ABSTRACT

Vanillin imprinted poly(ethersulfone) (PES) hollow fiber membrane was spun using dry-wet spinning method, the membrane was then prepared as a filter with an effective area of 152 m²/g. One main feature of this system is the vanillin-imprinted polymer particles embedded in hollow fiber membrane which is possible to be use as filtration materials for vanillin separation. In the present study, the vanillin-imprinted polymer particles was prepared by copolymerization of covalently linked vanillin methacrylate monomer and methacrylic acid in divinylbenzene segments followed by embedding in poly(ethersulfone) hollow fiber membranes with different contents of the vanillin-imprinted particles at 0, 2.5, 5.0, 10 and 15 wt %. The separation ability of the prepared hollow fiber membrane was measured using 100 mM aqueous solutions containing each vanillin and its analog towards the imprinted membrane by examined the permeation flux and separation factor. The value of the separation factor was 32 for 10 wt % loading with 93 l/m²h flux, while for 2.5 wt %, the values of separation factor and the permeation flux were 9.5 and 22 l/m²h, respectively. The rate of vanillin separation increased for the imprinted hollow fiber membranes due to the larger amount of binding sites, comparing with non-imprinted polymers. These experimental evidences indicated the importance of alternative tailored-made separation of vanillin mixture.

1. INTRODUCTION

The utilization of hollow fiber membranes in separation process has attracted much attention owing to its promising properties for compact fashion and high efficient performance on water treatment. The selectivity of hollow fiber membrane for a targeted molecule is a key factor determining the success of a membrane separation process.
In addition, the hollow fiber configuration led to numerous commercial applications in various fields such as for blood dialysis in the medical field (Tullis 2002), wastewater treatment (Naghizadeh 2008), gaseous separation (Lemanski 2002) and azeotropic mixture separation (Li 2006).

Recently, many efforts have been made to prepare functional hollow fiber membranes showing tailored-made selectivity towards specific molecules in order to separate chemical analog molecule components in a substance mixture. Among them, hollow fiber membranes showing molecular imprint functionality act as effective selectors. This is because in the molecular imprinting technology that the most applicable method can construct alternative polymeric materials for molecular recognition (Wulff 1995). It has been reported that hollow fiber molecularly imprinted membrane offers many advantages, when the support membranes having mechanical integrity has high selectivity of the imprinted polymer to the target molecules. In this strategy, Zhao (2008) demonstrated that bisphenol A could transfer from low concentration to high concentration for the poly(ethersulfone) (PES) hollow fiber membrane due to the large amount of binding sites. Meanwhile, Peimin and Bing (2009) reported that the blending trimethoprim-MIP and polysulfone membrane prepared to exhibit good recognition ability to trimethoprim as well as good flexibility and high mechanical strength. Therefore, this technique possesses the high possibility for broadening application, but, the information still is very limited.

In the present study, the covalent imprinting vanillin polymer particles were synthesized with precipitation terpolymerization including delayed monomer additions to the cored polyDVB spheres. Then, the particles were embedded in PES scaffold using dry-wet spinning method for preparation of imprinted hollow fiber membranes. The recognition property to the template vanillin was evaluated. For vanillin, generally, it is widely used as flavoring in sweet foods such as ice creams, cakes and soft drinks in food industries. Therefore, vanillin is important agent used for flavoring or for a precursor of drugs. Early in the 20th century, chemist found that lignin was a source of vanillin. However, the vanillin obtained from waste lignin contained high level of impurities (Pearl 1942 and Sarkanen 1971). Therefore, the successful purification to the vanillin is attractive for their complicated mixture. So, using vanillin-imprinted polymer embedded in hollow fiber membrane is one of alternative method to improve the separation of vanillin in the lignin mixture and is meaningful as an application. Therefore, this work describes the preparation of the vanillin-imprinted polymer particles. Then, the properties of vanillin separation were studied by using imprinted hollow fiber membranes to optimize their separation conditions.

2. EXPERIMENTAL SECTION

2.1 Reagents and Apparatus
Vanillin (≥ 98%) was purchased from Sigma (St. Louis, MO, USA) and purified by crystallization method. Tetrahydrofuran (THF), chloroform, divinylbenzene (DVB), acetone, azobisisobutyronitrile (AIBN), acetonitrile (HPLC grade), methacrylic acid (MAA), polyethylene glycol (PEG 600) (MW=600), N-methyl-2-pyrrolidone (NMP), acetic acid, sodium hydrogen carbonate and ethanol were purchased from Nacalai Tesque Inc (Kyoto,
Japan). The DVB was purified three times using a silica gel column to remove inhibitor prior used, while AIBN was purified by crystallization method. Sodium hydroxide was purchased from Wako Pure Chemical Industries., Ltd. (Japan). Meanwhile, triethylamine (TEA) was purchased from Tokyo Chemical Industry Co. Ltd (Japan). Methacryloyl chloride (MAC) was purchased from Tokyo Kasei Industry Co. (Tokyo, Japan). Prior used for the synthesis vanillin monomer, MAC was distilled under vacuum to remove the inhibitor prior. Magnesium sulfate was purchased from Kanto Chemical Co. Inc (Japan).

Poly(ethersulfone) (PES) (MW=50,000) was purchased from BASF (Ludwigshafen, Germany) and used as delivered.

2.2 Preparation of vanillin methacrylate and vanillin-imprinted polymer

Briefly, vanillin methacrylate (Scheme 1) was synthesized by esterification of vanillin (3.06 g, 20 mmol) and MAC (8.36 g, 80 mmol). Here, the methacrylate group was introduced to the vanillin framework in the presence of TEA (8.08 g, 80 mmol) by following the procedure. Firstly, vanillin was added in dry THF (100 mL) containing TEA and then, the MAC monomer was added drop wise under stirring at room temperature. Then, the esterification reaction was carried out for 24 hours. The white precipitate of TEA salt was removed by filtration after the reaction. The evaporated THF solution was dissolved in chloroform and washed with an aqueous sodium hydrogen carbonate solution and then with water. The organic layer was dried over with magnesium sulfate. Then, the precipitated crude VMA was obtained by the evaporation of the organic layer and purified by a re-crystallization in ethanol to obtain a final product (white in color, 70.6 % yield).

![Scheme 1. Preparation of vanillin methacrylate monomer](image)

For vanillin-imprinted divinylbenzene particles were obtained by conventional surfactant free polymerization was applied to core-shell imprinting method (Zhao 2001). The crosslinker DVB 13.02 g (100 mmol) was added in the mixture of 220 ml acetone, 30 ml water and the free radical initiator AIBN (1 mmol) was added into the solution. The mixtures were poured into a 500 ml three-neck round bottom flask. The flask was kept in an oil bath equipped with an agitator (BL 3000; Heidon/Shinto Scientific Co. Ltd.), a condenser and a capillary tube for nitrogen gas. The solution in the flask was deoxygenated with nitrogen gas for 30 minutes at room temperature, while the stirring speed was kept at 300 rpm. The temperature of the flask was increased up to 65 °C under continuous nitrogen atmosphere. After 3 hours, the template VMA 4.40 g (20 mmol) and the functional monomer MAA 1.72 g
(20 mmol) were dissolved in 50 mL acetone was dropped into the solution. The polymerization was continuously carried out by the process reached 24 hours. The precipitated polymer was separated and washed with a mixture of acetone and water and dried under vacuum condition. The white powder of dried polymer was hydrolyzed with 1 M NaOH and small amount of ethanol solution at 50 °C for 12 hours to remove the template. The core-shell imprinted polymers were washed with water until neutral and dried under vacuum condition. As a control, the non-imprinted polymer (NIP) in the absence of the VMA was prepared and treated by the same method. The obtained vanillin-imprinted polymer particles could be characterized using the following measurements such as Fourier transform infrared (FT-IR) spectrum (IR Prestige-21 FTIR 8400s; Shimadzu Corp., Japan) and scanning electron microscope (SEM) (JSM-5310LVB; JEOL, Japan).

2.3 Preparation of the hollow fiber imprinted membrane by dry-wet spinning process

In 44 mL NMP as dope solution, PES (20 g) was dissolved and added to 36 g of PEG 600 and MIP particles obtained. Then, the mixture was stirred at 50 °C to prepare the viscous solution. The content of MIP particles was varied by 0, 2.5, 5, 10 and 15 wt % in the PES dope solution. Both the dope solutions containing MIP spheres and the aqueous NMP solution (1:1 v/v %) were extruded through the spinneret at the rates of 3 mL/min and 2.5 mL/min, respectively, to mix together by using a high pressure gear pump (GP Driving Unit CDS-18G-0.8X1, Kyowa Fine Tech. Co. Ltd.). The extruded spinning solution was introduced into a water bath located below the nozzle. Then, the extruded spinning solution was coagulated at 25 °C in water to form hollow fibers. The hollow fiber membranes were treated with excess of hot water at 90 °C for 3 times in order to eliminate the NMP and PEG and then were dried.

2.4 Batch binding and permselective separation of vanillin analog

To evaluate the binding ability of the vanillin-imprinted hollow fiber membranes, the vanillin-imprinted hollow fiber membranes were cut into 20 cm and were bundled. Both ends of the bundled were fixed with polyurethane resin (U-10 FL, Loctite Corporation, USA) to form a module with 2 cm inner diameter. Each module contained 3 fibers for permselective experiments in 20 mL of the mixture solutions containing vanillin, syringaldehyde and p-hydroxybenzaldehyde with the initial concentration, 100 mM for each compound. The nitrogen gas pressure applied for filtration process was 0.1 kg cm⁻¹. The permeation flux (F) (l/m²h) was determined by Eq. 1.

\[ F = \frac{V}{St} \]

Herein, \( V \) was the volume of permeated solution (l), \( S \) for surface area of the membrane (m²) and \( t \) for permeation time (h). After permeation of solute mixture solution through the hollow fiber membrane, the vanillin and other analog concentration in the permeate solution was determined using high performance liquid chromatography (HPLC) (CCPE-II; Tosoh Corp.) equipped with UV detector set at 280 nm (Hitachi 655; Hitachi, Ltd.) and TSK-gel ODS-80Ts QA column (4.6 mm I.D, 75 mm length; Tosoh Corp.) (Son 2011).
3. RESULTS AND DISCUSSION

3.1 Characteristic of imprinted hollow fiber membranes

Each of the hollow fiber membranes was prepared with the phase transition technique of the dope solution involving the imprinted particles by using dry-wet spinning method to water coagulation medium. It is known that the water medium showed high solubility for NMP solvent, but not for PES and the vanillin-imprinted polymer powders. Thus, the polymer component was coagulated in the water medium and then the solidified hollow fibers showing opaque in appearance were obtained with satisfactory in strong membrane. Fig. 1 shows SEM images of cross-section for the vanillin-imprinted hollow fiber membranes (a) and (b). The images showed the presence of the embedded vanillin-imprint particles (VIP) in the hollow fiber membrane. Meanwhile, SEM images (d) and (e) show the PES hollow fiber membrane without vanillin-imprinted particles for comparison. The resultant hollow fiber membranes had an inner diameter around 0.59 mm and the thickness of the membranes was in about 98-100 μm. Besides, the outer diameter and the thickness of hollow fiber membrane embedded VIP spheres were 0.65 mm and 100 μm, respectively.

![Fig. 1 SEM images of cross-section of hollow fiber membranes](image)

In order to confirm the presence of the VIP in the PES scaffold, FT-IR spectra of the VIP powders, the PES membrane and PES-VIP membranes were compared as shown in Fig. 2. In a and b for the VIP and the PES scaffold, the IR bands at 1745 cm⁻¹ and 1238 cm⁻¹ were assigned to C=O stretching from the vanillin-imprinted powder and S(=O)₂ stretching for ethersulfone group of the PES, respectively. As references, the IR spectra of the PES including poly(DVB) spheres in the hollow fiber membrane could compared with the data of
the VIP membrane. In c-e, spectra for PES-VIP were present. It was found that the C=O group of vanillin methacrylate was present, while the S(=O)\textsubscript{2} stretching bands were shifted to 1246 cm\textsuperscript{-1}, relative to that of PES only (b). In addition, it was also clear that the appearance of 1745 cm\textsuperscript{-1} band represented the presence of the VIP in the membrane. Furthermore, the intensity of the S(=O)\textsubscript{2} peak near at 1909 cm\textsuperscript{-1} was decreased and the band at 946 cm\textsuperscript{-1} for the PES was disappeared in the PES-VIP hollow fiber membranes, meaning interaction between the VIP spheres and PES scaffold. These indicated that the VIP was successfully hybridized in the PES scaffold.

Fig.2 FT-IR spectra of (a) VIP particles, (b) PES membrane and PES-VIP membrane loading VIP particles with (c) 2.5, (d) 5, (e)10 and (f) 15 wt %
3.2 Vanillin binding to the imprinted membrane by permeation experiments

In order to study the recognition ability of resultant hollow fiber membranes to the vanillin template, a series of PES-VIP membranes were prepared by changing the content of the VIP particles. The binding capacities for vanillin were measured in various contents of VIP spheres in the membranes. The weight percents of the VIP changed were at 0, 2.5, 5, 10 and 15 wt % in each polymer solution and were used for phase transition technique in the dry-wet spinning process. The resultant membrane without VIP and with 10 wt % DVB particles had the binding ability to vanillin with 2.4 mmol/g and 21.1 mmol/g, respectively. When the content of the vanillin-imprinted powder was changed from 2.5, 5, 10 and 15 wt % in the membrane, the binding amounts of the vanillin was gradually increased at 63, 76, 88 and 84 mmol/g, respectively. There was a tendency on the increase of the binding capture of the vanillin by the PES-VIP membranes.

Fig. 3 shows permeation flux of the PES-VIP and PES hollow fiber membranes towards aqueous vanillin and vanillin analogs mixture with each 100 mM concentration. The permeation flux of the PES hollow fiber membrane without the VIP spheres was the lowest in the system. However, by increasing the VIP loading in the membrane, the values of the permeation flux were increased. For example, when the content of the VIP loading was changed from 0, 2.5, 5 and 10 wt %, the value of permeation flux was observed as 22, 35, 56 and 93 l/m²h, respectively. At higher than 10 wt % of VIP loading the value of the permeation flux of vanillin significantly was 92 l/m²h. The results indicated that the content of loading VIP particles should be controlled in certain range in order to obtain better performance of hollow fiber membrane. However, over 15 wt % loading, it was very difficult to have good membranes because of very brittle property.

Fig. 3 Comparison of volume permeation flux and membrane porosity of hollow fiber membranes and the VIP loading
As shown in Fig. 4 the ability of the VIP membrane to discriminate imprinted target vanillin and its analog was investigated. The data clearly showed that the value of separation factor for vanillin was increased, when the VIP loading was increased. In the PES-VIP with 10 wt % and 15 wt % loading in the membrane, the separation factor $\alpha$ was 32.1 and 31.6, respectively. In these loading amounts, the separation ability became constant. As seen, the membrane displayed a separation factor of 1 and 1.7 for $p$-hydroxybenzaldehyde and syringaldehyde, respectively. This meant that the both PES-VIP 10 wt % and 15 wt % showed a greater tendency towards vanillin uptake with higher selectivity. It was noted that high loading of the VIP particle in the membrane exhibited higher permeability of the solute solution through the hollow fiber membrane. Even though the lower residence time in the membrane for the solution, the 10 wt % and 15 wt % PES-VIP membranes had an effective separation of the vanilla component. In addition, while the VIP particles showed $\alpha = 6.8$ for vanillin, the imprinted membrane exhibited very high separation factor. This is a significant result in terms of recognition specificity in the present work. As considered in some degree of H-bonding interactions between the template and the imprinted sites, the template vanillin can be retained through the VIP spheres to affect vanillin selectivity. Therefore, the permeation performance had advantages to recognize vanillin in aqueous solution.

![Fig. 4 Separation factor of vanillin and vanillin analogs for each membrane](image)

As shown in Fig. 5 (a), the binding amounts of the vanillin substrate to the membranes were relatively small and increased along with the increase of vanillin concentration. But,
the PES-VIP membrane showed that the binding capacity increased gradually reaches a larger equilibrium value, when the concentration was increased. The difference in the imprinted and non-imprinted polymers was due to the presence of the formation of the specific recognition sites complementary to the vanillin templates. To analyze the binding behavior to the membranes, Scatchard equation which was commonly used for the evaluation of the binding characteristics of molecularly imprinted polymer to substrate compound, was used. Here, the value of $K_a$ for the vanillin-imprinted hollow fiber membrane was determined according to the Scatchard equation (Scatchard 1949).

$$[S]/C_e = -[S]K_a + nK_a$$  \hspace{1cm} (2)

where $K_a$ (mmol/L) is the equilibrium constant of the binding sites, $Q_{max}$ (mmol/g) is the maximum binding capacity of binding sites. Here, $Q$ (mmol/g) is the binding amount of polymer to vanillin and $C_e$ (mmol/L) is the equilibrium concentration of vanillin in solution.

According to the Scatchard equation, the data suggested that the membrane without the VIP formed a less class of equivalent binding sites to the vanillin to be $Q_m = 2.2$ mmol/g and $K_a = 9300$. The constant of $K_a$ and the maximum binding capacity of $Q_{max}$ for the vanillin were calculated to be 19800 mmol/L and 89 mmol/g, respectively, in the PES-VIP membrane. This ability of the PES-VIP membrane promised to be high recognition to the vanillin by the imprinted effect. As seen in Fig. 5 (b) and Table 1, the obtained value of the binding capacity of the PES-VIP hollow fiber membrane was about 40 times higher than that of the PES hollow fiber membrane without including the VIP particles. As compared between the VIP and DVB spheres, there was 4 times higher than the PES-DVB membrane in the PES-VIP membrane. It was clear that the PES-VIP membrane exhibited effective binding ability to vanillin compound.
Fig. 5 (a) Binding amount of vanillin in various concentration by using (a) PES-VIP 10 wt % hollow fiber membrane, (b) vanillin-imprinted powder, (c) PES-DVB hollow fiber membrane and (d) PES hollow fiber membrane; (b) Scatchard plots for vanillin onto PES-DVB and PES-VIP 10 wt % membranes

Table 1 The analogs binding capacities in PES, PES-DVB and PES-VIP (10 wt %) hollow fiber membranes and vanillin-imprinted particles determined from Scatchard plots

<table>
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<td>$K_a$ (mmol/L)</td>
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4. CONCLUSIONS

The hollow fiber membrane embedded the VIP spheres was prepared, when the loading content of the VIP in the PES scaffold was changed from 0 to 15 wt %. The imprinted hollow fiber membrane prepared to exhibit good adsorption capacities to vanillin. According to the Scatchard analyses, the vanillin-imprinted polymers exists a class of equivalent binding sites. This property was an advantage in eases for membrane adsorbents of vanillin in hollow fiber scaffold. Thus, this could promise many applications for recognition, separation and concentration of vanillin.

REFERENCES


