiple intense peaks as presented in AL spectra was not detected. This further proves that water bath process at 80°C removes the PEG content and generates the membrane’s porous structure. PEC interaction between CSAL membrane at all three mixing speeds were recognize through shifted 1638 cm\(^{-1}\) and 1560 cm\(^{-1}\) peaks to 1651 cm\(^{-1}\) and 1559 cm\(^{-1}\) upon addition of AL to CS. Furthermore, the peaks of 1651 cm\(^{-1}\) and 1559 cm\(^{-1}\) on CSAL membrane were much intensive comparative to CS membrane [25, 26, 34]. The broad band from 1560 cm\(^{-1}\) to 1651 cm\(^{-1}\) arose from overlapping of amide group CS and carboxylate group of AL[36]. Apart from that, the peak at 1376 cm\(^{-1}\) which highlights the N-O bonding remains constant but intensified upon addition of AL. Similarly, the increased intensity of carboxylic peaks at 1020 cm\(^{-1}\) and hydroxyl peak at 3347 cm\(^{-1}\) further indicates the presence of AL in the CSAL membrane[25, 26, 34]. On the side note, the intensity of all CSAL membrane at different speed were consistent as the concentrations of CS and AL were fixed.

3.1.2 Swelling Ratio

The swelling of a membrane provides information on the water uptake ability by the membrane and the degree of crosslinking if more than one polymer present. Fig. 3 presents the swelling curves of CS and CASL membrane at different speed.

![Fig. 3. Swelling curves of CS and CSAL membranes at different mixing speed](image)

Due to hydrophilic nature of AL, the membrane completely dissolved in UP water. The order of membrane swelling is as follow, 150CSAL >210CSAL > CS > 180CSAL. Several studies claimed that higher degree of crosslinking due to formation of PEC reflects in lower swelling ratio [25, 26]. This is due to reduction of protonated amino groups in CS and carboxylate groups of AL that are responsible for water uptake. In this study, the swelling reached at equilibrium after 30 min and presented with high swelling ratio for 150CSAL and 210 CSAL membrane than CS despite PEC formation. This is due to porous structure of CSAL membrane that allows water to enter the membrane skeletal structure and cover maximum surface area [36, 37]. Although porous CS membrane produced, the porosity of CSAL membrane much greater as CSAL membrane prepared with CS and AL containing 1:1 ratio of PEG. This indicates that the porosity of CSAL membranes is much prominent compared to CS membrane. Correspondingly, this also ensure that the homogeneity of the CSAL solution prior to casting and low
mixing speed also provide sufficient reactions between CS and AL. Apart from porosity factor, lower swelling of chitosan-alginate membrane reported despite porous membrane fabricated using different Pluronic F68 concentrations[39]. This was due to addition of calcium chloride to crosslink AL hence the interaction of carboxylate ions with water molecules will be reduced thus reflecting on lower swelling. However, in this study no crosslinker was added which suggest possible interaction carboxylate groups of AL with water molecules and leads to greater water uptake by the membranes. On the contrary, 180CSAL membrane has slightly lower swelling ratio compared to CS. This indicates higher degree of crosslinking between CS and AL and better homogeneity.

3.1.3 Porosity
Dry-wet weight method was performed to study the porosity of each membrane. 150CSAL has the highest porosity up to 94% while 180 CSAL membrane has the lowest porosity among all at 86. Meanwhile, CS and 210CSAL membrane have similar porosity of 88%. These finding coincide with the swelling curve in Fig.3 as 150CSAL membrane has the highest swelling which was hypothesized to have greater void fraction that allows water to enter the membrane skeletal structure and cover maximum surface area despite formation of PEC [38]. On the other hand, 180CSAL membrane swells the least which reflects on the lower porosity. This findings coincide with [31]as lower mixing through mechanical agitation expected to reflect on greater porosity.

3.1.4 UP water flux
The UP water flux was performed to study the workability of membrane for filtration at various operating pressure. Low operating pressure were studied for safety precautions purposes and effort for energy minimization maintained as the desired operating pressure for GW treatment set as low as possible. Table 3 presents the average UP water flux at different operating pressure ranging from 1 to 4 bar.

| Operating pressure (bar) | Units   | CS       | 150CSAL  | 180CSAL  | 210CSAL  |
|--------------------------|---------|----------|----------|----------|----------|
| 1                        | L/m²h   | 0.698±0.054 | 4.139±1.055 | 8.664±1.179 | 5.418±1.619 |
| 2                        | L/m²h   | 1.348±0.101 | 5.596±0.269 | 90.006±4.955 | 7.148±0.108 |
| 3                        | L/m²h   | 1.853±0.108 | 7.460±0.329 | n.a      | 9.578±0.066 |
| 4                        | L/m²h   | 2.383±0.054 | n.a      | n.a      | n.a      |

*UP water flux ± standard deviation, n.a: not available

In general, the study revealed increasing water flux trend with increased operating pressure. Dense structure of CS is less desirable for filtration process despite having porous structure. The dense structure of CS produces extremely low permeate flux ranging from 0.698 to 2.383 L/m²h when operated at 1-4 bar. Conversely, CSAL membrane unveiled improved water flux regardless of mixing speed and this proves that complexation of AL into CS helps to improves the dense structure of CS. 150CSAL and 210CSAL membranes have a comparable UP water flux ranging from 4.139-7.460 L/m²h and 5.418-9.578 L/m²h respectively. Meanwhile, 180CSAL membrane has significant water flux at pressure as low as 1 bar and at 2 bar the UP water flux recorded at 90.006 L/m²h. Thus, these findings highlight that the mixing speed do influence the membrane structure as proper dispersion leads to homogeneous solution. On the downside, 180CSAL membrane was inoperable beyond 2 bar as the membrane breaks and permeates passed through the membrane. Similar challenge faced with 150CSAL and 210CSAL membranes at pressure beyond 3 bar. A possible solution to overcome this challenge is to increase the concentration of AL as it will help to increase the structure of CSAL membrane and withstand at higher pressure.
3.2 Greywater Treatment

The previous subsection highlighted the minimal operating pressure without membrane rupture was 2 bar. Henceforth, GW treatment was operated at 2 bar and the treatment efficiency is as presented on Table 4.

Table 4. Greywater treatment efficiency using CS and CSAL membrane

| Parameters       | Unit | CS   | 150CSAL | 180CSAL | 210CSAL |
|------------------|------|------|---------|---------|---------|
| pH               | n.a  | 6.95 | 7.18    | 7.06    | 7.04    |
| Turbidity        | %    | 99.64| 99.44   | 99.43   | 99.16   |
| TSS              | %    | 100  | 100     | 100     | 100     |
| COD              | %    | 67.3 | 71.54   | 74.76   | 71.86   |
| Other organisms  | %    | 98.26| 93.31   | 98.06   | 99.01   |

As shown in Table 4, CSAL membranes offer excellent GW treatment efficiency compared to CS membrane. Altogether, CSAL membrane have a porous membrane skeletal, 100% TSS and 99% turbidity removal were achieved. All fabricated membrane met Canada and Italy non-potable GW reuse standard for turbidity<5 NTU and TSS<20mg/L[8, 9, 39]. In general, the particle size corresponding to TSS and turbidity falls within the range of 10-100 µm[41]. Henceforth, it can be deduced that the pore size of each membrane is much lower than 10 µm. On the other hand, CS membrane removed 67.3% of COD while CSAL membranes able to remove COD ranging from 71.54-74.76%. This highlights that regardless of mixing speed, PEC CSAL membranes has higher organic pollutant removal efficacy than CS membrane. Nonetheless, the permeate COD concentration was still higher than maximum allowable limit which is less than 100 mg/L. In terms of pathogen analysis, most literature evidence highlighted the presents of E.Coli and coliform bacteria in GW[41–43]. However, the GW used in this study did not detect both bacteria but presence of other organisms were reported 1.21×10⁵ cfu/100 mL. It was noted that increasing mixing speed from 150 rpm to 210 rpm reflected on higher pathogen removal efficiency up to 99.01%. 210CSAL membrane has slightly higher pathogen removal efficiency than CS membrane. This study showed an improvement on findings reported by[25] as the positively charged functional groups in CS reacted with AL’s negatively charged functional groups and limit the antimicrobial property of CS. Nevertheless, this study presented evidence that higher bacteria removal efficiency is achievable despite formation of PEC and increasing mixing speed found to enhance the interaction of CS and AL well. Despite 99% of pathogen removal was achieved, small amount of pathogen still escaped from the membrane pore and identified on the treated GW. Thus, addition of biocide to the membrane skeletal of CSAL membrane required to enhance the antimicrobial properties of membrane against Gram positive and Gram-negative bacteria. The GW flux was recorded at duration of 30 min and 180CSAL membrane presented with the highest flux followed by 150CSAL, 210CSAL and CS membrane at 10.26 L/m²h, 6.49 L/m²h, 6.20 L/m²h and 2.69 L/m²h respectively. Henceforth, it can be deduced that the CSAL membrane has the capability to treat GW efficiently although the complexation of CS and AL were done at low mixing speed.

4. Conclusion

In essence, this study investigated the feasibility of CSAL composite membrane fabrication techniques at low mixing speed with aim to apply in GW filtration treatment. This study disclosed the complexation of AL with CS improved the overall composite CSAL membrane structure. There were notable influences of mixing speed on formation of composite CSAL membrane structure in terms of swelling, porosity, and homogeneity of solution. Complexation of CSAL membrane significantly improved the water flux and GW treatment efficiency. In addition, GW treatment using 180CSAL membrane removed 99%, 100%, 74% and 98% of turbidity, TSS, COD and pathogens respectively. Apart from COD and pathogen concentration, GW removal efficiency of 180CSAL membrane meets the standard for non-potable reuse applications. As future work, it is recommended to study the influence of different AL concentrations on CSAL membrane properties to improve the organic pollutants removal. Besides that,
biocides with excellent antimicrobial properties can be added to the membrane skeletal to enhance the biocidal property of CSAL membrane. In addition, multiple cycle GW treatment operated under batch process can be explored to evaluate the flux decline mechanism of the membranes.

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