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A Novel Application of Oceanic Biopolymers — Strategic Regulation of Polymer Characteristics for Membrane Technology in Separation Engineering

Keita Kashima, Ryuhei Nomoto and Masanao Imai

Abstract

Membranes prepared from oceanic biopolymers have a high potential in membrane separation processes and water purification. It is anticipated to result in more biocompatible and lower-cost materials compared with artificial polymers. This chapter describes the excellent performance of oceanic biopolymer membranes in separation engineering and the regulation factors controlling membrane properties. In particular, chitosan and alginate were picked up as intelligent membrane materials to provide the promised molecular size recognition and other membrane properties. Future prospective strategies for a simple methodology for preparing stable membranes from oceanic biopolymers and the development of selective separation processing were reviewed.

Keywords: Membrane, oceanic biopolymer, chitosan, alginate, mechanical strength, mass transfer characteristics

1. Introduction

1.1. Overview of oceanic biopolymers in membrane separation technology

Membrane separation technology has been applied in various fields, such as the chemical industry, food production, pharmaceutical products, environmental sciences, and water purification, because it can be operated without heating and residual toxicity. Its energy cost was lower than conventional thermal separation technologies [1–4]. It can be employed for broad components by selecting optimum membranes.

Development of oceanic biopolymer membranes such as chitosan and alginate has exponentially increased due to increases in the demand for biocompatibility, environment adaptability,
renewability, and selective separation ability [5–6]. In the field of membrane science, most membranes have been made from petroleum-based polymers used as raw materials for the membrane body. Petroleum-based synthetic polymers such as polyethylene, polyamide, polyimide, and polysulfonate have been used as the main materials of the membrane body for a long time. The practical use of biopolymer membranes was less than synthetic polymer membranes, because controlling the physical and chemical properties of a biopolymer produced from natural bioresources was difficult in practical membrane applications. Cellulose-based membranes have been extensively used in practical applications since the development of the anisotropic cellulose acetate membrane in 1963 by Loeb and Sourirajan [7]. Applications of biopolymer materials have increased recently for membrane sciences [8]. Recent studies of biopolymer membranes are summarized in Table 1 referred to previous literatures [9-22]. In the past five years, oceanic biopolymers have attracted attention for their chemical functional ability. Investigations of oceanic biopolymer membranes, especially chitosan and alginate, for various applications have drastically increased.

| Authors         | Year | Membrane materials | Application                | Comments                  | Ref. |
|-----------------|------|--------------------|----------------------------|---------------------------|------|
| Torres et al.   | 2010 | eggshell           | biomedical application     | regenerative medicine     | 9    |
| Kashima et al.  | 2010 | calcium alginate   | membrane separation        | mass transfer characteristics | 10  |
| Kashima and Imai| 2011 | calcium alginate   | membrane separation        | mass transfer characteristics | 11  |
| Michalak and Mucha| 2012 | polyactic acid, dibutrylcellohexylic, chitosan | controlled release        | drug delivery system      | 12  |
| Wu and Imai     | 2013 | pullulan and κ-carrageenan | membrane separation      | dyes removal              | 13  |
| Lakra et al.    | 2013 | chitosan or cellulose blended polyethersulfone | membrane separation      | food industry             | 14  |
| Moraes et al.   | 2013 | chitosan and alginate | membrane separation        | environment science       | 15  |
| Nomoto and Imai | 2014 | chitosan           | membrane separation        | mass transfer characteristics | 16  |
| Ma et al.       | 2014 | chitosan           | biomedical application     | guided bone regeneration  | 17  |
| Uragami et al.  | 2015 | chitosan           | membrane separation        | pervaporative dehydration | 18  |
| Alias et al.    | 2015 | chitosan blended SiO2 | membrane separation        | proton battery            | 19  |
| Puspasari et al.| 2015 | cellulose          | membrane separation        | nanofiltration            | 20  |
| Livazovic et al.| 2015 | cellulose          | membrane separation        | water treatment           | 21  |
| Zhang et al.    | 2015 | calcium alginate and polyacrylamide | membrane separation      | nanofiltration            | 22  |

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Table 1. Recent investigations of biopolymer membrane and applications.

The common aim of membrane separation technology is to separate a target component from a mixture with the aid of permeation through the membrane, while rejecting other components. The key characteristics for practical use are as follows: mechanical strength, permeation flux, diffusivity of molecule, and micro-/nanostructure. This chapter describes the dominant factors in controlling important properties for practical membrane separation applications for oceanic polymer membrane, especially those of chitosan and alginate.

2. Chitosan membrane

Chitosan is a well-known sustainable and biocompatible oceanic biomaterial. It has been attracted in creating new polymer materials for broad application due to its nontoxicity,
biocompatibility, and biodegradability [5]. Chitosan is refined by removing an acetyl group from chitin, which is mainly produced in oceanic bioresources such as the shells of crabs and shrimps. Chitin is the second most abundant natural polymer in nature, after cellulose [23]. Chitosan is generally discarded as industrial waste around the world [24]. It is strongly expected to be useful as a biocompatible and reactive material for making functional gel membranes. Recent studies of various chitosan membranes are summarized in Table 2 and Table 3 referred to previous literatures [5-6, 12, 15-19, 24-46].

2.1. Chemical composition and membrane formation

Chitosan is a heteropolymer obtained by alkaline deacetylation of chitin at the C-2 position as shown in Figure 1 (a) and (b). Chitosan is generally defined by a deacetylation degree (DD [%]) of 60–100%. The deacetylation degree is estimated as follows:

\[
DD = \frac{n_{GS}}{n_{GS} + n_{AGS}} \times 100
\]

Here, \(n_{GS}\) and \(n_{AGS}\) is the molar number of glucosamine residues (acetylglucosamine residues) in the molecular chain. Chitosan has great potential for chemical modification because its molecular chain has a rich amino group and a hydroxyl group in the glucosamine residues [29].

![Chemical structure of chitosan showing β-1,4-D-glycoside linkage](image)

Figure 1. Chemical structure of chitosan showing β-1,4-D-glycoside linkage. (a) Chitin molecular chain consisting of poly-β-1,4-D-N-acetylglucosamine residues, (b) chitosan molecular chain consisting of poly-β-1,4-D-glucosamine residues.

The beneficial effects of chitosan are as a dietary fiber, such as its inhibition of fat digestibility [47] and its reduction of cholesterol [48]. The biodegradability and biocompatibility of chitosan are also suitable for biomedical applications [49].
| Authors                  | Year  | Membrane material                                      | Application                           | Regeneration factor          | Controlled properties of membrane                              | Comments                  | Ref.  |
|-------------------------|-------|---------------------------------------------------------|---------------------------------------|-------------------------------|----------------------------------------------------------------|---------------------------|------|
| Michalak and Mucha      | 2012  | chitosan blended polylactid acid and dibutyrylchitin    | controlled release                    | -                             | -                                                              | drug delivery system      | 12   |
| Tasselli et al.         | 2013  | chitosan membrane separation                            | concentration of glutaraldehyde       | mechanical strength, swelling ratio, adsorption of dye | hollow fiber membrane | 25   |
| Mores et al.            | 2013  | alginate blended chitosan membrane separation           | blended chitosan                      | swelling ratio, thickness, adsorption of herbicide | water treatment | 15   |
| Sun et al.              | 2014  | chitosan antibacterial medium                            | concentration of gallic acid          | antibacterial activity, mechanical strength | food packaging film   | 26   |
| Wanichapichat et al.    | 2014  | chitosan blended polysulfone membrane separation        | mixing ratio of chitosan and polysulfone | water permeation coefficient, rejection of fluoride and calcium | water treatment | 27   |
| Ma et al.               | 2014  | chitosan containing chitin whisker biomedicale application | containing ratio of chitin whisker   | mechanical strength, antibacterial activity | wound dressing | 5    |
| Bai et al.              | 2014  | chitosan containing nanotube bearing sulfonate polyelectrolyte | fuel cell                             | water uptake, proton conductivity, methanol permeability | direct methanol fuel cell | 24   |
| Nomoto and Imai         | 2014  | chitosan membrane separation                            | concentration of NaOH for neutralization of chitosan | mechanical strength, porosity, water permeation flux, effective diffusion coefficient | mass transfer characteristics | 16   |
| Shemvietl et al.        | 2014  | chitosan supported on PPEES membrane membrane separation | pH of tripolyphosphate solution as cross-linker | water flux, water uptake, salt rejection | water treatment | 28   |
| Han et al.              | 2014  | alginate and chitosan membrane separation               | -                                     | -                             | wound dressing | 29   |
| Karim et al.            | 2014  | chitosan containing cellulose nanocrystalline membrane separation | with or without cross-linking by glutaraldehyde | dyes rejection, porosity, mechanical strength | dyes purification | 30   |
| Dudek et al.            | 2014  | chitosan containing ion oxide nanoparticles membrane separation | containing ratio of ion oxide, additive sulphuric acid or glutaraldehyde | water permeation coefficient of water and ethanol | pervaporative dehydration | 31   |
| Kumar et al.            | 2014  | polysulfone blended chitosan and functionalized chitosan membrane separation | functionalization of chitosan molecular chain | heavy metal rejection, adsorbing activity | heavy metal purification | 32   |
| Bueno et al.            | 2014  | chitosan and alginate based biomedicale application      | containing ratio of surfactant (Phosphate FA) | porosity, mechanical strength | wound dressing | 6    |
| Ma et al.               | 2014  | chitosan biomedicale application                         | cross-linking with tripolyphosphate   | mechanical strength, biocompatibility | guided bone regeneration | 17   |

PES: polyethersulfone, PDMCHEA: poly (2-methacryloyloxy ethyltrimethylammonium chloride-co-2-hydroxyethylacrylate), PPEES: poly (1, 4-phenylene ether ether sulfone), PVP: polyvinylpyrrolidone
Chitosan is dissolved in an acid aqueous solution, such as acetic acid. To form a water-insoluble chitosan membrane, the acetic acid has to be neutralized by basic components. The authors have reported preparation of chitosan membrane using casting methods [16]. For example, 4 g of chitosan was dissolved in 198 mL of 1.7 mol·L⁻¹ acetic acid aqueous solution. The solution was mixed magnetically for 12 h at room temperature to obtain a mature solution. Some insoluble matter was removed by vacuum filtration using a filter paper (Grade No. 1, ADVANTEC, Japan). The concentration of the chitosan casting solution was 0.02 g-chitosan·mL⁻¹. Ten grams of the casting solution was dispensed in a glass Petri dish (inner diameter 7.75 cm) and dried in a thermostatic chamber at 333 K for 24 h. A dried chitosan membrane formed on the glass Petri dish. A 20 mL of sodium hydroxide (NaOH) aqueous solution was directly introduced onto the dried chitosan membrane. The chitosan membrane was continuously immersed for 3 h in NaOH solution for neutralization. The concentration of the supplied NaOH ranged from 0.1 to 5 mol·L⁻¹. In this case, the stoichiometric equivalent concentration of NaOH was estimated to be 0.83 mol·L⁻¹. After neutralization, the swollen membrane was easily separated from the glass Petri dish and was washed fully with pure water to remove excess NaOH.

2.2. Dominant role of the acid–base neutralization in chitosan membrane characteristics

The authors previously reported the dominant role of the acid–base neutralization process in forming chitosan membranes for controlling some membrane properties [16].

2.2.1. Mechanical strength

The mechanical strength, maximum tensile stress (Figure 2a), and maximum strain (Figure 2b) at membrane rupture presented bell-shaped curves with peaks when the NaOH concentration increased. For an 81% DD chitosan membrane, the maximum stress and the maximum strain reached maximum values of 8.6 MPa and 80.5%, respectively, in a membrane prepared with 1 mol·L⁻¹ NaOH. This concentration was almost the same as the stoichiometric equivalent concentration (0.83 mol·L⁻¹). In contrast, in a 98% DD chitosan membrane, the maximum stress and the maximum strain increase to 17.9 MPa and 134% when the membrane was prepared with 2 mol·L⁻¹ NaOH.

![Figure 2](http://dx.doi.org/10.5772/61998)
| Authors          | Year | Membrane materials                  | Application            | Regeneration factors                  | Controlled properties                              | Comments                          | Ref. |
|------------------|------|-------------------------------------|------------------------|---------------------------------------|---------------------------------------------------|-----------------------------------|------|
| Sajjan et al.    | 2015 | GTMAC grafted chitosan              | membrane separation    | mixing ratio of chitosan              | hydrophilicity, water/isopropanol selectivity      | pervaporative dehydration         | 33   |
| Bibi et al.      | 2015 | chitosan containing carbon nanotube | membrane separation    | with or without carbon nanotube       | pore size, swelling ratio, adsorption of naphtalene | water treatment                   | 34   |
| Ji et al.        | 2015 | chitosan blended PDMCHEA            | membrane separation    | mixing ratio of PDMCHEA               | water flux, mechanical strength, hydrophilicity     | nanofiltration membrane           | 35   |
| Uragami et al.   | 2015 | chitosan                            | membrane separation    | molecular weight and degree of deacetylation | permeation flux, water/ethanol selectivity          | pervaporative dehydration         | 18   |
| Premakshi et al. | 2015 | chitosan                            | membrane separation    | additive concentration of zeolite     | mechanical strength, permeation flux, selectivity   | pervaporative dehydration         | 36   |
| Santamaria et al.| 2015 | chitosan                            | fuel cell              | concentration of chitosan, ratio of chitosan and phosphogluconic acid | membrane thickness, conductivity                    | hydrogen-oxygen fuel cell          | 37   |
| Zhu et al.       | 2015 | PES and PVP blended chitosan and montmorillonite | membrane separation    | additive concentration              | water flux, salt rejection                         | dyes purification                 | 38   |
| Li et al.        | 2015 | chitosan                            | biomedical application | concentration of genipin as a cross-linker | swelling ratio, mechanical strength                | cultivation medium of epithelial cells | 39   |
| Alias et al.     | 2015 | chitosan                            | membrane separation    | mixing ratio of chitosan and SiO₂     | pure size, water uptake                             | proton battery                    | 19   |
| Hegab et al.     | 2015 | chitosan                            | membrane separation    | surface modification by using graphene oxide | hydropathicity, NaCl rejection, water flux, antifouling activity | reverse osmosis                   | 40   |
| Zhang et al.     | 2015 | poly (vinyl alcohol) blended chitosan | biomedical application | blending ratio of chitosan            | mechanical strength, water vapor, oxygen permeability, antibacterial activity | wound dressing                   | 41   |
| Panda et al.     | 2015 | chitosan coated iron-oxide-polyacrylonitrile | membrane separation    | chitosan coating, concentration of Fe₃O₄ | permeability, WVCO, pure size, hydrophilicity, mechanical strength | remove of humic acid              | 42   |
| Antunes et al.   | 2015 | chitosan and arginine               | biomedical application | blending ratio among chitosan, cationic chitosan, carbon nanotubes and silicon coagulant | hydrophobicity, mechanical strength                | wound regeneration                | 43   |
| Song et al.      | 2015 | chitosan containing carbon nanotube | antibacterial medium   | blending ratio of chitosan and polyacrylamide/poly styrene | hydrophilicity, mechanical strength                | surface modification              | 44   |
| Wang and He      | 2015 | chitosan blended copolymer of polyacrylamide/poly styrene | fuel cell              | blending ratio of chitosan and polyacrylamide/poly styrene | methanol permeability, water uptake, mechanical strength | methanol alkaline fuel cells       | 45   |
| Malini et al.    | 2015 | chitosan contained ZnO              | antibacterial medium   | combined with ZnO nanocomposite particles | antibacterial activity, antifouling activity       | nanocomposite membrane           | 46   |

GTMAC: Glycidyltrimethylammonium chloride, PES: polyethersulfone, PDMCHEA: poly (2-methacryloyloxy ethyl trimethylammonium chloride-co-2-hydroxyethylacrylate), PVP: polyvinylpyrrolidone
2.2.2. Water permeation flux

Figure 3 demonstrates that the water permeation flux and the volumetric void fraction of the swollen membrane were almost linearly correlated. The NaOH concentration in the neutralization process enhanced both the water permeation flux and the void fraction in the membrane. Neutralization using a high NaOH concentration weakens hydrogen bonding between chitosan polymer chains. The void fraction in the swollen membrane can assumed to be the volume of a water permeation channel occupying the membrane. This result suggests that the membrane structure involving water permeation was dominantly regulated by the NaOH concentration during neutralization.

![Figure 3. Correlation between the water permeation flux and the void fraction of 81% deacetylation degree chitosan membrane in reference [16]. The concentrations of NaOH used in the neutralization process are indicated at adjacent to keys, respectively.]

2.2.3. Mass transfer characteristics

The effective diffusion coefficient of the model components was evaluated based on the mass transfer flux. The membrane was sandwiched between twin mass transfer cells. The feed solution contained the model components (urea 60 Da, Methyl Orange 327 Da, Rose Bengal 1017 Da, and Sirius Red 1373 Da) at the desired concentrations, and the stripping solution was deionized water. The overall mass transfer coefficient $K_{OL}$ was evaluated from the mass transfer flux according to Eq. (2).

$$\ln \left(1 - \frac{2C_s}{C_{fi}}\right) = -\frac{2AK_{OL}}{V}t$$

(2)

Here, $C_s$ and $C_{fi}$ are the concentrations of the stripping and initial feed solutions, $A$ is the mass transfer area of the membrane, $V$ is the volume of aqueous phase in each transfer cell, and $t$ is the operation time.
The overall mass transfer coefficient $K_{OL}$ included the film mass transfer resistances ($k_{L1}^{-1}$ and $k_{L2}^{-1}$) and the membrane mass transfer coefficient ($k_m$) as seen in Eq. (3).

$$K_{OL}^{-1} = k_{L1}^{-1} + k_{m}^{-1} + k_{L2}^{-1}$$  

(3)

The aqueous phases in the mass transfer cells were sufficiently stirred to attain a fully developed turbulent condition ($Re > 10^4$). The film mass transfer resistances ($k_{L1}^{-1}$ and $k_{L2}^{-1}$) within the overall mass transfer resistance ($K_{OL}^{-1}$) were ignored under fully turbulent conditions. This directly indicated the membrane mass transfer coefficient ($k_m$). The effective diffusion coefficient was evaluated from $k_m$ using Eq. (4):

$$k_m = \frac{D_{eff}}{\ell}$$  

(4)

The initial membrane thickness in the swollen state ($\ell$) was measured with a micrometer (Mitutoyo Corporation, Kanagawa, Japan).

Figure 4 depicts the change in the effective diffusion coefficient in the chitosan membrane with the molecular weight of the tested components for 81% $DD$. The effective diffusion coefficient of a chitosan membrane prepared from NaOH of 1 mol·L$^{-1}$ changed dramatically at a molecular size corresponding to Rose Bengal (1017 Da). This result suggested that the size distribution of the mass transfer channel in the membrane was monodisperse and similar to the molecular size of Rose Bengal.

The effective diffusion coefficient of a membrane prepared from 5 mol·L$^{-1}$ NaOH greatly increased relative to a membrane prepared from 1 mol·L$^{-1}$. The molecular diffusion channel
formed by the polymer networks became enlarged due to the higher NaOH concentration employed.

The dominant role of the acid–base neutralization process in chitosan membranes was revealed to control membrane properties involving mechanical strength, the water permeation flux, and the effective diffusion coefficient.

2.2.4. Morphology of chitosan membrane

Figure 5 presents scanning probe microscope (SPM) photographs of chitosan membrane surfaces. The chitosan membrane made from 1 mol L\(^{-1}\) NaOH had a very smooth surface. In contrast, the membrane made from 5 mol L\(^{-1}\) NaOH had a somewhat rough surface.

2.3. Other regulation factors

2.3.1. Deacetylation degree

The deacetylation degree (DD) of a chitosan membrane can be stoichiometrically controlled by an acetic anhydride additive. Effects of the deacetylation degree on membrane properties, such as water permeation flux, have been found [50]. The water permeation flux of a membrane prepared from 99.2% DD chitosan was remarkably enhanced about 100-fold compared with a 76.5% DD chitosan membrane. The water permeation flux increased exponentially with increasing deacetylation degree from 81.8% to 92.2% [51].

Increasing the deacetylation degree enhances the surface hydrophilicity of the membrane surface because the acetamido groups on the chitosan membrane are converted into amino groups. This advances the effective formation of hydrogen bonds between the amino and hydroxyl groups and between the amino groups in the chitosan molecules, thus resulting in a dense molecular chain in the membrane [18].

2.3.2. Molecular weights of chitosan

Chitosan membranes prepared by Uragami and coworkers from different molecular weights (13–201 kDa) were tested during pervaporation dehydration of an ethanol aqueous solution.
The permeation flux decreased with increasing molecular weight from 13 kDa to 90 kDa, then increased from 90 kDa to 201 kDa. In contrast, the water permeation selectivity from the ethanol aqueous solution increased remarkably with increasing molecular weight up to 90 kDa. Over 90 kDa, the selectivity decreased. These results were understood to indicate that the 90 kDa molecular weight effectively formed entanglements and thus produced the strongest hydrogen bonds between the molecular chains of chitosan [18], although the mechanical strength increased with increasing average molecular weight of chitosan [52].

2.3.3. Addition of a cross-linker

Basically, chitosan can be formed into an insoluble membrane by acid–base neutralization in the casting solution without using a cross-linker. However, the addition of a cross-linker to improve membrane characteristics was carefully investigated.

The most prominent effect of an additive cross-linker is improved mechanical strength. Figure 6 depicts the change of mechanical strength of chitosan membrane (maximum stress vs. maximum strain at membrane rupture) with increasing amount of cross-linker. In a common trend, increasing the amount of cross-linker forms a rigid membrane. The addition of genipin as a cross-linker increased the maximum stress and reduced the maximum strain at membrane rupture [39]. Increasing added amounts of glutaraldehyde, methanol with ethylene glycol diglycidyl ether, and gallic acid also increased the mechanical strength. However, excess addition of cross-linker formed rigid and fragile structures on the chitosan membrane [25–26, 53].

![Figure 6. Change of mechanical strength of chitosan membranes with increasing amount of cross-linker. ●: chitosan membrane cross-linked with genipin [54]. ■: chitosan membrane cross-linked with methanol and ethylene glycol diglycidyl ether [53]. ▲: chitosan membrane cross-linked with glutaraldehyde [25]. ◆: chitosan membrane cross-linked with gallic acid [26], ▼: chitosan cross-linked with tripolyphosphate [55]. Arrows indicate increasing additive amount of each cross-linker.](Image)
Other researchers have reported that cross-linking with sodium tripolyphosphate enhanced the mechanical strength of chitosan membrane [17]. From another viewpoint, Shenvi and coworkers determined the effect of the pH value of the cross-linking solution on the membrane properties. A chitosan membrane cross-linked by tripolyphosphate solution at pH 5 realized a higher rejection rate of NaCl and MgSO\textsubscript{4} than a membrane cross-linked at pH 9 [28].

The enhancement of pervaporative dehydration ability of water–alcohol mixtures by adding cross-linker has been frequently reported [56]. A chitosan membrane cross-linked with toluene-2,4-diisocyanate exhibited high pervaporative dehydration ability with an isopropanol aqueous solution in which the selectivity of water $\alpha$ was performed as 472 [57]. The selectivity of water $\alpha$ was calculated using the following equation:

$$ \alpha = \frac{y}{x} \left(1 - \frac{x}{y}\right) $$ (5)

Here, $y$ is the permeate weight fraction of water and $x$ is the feed weight fraction of water.

### 2.3.4. Hybrid approaches with other materials

Some hybrid approaches using chitosan and other materials have been proposed to overcome problems in practical use [35]. To make a porous structure on a chitosan membrane, SiO\textsubscript{2}, a porogen agent, was mixed with chitosan cast solution and removed from the membrane. The average pore size reached a maximum of 8.5 μm when the mixing ratio of chitosan and SiO\textsubscript{2} was 1:2 [19].

Chitosan membranes are frequently combined with nanomaterial to form a composite medium. A chitosan membrane composited with a multi-walled carbon nanotube was modified by adding perfluorooctanesulfonyl fluoride (PFOSF). The added PFOSF enhanced antibacterial activity due to its remarkable hydrophobicity. The mechanical strength increased with increasing multi-walled carbon nanotubes [44]. Chitosan composited with ZnO nanoparticles was also investigated for antibacterial activity [46]. Chitosan membrane has a good potential as a composited nanomaterial medium for biologically based nanotechnology.

### 2.3.5. Chemical modification of the chitosan molecular chain

Chitosan has great potential for chemical modification. Functionalized chitosan is often used as the main membrane body, coating agent, or additive agent for functionalization of surface modifications. Graphene oxide functionalizing a chitosan membrane as a surface modification agent on a commercial polyamide membrane has been investigated. The water flux and NaCl rejection of the chitosan membrane were increased by the modification, due to the formation of a dense, thin layer of graphene-oxide-functionalized chitosan, which is better than natural chitosan membrane [40]. Kumar and coworkers prepared various chitosan membranes: a natural chitosan blended with polysulfone membrane, an N-succinylchitosan blended with polysulfone membrane, and an N-propylphosphonoyl
chitosan blended with polysulfone membrane. These membranes were applied to a heavy metal purification process. N-succinylchitosan blended with polysulfone membrane sufficiently purified Cu, Ni, and Cd [32].

3. Alginate membrane

Alginate is abundantly and sustainably produced by marine biological resources, especially brown seaweed. It has been widely applied in the food industry [58] and as a thickener [59], a suspending agent [60], an emulsion stabilizer [61], a gelling agent [62], and a film-forming agent [63]. In addition, alginate was continuously developed as useful materials for biomedical applications, especially for controlled delivery of drugs and other biologically active compounds and for the encapsulation of cells [64]. In recent pioneering works, alginate has developed as membrane material with excellent molecular selectivity for water-soluble components [65]. Recent studies of various alginate membranes are listed in Table 4 and Table 5 referred to previous literatures [10-11, 15, 22, 66-95].

3.1. Chemical composition and membrane formation of alginate

The molecular chain of alginate is constructed of a block copolymer of β-D-mannuronate (Figure 7a) and α-L-guluronate (Figure 7b) [96]. These two uronates construct a polymeric block in an alginate polymer chain with the following three types of block: homopolymeric blocks of α-L-guluronate (GG blocks), blocks with an alternating sequence in varying proportions of guluronate and mannuronate (MG blocks), and homopolymeric blocks of β-D-mannuronate (MM blocks) [97]. GG blocks chelate alkaline earth-metal ions because of the spatial arrangement of the pyranose ring and the hydroxyl oxygen atoms, and thus create a much stronger interaction than MM blocks and MG blocks [98–99].

![Figure 7](image-url)  
**Figure 7.** Residues of alginate molecular chain. (a) β-D-mannuronate. (b) α-L-guluronate. (c) Chelation of homopolymeric blocks of α-L-guluronate junction with calcium ions. Alginate was cross-linked by divalent cations according to the “Egg-box” model.
| Authors            | Year | Membrane material | Application                          | Regulation factor                  | Controlled properties of membrane | Comments            | Ref. |
|--------------------|------|-------------------|--------------------------------------|-----------------------------------|----------------------------------|---------------------|------|
| Toti and Aminabhavi| 2004 | sodium alginate   | membrane separation                  | containing ratio of PVA and PEG   | swelling ratio, water permeability, water/isopropanol selectivity | pervaporative dehydration | 66   |
| Kalyani et al.     | 2008 | sodium alginate   | membrane separation                  | with or without phosphoric acid as a cross-linker | swelling ratio, water permeation flux, water/ethanol selectivity | pervaporative dehydration | 67   |
| Kashima and Imai   | 2010 | calcium alginate  | membrane separation                  | concentration of CaCl$_2$ as a cross-linker | mechanical strength, swelling ratio, water permeation flux, effective diffusion coefficient | mass transfer characteristics | 10   |
| Saraswat et al.    | 2011 | calcium alginate  | blended dextrin membrane separation   | blending ratio of alginate and dextrin | swelling ratio, water permeability, water/isopropanol selectivity | pervaporative dehydration | 68   |
| Li et al.          | 2011 | sodium alginate   | membrane separation                  | blending ratio of gelatin         | crystallinity, water uptake, water permeability, water/CH$_3$OH selectivity | hollow fiber | 69   |
| Taskin et al.      | 2011 | sodium alginate   | material science                      | grafting time and temperature, concentration of hexafluorophenol | swelling ratio, hydrophilicity | hydrophilic material | 70   |
| Chen et al.        | 2011 | sodium alginate   | membrane separation                  | containing boric acid             | adsorption ability of Cu(II) | adsorption of Cu(II) | 71   |
| Kashima and Imai   | 2011 | calcium alginate  | membrane separation                  | homopolymeric blocks of α-L-guluronate | mechanical strength, water permeation, mass transfer characteristics | mass transfer characteristics | 11   |
| Li et al.          | 2012 | sodium alginate   | blended PVA and PSf                   | blending ratio of PVA             | crystallinity, water uptake, water vapor flux | dehumidification | 72   |
| Nigiz et al.       | 2012 | sodium alginate   | containing zeolite                    | containing ratio of zeolite       | water permeation flux, water/ethanol selectivity | pervaporative dehydration | 73   |
| Sajjan et al.      | 2013 | sodium alginate   | blended chitosan-wrapped MWCNTs       | blending ratio of chitosan-wrapped MWCNTs | swelling ratio, permeation flux, water/isopropanol selectivity | pervaporative dehydration | 74   |
| Flynn et al.       | 2012 | sodium alginate   | membrane separation                  | membrane thickness               | permeation flux, water/ethanol selectivity | pervaporative dehydration | 75   |
| Shi et al.         | 2013 | calcium alginate  | containing CaCO$_3$, PAA and PVA      | containing with or without CaCO$_3$, PAA and PVA | swelling ratio, drug release ability | biomineralization | 76   |
| Chen et al.        | 2013 | sodium alginate   | containing APTESOS                    | containing APTESOS               | adsorption ability of Cr(III) | adsorption of Cr(III) | 77   |
| Zhu et al.         | 2013 | sodium alginate   | membrane separation                  | concentration of sodium tetrave | CO$_2$ permeability, CO$_2$/N$_2$ selectivity | CO$_2$ separation | 78   |
| Asoor et al.       | 2013 | sodium alginate   | containing phosphenite                | containing ratio of phosphenite   | water permeation flux, water/ethanol selectivity | pervaporative dehydration | 79   |
| Mura et al.        | 2013 | alginate blended chitosan | membrane separation | blended chitosan                   | swelling ratio, thickness, adsorption of hepartin | water treatment | 15   |

APTESOS: 3-aminopropyltriethoxysilane, MWCNTs: multiwalled carbon nanotubes, PAA: polyacrylic acid, PAN: polyacrylonitrile, PEG: polyethylene glycol, PSf: polysulfone, PUA: poly (urethane-amine), PVA: poly (vinyl alcohol).
| Authors            | Year | Membrane material                               | Application                     | Regulation factor       | Controlled properties of membrane                                      | Comments                        | Ref |
|--------------------|------|-------------------------------------------------|---------------------------------|-------------------------|------------------------------------------------------------------------|---------------------------------|-----|
| Zhang et al.       | 2014 | sodium alginate supported on polypropylene     | membrane separation             | kind of cross-linking metal ion | mechanical strength, hydrophilicity, permeation flux, water/acetic acid selectivity | pervaporative dehydration       | 80  |
| Gao et al.         | 2014 | sodium alginate and hyaluronic acid supported on PAN | membrane separation             | concentration of Ca\(^{2+}\) as a cross-linker, creating sequence of alginate and hyaluronic acid | swelling ratio, hydrophilicity, permeation flux, water/ethanol selectivity | pervaporative dehydration       | 81  |
| Kaula and Ray      | 2014 | sodium alginate blended PVA                    | membrane separation             | blending ratio of alginate and PVA | mechanical strength, permeation flux, water/dioxane selectivity         | pervaporative dehydration       | 82  |
| Kaula and Ray      | 2014 | sodium alginate blended CMC                    | membrane separation             | blending ratio of alginate and CMC | permeation flux, benzene/cyclohexane selectivity                        | pervaporative separation        | 83  |
| Yang et al.        | 2014 | sodium alginate blended PVA                    | fuel cell                       | blending ratio of sodium alginate and PVA, time of crosslinking with glutaraldehyde | swelling ratio, ionic conductivity, methanol permeability              | direct methanol fuel cell       | 84  |
| Cabello et al.     | 2014 | alginate blended carrageenan                   | fuel cell                       | blending ratio of alginate and carrageenan | mechanical strength, water uptake, proton conductivity, methanol permeation flux | direct methanol fuel cell       | 85  |
| Cao et al.         | 2014 | sodium alginate containing graphene oxides     | membrane separation             | containing ratio of graphene oxides | hydrophilicity, crystallinity, swelling ratio, permeation flux, water/ethanol selectivity | pervaporative dehydration       | 86  |
| Yoo and Ghosh      | 2014 | calcium alginate                               | biomedical application          | concentration of alginate and CaCl\(_2\), cross-linking time | membrane thickness                                                     | microporous hollow fiber        | 87  |
| Kamuren et al.     | 2015 | sodium alginate blended PVA                    | biomedical application          | blending ratio of sodium alginate and PVA | water uptake, mechanical strength, release property, adsorption of BSA | wound dressing                   | 88  |
| Li et al.          | 2015 | calcium alginate                               | biomedical application          | concentration of ethanol as solvent of CaCl\(_2\) | swelling ratio, thickness, mechanical strength | pharmaceutical products        | 89  |
| Zhang et al.       | 2015 | calcium alginate blended polyacrylamide        | membrane separation             | with or without polyacrylamide | water permeation flux, adsorption of BSA (antifouling activity), rejection of Brilliant Blue | nanofiltration                  | 22  |
| Sanyo et al.       | 2015 | calcium alginate                               | edible film                     | concentration of alginate and calcium glucose, heat treatment | thickness, mechanical strength, color | membrane preparation           | 90  |
| Zhao et al.        | 2015 | calcium alginate                               | membrane separation             | concentration of sodium alginate, modification by PEG | water permeation flux, rejection of PEG and methylene blue, antifouling activity | ultrafiltration, nanofiltration | 91  |
| Jie et al.         | 2015 | calcium alginate containing carbon nanotubes   | membrane separation             | containing ratio of carbon nanotubes | mechanical strength, antifouling activity, water permeation flux, dye rejection | nanofiltration                  | 92  |
| Kirdponpattara et al. | 2015 | alginate blended cellulose                    | biomedical application          | blending alginate and bacterial cellulose | pore size, void fraction, mechanical strength, bio-compatibility | tissue engineering              | 93  |
| Shao et al.        | 2015 | sodium alginate blended cellulose loaded with AgSD | biomedical application          | loaded ratio of AgSD | swelling ratio, antibacterial ability | wound dressing                  | 94  |
| Uragami et al.     | 2015 | alginate blended DNA                           | membrane separation             | kind of cross-linking metal ion | hydrophilicity, swelling ratio, density, water/ethanol selectivity | pervaporative dehydration       | 96  |

AgSD: silver sulfadiazine, CMC: carboxymethyl cellulose, DNA: deoxyribonucleic acid, PEG: polyethylene glycol, PVA: poly (vinyl alcohol).
Sodium alginate easily forms a cross-link with the presence of divalent cations such as Ca\(^{2+}\), resulting in a highly compacted and dense gel network. GG blocks are constructed mainly of a cross-linked zone with Ca\(^{2+}\). This is called an “Egg-box junction” (Figure 7c), where the ions were assimilated to “Eggs” [100].

Sodium alginate forms a cross-link in the presence of divalent cations such as Ca\(^{2+}\), resulting in a highly compacted gel network. Homopolymeric blocks of α-L-guluronate are constructed mainly of a cross-linked zone with divalent cations. This section describes the impact of this kind of divalent cations and the mass fraction of homopolymeric blocks of α-L-guluronate in an alginate polymer chain \(F_{GG}\).

The authors previously reported the preparation of alginate membrane described below [10–11]. A 20 mL sodium alginate aqueous solution (10 g \cdot L\(^{-1}\)) was placed in a Petri dish. The solution was gradually dried at a mild temperature in a desiccator (298 K) or an electrical dryer (303 K) for 24 h to prevent heat degradation. A dried, thin film of sodium alginate was obtained on the Petri dish.

An electrolyte aqueous solution (CaCl\(_2\), SrCl\(_2\), and BaCl\(_2\)) was directly introduced onto the dried, thin sodium alginate film as a source of divalent cation for cross-linking. The concentration range of the electrolyte aqueous solutions was 0.1–1.0 mol \cdot L\(^{-1}\). A stable alginate membrane was quickly formed in the Petri dish at room temperature. After 20 min, the prepared swollen membrane was spontaneously separated from the surface of the Petri dish. The membrane remained in the electrolyte aqueous solution for further 20 min. The membrane was totally immersed in the electrolyte aqueous solution for 40 min. The prepared membrane was repeatedly washed with pure water to remove excess electrolyte, and then stored in pure water.

### 3.2. Effect of homopolymeric block of α-L-guluronate \(F_{GG}\)

The authors previously reported that membrane properties are evidently controlled by the mass fraction \(F_{GG}\) [11, 65, 101]. At first, the mass of GG blocks in the actual alginate polymer chain was determined by acid hydrolysis combined with Bitter–Muir’s carbazole sulfuric acid method [102]. The actual alginate was separated into three fractions (GG block, MM block, and MG block) by the acid-hydrolysis method. Acid-hydrolysis protocols were employed according to a previously published method [11, 103]. Their obtained fractions were then determined by Bitter–Muir’s carbazole sulfuric acid method using an optical density of 530 nm (UV-1200, Shimadzu, Kyoto, Japan). The calibration curve for mannuronic acid lactone was obtained and used as the standard component of uronic acid. These methods produced good intensity and accuracy of coloration [104].

The mass of the GG block \(W_{GG}\) was obtained from a fractional solution of the GG block by acid hydrolysis. The masses of the MM block \(W_{MM}\) and MG block \(W_{MG}\) were determined in the same way. The mass fraction of the homopolymeric blocks of α-L-guluronate \(F_{GG}\) was then calculated using the following formula:
$F_{GG} = \frac{W_{GG}}{W_{GG} + W_{MM} + W_{MG}}$  \hfill (6)

$F_{GG}$ was therefore shown to be a key factor in regulating membrane properties. In this study, two sodium alginates were examined, $F_{GG}$ 0.18 and $F_{GG}$ 0.56. Calcium alginate membrane prepared from five types of sodium alginate ($F_{GG}$ 0.18, 0.26, 0.35, 0.45, and 0.56) were regulated by mixing with two types of sodium alginate ($F_{GG}$ 0.18 and 0.56).

### 3.2.1. Mechanical strength

The effect of $F_{GG}$ on mechanical strength is depicted in Figure 8. The mechanical strength was determined based on the membrane deformation. The maximum stress was defined at the rupture of the membrane. This value increased with increasing $F_{GG}$. In contrast, the maximum strain decreased with increasing $F_{GG}$. The mechanical properties of the calcium alginate membrane changed from elastic to plastic transfer, depending on $F_{GG}$.

![Figure 8. Effect of $F_{GG}$ on mechanical strength of calcium alginate membrane [11].](image)

### 3.2.2. Mass transfer characteristics

An alginate membrane performs superior molecular size recognition on low-molecular-weight components from 60 Da to 600 Da [10]. Figure 9 demonstrates that the effective diffusion coefficient in the membrane ($D_{eff}$) of saccharides (glucose, G, 180 Da; maltose, M, 324 Da; raffinose, R, 504 Da) can be efficiently changed by regulating $F_{GG}$. The effective diffusion coefficient in the membrane prepared from $F_{GG}$ 0.56 alginate was proportional to the $-4.6$th power of the molecular volume. The diffusion coefficient in bulk aqueous phase ($D_0$) was
inversely proportional to the 0.6th power of the molecular volume [105]. In contrast, the effective diffusion coefficient in the membrane prepared from \( F_{GG} \) 0.18 alginate was proportional to the \(-2.9\)th power of the molecular volume. The higher \( F_{GG} \) membrane exhibited more sensitive molecular size recognition. “Egg-box junction” zones constructed from calcium ions and homopolymeric blocks of \( \alpha \)-L-guluronate dominantly regulated the mass transfer mechanism of the alginate membrane.

![Graph showing the relationship between molecular volume and diffusion coefficients](image)

**Figure 9.** The effective diffusion coefficient changed remarkably in our experimental range from 180 Da to 504 Da. The symbol ◆ indicates the diffusion coefficient in bulk aqueous solution. Temperature: 303 K. Agitation rate: 14.2 s\(^{-1}\) [65].

The effect of \( F_{GG} \) on the mass transfer characteristics was evaluated using a permeation test with urea aqueous solution as a typical molecule model. The effective diffusion coefficient \( (D_{eff}) \) of urea in the membrane decreased with increasing \( F_{GG} \). Figure 10 illustrates the correlation of the volumetric void fraction of the swollen membrane with the ratio between the effective diffusion coefficient of urea in the membrane and the diffusion coefficient in bulk aqueous phase \( (D_0) \). Both the effective diffusion coefficient and the volumetric water fraction were restrained by increasing \( F_{GG} \). The strong dependency of the effective diffusion coefficient of urea on the void fraction contributes to good understanding of the formation of a mass transfer channels in the alginate membrane. These channels are speculated as being monodisperse in a similar size with urea molecule. The mass transfer channel was governed by the mass fraction of homopolymeric blocks of \( \alpha \)-L-guluronate \( (F_{GG}) \).
3.2.3. Morphology of the alginate membrane

Figure 11 presents SPM photographs of the calcium alginate membrane surface. The distribution of membrane asperity clearly decays with increasing $F_{GG}$. Especially in higher $F_{GG}$ conditions, many of the GG blocks formed a higher population density of Egg-box junction chelating with Ca$^{2+}$, and the atomic force of the polymer networks was uniform.

Figure 10. Correlation of the volumetric void fraction of the swollen membrane with the effective diffusion coefficient of urea [11].

Figure 11. Scanning probe microscope photographs of calcium alginate membrane surface. (a) $F_{GG} = 0.18$, (b) $F_{GG} = 0.56$. 
3.3. Effect of cross-linking divalent cations

The authors prepared a stable alginate membrane cross-linked with CaCl$_2$, SrCl$_2$, and BaCl$_2$. These membranes are sufficiently stable in aqueous phase to apply for practical use.

3.3.1. Water permeability

The water permeation coefficient was evaluated based on the pure water permeation flux as presented in Figure 12. It was decreased logarithmically with increasing concentration of cross-linker. This suggests that the number of permeation channels and/or the size of the permeation channels decreased with increasing concentration of cross-linking ions. The effect of cross-linker concentration on water permeability appeared strongly in the BaCl$_2$ used, suggesting that Ba$^{2+}$ structures have a much stronger interaction in α-L-guluronate block. Binding of divalent cation to the three kind of copolymer blocks have been investigated [106–107]. The following orders of binding strength indicated by sign of equality were reported:

\[
\begin{align*}
\text{GG block: } & \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} \\
\text{MM block: } & \text{Ba} > \text{Sr} \approx \text{Ca} \approx \text{Mg} \\
\text{MG block: } & \text{Ba} \approx \text{Sr} \approx \text{Ca} \approx \text{Mg}
\end{align*}
\]

Hence, the alginate membrane cross-linked with BaCl$_2$ constructed a dense polymer network due to strong bonding between alginate molecular chain and Ba$^{2+}$.

![Figure 12. Effect of concentration of cross-linking electrolyte solution on water permeation coefficient.](image)

3.3.2. Volumetric water fraction

The volumetric water content of a swollen membrane can be assumed to an indicator of the void fraction of the membrane structure [108]. Figure 13 illustrates the effect of the concentration of electrolyte solution on the void fraction of the membrane. The void fraction decreased
with increasing concentration of the cross-linking electrolyte solution. An alginate membrane cross-linked with BaCl$_2$ was highly densified by the provided Ba$^{2+}$.

![Graph](image_url)

**Figure 13.** Effect of concentration of cross-linking electrolyte solution on void fraction of swollen alginate membrane.

### 3.4. Other regulation factors for controlling membrane properties

#### 3.4.1. Addition of cross-linker other than metal ions

Conventional cross-linkers forming a polymer membrane were also examined to realize the alginate membrane. Glutaraldehyde is most commonly employed as a cross-linker to form sodium alginate membranes [83–84]. These membranes cross-linked with glutaraldehyde were developed for use in organic dehydration by pervaporation [66, 79, 82]. A sodium alginate membrane cross-linked with phosphoric acid was prepared for pervaporative dehydration of ethanol aqueous solution [67]. This resulted in $3.5 \times 10^{-2}$ kg·m$^{-2}$·h$^{-1}$ of permeation flux and 2182 of selectivity as defined by Eq. (4). A sodium alginate membrane cross-linked by sodium tartrate was characterized by CO$_2$ capture from CO$_2$/N$_2$ [78].

#### 3.4.2. Hybrids with other polymers or materials

Many efforts have been made to enhance the performance of the alginate membrane by blending it with different hydrophilic polymers. An alginate-blended DNA membrane cross-linked with Mg$^{2+}$ or Ca$^{2+}$ was investigated with regard to the permeation flux of ethanol aqueous solution for pervaporation [95]. The permeation flux and selectivity of a calcium alginate membrane with DNA in pervaporative dehydration for an ethanol aqueous solution were measured as $1.2\times10^{-2}$ kg·m$^{-2}$·h$^{-1}$ and 5500, respectively. In contrast, a magnesium alginate
membrane with DNA exhibited a permeation flux and selectivity of $1.2 \times 10^{-2} \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and 6500.

Hybrid membranes of sodium alginate and dextrin cross-linked with glutaraldehyde had a permeation flux of $9.65 \times 10^{-2} \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ permeation flux and a selectivity of 8991 in pervaporative dehydration for an isopropanol aqueous solution [68].

Alginate membranes are frequently combined with nanomaterials to form a composite medium. A calcium alginate membrane containing multi-walled carbon nanotubes was prepared as a new nanofiltration membrane. It had high mechanical strength, antifouling ability, and high rejection of small organic molecules (Congo Red, 697Da) [92].

4. Conclusion

Strategic regulation of an oceanic biopolymer membrane to control its characteristics in membrane separation technology was demonstrated. An oceanic biopolymer chitosan membrane can be easily prepared by casting chitosan in dilute aqueous organic acids and neutralizing it with an alkaline aqueous solution. The dominant role of neutralization for chitosan membrane involves the mechanical strength, the permeation flux, and the mass transfer characteristics. Other regulating factors, such as the deacetylation degree, the average molecular weight, and the addition of a cross-linker were presented.

A calcium alginate membrane performs superior molecular size recognition on low-molecular-weight components from 60 Da to 600 Da due to a dense polymer network consisting of homopolymeric blocks of α-L-guluronate and calcium ions. The kind of cross-linking ion used is also able to control the membrane properties. Barium ion performed a stronger cross-linker in the alginate membrane rather than Ca$^{2+}$ and Sr$^{2+}$, and a highly complex structure was formed. The mass fraction of homopolymeric blocks of α-L-guluronate and cross-linking metal ions were impact factors in regulating the mass transfer characteristics, water permeability, and mechanical strength.

These oceanic polymers are biodegradable, biocompatible, environmentally friendly, stable, and easily available from renewable agricultural resources. In the future, oceanic biopolymer membranes should be developed as an alternative to artificial polymer membranes.

Nomenclature

$A$ Area of membrane surface [m$^2$]

$C_f$ Initial concentration in the feed solution [mol · L$^{-1}$]

$C_s$ Concentration in the stripping solution [mol · L$^{-1}$]

$D_0$ Diffusion coefficient in a bulk aqueous phase estimated from Wilke–Chang’s empirical formula [m$^2$ · s$^{-1}$]
DD Deacetylation degree [%]

$D_{\text{eff}}$ Effective diffusion coefficient [m$^2 \cdot $s$^{-1}$]

$F_{\text{GG}}$ Mass fraction of GG block in alginate determined by Eq. (5) [-]

$K_{\text{OL}}$ Overall mass transfer coefficient [m$ \cdot $s$^{-1}$]

$K_{\text{OL}}^{-1}$ Overall mass transfer resistance [(m$ \cdot $s$^{-1}$)$^{-1}$]

$k_{m}$ Membrane mass transfer coefficient [m$ \cdot $s$^{-1}$]

$k_{L1}$ Film mass transfer coefficient in the feed phase [m$ \cdot $s$^{-1}$]

$k_{L2}$ Film mass transfer coefficient in the stripping phase [m$ \cdot $s$^{-1}$]

$\ell$ Membrane thickness in the initial state [m]

$n_{\text{AGS}}$ Molar number of acetylglucosamine residues in polymer chain of chitin or chitosan [mol]

$n_{\text{GS}}$ Molar number of glucosamine residues in polymer chain of chitin or chitosan [mol]

$Re$ Reynolds number [-]

$t$ Time [s]

$V$ Volume of aqueous solution in the transfer cell [m$^3$]

$W_{\text{GG}}$ Mass of GG block in sodium alginate [kg]

$W_{\text{MG}}$ Mass of MG block in sodium alginate [kg]

$W_{\text{MM}}$ Mass of MM block in sodium alginate [kg]

$x$ Feed weight fraction of water in pervaporation [-]

$y$ Permeate weight fraction of water in pervaporation [-]

$\alpha$ separation factor on pervaporative dehydration defined by Eq. (4) [-]

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