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1 **Investigating the feasibility of using Polysulfone-Montmorillonite Composite**  
2 **Membranes for Protein Adsorption**

3  
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18 **Abstract**

19 The feasibility of immobilisation of montmorillonite (MMT) in polysulfone (PSf) to  
20 form mixed matrix membrane (PSf/MMT) to serve as the adsorbent for BSA proteins  
21 from a model white wine solution was investigated. Pristine PSf and modified  
22 PSf/MMT membranes were synthesized using the phase inversion method and  
23 characterized using various surface techniques. Addition of MMT particles in the  
24 polysulfone matrix enhanced the hydrophilicity of the membrane surface and promoted  
25 the formation of a more porous structure in the PSf/MMT membrane, resulting in  
26 greater permeance but lower rejection in comparison to the PSf membrane. In addition,  
27 imaging analysis demonstrated recognition of protein adsorption on the adsorptive areas  
28 of the MMT particles within the PSf/MMT membrane matrix which confirmed the  
29 hydrophobic interactions between the MMT particles and BSA protein molecules. The  
30 finding is a significant step for subsequent research to examine the possible applications  
31 of clay-filled polymers in selectively removing protein from wine.  
32

33 **Keywords:** XPS imaging; protein separation; adsorption; montmorillonite, polysulfone  
34 membrane, mixed matrix membrane.  
35

36 **Abbreviations**

37 BSA bovine serum albumin

38 MMT montmorillonite

39 NMP N-methyl-2-pyrrolidone

40 PSf polysulfone membrane

41 PSf/MMT polysulfone montmorillonite composite membrane

42 PSf\_F PSf membrane after filtration test with model wine solution

43 PSf/MMT\_F PSf/MMT membrane after filtration test with model wine solution

44 SEM Scanning Electron Microscope

45 XPS X-ray Photoelectron Spectroscopy  
46  
47  
48

## 1 **1. Introduction**

2 Bentonite, comprising predominantly montmorillonite (MMT, a member of the smectite  
3 group), has been extensively used to prevent the protein haze-forming in white wines  
4 for more than 70 years (Ferreira et al., 2001; Hsu and Heatherbell, 1987). The process,  
5 known as fining, is primarily driven by hydrophobic interactions where positively  
6 charged proteins are agglomerated onto the surface of negatively charged clay particles.  
7 Studies have shown that bentonite significantly swells and behaves like a series of small  
8 plates upon agitation in water. This results in a very large surface area which can adsorb  
9 as much as several times as in its dry condition (Sarmiento et al., 2000a; Siddiqui, 1968).  
10 However, because of its enormous availability, low cost, and the lack of available  
11 commercial processes for its separation/ regeneration from the wine, bentonite is usually  
12 used once and then discarded into the environment. This results in significant losses of  
13 wine captured in the slurry, and a high impact on the environment (Blade and Boulton,  
14 1988; Ferreira et al., 2001; Hsu and Heatherbell, 1987; Salazar et al., 2006a; Sarmiento  
15 et al., 2000a; Siddiqui, 1968; Waters et al., 2005). A recent article reported that the  
16 estimated total cost to the world wine industry of bentonite fining in its current form  
17 exceeds US\$1 billion (Majewski et al., 2011).

18  
19 Recently many researchers have looked for alternative methods to remove proteins from  
20 white wine. Different techniques have been employed, such as ultrafiltration (Flores et  
21 al., 1990; Hsu and Heatherbell, 1987; Hsu et al., 1987), proteolytic enzymes (Waters et  
22 al., 1992), flash pasteurization (Pocock et al., 1998), or using polymers or metal oxides  
23 (Pashova et al., 2004a; Pashova et al., 2004b; Salazar et al., 2006b; Salazar et al., 2007;  
24 Sarmiento et al., 2000a; Sarmiento et al., 2000b). Ueda et al. (Ueda et al., 1995) and Lit  
25 et al. (Liu et al., 2008) used polymer membranes for protein recovery. Avramescu et al.  
26 (Avramescu et al., 2003a; Avramescu et al., 2003b; Avramescu et al., 2003c) developed  
27 new protein adsorber membranes by the incorporation of various types of ion exchange  
28 resins into the polymer membranes.

29  
30 Researchers examining separations other than protein have reported the application of  
31 clay-filled polymer membranes in adsorption processes for gas separation,  
32 pervaporation and wastewater treatment (Adoor et al., 2006; Anadão et al., 2010;  
33 Choudalakis and Gotsis, 2009; Defontaine et al., 2010; Kim et al., 2006; Picard et al.,  
34 2007; Villaluenga et al., 2007; Wang et al., 2004). It has been reported that the  
35 incorporation of inorganic particles in the polymer membranes suppresses the formation  
36 of macro-voids and enhances the formation of micro-pores. This results in increased  
37 permeance and enhances the mechanical and thermal stabilities of the membrane. In  
38 addition, the composite membrane (commonly referred to as a mixed matrix membrane)  
39 can be reused in multiple adsorption/desorption cycles, thus reducing the amount of  
40 waste and the environmental impact compared to conventional clay based adsorption  
41 processes (Aerts et al., 2000a; Aerts et al., 2000b; Bottino et al., 2001; Clarizia et al.,  
42 2004; Nagarale et al., 2005; Tezuka et al., 2006; Uragami et al., 2005; Vankelecom et  
43 al., 1997; Yang et al., 2008; Yang et al., 2007).

44  
45 These studies reported the *physical* improvements of using clay-polymer membranes  
46 over pristine polymer membranes, and their uses in different applications, but to date  
47 there has been no study to examine the application of clay-polymer membranes for  
48 protein adsorption. Thus, the main focus of our work is investigating the feasibility of

1 the immobilisation of clay particles, in particular MMT, in polymeric materials to form  
2 mixed matrix membranes to serve as the adsorbent for BSA proteins from the model  
3 white wine solutions. The membrane was used to act as a support substrate for the  
4 MMT particles slowing the adsorption and intercalation within the MMT to proceed  
5 without using a bentonite slurry. Polysulfone (PSf) was chosen as the membrane  
6 polymer due to its thermal, biological, and chemical stability (Charcosset, 1998). An  
7 evaluation of membrane morphology, membrane protein rejection and changes of the  
8 membrane surface chemistry with the adsorption process was combined to clarify the  
9 key question of this research: “How does addition of MMT particles in the PSf  
10 membrane affect membrane structure and BSA protein adsorption”  
11

## 12 **2. Materials and Methods**

### 13 2.1 Materials

14 Polysulfone (PSf) in pellet form with  $M_w = 35,000$ , N-methyl-2-pyrrolidone (NMP,  
15 >99.5%), potassium D-tartrate monobasic and ethanol were all supplied by Sigma  
16 Aldrich, MO, USA. Bovine serum albumin (BSA, Fraction V IgG free) was supplied by  
17 Gibco, NY, USA. All chemicals were used as received without further purification. The  
18 inorganic particles dispersed in PSf polymer were sodium montmorillonite from Sigma  
19 Aldrich, MO, USA. As shown in Fig. 1, the MMT particles were approximately  
20 spherical and had an average particle size below 30  $\mu\text{m}$ .  
21

### 22 2.2 Membrane preparation

23 In this paper, two types of membranes, namely polysulfone (PSf) and polysulfone  
24 montmorillonite composite (PSf/MMT), were prepared via the phase inversion by the  
25 immersion precipitation method. The ratio of polysulfone, solvent and MMT powder  
26 used is summarised in Table 1. A homogeneous polymer solution consisting of PSf and  
27 NMP with suitable weight ratio (Table 1) was initially prepared by continuous stirring  
28 for several hours at room temperature until all polysulfone pellets were completely  
29 dissolved. The required amount of MMT powders was added into the polymer solution  
30 and then stirred for at least six hours at 400 rpm until the solution became visually  
31 homogeneous. The casting solution was degassed for 5 min at room temperature and  
32 then poured onto a smooth glass plate and spread to a thin film with an Elcometer 3700  
33 Doctor Blade doctor blade with reservoir. Membrane casting was performed using an  
34 Elcometer 4330 Basic Motorised Film Applicator (Elcometer Limited, Manchester,  
35 United Kingdom), with casting speed and film thickness set at 6  $\text{cm}\cdot\text{s}^{-1}$  and 250  $\mu\text{m}$   
36 respectively. After casting, the coated glass plate was immersed for coagulation in a de-  
37 ionised water bath at room temperature until the membrane detached from the glass  
38 surface. The resulting membranes were washed with de-ionised water several times to  
39 remove all solvents and left to dry in a fume hood at room temperature.  
40

### 41 2.3 Filtration tests

42 Protein rejection tests were carried out using a dead end pressure filtration cell  
43 (Steriltech<sup>TM</sup> HP4750 Stirred Cell, Steriltech, WA, USA) at room temperature. Model  
44 wine solution with 600  $\text{mg}\cdot\text{L}^{-1}$  bovine serum albumin, 120  $\text{mL}\cdot\text{L}^{-1}$  ethanol, 2  $\text{g}\cdot\text{L}^{-1}$   
45 potassium tartrate buffer, and deionised water with pH 3.8 was used to measure the  
46 permeance (membrane flux divided by filtration pressure) and rejection of the  
47 membrane. This has characteristics and pH comparable to model wine solutions used by  
48 previous researchers (Sarmiento et al., 2000a; Slatner et al., 1999) which is based on the

1 work of Blade and Boulton (Blade and Boulton, 1988). Before each measurement, the  
2 circular membrane samples with the diameter of 49 mm were cut from the membranes  
3 and immersed in de-ionised water overnight. This allows for the MMT to swell to the  
4 maximum extent, which can increase the adsorption ability of the protein (Blade and  
5 Boulton, 1988). The membrane coupon was installed in the cell and firstly was run with  
6 100 ml of de-ionised water to precondition the membrane to a steady state compaction  
7 and removed any weakly attached particles. Model white wine solution was then poured  
8 into the cell magnetically stirred at 500 rpm. The pressure was initially kept constant at  
9 5 bar. Time for the liquid to permeate 5 ml was recorded starting from 10 ml (the first  
10 clear reading on the measuring cylinder) to 30 ml in order to determine the membrane  
11 permeance. For each type of membrane, three different membrane samples were used  
12 for filtration test. Thus, the values reported in this paper are average values. The  
13 samples of PSf and PSf/MMT membranes after they have been used in filtration with  
14 model wine solution were named PSf\_F and PSf/MMT\_F respectively.

15  
16 The concentration of BSA protein in permeate and feed solution was measured using an  
17 Agilent 8453 UV-vis spectrophotometer (Agilent Technologies, CA, USA) at the  
18 absorbance of 280 nm. The absorbance-concentration standard curve was initially  
19 developed from 10 standard concentrations from 50 mg.L<sup>-1</sup> to 700 mg.L<sup>-1</sup>. The protein  
20 rejection (R, %) is defined as  $(1-(C_p/C_f)) \times 100\%$  where  $C_p$  and  $C_f$  denote the BSA  
21 concentrations of the permeation and the initial feed solution respectively.

#### 22 23 2.4 Membrane characterisation

24 The morphology of the membrane surfaces and the distribution of the MMT particles  
25 within the polymer structure were characterised using a Philips XL30 S-FEG Scanning  
26 Electron Microscope (SEM) (FEI, Eindhoven, The Netherlands). Cross-sections of the  
27 membranes were prepared by breaking the membranes in liquid nitrogen and then  
28 coating with platinum using a sputter coater Polaron SC 7640 (Quorum Technologies,  
29 East Sussex, UK) at 1.1 kV for 180 s. The topography of the membranes was studied  
30 using Atomic Force Microscopy (AFM, Digital Instruments NanoScope IIIa, Veeco,  
31 NY, USA) in contact mode with a scan size of 60  $\mu\text{m}$  x 60  $\mu\text{m}$ . The topography was  
32 evaluated using two parameters: the average surface roughness ( $R_a$ ) and skewness ( $S_k$ ).  
33 The average surface roughness represents the average distance between the surface and  
34 a mean centreline, whereas the skewness describes the degree of asymmetry of the  
35 distribution. A negative skewness value indicates that the sample has more valleys than  
36 peaks, and the reverse for a positive skewness value (Thomas, 1999). Roughness data  
37 were obtained from a minimum of two samples with 4 different regions on each sample.  
38 The values reported are the averages of these measurements.

39  
40 The hydrophobicity of the membranes were characterised based on their wettability  
41 which was evaluated by contact angle data. Contact angle measurements were made  
42 using the sessile drop method using a KSV CAM 101 instrument (KSV Instruments  
43 Ltd., CT, USA). A droplet of deionised water was placed on the membrane surface  
44 which was fixed flat on a glass slide using double-sided carbon tape at room  
45 temperature. For each PSf or PSf/MMT membrane, three different specimens were  
46 prepared at several regions for each specimen with measurements taken from both sides  
47 of the droplet. The measurements were immediately taken after the droplet was on the

1 membrane surface, and then at 5 s intervals until the water had completely  
2 absorbed/permeated into the membrane.

3  
4 Pores on the membrane surfaces were analysed using SEM and ImageJ imaging  
5 software (National Institute of Health, Washington DC, USA) to obtain quantitative and  
6 qualitative information about pore sizes and morphologies. About 15 SEM images at  
7 magnification of 10,000x were acquired at random locations for each sample. From  
8 these images, a minimum of 10-15 random areas with around 1,000 pores were analysed  
9 using ImageJ. The obtained information included Feret diameter, area, circularity and  
10 perimeter of individual pores. The Feret diameter is the longest distance between any  
11 two points on the boundary of the pore.

12  
13 To examine the surface chemical composition of the collected membranes, in particular  
14 the protein adsorption onto its surfaces, the membranes were analyzed with X-ray  
15 Photoelectron Spectroscopy (XPS) using a Kratos Ultra Axis DLD (Shimadzu,  
16 Manchester, UK). The excitation source in use was Al K $\alpha$  (1486.6 eV). The pressure  
17 during analysis was between  $1 \times 10^{-9}$  and  $1 \times 10^{-8}$  Torr. To prepare the samples for the  
18 XPS examination, small pieces of the top and bottom surfaces of each membrane were  
19 mounted on a sample bar using double sided carbon conductive adhesive tape. MMT  
20 powders were pressed onto the double side carbon tape which was glued on the bar, and  
21 then shaking to remove loose material. The cross section of each membrane was tightly  
22 sandwiched between two aluminium sheets and installed in the sample bar for the  
23 chemical analysis of the exposed cross sections. To obtain the surface chemical  
24 composition of the membranes, and corresponding images of all elements of interest,  
25 the analysis included the survey scans and narrow scans and then imaging as described  
26 in Table 2.

27  
28 In the current study, elemental images were obtained for carbon (C 1s), aluminium (Al  
29 2p), silicon (Si 2p), nitrogen (N 1s) and oxygen (O 1s). The binding energy was chosen  
30 from the narrow scans to include a specific photoelectron peak. The step size was  
31 chosen at 0.2 eV. At each step size of binding energy, image with high resolution of  
32 256x256 pixels was taken and was subsequently processed to obtain elemental maps  
33 using CasaXPS version 2.3.12. More detail of the processing procedures of the data set  
34 can be found in the CasaXPS manual (Casa Software Ltd., 2009).

### 36 **3. Results and discussion**

#### 37 **3.1 Membrane morphology**

38 The morphology of the membrane surfaces and the distribution of the MMT particles in  
39 the membrane structure were characterized using SEM. Figure 2 shows the typical  
40 morphologies of the top and the bottom surfaces of PSf and PSf/MMT membranes. As  
41 typical for phase inversion membranes, the top surface is defined as the side that is  
42 exposed to the air during casting whereas the bottom surface is in contact with the glass  
43 plate. It was found that pore formation varied between the top and bottom surfaces of  
44 each membrane. High densities of pores were observed on the top surfaces of both PSf  
45 and PSf/MMT membranes whereas few pores were found at the bottom of the  
46 membranes. The formation of a large number of pores at the top surface might relate to  
47 the membrane casting process. It is suspected that further optimisation of the membrane  
48 casting procedure is required to cast an optimal membrane for fining operations and is

1 therefore the focus of future work. This would include increasing the immersion time in  
2 the water bath (to provide further time for non-solvent penetration and macropore  
3 formation in the lower surfaces) and further degassing of the solvent (air may have  
4 either produced defects and/or escaped through the membrane film after casting and  
5 promoted the formation of surface pores as observed). Optimisation of the membrane  
6 was not the aim of this work however, and for this preliminary investigation all  
7 membranes were cast in a consistent manner and therefore changes produced by the  
8 presence and absence of clay particles can be compared relative to each other and robust  
9 conclusions that can be translated to optimised membranes (which are the subject of  
10 future work) can be made on this basis. .

11  
12 The pore-size distributions of the PSf and PSf/MMT top surfaces were characterized  
13 using ImageJ and shown in Fig. 3a. Pores were found with a quite regular distribution  
14 all over the top surface of the membranes. Also the proportion of pores with the  
15 diameter from 0.3 to 1  $\mu\text{m}$  on the PSf top surface (64.2%) was higher than on the  
16 PSf/MMT top surface (47.3%). For the case of larger pores with the diameter from 1 to  
17 3  $\mu\text{m}$ , the pore proportion on the PSf surface was about 35.5% relative to PSf/MMT  
18 surface. It was also observed that there was no pore with the diameter larger 3.5  $\mu\text{m}$  on  
19 the PSf top surface whereas approximately 8% of this pore type was found on the  
20 PSf/MMT surface. It appears that that addition of MMT into the polymer solution  
21 weakens the interaction among polymer molecules and expands the spacing between  
22 them in the solutions, thus enhancing the diffusion rate of the solvent (Yan et al., 2007).  
23 This resulted in larger pores on the PSf/MMT top surface compared to the PSf one. The  
24 appearance of larger pores on the PSf/MMT top surface had an effect on the number of  
25 pores per unit area. It can be seen from Fig. 3b that the average number of pores on the  
26 PSf and PSf/MMT surfaces per square micron was 0.12 and 0.1 respectively. However  
27 this difference is not statistically significant within the errors of the data collected.

28  
29 To further examine the membrane structure, several cross sections of the membranes  
30 were prepared and studied. The typical cross section of PSf membrane is shown in Fig.  
31 4. In general, the membrane had an asymmetric structure across the cross-section. Four  
32 distinct layers were observed across the cross section: a thin dense skin layer (1) at the  
33 top surface, supported by an irregular micro-tubular pores layer (2) with an open macro-  
34 void structure (3), and porous sponge-like layer (4) at the bottom of the cross section.  
35 Incorporation of MMT particles in polysulfone solutions resulted in significant changes  
36 in the membrane structure as can be seen in Fig. 5. The MMT particles were distributed  
37 across the membrane thickness and tightly held within the porous polymer matrix. The  
38 PSf/MMT presented an interconnected porous structure, without evidence of macro-  
39 voids in the open pore structure (large holes (4) observed in Fig. 5a were not macro-  
40 voids, but were likely formed as the particles detached off the membrane network  
41 during fracturing the membrane for SEM observation). It has been reported that the  
42 formation of macro-voids relates to the diffusion rate of different phases in the casting  
43 solution (Smolders et al., 1992; Vandezande et al., 2009). In particular, the difference in  
44 concentration between NMP solvent and polymer in the casting solution resulted in the  
45 difference in their diffusion rates and hence promoted the formation of macro-voids in  
46 the PSf membrane (Vandezande et al., 2009). In contrast, introduction of solid particles  
47 into the polymer solution increased the viscosity of the casting solution and promoted  
48 the formation of nuclei in solution resulting in delayed diffusion which suppressed the

1 growth of macro-voids formation in the PSf/MMT membrane (Vandezande et al.,  
2 2009).

3  
4 It was expected that the differences in the morphologies between the PSf and PSf/MMT  
5 membranes, would contribute to the permeance and rejection ability of these  
6 membranes with BSA model wine solution. The formation of larger size of the pores at  
7 the PSf/MMT surfaces could enhance the flow of the model wine solution, thus causing  
8 a higher BSA permeance over the pristine PSf membrane, as discussed in more detail  
9 later. In addition, the absence of the macrovoids within the PSf/MMT membrane may  
10 enhance the mechanical strength of the membrane during high pressure applications.

### 11 3.2 Membrane topography

12 The topography of the membrane surfaces was characterized using AFM. 3-D imaging  
13 of typical topographies of the PSf and PSf/MMT membranes are shown in Fig. 6 and  
14 the corresponding surface roughness values are presented in Fig. 7. The results revealed  
15 that the bottom surfaces of the PSf and PSf/MMT membranes were macroscopically  
16 smooth with the average surface roughness of  $35.2 \pm 13.8 \mu\text{m}$  and  $108.62 \pm 8.3 \mu\text{m}$   
17 respectively. In contrast, the presence of a significant number of pores on the top  
18 surfaces of these membranes unduly affected the average surface roughness  
19 measurements, and resulting in the negative skewness values (Fig. 7b). The average  
20 surface roughness of PSf and PSf/MMT top surface were  $350.2 \pm 36.5 \text{ nm}$  and  $965.8 \pm$   
21  $192.3 \text{ nm}$  respectively. It was also found that that the larger pores were observed on the  
22 PSf/MMT top surface which is consistent with the SEM observations.

23  
24 The smoother PSf top surface resulted in its smaller absolute surface area. The data  
25 analysis shows that the surface area of PSf and PSf/MMT membranes were  $4,688 \pm 156$   
26  $\mu\text{m}^2$  and  $6,142 \pm 915 \mu\text{m}^2$  respectively in the same projected area of  $3,600 \mu\text{m}^2$ . The  
27 increment of the surface area and the surface roughness value of the PSf/MMT  
28 membrane compared to the PSf one indicates that the addition of MMT particles  
29 enhances the effective filtration area and probably the hydrophobic property, and thus  
30 improving the permeation through the modified PSf/MMT membrane.

### 31 3.3 Contact angle measurements

32  
33 The hydrophobic nature of the PSf and PSf/MMT membranes was characterised by  
34 recording contact angle measurements. The contact angle was immediately taken within  
35 one second after the water droplet was on the membrane surface. The water contact  
36 angle on the PSf top surface was  $89.4 \pm 2.3^\circ$ , indicating the hydrophobic nature of the  
37 surface. In contrast, the PSf/MMT surface showed a much more hydrophilic surface  
38 with a much lower contact angle of  $70.4 \pm 3.2^\circ$ . The changes of water contact angle with  
39 time are subsequently observed until the water droplet adsorbed completely into the  
40 membrane and shown in Fig. 8. It was observed that the droplet spread out quickly upon  
41 impact. The contact angle decreased rapidly within the first 30 s and subsequently  
42 reduced linearly. The water droplet was completely adsorbed on the PSf membrane in  
43  $35 \pm 3 \text{ min}$  whereas it took only  $12 \pm 1 \text{ min}$  on the PSf/MMT membrane top surface.  
44 This indicated that addition of MMT particles enhanced the hydrophilicity of the  
45 PSf/MMT membrane, and it would contribute to lower BSA protein adsorption because  
46 of the reduced hydrophobic interaction between membrane surface and protein.  
47  
48



### 3.4 Flux and rejection measurements

Filtration tests of the model white wine solution through the PSf and PSf/MMT membranes were performed to evaluate their permeate permeance and BSA protein rejection. Figure 9 represents the corresponding permeance of the PSf and PSf/MMT membranes respectively. It was observed that model wine solution was not permeable through the PSf membrane at 5 bar, but can easily flow through the PSf/MMT membrane at the same pressure. The pristine PSf membrane instead required an operating pressure of 20 bar. It was observed that the PSf membrane permeance was initially at  $5.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$  and subsequently declined to zero after approximately half an hour. The permeance through the PSf/MMT membrane decreased from  $77.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$  at the beginning to  $15.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$  at the end of the filtration test, which was significantly higher than that of the PSf membrane. The differences in permeance induced the BSA protein rejection between PSf and PSf/MMT membranes. It was found that the rejection of the PSf/MMT membrane at 5 bar was  $33.8 \pm 5.2 \%$ , whilst the PSf rejection was  $68.5\% \pm 17.9$  at much higher operation pressure of 20 bar.

The differences in operating pressure, permeance and rejection ability of PSf and PSf/MMT membranes with model wine solution were expected to be linked to their surface properties. Schneider et al. (Schneider et al., 1988) reported that the pressure required to push the flow through the microporous hydrophobic membranes is inversely proportional to the pore radius. As such, the formation of the denser skin layer, at the PSf top surfaces hindered the flow of wine solution, and thus required higher pressure and longer filtration times resulting in lower BSA permeance. The denser structure at the PSf surface also rejected protein molecules. In addition, the hydrophobic nature of the PSf membrane enhanced the hydrophobic interaction between the membrane surface and protein, causing concentration polarisation and probably fouling, and correspondingly a higher rejection of BSA protein molecules as observed. In contrast, the porous structures of the PSf/MMT membrane surface, its higher surface area and its hydrophilic nature induced a higher permeance but lower protein rejection.

From these observations, it can be concluded that the permeance increased with the decrease in rejection of the membrane, which was coincident with the hydrophilic nature and increasing size of pores on the surfaces as would be expected from a porous membrane separating a large protein like BSA, where separation is mainly via a size exclusion (porous flow) mechanism. However a size exclusion mechanism is not selective towards the removal of haze causing proteins – other similar or larger sized components important to the quality of the wine (e.g. taste, colour and mouth feel) would be non-selectively removed as well. Consequently ensuring that the membranes separate components mainly via the more selective adsorption mechanism is crucial in ensuring that wine proteins are selectively removed. Note that BSA has adsorption properties (i.e. isoelectric point of around 4.3) within the range of wine haze proteins (Slatner et al., 1999) and so is a suitable model compound to investigate wine fining by adsorption. As a result of having the potential for separation via both adsorption and size exclusion, the separation mechanism of the more open (porous) PSf/MMT mixed matrix membrane is more complicated. Therefore the selectivity mechanism was explored further by XPS analysis.

### 3.5 Surface chemistry of the membranes.

1 To examine the surface chemical composition of the collected membranes, the  
2 membrane surfaces were analyzed with XPS. In addition, high spatial resolution XPS  
3 imaging was used to examine where the BSA protein was on both the membrane  
4 surfaces and within the membrane cross-section. Therefore, the top and bottom surfaces  
5 and cross section of each membrane were analyzed. In addition, the chemical  
6 composition of MMT particles was also analyzed. Typical survey scans of the MMT  
7 particles, the top surfaces of PSf and PSf\_F membranes are shown in Fig. 10. From the  
8 survey scans, the surface chemical compositions of each sample were calculated and  
9 presented in Table 3.

10  
11 As can be seen in Fig. 10a and Table 3, the compositions of the MMT powders include  
12 silicon (Si 2p), aluminium (Al 2p), oxygen (O 1s), calcium (Ca 2p), sodium (Na 1s),  
13 and adventitious carbon (C 1s) which were in agreement with literature (Barr et al.,  
14 1995). The survey spectra of the top, bottom surfaces and cross section of the PSf  
15 membrane showed three single peaks of C 1s, O 1s and sulphur (S 2p) at the binding  
16 energy of 284.5 eV, 532.5 eV and 167.5 eV respectively. For the polysulfone  
17 membranes after they have been used in filtrations with the model wine solution (PSf\_F  
18 as defined in 'Materials and Methods' section), a fourth peak appeared at the binding  
19 energy of 399.5 eV which is the proteinaceous N 1s peak (Fig. 10c). A trace of nitrogen  
20 was found on both the top and bottom surfaces of the PSf\_F membrane, but at a  
21 different concentration. The nitrogen proportion at the top surface (5.8%) was much  
22 smaller than that at the bottom surface (12.7%) of the PSf\_F membrane. In addition,  
23 typical XPS images of C 1s, O 1s and N 1s at the PSf\_F bottom surface in Fig. 11  
24 confirmed very good adsorption of protein on the PSf surface.

25  
26 Evidence of nitrogen was found on both the top and bottom surface of the PSf\_F  
27 membrane. However, chemical analysis, and N 1s imaging of its cross section, revealed  
28 that there was no detectable trace of nitrogen across the membrane thickness. From  
29 these observations, it can be suggested that the separation of BSA by the PSf membrane  
30 mainly relates to its morphology, particularly the number of pores and pore size on the  
31 membrane surface (Fig. 2). The smaller the pores were at the bottom surface, the higher  
32 protein selectivity was achieved. In addition, hydrophobic nature of the PSf membrane  
33 may also contribute to the adsorbed protein on the membrane surface. However, the  
34 observation of limited protein adsorption across the thickness of the membrane where  
35 its structure mainly composed of open pores and macro-voids suggested that  
36 morphology is more important factor than the hydrophobicity in protein separation  
37 membrane.

38  
39 It is noted that the changes in surface chemistry observed here are only for the 10 nm  
40 outermost layer within the XPS depth of analysis (Briggs and Seah, 1990). Thus, the  
41 evidence of Si 2p and Al 2p peaks in the surface compositions of PSf/MMT and  
42 PSf/MMT\_F membranes (Table 3) confirmed the presence of MMT particles within 10  
43 nm at the top and bottom surfaces of the membrane. Like the PSf\_F membrane,  
44 nitrogen was found on both the top and bottom surfaces of the PSf/MMT\_F membrane,  
45 but in a lesser amount. There were 1.8% and 5.2% of nitrogen on the top and bottom  
46 surfaces of the PSf/MMT\_F membrane. The differences in the nitrogen proportion  
47 detected on the surfaces between PSf\_F and PSf/MMT\_F membranes were again in

1 relation to the amount and size of pores distributed on the membrane surface as well as  
2 the hydrophobicity of the surface, as discussed in the previous paragraph.

3  
4 In contrast to the PSf\_F cross section (with no detectable nitrogen), 2.2% of nitrogen  
5 was found in the PSf/MMT\_F cross section. That indicated that the BSA protein was  
6 probably trapped inside the pore network in the PSf/MMT\_F membrane. To further  
7 understand whether the adsorption was due to the membrane structure or the  
8 hydrophobic interactions between the active sites on the MMT particles and BSA  
9 protein, XPS imaging of C 1s, O 1s, N 1s, Al 2p and Si 2p were obtained. Figure 12  
10 shows the images taken from an area within the cross section of the PSf/MMT\_F  
11 membrane. It was observed that the analysis area of 100 x 100  $\mu\text{m}$  was completely  
12 covered with carbon (Fig. 12a). The presence of Al 2p (Fig. 12d) and Si 2p (Fig. 12e)  
13 indicated the presence of MMT particles within the cross section surface in an island-  
14 like formation (corresponding to MMT particles). It was also found that the MMT  
15 surface was covered by nitrogen, as can be seen in Fig. 12c-f. This evidence indicated  
16 that the protein adsorption mechanism of the PSf/MMT\_F cross section did not relate  
17 solely to its morphology, but occurred on the functional adsorptive sites of the MMT  
18 particles.

19  
20 The difference in chemical analysis between the PSf and PSf/MMT membranes was  
21 again in good agreement with the morphology observations, hydrophobicity and the  
22 measurements of the permeance and rejection. The hydrophobic nature along with the  
23 denser structure with lower porosity at the top and bottom surfaces of the PSf  
24 membrane resisted flow, but enhanced the protein selectivity at these surfaces. In  
25 contrast, the porous sublayer along the membrane thickness had no effect on the  
26 separation characteristics of the PSf membrane. Thus, the separation of the protein on the  
27 PSf membrane was solely related to their hydrophobic nature and dense structure at the  
28 top and bottom surfaces.

29  
30 Incorporation of MMT particles in the polysulfone matrix enhanced the hydrophilicity  
31 of the surface and promoted the formation of a more porous structure in the PSf/MMT  
32 membrane, resulting in greater permeance but lower rejection in comparison to the PSf  
33 membrane. However, evidence of protein on the PSf/MMT top, bottom surfaces, and on  
34 the MMT particle surfaces within the PSf/MMT cross section confirmed that the protein  
35 adsorption mechanism in this case occurred both onto the geometric area and on the  
36 functional adsorptive site of the MMT particles.

#### 37 38 **4. Conclusions**

39 PSf/MMT composite membrane with 10% polysulfone and 10% montmorillonite was  
40 synthesised using the phase change method. The structure and adsorption ability of the  
41 PSf/MMT membrane were systematically examined and compared to that of  
42 unmodified PSf membrane. It was observed that the PSf membrane posed a denser  
43 structure which was mainly linked with the size of pores at the top and bottom surfaces.  
44 This in turn required higher pressure to induce the flow transport, and hence lower  
45 permeance. However, due to its denser structure and hydrophobic nature, the BSA  
46 protein rejection of the PSf membrane was higher and mostly occurred at the membrane  
47 surfaces which led to undesired fouling. In addition, the occurrence of macrovoids along

1 the membrane thickness can contribute to the mechanical failure of the membrane  
2 during high pressure applications.

3  
4 Inclusions of MMT particles inside the polymer solution resulted in the formation of the  
5 membrane with a porous structure and a hydrophilic surface, which in turn reduced the  
6 hydrophobic interaction at the surface and required a lower pressure to obtain an  
7 acceptable permeance. This therefore reduced fouling and enhanced permeability  
8 respectively. The MMT particles were found to be well-distributed along the thickness  
9 of the membrane which could contribute to the improvement in mechanical stability of  
10 the membrane under high applied pressure. Most importantly, it was demonstrated that  
11 there was targeted protein adsorption on the adsorptive areas of the MMT particles  
12 within the membrane matrix, confirming that there are hydrophobic interactions  
13 between the MMT particles and BSA protein molecules. This means that the mixed  
14 matrix membrane works as intended - it supports the MMT particles without blocking  
15 the adsorption sites within the polymer matrix. This indicates that it is possible to make  
16 a membrane with this system that is able to be porous enough to allow the molecules  
17 responsible for wine's flavour and texture to pass through whilst removing the  
18 unwanted proteins. Therefore, these findings are a significant step to better  
19 understanding the fundamental knowledge in adsorption ability of MMT particles and to  
20 predict the possible applications of using clay-filled polymer membrane to remove  
21 protein from wine in a membrane type module, opening up the possibility of continuous  
22 wine fining operations.

23  
24 Due to the adsorption of BSA protein on the MMT particles, it will be necessary to  
25 regenerate the PSf/MMT membrane once the MMT active sites are saturated with BSA  
26 proteins. The interactions between the BSA protein and MMT particles at different  
27 conditions of pH and ethanol content are currently being investigated to determine the  
28 reversibility of the MMT. So far it has been found that changing the pH is an effective  
29 way to desorb BSA protein from the MMT particles, and thus regenerate the PSf/MMT  
30 membrane. However, the details of the protein-MMT interactions are under study and  
31 will be part of a future publication. Also the lifetime/reusability of these types of  
32 membranes in the wine fining application has yet to be assessed, but will be an  
33 important aspect in terms of industrial viability and adoption.

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25  
26  
27



1 Fig. 1: Micrograph of MMT particles. The insert image on the bottom right of the image  
2 shows the shape of a typical MMT particle.

3 Fig. 2: Typical SEM images of the (a) top, and (b) bottom surfaces of PSf membrane,  
4 (c) top, and (d) bottom surfaces of PSf/MMT membrane.

5 Fig. 3: (a) Size distribution of pores on the PSf and PSf/MMT top surfaces, and (b)  
6 number of pores per square micrometer on the PSf and PSf/MMT top surfaces.

7 Fig. 4: Typical images of (a) PSf cross section, (b, c) enlargement of selected areas in  
8 (a).

9 Fig. 5: Typical images of (a) PSf/MMT cross section, and (b,c) enlargement of selected  
10 areas in (a) showing the distribution of MMT particles within the polymer matrix.

11 Fig. 6: 3D images of the (a) PSf top surface, (b) PSf bottom surface, (c) PSf/MMT top  
12 surface, and (d) PSf/MMT bottom surface. Images are of 60  $\mu\text{m}$  sample square.

13 Fig. 7: Changes of (a) average surface roughness and (b) skewness resulting from the  
14 incorporation of MMT particles in the polysulfone membranes.

15 Fig. 8: Measurements of contact angle with time. The dotted line indicates the standard  
16 deviation of the measurements.

17 Fig. 9: Average permeance for PSf and PSf/MMT with corresponding pressure.

18 Fig. 10: Typical XPS survey scans of (a) MMT particles, top surface of (b) PSf  
19 membrane, and (c) PSf\_F membrane (the arrow indicates the presence of nitrogen  
20 peak).

21 Fig. 11: Photoelectron (a) C 1s, (b) O 1s, and (c) N 1s images acquired from the same  
22 area on the PSf\_F bottom surface. Bright areas in the images are enriched in PSf\_F  
23 bottom surface. The analysis area was 110 x 110  $\mu\text{m}$ .

24 Fig. 12: XPS images from PSf/MMT\_F cross section (a) carbon distribution, (b) oxygen  
25 distribution, (c) nitrogen distribution, (d) aluminium distribution, (e) silicon distribution,  
26 and (f) overlay of silicon and nitrogen showing blend composition. The analysis area  
27 was 110 x 110  $\mu\text{m}$ .

28

29 Table 1: Membrane preparation conditions

30 Table 2: Summaries of XPS parameters in this study

31 Table 3: Surface compositions (atomic %) of the samples following various conditions.

32