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1 **Preparation and benchmarking of highly hydrophilic polyaniline poly(2-**
2 **acrylamido-2-methyl-1-propanesulfonic acid) PANI PAMPSA membranes**
3 **in the separation of sterols and proteins from fruit juice**

4
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14
15 **Abstract**

16 A straightforward approach is presented to prepare highly hydrophilic ultrafiltration
17 polyaniline poly(2-acrylamido-2-methyl-1-propanesulfonic acid (PANI PAMPSA)
18 membranes. Their application in the fractionation of phytosterols and proteins from fruit juice
19 is described. The poly(2-acrylamido-2-methyl-1-propanesulfonic (PAMPSA) is added to the
20 aniline during the polymer synthesis and the membrane is prepared via phase inversion forming
21 a highly hydrophilic and mechanically stable ultrafiltration membrane of 200 µm thickness and
22 pure water flux of 126 LMH at 1 bar. The membrane so produced is benchmarked against a
23 hydrophilic commercial regenerated cellulose acetate membrane (RCA) for the separation of
24 phytosterols and proteins from orange juice. Cross-flow filtration experiments show
25 comparable protein separation efficiency of the membranes but better rejection of phytosterols
26 for the commercial RCA membrane. Both commercial and lab prepared membranes are subject
27 to fouling, with the PANI PAMPSA membrane showing higher irreversible fouling.
28 Nevertheless, the PANI PAMPSA membrane showed a good cleaning efficiency of 74 % after
29 three fouling-cleaning cycles. Overall, this work has demonstrated the possibility of use PANI
30 PAMPSA for ultrafiltration application and provided a better understanding of its fouling
31 ability when compared to a commercial membrane in a multicomponent system.

32
33 **Keywords:** biocompounds, sterol, fruit juice, polyaniline, ultrafiltration, fouling

34

35 **1.0 Introduction**

36 Membrane separation has recently and increasingly become a key unit operation in many
37 industries, with the food and water sectors representing the main areas where membranes have
38 showed the greatest impact. An emerging area for membrane applications is the recovery of
39 bioactive compounds that are found in foods and have specific metabolic and physiological
40 actions that are relevant to the nutraceutical, pharmaceutical and food industries. Unlike other
41 energy-intensive techniques, membrane separation offers an energy-efficient alternative for the
42 recovery of biocompounds from plants and by-products of agro-industrial application[1]. The
43 current extraction and recovery methods include soxhlet, maceration and hydrodistillation and
44 make use of organic solvents, agitation and high temperatures [2].The extensive use of solvents
45 and the prolonged extraction times is not economically viable and the instability of some of the
46 bioactive compounds to the high temperatures represent a further challenge. Other relatively
47 greener cold extraction techniques include extraction using supercritical fluid, pressurised
48 liquids, ultrasound [3], microwave radiations etc [3,4]. Nevertheless, these techniques have
49 limited application in manufacturing because their scaling-up is challenging and have high
50 operational and maintenance cost [5].

51 In previous work we have demonstrated the principle of using ultrafiltration to separate
52 phytosterols from proteins in orange juice [7] with RCA membranes displaying the highest
53 permeate flux, the highest transmission of phytosterols from orange juice, and the highest
54 fouling index and cleaning efficiency, when compared to the polyethersulfone (PES)
55 membrane and polyvinylidene fluoride (PVDF) material. RCA membranes are widely used in
56 fruit juice processing to separate bioactive compounds such as phenolics and proteins from
57 fruit juice such as kiwi [8] , apple [9] and pomegranate juice [6]. RCA membranes are relatively
58 cheap and are categorized as hydrophilic membranes, which means that they are able to provid
59 a good resistance to fouling [10]. The surface science of membrane fouling and cleaning

60 processes was a focus of our previous work [11], whilst optimizing the ultrafiltration process
61 to fractionate the targeted sterol compounds. Despite the great potential of membrane
62 technology in fruit juice processing for the recovery of active biocompounds using
63 commercially available membranes [12,13] the widespread use of this technology is still
64 limited because of the tendency of these membrane to foul. Hence, in this work we focused on
65 investigating the ultrafiltration process for the fractionation of sterols from protein in orange
66 juice using a novel developed membrane material – PANI PAMPSA- as it is believed that the
67 development of more fouling resistant materials in food processing is worthy of investigation.
68 Fouling resistant membrane materials to facilitate the widespread use of membrane technology
69 are the focus of many research areas [14,15]. Among these, polyaniline is a conducting polymer
70 that has been extensively used in membrane fabrication for its versatility, redox chemistry and
71 charge switchability of the membrane surface. PANI doped with organic acids such as
72 PAMPSA, polystyrenesulfonic acid PSSA etc. have shown improved hydrophilicity, making
73 them excellent candidates for antifouling membranes[16]. In addition, the membranes are easy
74 to prepare and possess good chemical stability[17]. Recent work has reported the post-
75 modification of this membrane for solvent resistant nanofiltration [16,17] and investigated its
76 electrical responsive behaviour [18]. However these studies have been carried out in pure
77 solvents and there is a lack of data on the membrane performance in complex systems that
78 mimic real case scenarios as well as the fouling behaviour of the membrane.

79 Hence, in this study, we exploited the key improvement by incorporating hydrophilic
80 PAMPSA on the PANI backbone to prepare a low fouling ultrafiltration PANI PAMPSA
81 membrane. We believe this to be the first study reported in the literature to investigate
82 polyaniline based membrane performance for the recovery of phytosterols and proteins from
83 fruit juice. The fabrication method offers a simple and straightforward approach to prepare a

84 highly hydrophilic membrane that is benchmarked against a commercial RCA membrane to
85 assess filtration and membrane fouling performance.

86

87 **2.0 Experimental Methods**

88 **2.1 Materials**

89 Aniline, ammonium persulfate (APS), hydrochloric acid (HCl), HPLC grade acetone, DMF,
90 DMAc, Toluene, N-methyl-2-pyrrolidone (NMP) and 4-methyl piperidine (4-MP) were
91 purchased from Sigma-Aldrich (UK). Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)
92 (PAMPSA) was purchased from Sigma Aldrich (Merck, UK) and has average molecular
93 weight of 2,000,000 Da. PET/PBT backing layer- Novatexx 2484 (120 µm) was supplied by
94 Freudenberg Filter technologies (Germany). All solutions were prepared with deionised (DI)
95 water produced from an ELGA deioniser (PURELAB Option). Acetic anhydride, sulphuric
96 acid, chloroform and methanol were purchased from *Merck*, UK. Standards for characterisation
97 such as stigmasterol and butylated hydroxytoluene (BHT) were purchased from *Sigma Aldrich*,
98 UK. The cleaning was carried out using 0.5 % (w/w) *P3-Ultrasil 11* from *Henkel Ecolab*, US,
99 a commercial cleaning agent which widely used in food processing using membrane filtration.
100 Orange juice not from concentrate (NFC) was sourced from *Cobell*, UK. The phytosterols and
101 protein concentration of the orange juice used in this study is 0.2 – 0.3 mg/mL and 0.8 – 1.0
102 mg/mL respectively, as described previously in [7]. These values are in agreement with
103 previous studies [19-21].

104

105 **2.2 Synthesis of PANI PAMPSA powder**

106 PANI-PAMPSA powder was synthesised by oxidative polymerisation of aniline in PAMPSA
107 using a procedure developed in our research group [17]. Two solutions were made: solution 1
108 made with the concentration of 0.2 M aniline and 0.05 M PAMPSA and solution 2 with the

109 concentration of 0,2 M APS, solution 2 was added to the solution 1 slowly in 24 h The obtained
110 dark green PANI-PAMPSA product was filtered and washed firstly with DI water 3 times and
111 then with acetone 3 times until the pH of the filtrate became neutral. The procedure allowed
112 for the removal of impurities, unreacted material and PANI oligomers. The obtained cake layer
113 was then dried in a vacuum oven at 65 °C for 24 h. A dark green powder was obtained. As a
114 control PANI was synthesised using HCl as dopant following the recipe from our previous
115 work [17]. The average molecular weight was determined by Gel permeation chromatography
116 (GPC) as 49,975 g mol⁻¹ with a polydispersity of 1.65.

117 **2.3 Membrane fabrication and characterisation techniques**

118 The powder (20% wt) was dissolved in a mixture of NMP, 4-MP and THF (10% of the total
119 solvent) and the solution was left stirred for overnight. All membranes were cast on a bench
120 top laboratory caster. The Novatexx 2484 membrane backing layer was secured using scotch
121 tape on a flat glass plate. An adjustable casting knife was used to cast 200 µm thick films using
122 an adjustable film applicator (Elcometer 4340 automatic film applicator, Elcometer, UK).
123 Evaporation time of 30 s was used before immersing the casted membrane solution into a DI
124 water coagulation bath (Fig S1). The membrane was kept immersed in DI water at room
125 temperature for at least 24 h before suing it for characterisation and filtration experiments.

126

127 **2.3.1 Fourier transform infrared spectroscopy FTIR**

128 The chemical structure and the incorporation of the sulfonic groups of the PAMPSA to the
129 PANI backbone was studied by FTIR. The FTIR spectra of dry PANI PAMPSA (both powder
130 and membranes) were obtained using a Spectrum 100™ – FTIR Spectrometer (PerkinElmer,
131 USA) fitted with an attenuated total reflectance (ATR) detector. A background scan was run
132 prior to sample testing and spectra were recorded from 4000 to 650 cm⁻¹ in transmission mode
133 with a spectral resolution of 4 cm⁻¹ and 64 scans.

134 **2.3.2 Field emission scanning electron microscopy FSEM**

135 Membrane morphology was studied using FSEM (JSM-6301F, JEOL, Germany). Lab made
136 membranes and commercial RCA membranes were prepared by freeze fracturing them in
137 liquid nitrogen and drying them in vacuum overnight. Before the analysis was performed the
138 samples were coated in chromium using a sputter coater (Q150T S, Quorum) under argon for
139 5 min.

140

141 **2.3.3 Dynamic contact angle**

142 PANI PAMPSA and PANI membrane hydrophilicity was studied by dynamic contact angle
143 analysis. (Contact Angle System OCA 15Pro, Dataphysics, Germany). The instrument consists
144 in an automatic dispenser system equipped with a long needle glass syringe which dispense a
145 small drop of liquid, and a mobile platform where the membrane was fitted. Once the drop
146 leaves the needle the instrument starts to measure the variation of angle with time. A double
147 side tape glued to the support layer was used to keep the membrane flat on the platform. The
148 analysis was performed using sessile drop technique (4 μL) and data were recorded for 60 s
149 and repeated 2 times. Water was used as liquid. the technique gives an important data to
150 measure the wetting characteristic of the membrane

151

152 **2.3.4 Zeta potential**

153 Membrane surface charge measurement was carried out by using Zetasizer nano series model
154 ZS, Malvern-Panalytical, UK. Zeta potential planar cell (ZEN 1020) along with tracer particles
155 (Latex beads, polystyrene 0.3 μm mean particle size). Both the magnitude of the particle
156 electrophoresis and the electro-osmosis generated by the wall zeta potential were used to
157 calculate the zeta potential at the wall surface.

158

159 **2.3.5 Dynamic mechanical analysis DMA**

160 The mechanical properties of the membrane were studied using a dynamic mechanical analyser
161 (Mettler-Toledo, DMA1, STAR System) up to a temperature of 100°C with a heating rate of
162 1K min⁻¹. The membranes were cut into strips of 20 mm (L) x 5.0 mm (W) and secure on a
163 clamp in dual cantilever mode.

164

165 **2.4 Evaluation of membrane performance**

166 Two polymeric membranes were used; (1) A commercial flat-sheet regenerated cellulose
167 acetate (RCA) membrane (RC70PP) with 10 kDa MWCO supplied by Alfa Laval, Denmark
168 and (2) A lab synthesised PANI PAMPSA membrane (MWCO ~ 10 kDa, Fig S3). The MWCO
169 of PANI PAMPSA membrane was determined following the HPLC characterisation procedure
170 as detailed in authors previous works (please see SI) and [18, 28]. The RCA 10 kDa
171 commercial membrane was conditioned with deionised water (DI) water at 60 °C to remove
172 glycerol preservative applied by the manufacturer. The PANI PAMPSA membrane was
173 conditioned with DI water at 20 °C to ensure wetting of the membrane. Filtration experiments
174 were carried out on each of the membranes using a cross-flow membrane filtration system
175 *LabStak M10* manufactured by *DSS* (now *Alfa Laval*), Denmark. A schematic design of the
176 M10 filtration system applied in this study is illustrated in Fig. 1 [11]. The ultrafiltration steps
177 have been described in detail by Abd-Razak et al.[7]. Pure water flux (PWF) measurements
178 were determined for each membrane using DI water prior to fouling (before filtration), after
179 fouling (after filtration) and after chemical cleaning.

180

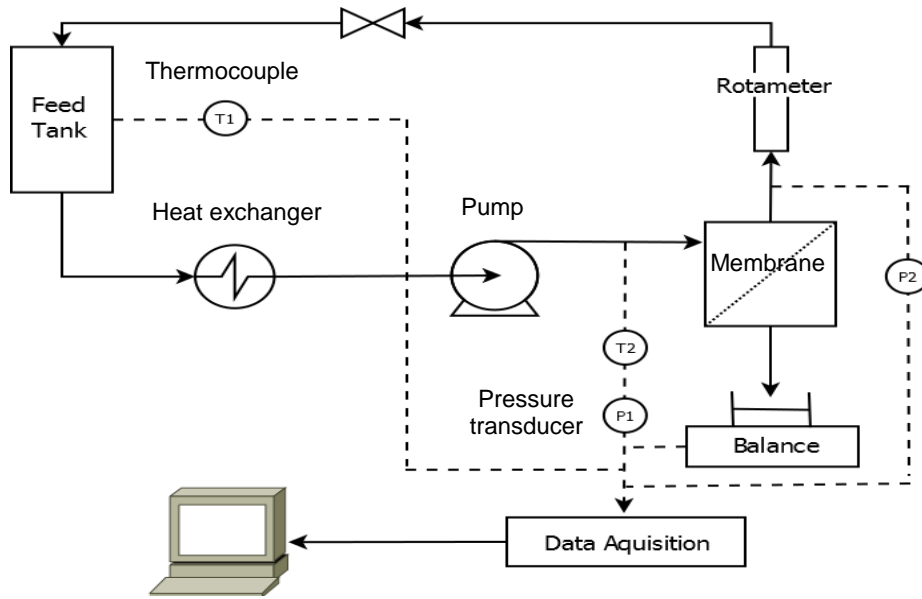


Fig. 1: A schematic diagram of the M10 filtration system

2.4.1 Pure water flux and permeate flux analysis

During all the filtration tests a pre-conditioning step was performed for the permeate flux to reach steady state. Pure water flux (Equation 1) is defined as follows:

$$J_w = \frac{V}{A \times \Delta t} \quad (1)$$

Where V (L) is the permeate volume; A (m²) is the membrane effective filtration area and Δt (h) is the filtration time. The general equation (2) was used to calculate the permeate flux through a membrane.

$$J = \frac{\Delta P}{\mu R} \quad (2)$$

196 where J is the flux through the membrane (m s^{-1}), ΔP (Pa) is the transmembrane pressure
197 (TMP), μ is the dynamic viscosity (Pa s) and R represents the total resistance (m^{-1}). A
198 membrane displays resistances when fouled and these can be characterised by the resistance
199 (J) in series model as shown in equation (3) and (4) [22].

200

$$201 \quad J = \frac{\Delta P}{\mu (R_m + R_{cp} + R_f)} \quad (3)$$

202

$$203 \quad R_f = R_{ir} + R_r \quad (4)$$

204

205 where R_m is the conditioned virgin membrane resistance, R_{cp} is the resistance due to
206 concentration polarisation, R_f is the fouling resistance, R_{ir} is the irreversible fouling resistance
207 and R_r is the reversible fouling resistance. The rejection (R) of total phytosterols and protein
208 during filtration were calculated by equation (5).

209

$$210 \quad R = \left(1 - \frac{C_p}{C_r}\right) \times 100 \quad (5)$$

211

212 where C_p is the solute concentration in the permeate and C_r is the solute concentration in the
213 retentate. In this case, the retentate was recycled back into the feed tank. The cleaning
214 efficiency (CE) is calculated according to equation (6) [5].

215

$$216 \quad CE = \left(\frac{WP_1}{WP_0}\right) \times 100\% \quad (6)$$

217

218 where WP_0 is the pure water permeability (LMH) of the virgin membrane and WP_1 is the pure
219 water permeability after the cleaning. The pH of orange juice was found to be pH 3.45. Orange
220 juice contains 0.2 – 0.3 mg/mL phytosterols and 0.8 – 1.0 mg/mL protein.

221

222 **2.4.2 Analyses of compounds**

223 **2.4.2.1 Total phytosterol**

224 The amount of total phytosterols in all filtration samples was determined based on the
225 Liebermann-Buchard (LB) method using stigmasterol as standard and a spectrophotometer
226 (Cary 100, *Agilent*, USA) as described in detail by Abd-Razak et al. [11]. The total phytosterol
227 content (TPC) was calculated using the standard photometric formula in equation (7) [23,24]:

$$228 \quad \text{TPC} = C_s \times \frac{A_u}{A_s} \quad (7)$$

229 where C_s = standard concentration, A_u = Absorbance of the sample, A_s = Absorbance of the
230 standard. All measurements were carried out in triplicate and the results were averaged.

231

232 **2.4.2.2 Proteins**

233 Protein concentration was analysed by the Bradford method [25, 26] using bovine serum
234 albumin (BSA) as standard and a spectrophotometer (Cary 100, *Agilent*, USA) as described
235 previously by Abd-Razak et al. [11]. The assay is based on the binding of the acidic dye
236 solution Coomassie Brilliant Blue G-250 to protein at maximum absorbance from 465 to 595
237 nm [26].

238

239

240

241

242 **3.0 Results and discussion**

243 **3.1 Characterisation of PANI PAMPSA membrane**

244 **3.1.1 FT-IR**

Fig. 2 shows the FT-IR spectrum of PANI PAMPSA membrane. The vertically dashed lines represent peak widths. The absorption bands at approximately 1225-1113 and 1038 cm^{-1} correspond to the asymmetric and symmetric stretching of $-\text{SO}_2-$ in the PAMPSA respectively [16, 17]. The peak at 1166 cm^{-1} could be assigned to the vibrational band of the nitrogen quinone on the PANI [17] (Fig. S2). The PANI PAMPSA spectrum showed characteristic peaks at 1497 cm^{-1} and 1590 cm^{-1} corresponding to the benzenoid and quinoid form of PANI. Finally, the methyl groups of PAMPSA give rise to absorption bands at 1420 and 1382 cm^{-1} . These results are consistent with previous FTIR results [16, 17] and confirm that the obtained polymer is PANI PAMPSA.

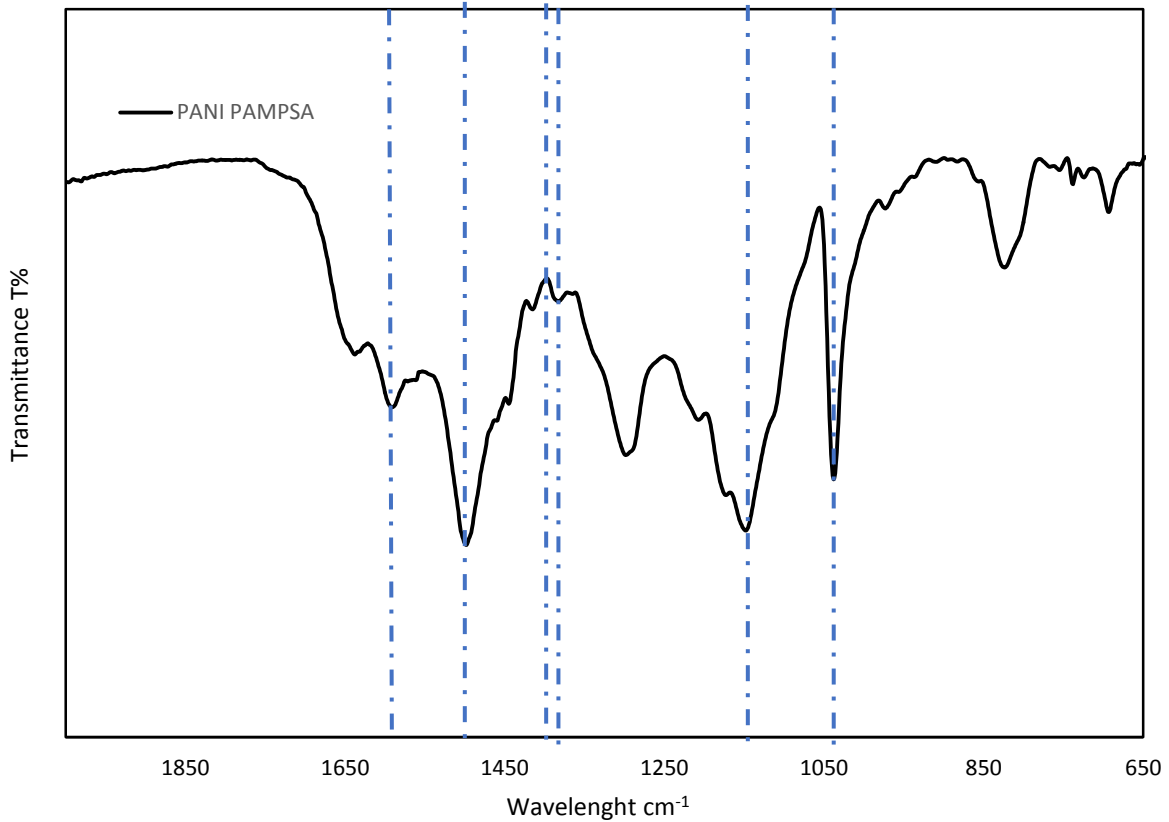


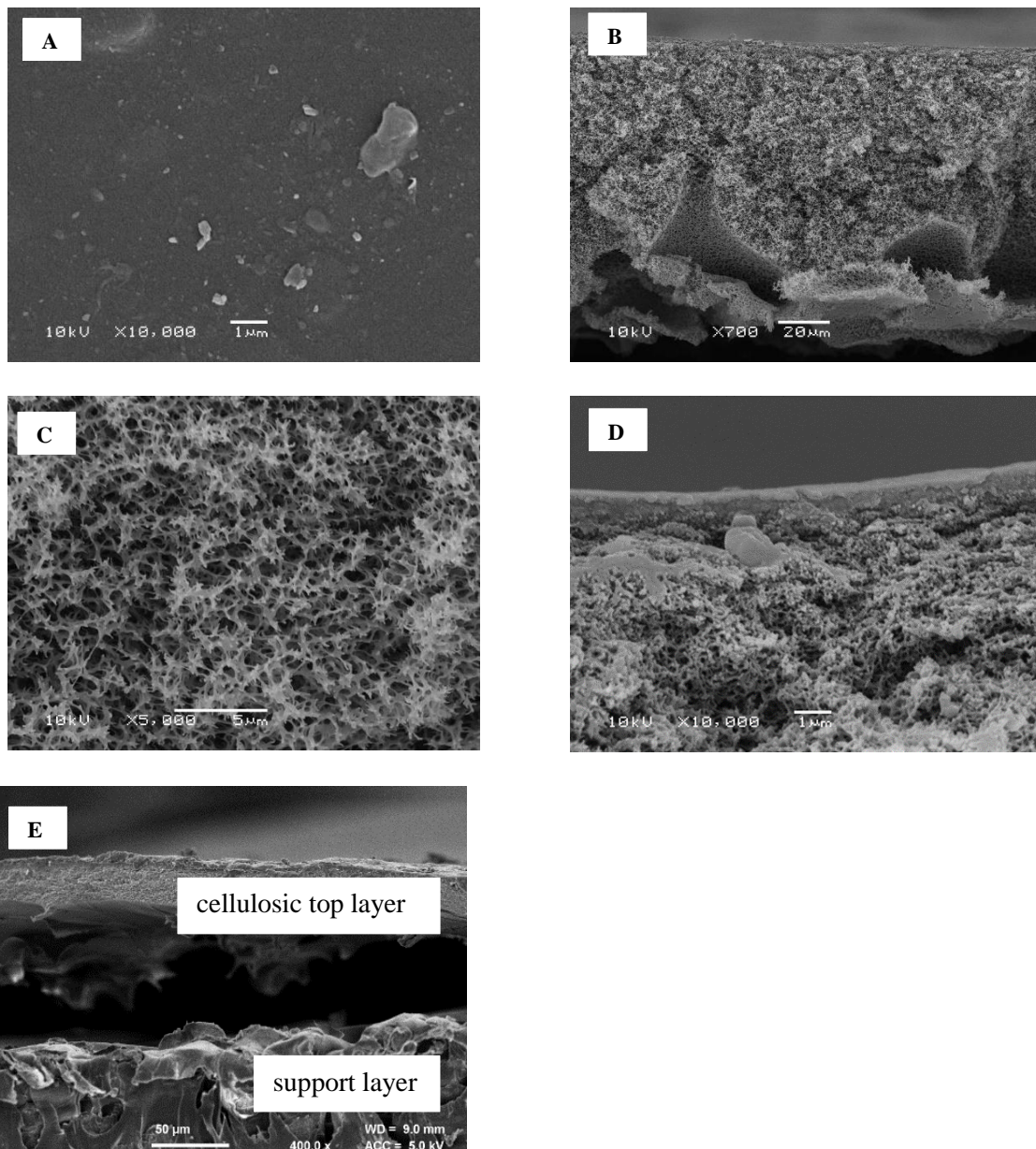
Fig. 2: FT IR spectrum of PANI PAMPSA membrane

245 3.1.2 Characterisation of membrane morphology

246 Fig. 3 reports the morphologies of the lab synthesised PANI PAMPSA membrane at different
 247 magnification. The surface appears smooth with no defects. The cross-sectional images of
 248 membrane show a typical morphology of a phase inversion membrane: a denser skin layer, a
 249 transition region and a relatively porous layer. The backing layer has been removed in SEM
 250 analysis. The use of larger acid like PAMSA could produce a greater intermolecular spacing
 251 between the PANI chains and therefore expanded the membrane pore structures, resulting in
 252 the formation of a loose membrane topology with higher porosity and larger pore sizes. It is
 253 important to note that no macrovoids were formed in the membrane. The membrane
 254 microstructure is influenced by the viscosity of the membrane solution and de-mixing kinetics.
 255 A greater viscous hindrance slows down the de-mixing rate and favours formation of ‘sponge-

256 like' substructures while inhibiting the formation of large macrovoids. The RCA 10 kDa
257 membrane consists of a dense cellulosic top layer and a porous support layer as shown in Fig.
258 3 (e). The support layer of RCA 10 was prepared from polypropylene (PP). It can be seen that
259 the top layer was easily detached from the support layer during the SEM analysis. However,
260 the membrane was not affected during the ultrafiltration process.

261

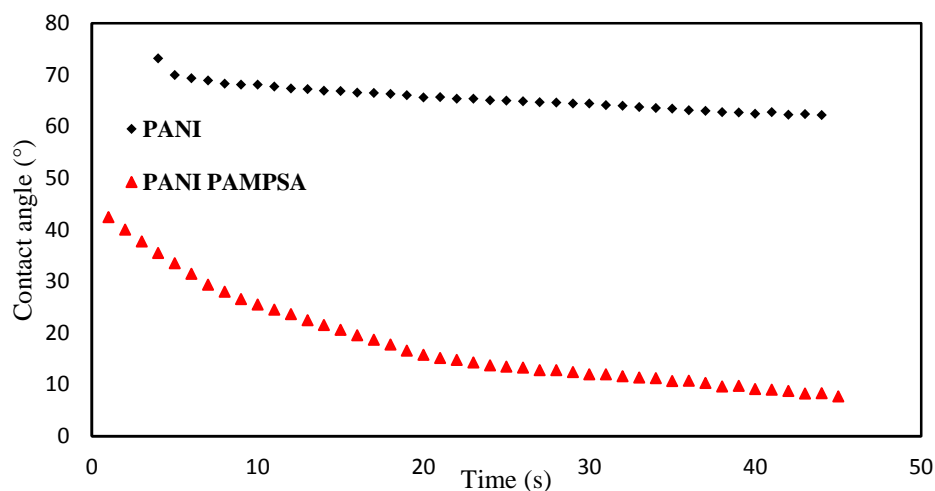


262

263 Fig. 3: SEM images of PANI PAMSA membrane (A) surface and (B-D) cross-sections and
264 RCA membrane (E) cross-section.

265 3.1.3 Membrane surface hydrophilicity

266 The hydrophilicity of the prepared PANI PAMPSA membrane was investigated via dynamic
267 contact angle technique and compared with hydrophilicity of the unmodified PANI membrane.
268 The incorporation of the big polyacid group during synthesis can impart hydrophilic properties
269 to the membrane due to the presence of the sulfonic acid groups. In addition, PAMPSA can
270 also form hydrogen bonding with water, hence an increase in the water permeation rate and
271 rapidly decrease of contact angle should be expected for PANI PAMPSA membrane [27, 28].
272 Fig. 4 reports the contact angle results for the PANI and PANI PAMSA membranes. PANI
273 PAMPSA shows a rapid decrease of the water contact angle over time with an initial value of
274 42 ° and a rapid reducing rate of the 77 % after 55 s. In contrast, PANI membrane shows a
275 slower reducing rate and an initial angle of 73 °. Contact angles values rapidly change over
276 time and did not reach a steady value. Membranes that show a contact angle below 90° are
277 considered hydrophilic, however, PANI PAMPSA membrane could be considered highly
278 hydrophilic because of the rapid change over time and its initial angle (below 50 °). It could
279 also be hypothesised that the increased hydrophilicity of PANI PAMPSA will increase its
280 fouling resistance making it a good candidate for a benchmarking against the very hydrophilic
281 commercial RCA membrane which has shown a contact angle of 11 ° as reported in a previous
282 work [11].



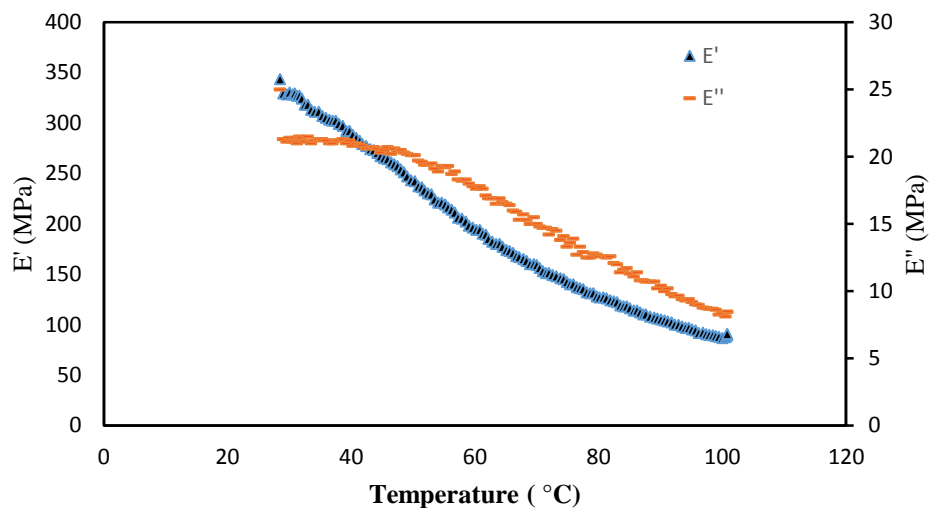
283

284 Fig. 4: Contact angle over time for PANI PAMPSA and PANI membrane. Data are average of
285 2 membrane samples from 2 different batches.

286

287 **3.1.4 Mechanical stability of PANI PAMPSA membrane**

288 Previous works have reported PANI PAMSA membranes with a greater flexibility and
289 improved mechanical stability due to the ionic bonds and double-stranded network between
290 polymer acids and PANI chains [28, 29]. To further characterise the elastic behaviour of the
291 prepared PANI PAMPSA membrane, the mechanical response of the membrane at different
292 temperature was investigated. The degree of stiffness of the material or storage modulus was
293 measured, and the data are reported in Fig. 5. It is noted that the initial value of the storage
294 modulus at 324 MPa decreases with temperature increases, indicating a decreasing in stiffness
295 of the polymer chains. The hump of the loss module E'' curve can be attributed to an increase
296 in molecular motion, but the absence of an evident step decrease for E' curve does not indicate
297 any transition or physical change. The absence of any transition between 25 and 100 °C gives
298 an indication of the membrane response in that temperature range, confirming the mechanical
299 stability and flexibility of the synthesised membrane and its applicability in processes where
300 temperatures higher than ambient values are required, or cleaning steps are performed with hot
301 solutions.



302

303

304 Fig. 5: Dynamic mechanical analysis of PANI PAMPSA membrane. Data are average of 2

305 membrane samples from 2 different batches.

306

307 3.2 Permeate flux analysis

308 Fig. 6 shows the time course of permeate flux for the ultrafiltration of orange juice using PANI

309 PAMPSA and RCA membranes. The ultrafiltration was stopped at 60 min. It can be seen that

310 the lab made membrane and the commercial RCA have comparable permeate fluxes of 31 ± 2

311 $\text{L m}^{-2} \text{h}^{-1}$ and $29 \pm 1 \text{ L m}^{-2} \text{h}^{-1}$ at the beginning of the filtration. The initial permeate flux

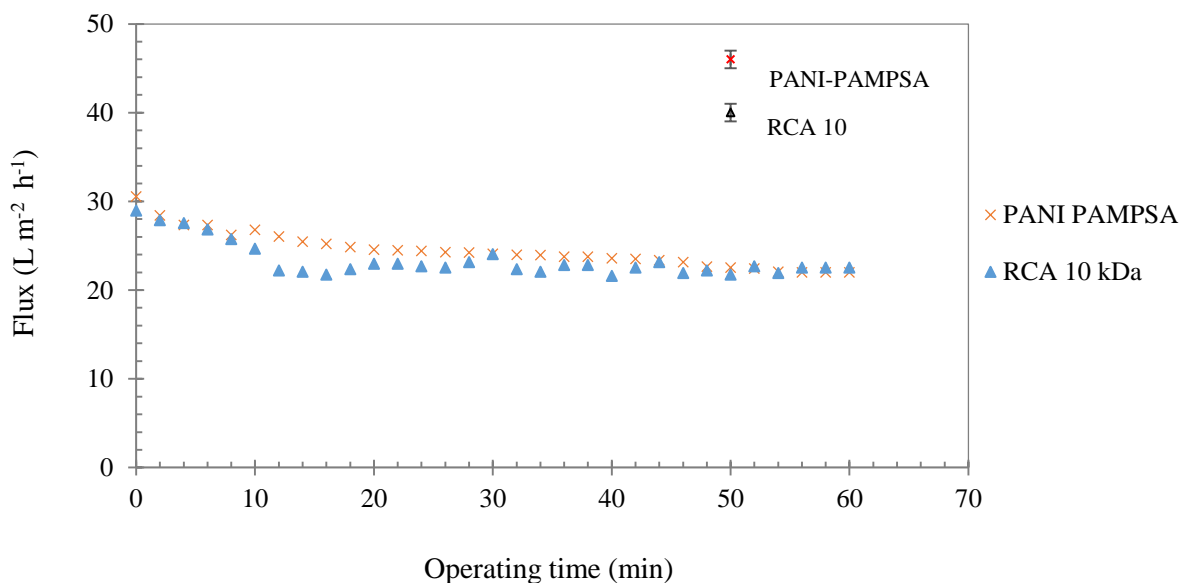
312 continued to decline gradually with filtration time until it reached a steady-state value at *ca.* 22

313 $\text{L m}^{-2} \text{h}^{-1}$. The permeate flux of PANI PAMPSA and RCA membranes dropped to $22 \text{ L m}^{-2} \text{h}^{-1}$

314 ¹, indicating a flux decline of 29 % and 24 % respectively. The decrease of permeate flux can

315 be described by the effect of membrane fouling phenomena [5, 25].

316



317

318 Fig. 6: Time course of permeate flux using PANI PAMPSA and RCA membranes. The largest

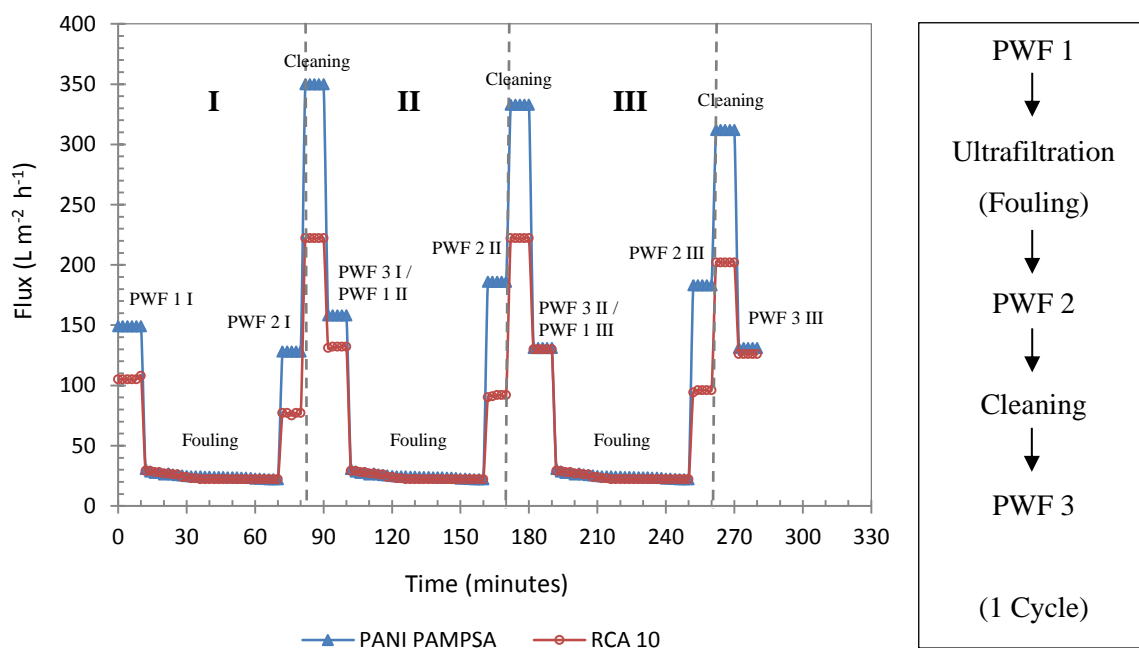
319 error for this dataset is $\pm 2 \text{ L m}^{-2} \text{h}^{-1}$.

320 3.2.1 Pure water flux

321 Pure water flux (PWF) values were measured for both membranes using DI water. The
322 experiments were performed under three different conditions (i) before fouling, (ii) after
323 fouling and (iii) after cleaning over three different cycles. Fig. 7 shows the PWF of tested
324 membranes at a TMP of 1.0 bar and at 20 °C. PANI PAMPSA and RCA membranes presented
325 the pure water flux of 128 - 186 L m⁻² h⁻¹ and 77 - 132 L m⁻² h⁻¹ respectively, for three
326 different cycles. According to the results, RCA membrane showed lower pure water fluxes than
327 the PANI PAMPSA membrane and the pure water flux before fouling (PWF 1) was reduced
328 after fouling (PWF 2) for RCA membrane in all cycles. For the PANI PAMPSA membrane, a
329 loss in performance was observed only during Cycle I with PWF before fouling (PWF 1 I)
330 reducing after fouling (PWF 2 I). As expected, the ultrafiltration process was affected by the
331 membrane fouling, thus, a cleaning method was required to regenerate the membrane.

332 The cleaning stage was performed using the commercial cleaning agent named Ultrasil
333 11 which is widely used in food process research using membrane [30] and has pH 11. Fig. 7
334 demonstrates that for the RCA membrane, cleaning method was effective in regenerating the
335 membrane with the pure water flux after cleaning higher than that seen after fouling (eg: PWF
336 3 I > PWF 2 I). However, the PANI PAMPSA membranes behave differently in Cycle I and
337 Cycle II: the fluxes after cleaning were lower than the fluxes after fouling (eg: PWF 3 II < PWF
338 2 II). This behaviour was not expected but it could be due to the PANI membrane being
339 sensitive to high pH. The different behaviour in cycle II and III showed by PANI PAMPSA
340 can be explained as a response to the variation of pH experienced by the membrane after
341 cleaning with ultrasil-11, at pH 11. It could be hypothesised that PANI PAMPSA undergoes
342 configurational changes leading to variation in the pore dimension and hence the permeability.
343 In a previous work [18], the pH dependence of PANI doped membrane has been highlighted
344 and it was found that exposure to alkaline environment causes the swelling of the membrane

345 and subsequent pore constriction. However, it is also be considered that with the increase of
 346 solution pH, the positive sites of the PANI PAMPSA can be deprotonated and this can further
 347 affect the membrane filtration performance After the cleaning step in cycle I, the flux observed
 348 after fouling in cycle II and cycle III is higher than the pure water flux suggesting a pore-
 349 opening effect of the cleaning agent. The Ultrasil-11 with basic pH does not affect the RCA
 350 membrane, however PAMPSA and PANI possess charged functional groups which are affected
 351 by the pH of the feed solution [18]. As Ultrasil-11 is a common cleaning agent for restoring
 352 membrane flux and de-foul membranes used in food industry, it was selected for the cleaning
 353 step and compare the ultrafiltration performed by the two membranes. However the influence
 354 of pH on PANI membrane performance during cleaning steps is not fully understood and was
 355 not addressed in this work where the focus was on understanding the performance of these
 356 novel membranes in complex multicomponent systems.



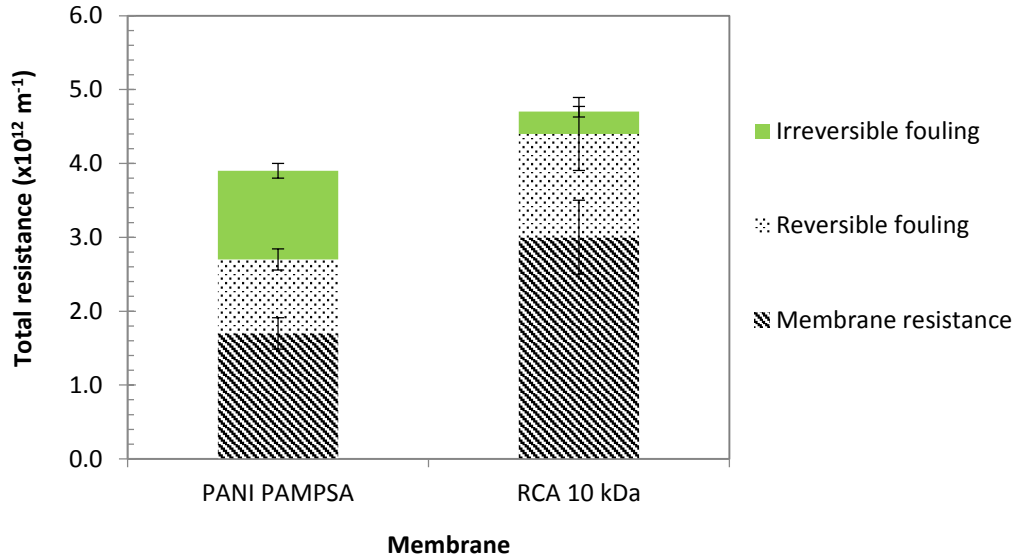
357
 358 Fig. 7: Pure water fluxes of two membranes tested; PANI PAMPSA and RCA.

359
 360 The cleaned membranes present a higher permeate flux when compared to the PWFs
 361 and this can be explained as a result of cleaning agents such as Ultrasil 11 (used in this study)

362 that can foul the membrane with surfactants. Surfactants may lead to a flux which can
363 occasionally be higher than the pure water flux obtained when using a clean membrane. If
364 surfactants coat a fouled membrane, the flux can still be higher than that seen for a clean
365 membrane. Hence, to have a better indication of surface conditions, other techniques such
366 electron microscopy can be used to determine whether the membrane is physically clean and
367 with no feed related foulants being present. After rinsing and further feed processing, these
368 surfactants desorb from the surface, and flux may then be more representative of the
369 interactions that have occurred between the polymer and the feed materials.

370 The total resistances were calculated from the flux data. A test for concentration
371 polarisation was carried out and the results showed that concentration polarisation is not an
372 important fouling related resistance in this system. Fig. 8 shows the total resistances including
373 membrane, reversible fouling and irreversible fouling for the membranes tested. The
374 conditioned virgin membrane resistances before fouling for PANI PAMPSA and RCA
375 membranes were $1.7 \times 10^{12} \text{ m}^{-1}$ and $3.0 \times 10^{12} \text{ m}^{-1}$ respectively. These values increased after
376 fouling, to $3.9 \times 10^{12} \text{ m}^{-1}$ and $4.7 \times 10^{12} \text{ m}^{-1}$ respectively, which were 1.6 and 2.3 times more
377 than those seen before fouling. Thus, it can be concluded that both membranes became fouled
378 during filtration. The RCA membrane displayed higher total membrane resistance and this is
379 reflected in lower pure water flux for RCA in Fig. 7. Table 1 shows the percentages of total
380 resistances including membrane resistance, reversible fouling and irreversible fouling. For
381 RCA 10 kDa membrane, the increase in the total resistance after fouling was mainly due to
382 reversible fouling ($30 \pm 5\%$) rather than irreversible fouling ($6 \pm 2\%$). Irreversible fouling (31
383 $\pm 2\%$) showed higher percentage compared to reversible fouling ($26 \pm 2\%$) for PANI PAMPSA
384 membrane as shown in Table 1. It was clear that RCA 10 kDa membrane was easily cleaned
385 compared to PANI PAMPSA, as it showed the lowest percentage of irreversible fouling.

386



387

388 Fig. 8: Total resistances including membrane, reversible fouling and irreversible fouling

389

390 **Table 1** Percentages of the breakdown of total resistances

	PANI PAMPSA	RCA 10kDa
Membrane resistance (%)	44 ± 4	64 ± 5
Reversible fouling (%)	26 ± 2	30 ± 5
Irreversible fouling (%)	31 ± 2	6 ± 2

391

392

393 The cleaning efficiency was calculated by comparing the pure water permeability

394 before and after cleaning [6]. RCA membrane exhibited higher cleaning efficiencies with 98 ±

395 1 % compared to PANI PAMPSA membrane (74 ± 11 %) (Fig. S4). This may suggest that the

396 fouling resistance was removed by the cleaning agent for the fouled membranes [30] . From

397 this result, it can be noted that the chemical cleaning method using 0.5 wt % Ultrasil-11 was

398 highly effective in regenerating RCA membrane, but less effective in regenerating PANI

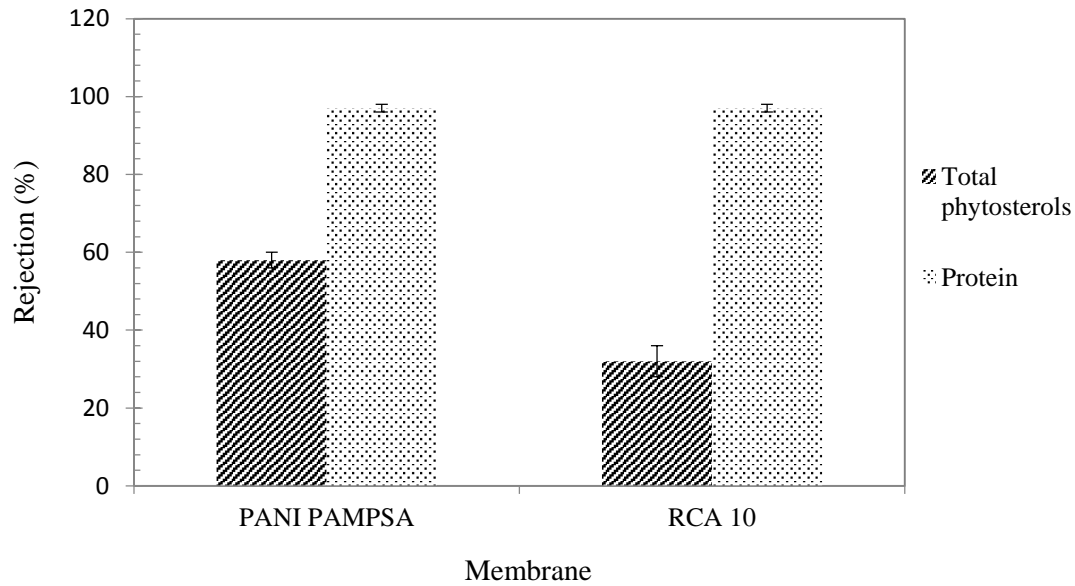
399 PAMPSA membrane. This may suggest that the PANI membrane is pH sensitive at high pH of

400 cleaning process which affected the membrane surface charge.

401 3.2.2 Rejection of key compounds

402 Ultrafiltration was used to enable the separation of phytosterols from protein in orange juice.
403 The separation efficiency and the effect of membrane fouling were studied by measuring the
404 rejection of key compounds such as phytosterols and proteins content. Samples from the feed,
405 retentate and permeate streams were collected and characterised for both compounds. Fig. 9
406 illustrates the rejection of compounds by PANI PAMPSA and RCA membranes. As previously
407 reported, the RCA membrane presented good separation efficiency with 32 ± 4 % rejection
408 towards phytosterols [11]. The lowest rejection of phytosterols by the tested membrane
409 indicates the best separation efficiency. It can be seen in Fig. 9, PANI PAMPSA membrane
410 showed higher rejection of phytosterols with 58 ± 2 %. Meanwhile for the protein content, both
411 membranes showed higher rejection of protein of 97 ± 1 %. The molecular weight of proteins
412 in orange juice were in the range 12 kDa to 71 kDa [31]. Thus, the higher molecular weight
413 compounds were rejected by smaller pore size membrane and this increased the fouling layer
414 [32]. It is possible that the membrane was fouled by protein-based compounds or other
415 hydrophilic sub micelles [33, 37]. This data was supported by the flux declining results in Fig.
416 6 showing that the membrane has been fouled during the filtration. From this rejection results,
417 it can be concluded that the protein can be removed from the sterols stream by using both PANI
418 PAMSA and RCA membrane but PANI membrane showed a good result in term of the protein
419 rejection which is comparable to the commercial RCA membrane. As reported in our previous
420 study [7], cake fouling was the dominant mechanism for RCA 10 kDa membrane, as proteins
421 were highly rejected by the 10 kDa membrane. As the PANI PAMPSA membrane has a similar
422 MWCO of 10 kDa (Fig. S3), it is postulated that the PANI-PAMPSA membrane was also
423 fouled with a cake of proteins as both membranes showed higher rejection of protein of 97 ± 1
424 % (Fig. 9).

425



426

427 Fig. 9: Rejection of phytosterols and protein by PANI PAMPSA and RCA membranes.

428 **3.2.3 Mass balance of key compounds**

429 Table 2 illustrates a mass balance for the ultrafiltration of total phytosterols and protein using
 430 PANI PAMPSA and RCA membranes. The initial volume of the orange juice for the
 431 ultrafiltration was 3000 mL. The total phytosterols present in feed solution were 259 ± 11 mg/L.
 432 The yields of total phytosterols in the permeate for PANI PAMPSA and RCA membranes were
 433 23 ± 2 mg/L and 43 ± 2 mg/L respectively. The mass concentration ratio of sterol to protein
 434 was increased from feed to permeate streams for both membranes. For PANI membrane, the
 435 mass concentration ratio of sterol to protein changed from 0.27 in the feed to 3.00 in the
 436 permeate. The mass concentration ratio of sterol to protein increased from 0.27 in the feed to
 437 5.00 in the permeate for the RCA membrane. The permeate from the RCA membrane showed
 438 the higher ratio of sterols to protein compared to PANI membrane. The 18 % loss of
 439 phytosterols in the system for PANI membrane and 21 % loss for RCA membrane were
 440 presumably due to the fouling effect during the filtration [25]. It is hypothesised that the sterols
 441 were trapped by the fouling layer and did not pass through the membrane. The protein mass in
 442 the feed solution was 947 ± 23 mg/L. The yields of proteins in the permeate for PANI PAMPSA

443 and RCA membranes were 8 ± 2 mg/L and 9 ± 2 mg/L respectively. The losses of the feed
 444 proteins for both membranes were presumably due to the adsorption of protein solute inside
 445 the membrane pores or on the membrane surface [25]. It can be noted that the highest recovery
 446 of phytosterols in the permeate (43 ± 2 mg/L) was obtained by using RCA membrane.

447

448 Table 2: Mass balance for total phytosterols and protein by UF process of orange juice with
 449 different membranes; (a) PANI PAMPSA and (b) RCA 10.

(a) PANI PAMPSA						
	Feed	Final retentate		Total permeate		Total (%)
Volume (mL)	3000	2300	77%	700	23%	100
Total sterols (mg)	742	539	73%	69	9%	82
Protein (mg)	2772	2212	80%	23	1%	81
Mass concentration ratio (sterols to protein)						
	0.27			3.00		

(b) RCA 10						
	Feed	Final retentate		Total permeate		Total (%)
Volume (mL)	3000	2150	72%	850	28%	100
Total sterols (mg)	810	504	62%	135	17%	79
Protein (mg)	2910	2408	83%	26	1%	84
Mass concentration ratio (sterols to protein)						
	0.27			5.00		

450

451

452 **3.3 Surface charge of PANI PAMPSA membrane**

453 The PANI PAMPSA membrane's fouling tendency was further studied via surface charge
454 analysis. A surface exposed to an aqueous environment assumes an electric surface charge
455 which arises either from dissociation or protonation of surface functional groups or from
456 selective adsorption of ions. The pristine PANI PAMPSA membrane showed a negative Z
457 potential of -16 mV. It is usually accepted that the negative charges of PAMPSA are balanced
458 by the positive charges of the PANI backbone, however it has been reported that the polymer
459 matrix is negatively charged due to the dissociation of the macromolecular acid with a pKa of
460 0.87 [34]. After fouling and decrease in the permeate flux, the PANI PAMPSA membrane was
461 extensively cleaned with a solution at pH 11.7 and then rinsed with water increasing the z
462 potential to -11 mV. The minor change in the net surface charge towards less negative value
463 could be attribute to the buffer effects of the sulfonic and carboxylic groups of the PAMPSA
464 and the irreversible adsorption of charged compounds onto the membrane surface [35].

465

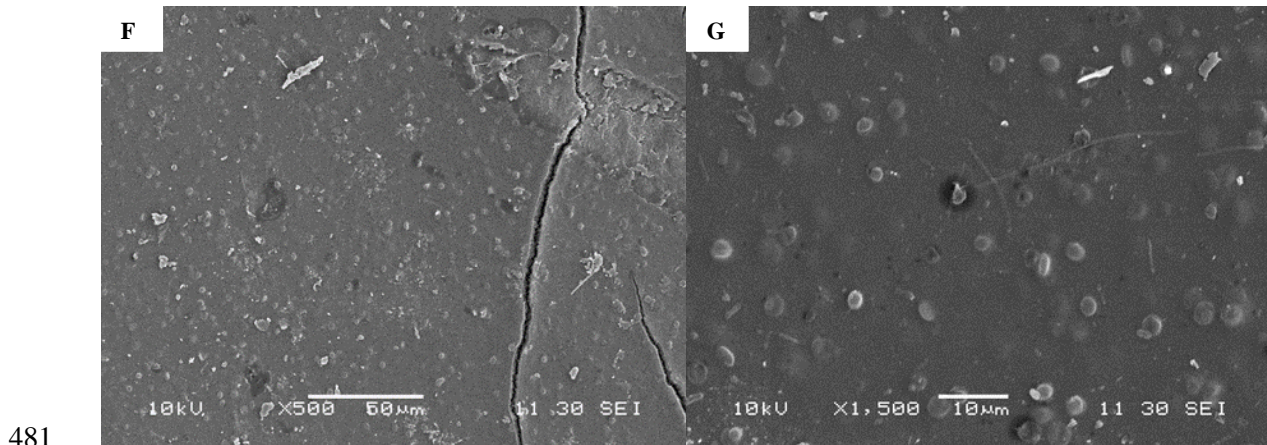
466 **3.4 Membrane fouling: visual study**

467 To assess membrane fouling and evaluate the effectiveness of the cleaning we carried out a
468 visual study of the PANI PAMPSA membrane and the RCA membrane surface using SEM.
469 Fig. 10 and Fig. display i) the surface of the pristine membrane ii) fouled membrane and iii)
470 the cleaned membrane.

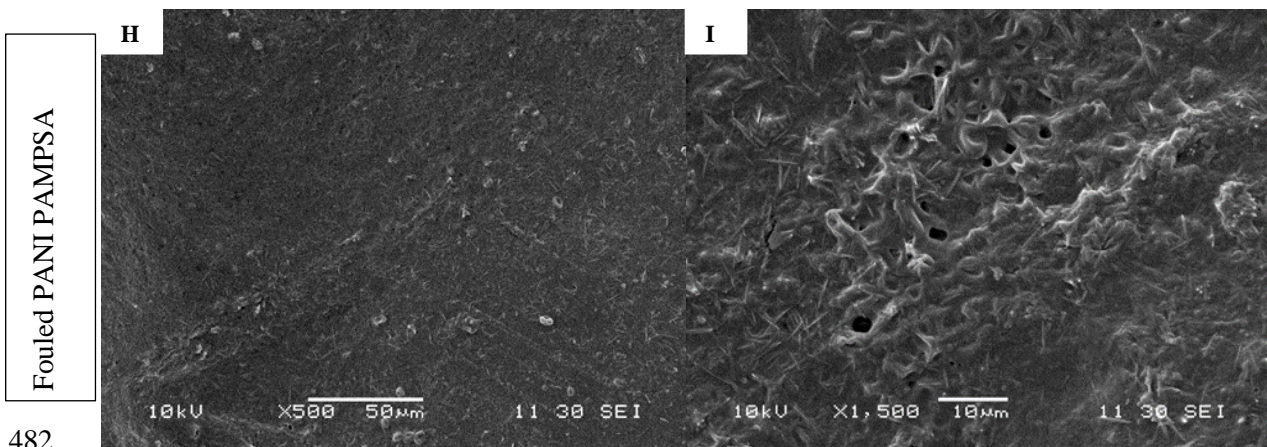
471 As reported in Section 3.1, the cleaning efficiency was superior for the RCA membrane
472 whereas the PANI PAMPSA membrane showed a higher irreversible fouling value. From SEM
473 it was possible to characterise the membrane before and after cleaning. The fouled membrane
474 shows the presence of a dispersed layer on the top of the membrane surface which appeared
475 rougher when compared with the pristine membrane. Interestingly, the cleaned membrane SEM
476 image shows a greater similarity to that of the pristine membrane, and shows no sign of the

477 dispersed layer. This result confirms the effectiveness of cleaning the PANI PAMPSA
478 membrane using 0.5 wt % Ultrasil-11. This formulation was able to remove the adsorbed matter
479 from the top surface.

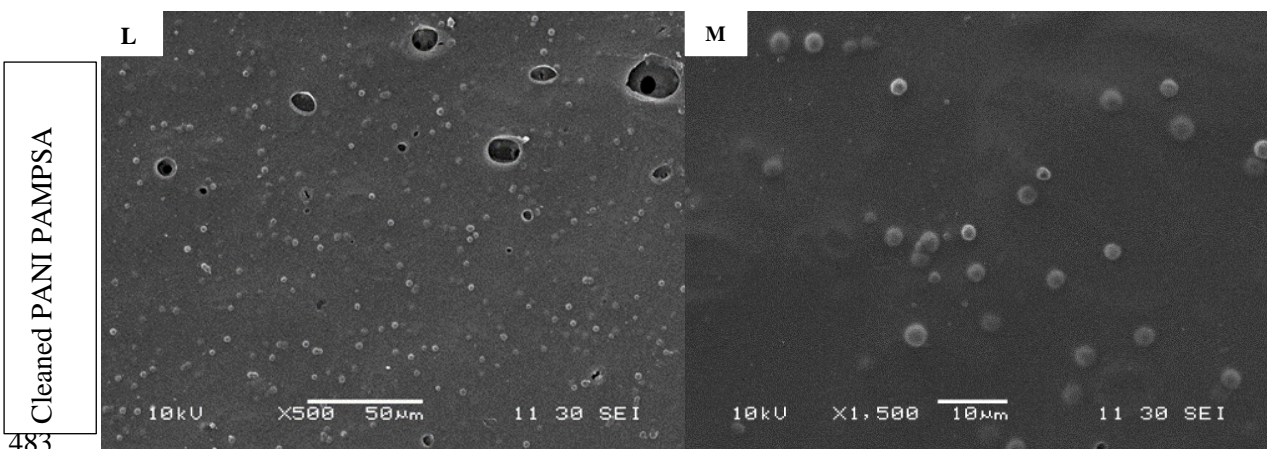
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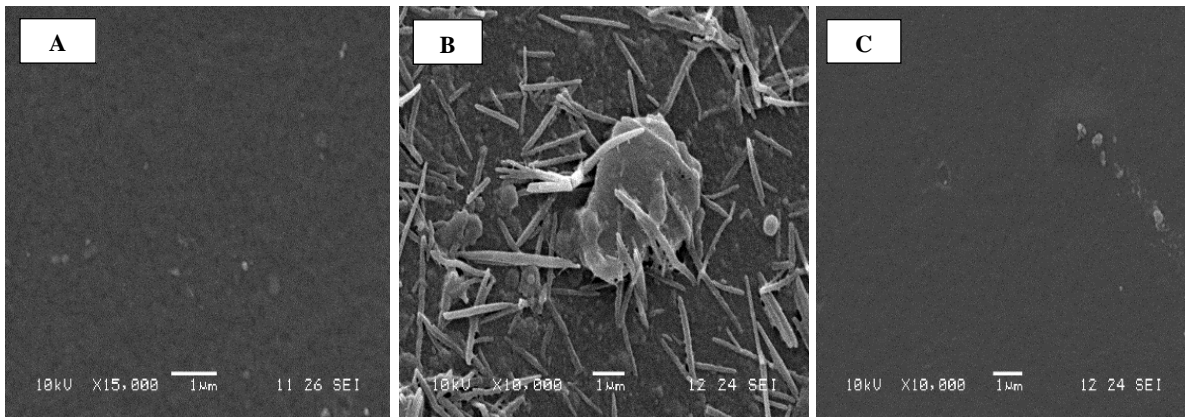


482



483

484 Fig. 10: SEM images of membrane surfaces of (F,G) pristine PANI PAMPSA; (H,I) Fouled
485 PANI PAMPSA and (L,M) cleaned PANI PAMPSA.



487

488 Fig. 11: SEM images of RCA membrane surfaces (A) conditioned membrane, (B) fouled
 489 membrane, and (C) cleaned membrane

490

491 **4.0 Conclusion**

492 In this work, the lab made PANI PAMPSA membrane was benchmarked against a commercial
 493 RCA membrane. The separation of phytosterols from protein in orange juice were investigated,
 494 focussing on both filtration performance and membrane fouling. The PANI PAMPSA
 495 membrane was synthesised via phase inversion in water from a solution of PAMPSA 20 wt%
 496 in NMP, 4-MP and THF. Physical and chemical characterisation showed that the presence of
 497 acid sulfonic groups imparted hydrophilicity to the PANI backbone, resulting in a decreased
 498 contact angle value of 77° after 60 s. The PANI PAMPSA membrane of 200 µm thickness
 499 showed a pure water flux of 126 Lm⁻²h⁻¹. Cross-flow ultrafiltration of orange juice showed
 500 that fouling occurs for both membranes with the PANI PAMPSA membrane showing slightly
 501 higher irreversible fouling than the RCA membrane. The cleaning efficiency was high for both
 502 membranes, with PANI PAMPSA membrane showing a value of 74% after 3 fouling-cleaning
 503 cycles. This study is the first reported in the literature to evaluate the PANI PAMPSA

504 membrane in a complex model system and benchmarks it against a commercially available
505 membrane.

506

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513

514 **Nomenclature**

515 *Abbreviation*

516	APS	Ammonium persulfate
517	LB	Liebermann-Buchard
518	MWCO	molecular weight cut-off
519	NMP	N-methyl-2-pyrrolidone
520	PANI	Polyaniline
521	PAMPSA	Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)
522	PWF	pure water flux
523	R	rejection ratio
524	RCA	regenerated cellulose acetate
525	TPC	total phytosterol content
526	UF	ultrafiltration

527

528 *Symbols*

529	A	absorbance	nm
530	C _p	solute concentration in the permeate	mg mL ⁻¹

531	C_r	solute concentration in retentate	mg mL^{-1}
532	ΔP	transmembrane pressure	bar or Pa
533	J	flux	$\text{L m}^{-2} \text{h}^{-1}$
534	P	pressure	bar or Pa
535	R	rejection ratio	%
536	R_{cp}	concentration polarisation resistance	m^{-1}
537	R_f	fouling resistance	m^{-1}
538	R_{ir}	irreversible fouling resistance	m^{-1}
539	R_m	membrane resistance	m^{-1}
540	R_r	reversible fouling resistance	m^{-1}
541	R_{tot}	total resistance	m^{-1}
542	T	temperature	$^{\circ}\text{C}$
543	t	time	sec or min or hr

544

545 ***Greek symbols***

546	ξ	zeta potential	mV
547	θ	contact angle	$^{\circ}$
548	ρ	fluid density	kg m^{-3}
549	μ	dynamic viscosity of fluid	Pa s

550

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