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MOLECULAR NANO-SIEVE APPROACH BY THE APPLICATION OF POLYPIPERAZINE (PPA) BASED MEMBRANE FOR THE RECOVERY OF WATER SOLUBLE AGARWOOD (AQUILARRIA MALACCENSIS) MARKER MOLECULES

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ABSTRACT

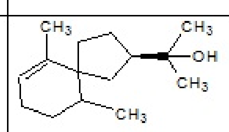
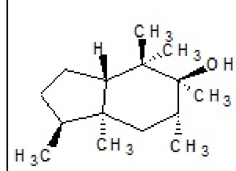
This study is the groundwork on the ability of nano-sieve technique in the recovery of water soluble agarwood marker compounds from agarwood hydrosol. To achieve this purpose, a polypiperazine (PPA) based nanofiltration (NF) membrane was used. The effectiveness of this membrane on the separation of agarwood marker molecules was analysed and FTIR results showed that most of marker compounds (i.e. agarospirol, jinkohol, jinkoh eremol and khusenol) has been successfully separated from the aqueous agarwood. However, the performance of the membrane in terms of flux and permeability is quite low, which is 23.30 L/m^2.h, with 6.76 L/m^2.h.bar, respectively. These initial findings will be used as the forecast to improve the future development of NF membrane, specifically *'tailor-made'* for the large scale production of agarwood marker compounds.

Keywords: agarwood, aquilarria malaccensis, nanofiltration, agarospirol, jinkohol, jinkoh eremol, khusenol.

INTRODUCTION

Compound Formula Structure Functional groups MW(Da) Agarospirol C15H26O Aromatic Hydroxyl Alkene Alkane 222.36 Jinkohol C15H26O Aromatic Hydroxyl Alkane 222.36Agarwood, or 'karas/gaharu' in Malay is the resin produced by Aquilarria Malaccensis tree, results from their defence mechanism against wounding (Chong *et al.* 2014), (Li *et al.* 2013). It is often occurs as dark coloured patches or streaks in the tree. The essential oil of agarwood is significantly prized, especially for perfume, incense, religious rituals and medicinal purpose. At present, hydro-distillation technique, utilizing water as solvent, is commercially being used to extract the agarwood oil from its wood (Islam *et al.* 2014), (Azah *et al.* 2013) (Naef *et al.* 2010). Although this method is widely applied in agarwood industry, it is still not yet proficient. This reason is because most main marker compounds of agarwood which are responsible for their aromatic scent as shown in Table-1 are from sesquiterpenoids groups which possess hydroxyl (OH) moieties, have the ability to form hydrogen bonding with water (Subasinghe *et al.* 2012), (Tajuddin *et al.* 2010) (Fadzil *et al.* 2013). This reflects to their possibility to dissolve in solvent during processing, leaving them in the by-product of distillation, known as distillate or hydrosol (Figure-1). As a consequence, they cannot be completely recovered and feasible product yield could not be achieved. Moreover, hydro-distillation is also not very useful for investigating the composition of genuine essential oils and aroma-active compounds because of the tendency in transformation processes due to high temperatures (Richter *et al.*, 2007) (Mohd *et al.* 2008). Thus, considering the demand and high value of these compounds, a new further alternative separation approach has to be explored. In this research, a commercial NF membrane based on polypiperazine amide (PPA) was applied for the extraction of agarwood marker compounds. The surface of PPA is hydrophilic due to the existence of semi aromatic/aliphatic polyamide as shown in Figure-2. Membrane technology does not require additional energy and also enables a high productivity. Isolation of agarwood marker compounds using membrane technology would bring benefits to the local agarwood industries to control the qualities of agarwood oil, as well as maximizing their profit through the utilization of low cost technology.

Table-1. Properties of agarwood sesquiterpenoids.

Compound & Formula	Structure	Functional groups	MW (Da)
Agarospirol $C_{15}H_{26}O$		Aromatic Hydroxyl Alkene Alkane	222.36
Jinkohol $C_{15}H_{26}O$		Aromatic Hydroxyl Alkane	222.36

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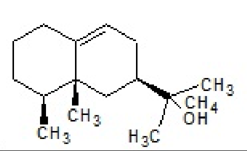
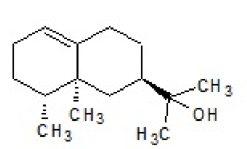
Jinkoheremol $C_{15}H_{26}O$		Aromatic Hydroxyl Alkene Alkane	222.36
Kusenol $C_{15}H_{26}O$		Aromatic Hydroxyl Alkene Alkane	222.36

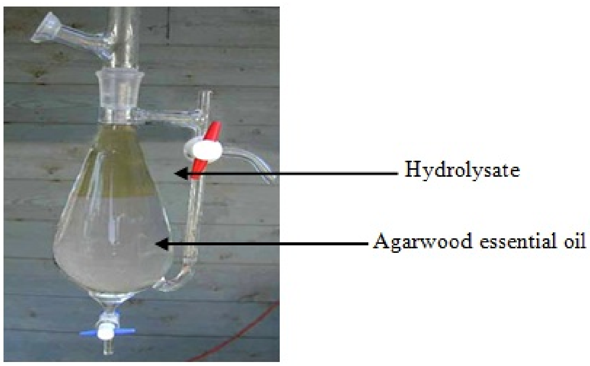


Figure-1. Production of agarwood essential oil by distillation.

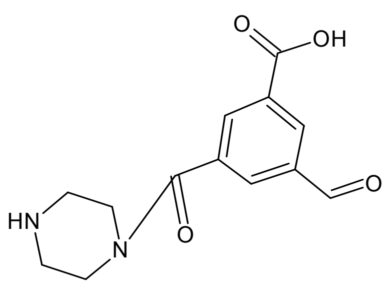


Figure-2. Chemical structure of polyiperazine (PPA).

MATERIALS

The hydrosol of agarwood was obtained from Kedaik Agarwood Sdn Bhd, a local industry located in Rompin, Pahang, Malaysia. The PPA (TS40) membrane was supplied by Sterlitech Corporation, with theoretical molecular weight cut-off (MWCO) of 200 Da. This membrane is a composite type, consists of thin polypiperazine top layer, supported by polymeric and non-woven bottom layer with '*spongy*' micropores. Other chemicals and solvent for analysis (acetone and methanol, both from Fischer Scientific (M) Sdn Bhd) were of reagent grade. The filtration unit was operated in dead end module using Amicon Stirred Filtration Cell (Model 8200). Analyses of both permeate and retentate was accomplished by FTIR.

EXPERIMENTAL PROCEDURE

Permeation process: Optimization of permeation process was performed by applying different transmembrane pressure (TMPs). 20 mL of feed solution (agarwood hydrosol) was poured into permeation apparatus and the volume of permeate collected in five minutes was measured. Permeate flux was calculated according to the following equation:

$J_v = V/ (t \times A)$

Where J_v is flux ($L/m^2.h$), V is volume of permeate in liter, t is time in hour and A is the effective area of the membrane, which is 0.00287 m^2. The filtration was carried out at different pressure to calculate the permeability coefficient (P_m), which is determined from the slope of the graph. Permeate and retentate stream were both analysed by FTIR.

Fourier Transform Infrared (FTIR): FTIR measures the frequencies at which the sample absorbs, and also the intensities of these absorptions. The frequencies are helpful for the identification of the sample's chemical make-up due to the fact that chemical functional groups are responsible for the absorption of radiation at different frequencies. FTIR is very helpful for the predictive assignment of chemical compounds. The spectrum of all samples (agarwood hydrosol, retentate and permeate) was recorded at range of 4000 – 400 cm^{-1} (mid infrared spectroscopy) at 4 cm^{-1} resolution (FTIR model: Nicolet Avatar 370 DTGS).

Scanning Electron Microscopy (SEM): Scanning Electron Microscopy (SEM) is a scientific instrument that uses a principle of a narrow beam of the electron with kinetic energies hits (1 to 25kV) the membrane sample. It allows a clear and concise view of the overall membrane structure. For this work, a scanning electron microscopy (Model: Zeiss Evo 50) was used to probe the morphological features of membranes. Small pieces of membrane were fractured cryogenically in liquid nitrogen, and sputtered by platinum, prior to viewing under SEM.

RESULTS AND DISCUSSION

Figure-3 illustrates the FTIR plots for feed (industrial agarwood hydrosol), retentate and permeates from membrane filtration process. Based on the generated wavenumbers (Table-2) bands in feed were identified as hydroxyl (O-H), aromatic alkane (C-C, C-H,) and alkene (=C-H) stretches. All of them resemble the functional groups of water soluble agarwood sesquiterpenoids as previously displayed in Table-1, thus supportively confirms the presence of these compounds in the hydrosol. H-O-H bond from water was also detected in feed since the agarwood hydrosol itself is a homogenous mixture of water and agarwood sesquiterpenoids. The FTIR characteristic of retentate is almost similar to feed except for the absence of H-O-H stretch in retentate. Permeate on the other hand, shows the presence of only O-H and H-O-H stretch, exhibiting an analogous chromatogram to the FTIR of pure water. From this evidence, it is postulated that, this PPA membrane has been successful in separating

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majority of agarwood sesquiterpenoids from its water fraction, by retaining them in retentate and allowing only water to pass through into permeate. This prediction is further strengthened by the fact that, MWCO of this PPA membrane is 200 Da. Definitely, agarwood sesquiterpenoids which have MW above 200 Da are not permeable to this membrane, as compared to water with MW of 18 Da. The significance size difference also explain their efficient segregation disregard the fact that, both water and agarwood components actually have the same ability to be pulled towards the hydrophilic vicinity of PPA membrane.

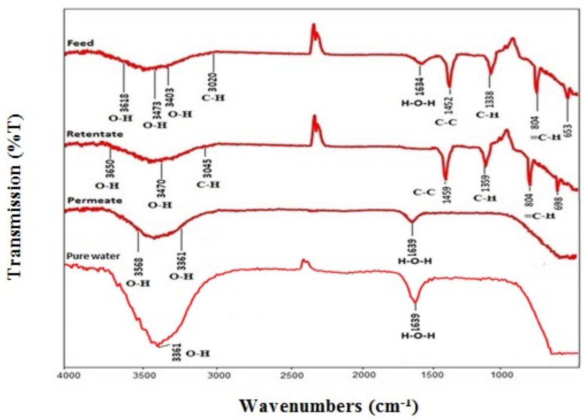


Figure-3. FTIR spectroscopy of feed, retentate, permeate and pure water.

Table-2. Vibrational bands assignments of feed, retentate, permeate and pure water [(Schulz *et al.* 2005), (Fang *et al.* 2011), (Li *et al.* 2013), (Santosa *et al.* 2013)].

Wavenumbers (cm^{-1})	Band assignment
3400- 3600	O-H (alcohol)
3000-3100	C-H (aromatic alkane)
1400- 1500	In ring C-C stretches (aromatic alkane)
1330-1370	C-H (alkane)
650-800	=C-H bending (alkene)
3300-3400	O-H (water)
1630-1640	H-O-H (water)

The graph of pure water flux vs pressure is presented in Figure-4 and summarized results are tabulated in Table-3. Regression coefficient, (R^2) is high (0.9975) indicating an outstanding linearity between pressure and flux. However, the flux and permeability (P_m) is quite low, which may be caused by the tight cross sectional structure of this membrane, as portrayed by Scanning Electron Microscopy (SEM) image in Figure-5. The average flux is 23.30 L/m².h, with 6.76 L/m².h.bar of P_m. Data from the graph showed that, the produced pure water fluxes in the pressure of 2-5 bars are approximately 10-35 L/m².h, constitutes the lower range of typical NF flux, which is 20-200 L/m².h. This is not feasible especially in large scale agarwood industry, as it will restrain the flow rate of water, consequently inhibiting a rapid separation process (Khalil *et al.* 2013), (Kumar *et al.* 2011), (Konwar *et al.* 2011), (Bergo *et al.* 2012), (Koris *et al.* 2011).

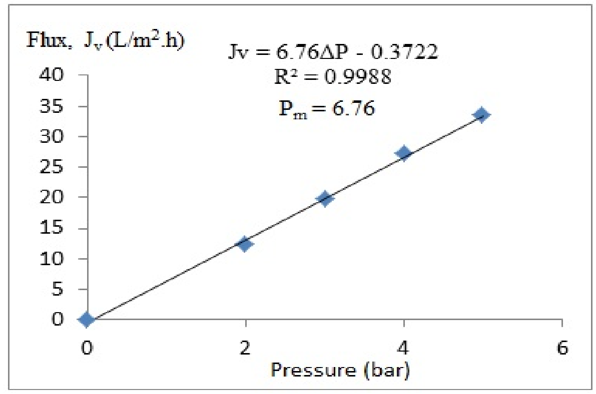
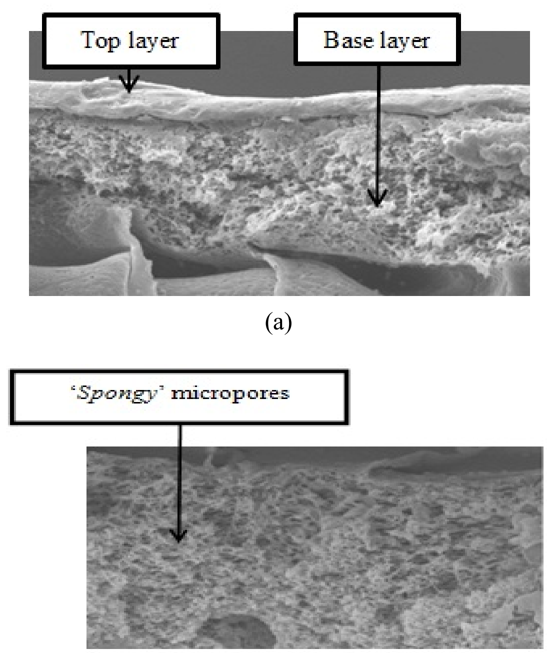


Figure-4. Flux of PPA membrane at different operating pressure.

Table-3. Performance characteristics of PPA membrane.

Membrane	Characteristics	
	P_m	Average flux (L.m².h)
PPA	6.76	23.20



(a)

(b)

Figure-5. SEM cross sectional image of PPA membrane (a) Top and base layer at 100x magnification (b) Base support layer at 300x magnification.

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CONCLUSIONS

The recovery of agarwood marker compounds using commercial polypiperazine (PPA) NF membrane yield a positive outcome. FTIR analysis showed that most of hydroxyl bearing components has been extracted into permeate. This might be a fundamental indicator of the successful separation of the agarwood sesquitpeneoids from their hydrosol. Nevertheless, additional studies should be carried out for a more detail clarification, especially on the biological and chemical information of these compounds. The endowed working flux is also low, and this seems to be not efficient, especially for bulk application. Therefore, the operational membrane properties are yet to be improved. Using this PPA membrane as reference prototype, a new formulation of thin film composite (TFC) NF membrane with the combination of *'fine-tuned'* flux and high rejection property is aimed to be customized towards the achievement of optimum industrial productivity.

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