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Excellent dyes removal and remarkable molecular size rejection of novel biopolymer composite membrane

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ABSTRACT

The κ -carrageenan mass fraction ($F_{\rm C}$) was a key factor to determine membrane character not only on mechanical strength but also on selected molecular permeability. It was defined as the following equation: $F_{\rm C} \equiv (\kappa C[g]/(P[g] + \kappa C[g]))$ and changed in desired range (0.33–0.83). This study reports the results of mass transfer and ultra-filtration experiments on model dye solutions, indicating Methyl Orange, Indigo Carmine, Bordeaux S, Brilliant Blue, and Rose Bengal, and the reference molecular weight are from 327 to 1017 Da. The fundamental parameters influencing the transport of dye such as experimental temperature, viscosity of the feed solution, initial dye concentrations have been determined. The effective diffusion coefficient of dye molecules in the biopolymer membrane was calculated. Outstanding molecular size recognition was appeared. The molecular weight cut-off values in $F_{\rm C}$ 0.33 membrane were 327 Da, and for $F_{\rm C}$ 0.66 membrane performed the results of 466 Da, respectively. The membrane changed from the wholly compact structure to the porous structure by an increase of the $F_{\rm C}$, and then, we proved the changes of membrane formation while $F_{\rm C}$ value increased scientifically based on a scanning electron microscope (SEM) observation.

Keywords: κ-Carrageenan; Pullulan; Composite membrane; Mass transfer; Diffusion coefficient; Water permeability

1. Introduction

Treatment of wastewater containing dyes is one of the most important ecological problems because the effluents containing the dyes are not only highly colored, but also toxic to aquatic life [1]. Concerning membrane operations, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are the most applied. However, UF presents low rejection values, whereas NF and RO are limited by the high osmotic pressures, which arise at high concentrations. The literature has provided different studies in which traditional methods are coupled with membrane processes [2–4]. Over the past two decades, membranes made from polymeric materials have become increasingly popular in industrial processes where reliable and repeatable purification or concentration is required. Membrane processes have wide industrial applications covering many existing and emerging use

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in the chemical, environmental, water treatment, pharmaceutical, and food industries. Among all types of membrane process, NF as one of the most promising membrane technologies has the advantages of low operation pressure, higher permeate, and high rejection for small molecules separation from water solution. NF is shown to be the most effective principal for the separation of dyes from wastewater with relatively low investment [5,6]. The rejection of the aromatic poly (m-phenylene isophthalamide) (PMIA) NF membrane for dyes Eriochrome black T, Eriochrome blue black B, and Alizarine red were all over 98%, with a flux about $80 L/m^2 h$, while the rejection for NaCl was only about 5.5% when tested at 0.4 MPa [7]. Two hydrophobic and one hydrophilic commercial membrane were selected to study the removal efficiencies of color and chemical oxygen demand (COD) from the real-dyehouse wastewater [8]. In another report on dye separation using polymeric hollow fiber membranes, excellent separation of Methylene blue (MB) from dye wastewater was obtained by micellar-enhanced UF using a combination of polysulfone hollow fiber UF membrane and sodium dodecyl sulfate surfactant the [9]. Further, the polysulfone-polyamide membranes exhibited molecular weight cut-off values in the range of 490–730 g/mole. They showed the rejections in the range of 60-97% for Reactive black-5 and Rhodamine-B for feed solutions containing 400-2,000 ppm dye with water flux of $10-35 \,\mathrm{mL/m^2}\,\mathrm{h}$ at $170 \,\mathrm{kPa}$ [10].

The biopolymers of marine algae origin are ubiquitous in surface waters and attracted to their potentialities. They present an enormous variety of structures, such as alginate, carrageenan, and chitosan. They are still under-exploited, and they should therefore be considered as an extraordinary source of biopolymer for membrane separation technology. In contrast, polysaccharides based on sugar unit repeating units, they are rich in -OH functional groups that form H bonds, in stereo-regular polysaccharides especially in bacterial polysaccharides such as pullulan, and a number of potential applications have been reported for pullulan as a result of its good filmforming properties. The great success as preparation of membrane used marine biopolymer is a tremendous extension of applications of marine polymers (casing, regenerate medical treatment, etc.) other than using in food industry. It is signaled that the development of membrane technology based on the sustainable and ecological polymer. Among the polysaccharides, starch and cellulose are the most frequently and massively modified, followed by carrageenans. Such marine algae as carrageenans should be pointed out that optimum growth conditions in terms of sufficiently supplied sun light, stable temperature and no-effect on climate change on ground, and therefore, the stable harvest is expected. Biopolymer membranes are biodegradable, and therefore, they have the potential to cut carbon emission and reduce CO_2 quantities in the atmosphere. It is significant research for membrane separation technology to utilize biopolymer membrane. Sanchuan et al. investigated the impacts of cellulose acetate membrane properties on reactive dye removal from dye/salt mixtures through NF process. They found that the properties of the NF membrane play an important role in dye removal rate, stable permeate flux, and their change of behaviors with operational conditions [11].

As the adsorption-separation research, Aleksandra et al. combined the Langmuir and Freundlich adsorption isotherms to study the adsorption capability for the removal of textile dyes with the novel chitosan/ montmorillonite membrane. They observed that the membrane exhibited high adsorption capacity at low concentration of dye. The Bezactiv orange adsorbed per unit mass of the adsorbent is high and is efficient than the other materials [12]. Papageorgiou et al. reported that the prepared Ca alginate/TiO₂ fibers exhibited high efficiency for the removal of Methyl orange from polluted water [13].

Carrageenan is a high-molecular-weight linear hydrophilic polysaccharide comprising repeating disaccharide units of galactose and 3,6-anhydrogalactose (3,6 AG), both sulfated and non-sulfated, joined by alternating α -(1,3) and β -(1,4) glycosidic links. The main carrageenan types, kappa, iota, and lambda, can be prepared in pure form by selective extraction techniques from specific seaweeds and plants within those species. Kappa forms strong, rigid gels in the presence of potassium ions, iota forms soft gels in the presence of calcium ions, lambda does not gel and is used to thicken dairy products.

The κ -carrageenan comes from a family of linear water-soluble polysaccharides extracted from different species of marine red algae with a primary structure based on an alternating disaccharide repeating unit of α -(1-3)-D-galactose-4-sulphate and β -(1-4) 3,6-anydro-D-galactose. It is largely used as thickening, gelling agent or texture enhancer or stabilizer in food, pharmaceutical [14] and cosmetic [15] industries. Indeed, in aqueous solutions and in the presence of several cations, κ -carrageenan forms, on cooling, thermoreversible gels. It is known that, in the presence of K⁺, thermo-reversible gelation of κ -carrageenan involves a coil-to-double helix conformational change, followed by aggregation of the ordered molecules in an infinite network [16] (Fig. 1).



Fig. 1. The schematic chemical structures of (a) κ -carrageenan; (b) ι -carrageenan; (c) λ -carrageenan; (d) crosslinked κ -carrageenan.

Pullulan is an extracellular glucan elaborated by a fungus of the genus Aureobasidium, commonly called 'black yeast', and was first discovered by Bauer (1938). Pullulan is a linear glucan consisting of repeating units of maltotriose joined by α -D-(1 \rightarrow 6) linkages (see Fig. 2). The polymer also contains some maltotetraose units. A number of potential applications have been reported for pullulan as a result of its good filmforming properties [17].

Pure pullulan film, however, performs weak mechanical strength property, which is difficult to use in membrane separation process. In our study, combinations of κ -carrageenan and pullulan give

membrane strengths and elasticity. Pure pullulan single component membrane (cross-linked by glutaraldehyde) was too weak to make a flat membrane in our study (Fig. 3).

2. Materials

Pullulan was provided by Hayashibara Biochemical Laboratory (Okayama, Japan). *κ*-carrageenan, glutaraldehyde and potassium chloride were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Glucose (MW 180 Da), Methyl Orange (MW 327.34 Da) Bordeaux S (MW604.48 Da) and Rose Bengal (MW



Fig. 2. The schematic chemical structure of pullulan.



Fig. 3. The pictures of pure pullulan membrane and κ -carrageenan/pullulan composite membrane.

1017 Da) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Brilliant Blue (MW 826.0 Da) was purchased from Sigma Chemical Co. (Perth, WA). Indigo Carmine (MW 466.37 Da) was purchased from Kokusan Chemical Works, Ltd. (Tokyo, Japan).

Model dye solutions were prepared by dissolving dyes in pure water at room temperature (approximately 25°C). Dye concentration in the aqueous solutions was determined by measuring UV absorbance (UVMINI-1240 Shimazu) at the wavelengths given in Table 1.

3. Experimental

3.1. The preparation of composite membrane

 κ -carrageenan and pullulan powders were dissolved in distilled water (70°C) using a magnetic stirrer to prepare film-forming solutions of various blend-weight ratios. All polymer solutions were prepared based on 3g total polymer weight dissolved in 97g of distilled water at 70°C for one hour. In addition, each was stirred for one hour at 70°C with

Table 1 The dye components concentration preparation of glutaraldehyde [18] (30–130 mM) was added. The polymer solutions were then cast 20 g onto for each Petri dish, followed by drying in an electrical blast-drying chest at 65° C for 24 h. Potassium chloride solution was introduced into the dried membranes (attached to the Petri dishes) [19] (0.1–1.0 M) for 24 h. The swollen membrane was spontaneously peeled from the Petri dish at $25 \pm 1^{\circ}$ C and washed by pure water cleanly for further testing. Membrane samples were tested in triplicate.

3.2. Photograph by Scanning Electron Microscopy (SEM)

The membranes were snapped under liquid nitrogen then dried in a vacuum freeze dryer (RLE-103, Kyowa Vacuum Engineering. Co. Ltd., Tokyo, Japan) (298 K) for 24 h. The membranes were then sputter coated with a thin film of Pt, using a sputter-coater (E-1010 Ion Sputter, Hitachi, Ltd., Tokyo, Japan). Images of cross sections of the membranes were obtained using a SEM (Miniscope TM-1000, Hitachi, Ltd.,) (Fig. 4).

3.3. Measurement of the composite membrane's mechanical strength

A rheometer (CR-DX500, Sun Scientific Co. Ltd., Tokyo, Japan) was used to determine the tensile strength and the percentage elongation at break. Three rectangular-strip specimens (10 mm wide, 40 mm long) were cut from each membrane for tensile testing. The initial grip separation was set to 20 mm, and the crosshead speed was set to 1 mm/s. The initial membrane thickness was measured using a micrometer (Mitutoyo, Kanagawa, Japan). The average thickness of the membrane strip was used to estimate the initial cross-sectional area of the membrane sample.

3.4. Water content (H_V)

The water content was measured as follows. Membranes were immersed in distilled water at 25° C for 1 day. The membranes were removed from the

Marker components	Molecular weight (MW) [Da]	Molecular size (MS)[Å]	Power terms (Referred from Fig. 9)	рН ^а	Structural formula
Methyl Orange (MO)	327	10.6	0.96	5.6	C ₁₄ H ₁₄ N ₉ O ₉ SNa
Indigo Carmine (IC)	466	11.9	1.9	5.4	$C_{16}H_8N_2Na_2O_9S_2$
Bordueax S (BS)	604	13.0	4.0	5.9	C ₂₀ H ₁₁ N ₂ Na ₃ O ₁₀ S ₃
Brilliant Blue (BB)	826	14.4	3.4	5.5	C ₄₅ H ₄₄ N ₃ NaO ₇ S ₂
Rose Bengal (RB)	1,017	15.8	3.6	5.8	$C_{20}H_2Cl_4I_4Na_2O_5$

^aMeasured from the dye aqueous solutions at 1 mM.



Fig. 4. SEM imagines of κ -carrageenan/pullulan membrane (cross-section).

water, tapped with filter paper to remove excess water on the membrane surface and weighed W_w in the wet state. The water content, H_V , is calculated from weights in the wet state, W_w , and in the dry state, W_d , as:

$$H_{\rm v} = \frac{(W_{\rm w} - W_{\rm d})/\rho_{\rm w}}{(W_{\rm w} - W_{\rm d})/\rho_{\rm w} + W_{\rm d}/\rho_{\rm m}} \tag{1}$$

Here, ρ_w and ρ_m are the densities of water and membrane, respectively.

3.5. Effective diffusion coefficient (D_{eff}) of dye molecules in the composite membrane

Molecular diffusion experiments were used a mass transfer setup (Fig. 5). The κ -carrageenan pullulan composite membrane was sandwiched between the



Fig. 5. The schematic image of the mass-transfer setup.

two halves of the glass made diffusion cell. The diffusion area was 24 cm². One of the diffusion cell was filled with 190 cm³ of water-soluble solution (1 mM) in distilled water, while the other diffusion cells received 190 cm³ of distilled water. The diffusion of solutes through the membrane was monitored by periodically removing 1 cm³ samples from both diffusion cells and determining the tested solute in the stripping side samples as detailed below.

It is supposed that since the concentrations in the two diffusion cells were uniform, the mass transfer flux was so small that the diffusion process can be regarded as a quasi-steady state. Accordingly, we can use Eqs. (2) and (3) to calculate the effective diffusion coefficients.

$$\ln\left(1 - \frac{2C_{\rm s}}{C_{\rm f}}\right) = -2A/VK_{\rm OL}t\tag{2}$$

$$K_{\rm OL}^{-1} = k_{\rm L1}^{-1} + k_{\rm m}^{-1} + k_{\rm L2}^{-1}$$
(3)

The mass-transfer resistances k_{L1}^{-1} and k_{L2}^{-1} in the overall mass transfer resistance K_{OL}^{-1} can be neglected because of the sufficiently turbulent conditions in the two diffusion cells during the experiment. K_{OL}^{-1} did not depend on the stirring rate, and therefore, it directly indicates the membrane mass-transfer coefficient ($k_{\text{m}} = D_{\text{eff}} l^{-1}$). The effective diffusion coefficient in the membrane (D_{eff}) was evaluated from k_{m} . The initial membrane thickness l in the swollen state was measured with a micrometer (Mitutoyo, Kanagawa, Japan).

The mass-transfer characteristics were evaluated from the effective diffusion coefficient estimated by



Fig. 6. The chemical structures of the dye molecules.

measuring the mass-transfer rate in the composite membrane. The dyes were employed to determine the size of the transfer channel in the membrane. The reference molecular size was from 327 to 1017 Da indicating Methyl Orange, Indigo Carmine, Bordeaux S, Brilliant Blue, and Rose Bengal. The chemical structures of the dyes molecule were shown in Fig. 6.

3.6. Measurement of the composite membrane separation performance

The dye solutions permeability experiment used a filtration cell (UHP-62 K, ADVANTEC, Ltd., Japan) had a volume of 200 mL and the membrane surface area of 21 cm². A magnetic stirring bar was installed in the membranes upper surface. The filtration cell was employed for both constant flux and constant pressure filtration. For operation in constant flux mode, a nitrogenous gas pump was connected to the inlet of the filtration cell and piped the permeate solution from the outlet. The weight of permeate solution was logged by electronic balance. The schematic representation of module and set-up are shown in Fig. 7. In our study, the permeate flux can be calculate by

$$J = \frac{W}{A\Delta t} \tag{4}$$

Here, *W* is the total mass of the water or solution permeated during the experiment; *A* is the membrane surface area; and Δt is the operation time. Rejection, *R*, is calculated using the following equation:



Fig. 7. The schematic representation of membrane permeation module.

$$R = 1 - \frac{C_{\rm P}}{C_{\rm F}} \tag{5}$$

where C_P is the concentration of permeate and C_F is the concentration of feed.

4. Results and discussion

4.1. Measurement of the composite membrane's mechanical strength

The lower $F_{\rm C}$ membrane ($F_{\rm C}0.33$) is convenient to investigate the influence dehydration by glutaraldehyde, because the lower $F_{\rm C}$ membrane ($F_{\rm C}0.33$) contains many hydroxyl groups bonding to pullulan. The polymeric framework of the κ -carrageenan/pullulan composite membrane became more densely populated with increasing glutaraldehyde concentration, and its mechanical strength was elevated. The mechanical stress increased with increasing glutaraldehyde concentration and then leveled off over 70 mM [20]. Authors set the concentration of glutaraldehyde and potassium chloride-immersion condition at 90 mM and 0.7 M, respectively. Fig. 8 represents the effect of $F_{\rm C}$ values on membrane mechanical strength. The maximum stress linearly increased with proportional to F_C values, and the maximum strain was appeared at 35%.

4.2. Measurement of the composite membrane separation performance

In Fig. 9, the logarithmic plots of diffusion coefficients (D_{eff}) in membrane plotted against the fraction of κ -carrageenan (F_{C}) in composite membrane, showing that the D_{eff} changes vary directly with the F_{C} value. On molecular range of 327–1017 Da, a high-molecular-weight component indicates a higher D_{eff} changes in the same composite membrane; however, on the Bordeaux S (604 Da) the D_{eff} changes is showed higher than Brilliant Blue (826 Da) and Rose Bengal (1017 Da). Therefore, we could predict that the changes of F_{C} value from 0.33 to 0.75 could regulate



Fig. 8. Effect of $F_{\rm C}$ on the maximum stress and the strain of κ -carrageenan/pullulan membrane. The concentration of GA and KCl were set at 90 mM and 0.7 M, respectively.



Fig. 9. Change of effective diffusion coefficient (D_{eff}) with mass fraction of κ -carrageenan (F_C). Empirical correlations were obtained, the power terms of F_C in empirical equations were summarized in Table 1.

the size of the mass transfer channel up to approximate 2 Å (Remainder of subtract molecular size of Methyl Orange (11 Å) from Bordeaux S (13 Å)).

Fig. 10(a) shows the logarithmic plot of the mass fraction of κ -carrageenan ($F_{\rm C}$) against to the effective diffusion coefficient ($D_{\rm eff}$) of Indigo Carmine, which indicated that $D_{\rm eff}$ should be severely dependent when $F_{\rm C}$ values were changed ($D_{\rm eff} \propto F_{\rm C}^{1.9}$). On the other hand, in Fig. 10(b), the water content ($H_{\rm V}$) of membrane had a weak potential for $F_{\rm C}$ values' changing ($H_{\rm V} \propto F_{\rm C}^{0.15}$). There is a great difference (approximately 12 times) between exponential terms.

So in Fig. 11 shows the dependence property based on the radicals of relational expressions that as mentioned in Fig. 9 and molecular sizes of dyes. The value of the radical was appeared at 3.3 $(D_{\rm eff} \propto volume of dye molecule)$, and therefore, authors came under review in the connection between water content (free volume) and mass transfer through membrane. The presumption that molecular transport is regulated by free volume was first introduced by Cohen and Turnbull (1959). The dye molecules diffuse into the membrane through the void of polymer chain (capillary model) or the free volume (free-volume model). The difference between the two models exists because of the assumption that void may exist in the membrane. The void of polymer chain plays the main role in transport and is neglected in dependence of the free-volume in the κ -carrageenan/pullulan composite membrane. Thus the molecular size distribution is the physical properties influenced by the variation of the mass fraction of κ -carrageenan (F_C), and in short, the dye molecule was smartly choosing the size which suitable to itself, and diffusing through the membrane.



Fig. 10. The effect of mass transfer of κ -carrageenan (F_C) in (a) D_{eff} of Indigo Carmine; and (b) water content (H_V).



Fig. 11. The dependence property based on the radicals of relational expressions that as mentioned in Fig. 9 and molecular sizes of dyes.



Fig. 12. The model of the dye molecule diffuse through the void of polymer chains.

Fig. 12 illustrates the model of the dye molecule diffuse through the void place of polymer chain. The information about the model is necessary, because the dye molecule can diffuse into the domain with a large free-volume fraction, and this domain is only the path of molecular diffusion. The variable void place (pores) of the polymer chains is activated and is the real factor to determine the transports.

4.3. Effect of temperature and viscosity of solutions on membrane permeability

Fig. 13 presents the permeate flux of pure water as a function of temperature. Along with an increase in temperature, the permeate flux increased linearly. $F_{\rm C}0.33$ membrane, the permeate flux of $0.13 \,{\rm g}\,{\rm m}^2\,{\rm s}^{-1}$ at 31°C was about 1.4 times higher than $0.09 \,{\rm g}\,{\rm m}^2\,{\rm s}^{-1}$ at 20°C, whereas $F_{\rm C}0.66$ membrane the permeate flux of $0.22 \,{\rm g}\,{\rm m}^2\,{\rm s}^{-1}$ at 31°C was about 2.2 times higher than $0.1 \,{\rm g}\,{\rm m}^2\,{\rm s}^{-1}$ at 20°C. These phenomena might be due to the effect of temperature on the viscosity of solution, the other reason might be that κ -carrageenan is sulfated only at C4 in the 1,3-linked galactose ring. The structure of κ -carrageenan allows the formation of double-helical segment that can form gel structure at



Fig. 13. Effect of feed temperature on permeate flux (pressure: 100 kPa).



Fig. 14. Effect of feed viscosity on permeate flux (pressure: 100 kPa).

the appropriate conditions of potassium concentration and temperature. The temperature has a dramatic effect on κ -carrageenan gel-structure. The relative high temperature can make polymer chain of κ -carrageenan more spongy and larger pores.

Authors adjusted the viscosity of feed solution with different concentrations of glucose solutions. Variation in the viscosity of glucose was studied on the membrane permeation performance as shown in Fig. 14. The membrane fluxes of $F_{\rm C}0.33$ and $F_{\rm C}0.66$ membrane filtration experiments were both impair with the elevated solution viscosities. According to Fig. 14, compared with the $F_{\rm C}0.33$ and $F_{\rm C}0.66$ membrane in permeability at different solution viscosity of the feed solution $F_{\rm C}0.66$ membrane had good permeation properties at low-viscosity solution, but dramatically decreased in the high viscosity of the glucose solution, whereas $F_{\rm C}0.33$ membrane has only a little change in permeation flux.

4.4. Membrane performance in dye separation

The experiments were aimed at evaluating the application of κ -carrageenan/pullulan membrane for the decolorization of dye solutions. The effects of the dye molecular weight and viscosity on the process were verified. The basic transport and separation properties of the membrane permeation were determined prior to the long-term experiment, which was shown in Fig. 15. It is likely that the worsening of membrane transport properties (in terms of membrane permeability to pure water) was cause by the high-molecular-weight dyes. Furthermore, it is also worth that the decreases in dye permeate flux is pronounced for the κ -carrageenan/pullulan membrane, which the size of separated particles is anticipated to be much similar with the mean pore size.



Fig. 15. Membrane flux permeation of various model dye solutions (pressure: 100 kPa). (Water; MO: Methyl Orange; IC: Indigo Carmine; BS: Bordueax S; BB: Brilliant Blue; RB: Rose Bengal).

4.5. Membrane performance in dye treatment

The selectivity of a membrane is usually represented by its molecular weight cut-off. This is defined as the minimum molar mass of a test solute that is 90% retained (or 95% depending on the manufacturer) by the membrane.

Fig. 16 shows that the plots of the rejection rate for tracer molecules according to their molar mass: the selectivity curve. The molecular weight cut-off values of $F_{\rm C}0.33$ membrane were 327 Da, and for $F_{\rm C}0.66$ membrane performed the results of 466 Da, respectively.

From Fig. 16, the rejections of Bordeaux S, Brilliant Blue and Rose Bengal were achieved 96–98%, which demonstrated that the κ -carrageenan/pullulan composite membrane had low-molecular-weight cut-off and good performance in dye treatment.

Different dye solutions were treated at 25°C and 100 kPa with κ -carrageenan/pullulan composite membrane, respectively. The decolorization effect of the membrane was shown in Fig. 17. It can be seen that



Fig. 16. The selective curve of κ -carrageenan/pullulan membrane for dye molecules.



Fig. 17. Photograph of the membrane performance in decolorization (F and P represent feed solution and permeate solution, respectively. The dyes used Methyl Orange (MO), Indigo Carmine (IC), and Rose Bengal (RB)).

the permeated solutions of Rose Bengal (1017 Da) was completely was colorless as pure water, the dyes were partially removed when the Methyl Orange (327 Da) and Indigo Carmine (466 Da) applied to larger molecule is expected high rejection.

5. Conclusions

Biopolymer κ -carrageenan/pullulan composite membrane was successfully prepared by the casting method. It has the sufficient mechanical strength enough for a practical use and the excellent mass transfer character especially on molecular size screening (327–1017 Da). The relationship between mass transfer character and the mass fraction of κ -carrageenan in the composite membrane was formulated based on the experiments of mass-transfer flux and pure water flux. The results provided a novel and simple method of preparation membrane and the size of mass transfer channel based on molecular-size indicators and suggested that different $F_{\rm C}$ values significantly affect the mass-transfer permeability. The membrane can be applied in the removal of dyes from aqueous solutions. The membrane with low-molecular-weight cut-off (the molecular weight cut-off value of $F_{\rm C}0.33$ ($F_{\rm C}0.66$) membrane was 327 Da (466 Da)) had good rejection in dye solution and had relatively highflux permeation, which were suitable to be applied in

desalination of dyes with low-molecular-weight. The dye treatment experiment indicated that the membrane showed good performance molecular weight higher than 1000 Da.

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Nomenclature

- A— area of membrane $[m^2]$ C_f initial concentration of feed solution [M] C_s concentration of stripping solution [M] D_{eff} effective diffusion coefficient $[m^2 s^{-1}]$ J— water-permeated flux $[g m^{-2} s^{-1}]$ K_{OL} overall mass-transfer coefficient $[m s^{-1}]$
 - K_{OL}^{-1} overall mass transfer resistance [(m s⁻¹)⁻¹]
 - $k_{\rm m}$ membrane mass-transfer coefficient [m s⁻¹]
 - k_{L1} membrane mass-transfer coefficient in feed phase [m s⁻¹]
 - k_{L2} membrane mass-transfer coefficient in stripping phase [m s⁻¹]

l — membrane thickness [m]

 ΔP — operational pressure [kPa]

 Δt — time [s]

V — volume of aqueous solution in the transfer cell [m³]

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