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1 **A Hybrid Super Hydrophilic Ceramic Membrane and Carbon Nanotube**

2 **Adsorption Process for Clean Water Production and Heavy Metal Removal**

3 **and Recovery in Remote Locations**

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15

16 **Abstract**

17 A novel hybrid membrane-adsorption process has been developed for the production of

18 clean water supplies. A 0.2μm ceramic membrane has been functionalised to produce a

19 super-hydrophilic surface on the microfiltration membrane capable of maintaining flux with

20 little or no fouling under normal operating conditions. The adsorbent used is a supported

21 epoxidised carbon nanotube material capable of removing heavy metals from solution. Both

22 the membrane and the adsorbent can be easily cleaned when necessary using only a

23 solution of readily available vinegar. The intended aim for this new water production system

24 is for the production of clean water in remote locations, in disaster relief zones and for

25 humanitarian purposes. Laboratory studies have shown that the membrane is capable of

26 maintaining flux over a significant period of time and even when tested with an extreme

27 foulant (used motor oil) performed admirably. The rejection properties of the membrane

28 are as expected for small pore microfiltration, i.e. microbial contamination is easily

29 removed. The adsorbent was shown to remove heavy metals (Cd, Hg, Ni, Co and Pb) to a

30 very high degree (>99.3% in all cases) and was easily regenerated to almost complete

31 adsorptive capacity. The hybrid-process was briefly deployed to the Rio Las Vacas
32 (Guatemala) as part of a basic feasibility study and the unit performed as expected. No
33 microbial contamination was detected in the permeate and the flux was maintained
34 consistently at one third of the clean water flux. This demonstrates the system is capable of
35 microbial removal and has good antifouling properties.

36

39 **1   Introduction**
40 The United Nations (UN) estimates that the world population reached 7.3 billion as of mid-
41 2015, implying that the world has added approximately one billion people in the span of the
42 last twelve years (UN. 2015). 60% of the global population lives in Asia (4.4 billion), 16 % in
43 Africa (1.2 billion), 10% in Europe (738 million), 9% in Latin America and the Caribbean (634
44 million), and the remaining 5% in Northern America (358 million) and Oceania (39 million).
45 China (1.4 billion) and India (1.3 billion) are the two largest countries of the world
46 representing 19 and 18% of the world's population respectively. The world population
47 continues to grow, although at a slower rate than in the recent past. Ten years ago, world
48 population was growing by 1.24 per cent per year and this figure is currently 1.18 per cent
49 per year or approximately an additional 83 million people annually. The world population is
50 projected to reach 8.5 billion by 2030 and to increase yet further to 9.7 billion by 2050. The
51 predicted population increase will add further stress to current already oversubscribed
52 infrastructure for water; either for drinking, sanitation or agricultural use and will
53 particularly affect developing regions which will see the largest percentage increase in
54 population.
55 The Joint Monitoring Programme (JMP) by the UN Children's Fund (UNICEF) and World
56 Health Organisation (WHO) reported in 2015 that 9% (663 million) of the world's population
57 have no access to an improved drinking water source, classified as unimproved and surface
58 water (UNICEF/WHO. 2015). The sub-Saharan Africa region makes up approximately 48% of
59 the total population with no access to clean water, Southern Asia being the second highest
60 with 134 million (20%). The same report also found that 2.4 billion people globally (1 in 3)
61 have no access to improved sanitation facilities, 934 million (39%) of them defecate in open

62 spaces. The majority of the population without access to clean drinking water and sanitation

63 are from rural areas (UNEP. 2008). As a result, local sources and/or localised treatment are

64 required. The most desirable source of drinking water for remote locations are from shallow

65 or deep wells drawing fresh groundwater (Winter. 1998). Shallow wells are considerably less

66 expensive than deep wells as they can be hand dug and do not require any specialised

67 drilling equipment (Pritchard et al. 2008). However, they rely on an aquifer sources of less

68 than 50m below ground which can fluctuate seasonally. Shallow wells are also prone to

69 contamination from surface water permeation, open space defecation being a prime

70 example (Pritchard et al. 2007). Deep water wells are also prone to contamination but the

71 likelihood if greatly reduced when compared to shallow wells (British Geological Survey

72 2001). Deep water wells require expensive and heavy drilling equipment due to the hard

73 rock basin that needs to be penetrated to reach the depths of the groundwater beneath

74 (Adelana & MacDonald. 2008). Several technology platforms exist that can be used for the

75 treatment of local water sources. These include physical processes, chemical treatment,

76 thermal processes, light based treatments, integrated systems and membrane technology

77 (Loo et al. 2012). Several of these technologies have been coupled to local energy

78 production systems for off-grid applications, such as solar stills, photo-voltaic driven

79 systems, solar-thermal systems, biomass and geothermal energy (Eltawil et al. 2009;

80 Chandel et al. 2015). Some future technologies have also been proposed that could come

81 online for local water generation; these include new methods for disinfection using

82 nanostructures, development of biosensors to confirm decontamination, deployment of

83 hybrid membrane bioreactor systems and development of novel membranes based on bio-

84 inspired systems (Shannon et al. 2008). However, due to simplicity and cost the Bio-sand

85 filter is currently often deployed for the generation of water in local or remote regions. Bio-

86 sand filters have been deployed as an alternative method for generating clean drinking

87 water from rainwater or a contaminated local source (Duke et al. 2006; Stauber et al. 2006;

88 Barnes et al. 2009; Pokhrel et al. 2009; Stauber et al. 2009). The untreated water passes

89 through a biological layer and multiple sized physical layers, pathogens are removed by

90 microorganisms in the bio-layer, layers of fine sand and gravel of increasing size then

91 remove any suspended solids. The negative aspects of bio-sand filters include the

92 requirement for sufficient hydraulic head to force the water through the bed. As a result,

93 the production rate of clean water can be slow and as the feed water level drops, the

94   production rate slows further. Particles can accumulate in the sand filters clogging the filter,

95   reducing the flow rate of clean water (Tellen et al. 2010). Typically, a bio-sand filter will be

96   constructed of concrete, therefore, they are heavy and vulnerable to damage making them

97   difficult units to transport to remote locations. Limited research has been conducted into

98   the removal of heavy metals by bio-sand filters, results reported have varied considerably

99   (Mwabi et al. 2011; Islam et al. 2014) Personal drinking water devices have been developed

100   that are able to produce clean drinking water from an untreated fresh water supply. These

101   devices have been made popular to the general public through advertisement campaigns on

102   social media, in particular the personal filter brand *LifeStraw* (Vestergaard Frandsen). These

103   units work well for bacteria, protozoa and viruses depending on the version of the filter

104   used, LifeStraw (0.2 μm) and LifeStraw Family or Mission (0.02 μm). These units are reliant

105   on a suitable local source of water being available and do not remove heavy metals.

106   The research group was approached by the clean water charity, Millions from One, to

107   produce a filtration platform that could treat a local contaminated water source, the Rio Las

108   Vacas in Guatemala, which contains a plethora of bacterial and heavy metal contaminants.

109   The challenge was to produce water that meets the WHO drinking water quality, although a

110   clear improvement in general water quality would be acceptable. One of the tributaries for

111   the Rio Las Vacas river passes through the Guatemala City dump, Fig 1a. This dump is

112   notorious for unauthorised dumping of hazardous and toxic material into the local

113   environment as witnessed during a tour of the surrounding area, Fig 1b. Furthermore, the

114   city cemetery is located directly above the dump and operates a plot lease scheme, i.e. if

115   payment is no longer made the plots are exhumed and any remains are reburied in mass

116   grave pits on site, coffins, rubbish and any other material is burned and cast over the cliff

117   into the dump. Locals have alleged that human remains have also found their way over the

118   cliff edge into the city dump. The raw sewage stream that forms part of the Rio Las Vacas

119   tributary is eroding the cliff edge. As recently as May 2015, a large mudslide due to erosion

120   carried 18 tombs from the edge of the cemetery down into the dump. Some 7,000 people

121   work in the dump, these workers or "Guajeros" known locally spend their lives collecting

122   plastic, metal and old magazines from out of the trash heap to sell to recyclers. Around

123   1,000 of these workers are children. Workers, local residents and children of Barrios (an

124   area downstream) regularly play and wash laundry in the contaminated waters. Fortunately,

125   they understand the water is not suitable for consumption.

126 In this work, a localised water purification system is developed that combines a sterilising

127 pre-filter to remove bacteria and protozoa followed by a post filtration heavy metal removal

128 unit. The sterilising pre-filter used was a super-hydrophilic functionalised ceramic 0.2 μm

129 filter, 0.2 μm being the minimum international standard for sterilisation (ASTM. 2015). The

130 permeate from the pre-filter is then passed through a heavy metal adsorption pack. The

131 adsorption pack contains supported epoxidised carbon nanotubes (SENTs) and are highly

132 efficient at removing heavy metals. The novel water purification system is extensively tested

133 in the laboratory and briefly deployed to an extremely polluted river water in Guatemala

134 City.

135

136 **2   Experimental**

137 *2.1   Ceramic Functionalisation*

138 Virgin (unmodified) Atech ceramic membranes (19-3.3 version Atech-Innovations GmbH,

139 Germany) with support and active layer manufactured from alpha alumina were initially

140 washed with hot mains tap water (approx. 42 °C) to remove any alumina dust from the

141 manufacturing process. The membranes were then rinsed with ultra-pure water (Millipore -

142 Elix 5). The membranes were placed inside a stainless steel housing (Memtech Ltd -

143 Membralox housing custom design) with an electrical heating tape (Electrothermal -

144 HT95515 glass fibre heating tape) wrapped around the external surface of the housing, see

145 Fig 2. In addition to the intact membrane a small broken alumina membrane piece from an

146 unmodified alumina membrane (Pall - Membralox 1.4 μm) was placed inside the housing on

147 top of the whole membrane, this fractured piece will functionalise in-situ and is used for

148 functionalisation analysis post treatment to avoid damaging the intact membrane. The

149 membranes were submerged in a 150 g/l solution of l-cysteic acid anhydrous (Acros

150 Organics) and left to effervesce until the air inside the membrane structure was removed.

151 Once the membranes stopped effervescing a condenser (Axium Process Ltd - custom design)

152 was attached to the housing and a coolant from a chiller unit (Huber) set at 4 °C was

153 circulated through the condenser jacket. After the set point temperature was achieved the

154 electrical heating tape controller (Electrothermal - MC242 1800W) was turned on and the

155 cysteic solution was allowed to reach a steady reflux temperature of approximately 105°C.

156 The solution was maintained at reflux for 72 hours. The heating tape was turned off and the

157 solution was allowed to return to room temperature, the remaining cysteic acid solution

158 was drained from the housing and stored for further functionalisation processes. The

159 membrane and membrane piece were then thoroughly washed at least 3 times in hot water

160 and deionised (DI) water respectively. The membranes were then stored in original

161 packaging under ambient conditions prior to scanning electron microscopy with energy-

162 dispersive X-ray spectroscopy (SEM-EDX) and thermogravimetric analysis (TGA). This is a

163 modified version of a patented fabrication process described previously (Lance Energy

164 Services. 2013).

165

166 *2.2   SENT Functionalisation*

167 4.33 g of ferrocene was dissolved in 80 ml of toluene in a volumetric flask with the aid of

168 sonication. The flask was then filled to produce a 0.233M solution. 3.45 g of 12 μm diameter

169 quartz wool for nanotube deposition was placed in a 34 mm inner diameter x 38 mm outer

170 diameter x 500 mm long quartz tube, which was then inserted into an SSP-354 Nanotech

171 Innovations table-top growth furnace such that the quartz wool was positioned at the front

172 of the growth zone (Orbaek et al. 2013). The instrument was calibrated as follows: The inert

173 gas flow regulator was set to 1.5 LPM (5% Hydrogen, 95% Argon as obtained from Matheson

174 Tri-Gas) and maintained for 25 minutes to remove any resident water vapour or other

175 environmental impurities. The injection and growth zone temperatures were set to 225°C

176 and 900°C respectively. Once the calibration was completed, 5 ml of the 5% by weight

177 solution of ferrocene dissolved in toluene was transferred into a 6 ml syringe clamped in

178 place by a syringe pump. The solution was injected into the tube furnace through a 9"

179 injection needle (Hamilton Syringe Company) in the middle of the injection zone at a rate of

180 3 ml/hr for 100 minutes along with the inert gas mixture, and chemical vapour deposition

181 (CVD) was initiated to deposit the multi-walled carbon nanotubes (MWNTs) on the quartz

182 wool. Ferrocene serves as a catalyst under high temperatures and catalyses the

183 decomposition of toluene. Subsequently, ferrocene recombines the carbon within toluene

184 to form MWNTs on the surface of the quartz wool. Both zones were cooled to 15°C after the

185 full volume of the precursor solution was injected and the inert gas flow was turned off after

186 a period of 50 minutes. Purification of the MWNTs was necessary before epoxidation,

187 because injection CVD is known to leave residual iron particles in the graphitic structure of

188 the nanotubes. The material was positioned at the front of the growth zone for purification.

189   Wet-Air Oxidation (WAO) and hydrochloric acid (HCl) sonication were the two techniques

190   utilised to effectively remove residual impurities. WAO oxidises elemental iron impurities to

191   iron oxide, thereby providing hydrochloric acid the ability to permeate the nanotubes and

192   leach out the iron particles, since iron oxide is soluble in HCl on the basis of polarity. An air

193   source was connected to a flow regulator set to a pressure of 1000 kPa, which was then

194   connected to a bubbler 50% with DI water. The bubbler, in turn, was connected to the

195   reactor chamber inlet containing the Quartz Wool-MWNTs. WAO was initiated as the

196   injection zone temperature regulator was set to 240°C and the growth zone temperature

197   regulator was set to 37.5°C. The growth zone temperature was set to a relatively low value

198   to minimise the risk of nanotubes burning during the oxidation process. After 2 hours and

199   45 minutes the WAO process was completed; the Quartz Wool-MWNT material was placed

200   in a beaker filled with 100 ml of 1M Hydrochloric acid and sonicated for 45 minutes in a

201   Branson 3510-DTH ultrasonic cleaner. The contents of the beaker were then filtered

202   through a 0.45 μm Polytetrafluoroethylene (PTFE) membrane and flushed with 1000 ml of

203   water. The purified quartz wool MWNTs were placed in an oven and dried for 10 minutes.

204   The purified Quartz Wool-MWNTs were functionalised through epoxidation to form SENTs.

205   A 250 ml round bottom flask was filled with 200 ml of dichloromethane (DCM). 3.85 g of

206   meta-chlorperoxybenzoic acid (m-CPBA) was then dissolved in the DCM by a magnetic

207   stirrer for 10 minutes. The remaining purified Quartz Wool-MWNT material was then placed

208   in this solution and stirred overnight with the same magnetic stirrer setup. The contents

209   were poured through a 0.45 μm PTFE membrane, under vacuum, while rinsed with 500 ml

210   of DCM. The functionalisation was complete after the SENT product was air dried in the back

211   of a fume hood for 24 hours. The progression of the filter medium preparation is shown in

212   Fig 3.

213   *2.3   Laboratory trials*

214   The super-hydrophilic functionalised ceramics were developed to produce a low fouling

215   membrane capable of high rejection of organic and particulate materials. Initial testing

216   focussed on oil-water emulsions as a representative highly fouling organic stream.   A

217   mixture of spent motor oil (courtesy of Trainer BMW, Swansea, UK) 1L in 39L of water, 2.5

218   v/v %, was created as a model feed solution. A standard pilot membrane filtration platform

219   was used to test the membrane and is described elsewhere (Williams. 2015). The minimum

220   operating volume of the pilot scale rig used, Fig 4, is 10 litres, therefore, the experiment was

run until 30 litres of permeate was collected or 1 hour was reached. The operating conditions of the experiment were as follows: Temperature – Ambient (uncontrolled), a temperature correction factor for microfiltration fluxes corrected for any fluctuations; membrane inlet pressure set and maintained at 2 barg; recycle flowrate set and maintained at 60 LPM; membrane retentate pressure – controlled by previous set points. Permeate samples were collected every 5 minutes for Total organic carbon (TOC) analysis (Shimadzu TOC-LCPH, Japan).

For the SENTs a 0.052 M cadmium acetate dihydrate solution was prepared by dissolving 1.8 g of cadmium acetate dihydrate in 150 ml of water to simulate heavy metal contaminated water. A 100 mL burette cleaned consecutively using a base bath with potassium hydroxide (KOH)/isopropyl alcohol, tap water, and DI water was packed with 0.5 g of the SENTs. 50 ml of the 0.052 M cadmium acetate dihydrate solution was poured through the adsorbent medium and an aliquot was collected at the bottom for UV-Vis analysis of adsorption capacity. The adsorption procedure was consecutively conducted two more times using the same adsorbent medium with the same concentration and quantity of cadmium acetate dihydrate solution. The procedure was then repeated (with the appropriate changes in the stock solution preparation, a distinct adsorbent medium sample, and three trials per metal to ensure repeatability) for a 0.01 M solution of mercuric chloride, 0.01 solution of nickel nitrate hexahydrate, 1 mM solution of cobalt chloride hexahydrate, and a 100 ppm solution of lead acetate trihydrate. These concentrations were selected to simulate cases of high industrial wastewater contamination. A time trial was conducted for each adsorption trial to determine, on average, the flow rate through the bed in ml/min.

For the renewal process, the adsorbent material was treated with 50 ml of 50:50 (by volume) DI water/acetic acid in the same burette after the three trials of cadmium filtration. The renewal process utilises a 50:50 volumetric solutions of DI water and acetic acid to desorb metal compounds through electrostatic repulsion. Another time trial was conducted to determine how quickly the adsorbent medium could be renewed. The resulting solution containing DI water, acetic acid, and cadmium acetate was then collected below in a beaker, and subsequently left for 4 hours at an ambient temperature of 25°C. The solution underwent natural evaporation to leave behind a caked residue of cadmium acetate. The effectiveness of the renewal procedure was then verified by conducting three additional

8

252 consecutive adsorption trials of cadmium acetate dihydrate, at the same concentration
253 previously used, with the renewed adsorbent medium.

254 To determine the maximum quantity of contaminated water the adsorbent medium could
255 purify before renewal was necessary, saturation trials were conducted. 50 ml of a 100 ppm
256 solution of lead acetate trihydrate was poured through 0.5 g of a freshly prepared
257 adsorbent medium and the aliquot was collected at the bottom for UV-Vis analysis to
258 determine adsorbent capacity. Following the adsorption process, the adsorbent medium
259 was rinsed with DI water to desorb any physically adsorbed lead and the resulting solution
260 was stored separately from the aliquot. This adsorbent procedure followed by rinsing with
261 DI water was consecutively conducted twelve times using the same adsorbent medium.
262 Eluent analysis using UV-Vis was performed after each aliquot was collected to determine
263 the changes in the adsorbent capacities as the trials progressed. The results of the
264 saturation trials were then analysed to determine the maximum volume of contaminated
265 water the medium could purify with greater than 99% adsorption capacity.

266 Calibration curves for each heavy metal compound were generated to determine the
267 adsorbent capacity of the medium. Initially, absorbance spectra were generated for 5 stock
268 solutions for each of the 5 metal compounds, for a total of 25 spectra. Then, the wavelength
269 at which each spectrum had a maximum absorbance was taken, with each metal compound
270 having a peak wavelength. The peak absorbance values at the respective peak wavelengths
271 for each metal compound were plotted against the stock solution concentrations such that
272 the absorbance values had a linear relationship with the standard molar concentrations
273 used. Upon the completion of the calibration curves, absorbance spectra were generated
274 for each of the aliquots for a total of 15 spectra. The peak absorbance value of each of these
275 spectra was located using the peak wavelengths determined from the stock solution
276 spectra. Given the peak absorbance value of each of the spectra, the concentration of the
277 aliquot could be determined using linear interpolation.

278

279 *2.4   Guatemala filtration platform*

280 In order to speed up the build process of the pilot system used for deployment, a small in-
281 house pilot scale polymeric MF/UF unit (Membranology, Swansea UK) was modified to fit
282 the 1000 mm ceramic membrane housing containing a membrane with $0.2m^2$ active surface
283 area, Fig 5. The rig is built using aluminium box frame (Valuframe Series 8), the pipework is

284 316L hygienic tri-clamp stainless steel (316L SS), excluding pipework connecting the rig to

285 the tanks. Pressure gauges, diaphragm seal for sanitary use, are included before and after

286 the membrane to monitor and control transmembrane pressure via the two diaphragm

287 valves.

288 A submersible pump (Karcher SDP7000) provided water from the stream to a 40L Low

289 density polyethylene (LDPE) feed tank. The feed is circulated through the membrane using a

290 centrifugal pump (Stuart Turner CH4-40) as previously mentioned the membrane inlet

291 pressure was controlled by diaphragm valves set to achieve 2 barg. This system was

292 redesigned to operate as a single pass system to avoid any build-up of large debris or

293 sediment in the feed tank, therefore, retentate was returned to the river water source. The

294 permeate from the membrane was collected in a 10L LDPE collection tank with a base valve.

295 The SENT pack was a simple polycarbonate tube with two screw in brass fittings, the base

296 fitting containing a mesh disc to maintain the CNTs within the pack, Fig 6. This pack was

297 secured to the base valve stem and when the membrane process was started up and online

298 the tank valve was opened and permeate water was gravity fed through the heavy metal

299 adsorption pack top to bottom producing metal free clean water.

300 **3   Results**

301 *3.1   Ceramic membrane characterisation and performance in laboratory trials*

302 The functionalisation of the membrane can be directly quantified by TGA and EDX. As a

303 result of the reaction between the alumina membrane and cysteic acid, the mass of the

304 resultant membrane will increase very slightly from that of the original membrane. This is

305 shown by TGA in fig 7. Prior to functionalisation the mass profile for the original ceramic

306 membrane falls linearly as the temperature is increased from approximately 75 °C to 600 °C

307 and then shows a distinctive dip and return at around 700 °C. The functionalised membrane

308 shows the same initial behaviour, but then at ~250 °C drastically reduces in non-linear

309 fashion. The same dip and return is evident at 700 °C, albeit at a lower mass level. This

310 change in weight loss profile is directly attributable to the removal of cysteic acid during the

311 experiment, i.e. the acid is burned away from the ceramic support membrane. As the

312 functionalisation reaction has no major physical effect on the pore size or surface of the

313 ceramic membrane, SEM alone will not confirm a successful reaction and elemental EDX is

314 required. As the cysteic acid contains a sulfonyl group an increase in sulphur is the easiest

315   indicator that functionalisation has occurred. Fig 8 shows an EDX map original ceramic

316   membrane and the functionalised membrane respectively. There is a clear increase in

317   surface sulphur content for the functionalised membrane.

318

319   The super-hydrophilic functionalised Atech 0.2 μm membrane demonstrated a rejection of

320   >99.5% over a series of experimental runs. The permeate samples were visibly clear in

321   comparison to the feed, see Fig 9. The membrane clean water flux prior to use was 1395

322   LMH/bar and during operation this dropped drastically to below 100 LMH/bar (minimum

323   readable permeate flowrate). The anticipated reduced fouling properties of the membrane

324   was not clearly evident during this initial set of experiments. The anti-fouling properties

325   became more apparent during longer operational periods, days rather than hours. The

326   initial drastic decline in flux is unpreventable due to the high concentration of oil

327   contamination in the feed. However, the reduced fouling behaviour stems from the

328   membrane flux remaining constant over a longer period, 1 to 2 weeks, after the initial

329   decrease in flux from fouling. Untreated membranes demonstrated a continual drop in flux

330   over this period beyond the early fouling stage. Post experiment treatment to attempt to

331   recover the initial flux was conducted and included a 2 wt% sodium hydroxide wash at 50°C

332   for 1 hour to remove organic foulant, followed by a 1% Citric acid to remove any inorganic

333   foulant. Unfortunately, the membrane flux recovery was only 12% of the original pre-

334   experimental specific clean water flux. Clear staining of the membrane was visible on both

335   the inside and outside surface and the conclusion was made that the used motor oil results

336   in irreversible fouling of the membrane due to surface and internal pore blocking.

337

338   *3.2   SENTs laboratory performance*

339   The interpolation of the average peak absorbance yielded post-adsorption of the heavy

340   metal concentrations gave average adsorption capacities of 99.39% for cadmium, 99.61%

341   for mercury, 99.70% for nickel, 99.72% for cobalt, and 99.97% for lead. Thus, for example,

342   heavy metal-contaminated sources as high as 750 μg/L can be filtered to meet the current

343   EPA Maximum Contaminant Level Goal of 1 μg/L. However, even in extreme cases, heavy

344   metal levels have not been found to exceed 100 μg/L in worldwide water sources (Meybeck

345   et al. 1990).

346 The renewal procedure devised allows for metals to be removed from the adsorbent

347 medium by natural evaporation. After the renewal of the adsorbent medium that was used

348 for the adsorption of cadmium acetate, three additional adsorbent trials with cadmium

349 acetate of the same concentration and quantity as before on the renewed medium

350 demonstrated that the adsorption capacity remained high at 99.45%. A two-sample T-Test

351 was conducted to compare the adsorbent capacity of the medium before and after the

352 renewal demonstrated the consistency of the adsorbent medium.

353 Saturation trials conducted with 100 ppm lead acetate trihydrate indicated that the

354 adsorbent capacity remained greater than 99.9% for 7 consecutive filtrations of 50 ml each,

355 and then quickly deteriorated to 55% within the next 5 trials indicating saturation. Thus 350

356 ml of the solution was adsorbed successfully by 0.5 g of the SENTs adsorbent medium, after

357 which regeneration was necessary. Time trials for the process demonstrated that the

358 adsorbent medium, on average, took 120 seconds to filter 50 ml of contaminated water,

359 while the renewal process took approximately 180 seconds for completion. For a scaled-up

360 version of the adsorbent medium suitable for domestic settings (200x the sample used in

361 the experiment), the adsorbent material can filter 5 L of water in 1 minute and be renewed

362 in just 1.5 min.

363

364 *3.3   Guatemala City trials*

365 The filtration platform trial was conducted over a 3 day period at the start of the dry season

366 in Guatemala (early November 2015). Throughout the trial period the membrane flux

367 performance was recorded as similar to that observed for clean water flux in the laboratory.

368 The initial flux rate declined almost instantly by 30% of the original clean water flux and

369 remained at this same level for the remainder of the trial period. This illustrates that the

370 super-hydrophilic surface functionalisation is assisting in the reduction of organic fouling of

371 the membrane surface.

372 An initial visual result from the water production system is presented in Fig 10a. The

373 difference in opacity between the feed (river water) and final product (post filtration and

374 adsorption) is stark, the product water is transparent whereas the feed is clearly

375 translucent. An onsite bacteria screening test (Watersafe) was conducted for the feed and

376 membrane permeate. The bacteria test takes 24 to 48 hours, a purple solution indicates a

377 negative result, a positive result changes from purple to yellow indicating bacteria is present

378 in the sample. As shown in fig 10b, the permeate sample remains a strong purple colour

379 whilst the feed sample has noticeably changed in comparison. The photo in Fig 10b was

380 taken after 24 hrs and after 48 hrs the feed sample colouration became even more

381 transparent purple and started to become yellow, while the permeate sample remained

382 unchanged. In addition to the basic screening test, bacterial growth within a laboratory

383 controlled area was conducted using nutrient agar plates and incubated for 24 hours at

384 35°C. The plate is shown in fig 10c and was split into 4 sections: feed, feed x10 dilution, feed

385 x100 dilution, permeate (from top right, clockwise). Bacterial growth was evident in the feed

386 section, there was some very minor growth at x10 dilution. There was no observable growth

387 in the feed x100 and no growth in the permeate. The lack of growth and very minor growth

388 at x100 and x10 dilution respectively indicates a low bacterial concentration in the feed and

389 confirms the result obtained in the basic screening test. No growth in the permeate section

390 demonstrates that the membrane successfully removed any bacteria present.

391 Unfortunately, metals analysis was not available onsite in Guatemala and while samples

392 were sent to a local laboratory, no results were received. Clearly a further deployment study

393 is required to properly validate the novel water treatment system and obtain long term data

394 for both membrane and adsorption performance, particularly during seasonal variations in

395 water quality.

396

397 *3.4 Prototype development*

398 Following the feasibility demonstration, the charity requested the construction of a low-cost

399 prototype unit that has the capability to be scaled up to produce 10,000 US gallons per day

400 of clean water, with minimal control systems and limited operator maintenance. Based on

401 estimates for the requirements of lactating women who engage in moderate physical

402 activity in above-average temperatures, the WHO suggest a minimum of 7.5 litres per capita

403 per day will meet the requirements of most people under most conditions. This water needs

404 to be of a quality that represents a tolerable level of risk. However, in an emergency

405 situation, a minimum of 15 litres is required. A higher quantity of about 20 litres per capita

406 per day should be assured to take care of basic personal and food hygiene. A desired level of

407 between 50 and 100 litres of water per person per day are needed to ensure that the most

408 basic needs are met and few health concerns arise (Howard & Bartram. 2003). Hence, a

409 system of such size would be capable of supporting 378 to 757 people per day based on 100

410   litres and 50 litres respectively. However, as water wastage is considerably less and the

411   typical use is more efficient than developed countries, this system, assuming a consumption

412   of 37 litres per person per day (proposed actual consumption in rural communities, data

413   from 'Millions from One' charity), would be capable of supporting a village of 1000 people

414   for basic personal and food hygiene needs. The Membranology rig used for the feasibility

415   trial has a retail value of £10,000. The main cost of the unit being the 316L SS pipe work,

416   membrane housing and/or installed membrane and additional monitoring. Consequently,

417   for the prototype system, see Fig 11, water regulations advisory scheme (WRAS) approved

418   polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (cPVC) was used for the

419   pipework. This reduces manufacturing cost, increases design flexibility and reduces weight

420   resulting in transportation savings. The internal frame utilised Valuframe Series 5 aluminium

421   box frame to significantly reduce the weight of the equivalent Series 8 frame. The prototype

422   system includes two LDPE conical tanks, feed (60L) and permeate (40L), both tanks contain

423   float level switches, low level in the feed tank to protect the pump from dry running and

424   high level in the permeate tank to avoid overflow and unnecessary water production. A

425   removable pre-filter screen, 20 mesh or 0.9mm, was installed on the feed tank outlet to

426   prevent debris blocking the 2mm membrane channels. The prototype also uses the same

427   Stuart Turner pump as the Membranology rig but the reduced size variant (CH4-30) with a

428   maximum supply pressure of 2.5 bar, suitable for microfiltration. The membrane selected

429   for the prototype was a bespoke Atech ceramic membrane. One of the design aims was for

430   the main filtration cabinet to have a minimal footprint with dimensions no larger than an

431   under counter refrigerator. Using a standard 1000 mm or 1200 mm membrane would result

432   in a particularly tall unit. For that reason, the membrane supplier was contacted and

433   supplied a membrane of 500mm in length along with the corresponding cPVC housing. The

434   membrane has a diameter of 52 mm and contains 211 channels each with a diameter of 2

435   mm. This equates to a filtration surface area of $0.66m^2$, when operated at 2 bar membrane

436   inlet pressure the unit produces 450 l/h or 119 (US)GPH of clean water. This is 33% of the

437   desired volume, thus, a minimum of 3 membranes would be required. Consideration should

438   also be given to the fact that these calculations are based on clean water fluxes, actual

439   permeate flow rate from a contaminated water source will be considerably less as observed

440   in the Guatemala study. A total of 6 to 8 membranes will provide enough permeate with

441   sufficient redundancy. The SENT adsorption pack was redesigned to be easily removable

442   from the system in the same way as the membrane housing. The pack is made from clear 25

443   mm PVC tubing bonded to two 25 mm PVC unions, the SENTs are layered between

444   polypropylene (PP) beads, the PP beads allow improved flow characteristics through the

445   pack, see Fig 12. 316L SS laser cut 20 mesh discs inside each union maintains the CNTs

446   within the pack. The largest outlays remain the ceramic membrane, membrane housing and

447   pipework, for this prototype only a single bourdon tube pressure gauge was included to

448   monitor membrane inlet pressure. This single one-off prototype unit has a retail value of

449   £3000, with mass production these costs would be significantly reduced. A full scale 10,000

450   (US)GPD per day unit would cost approximately £5000 to £8000. The new prototype unit is

451   currently undergoing a series of rigorous tests prior to further deployment activities.

452   **4   Future Work**

453   *4.1   Scalability*

454   The future of this system will require ongoing development as a result of feedback from in-

455   house testing and customers. It has already been established that a larger capacity system is

456   desirable and relatively easy to achieve. The footprint of the system will have to increase to

457   accommodate the increased number of membranes and SENT adsorption packs. This will

458   entirely depend on what would be considered most suitable for the end user, multiple

459   membranes and adsorption packs in one large system or multiple small systems in parallel.

460   For example, the most pragmatic decision for a production critical system such as the sole

461   supply of clean water to village would be to have more than one operable unit, therefore,

462   should one system fail or require maintenance then water production does not halt

463   completely. The increased capacity will also require larger feed tanks and permeate tanks or

464   a direct supply between the water source and system. The permeate storage tank would

465   have to be limited to ensure a regular turnover rate of fresh water to prevent contamination

466   or long term stagnation issues.

467   *4.2   Cleaning in Place (CIP)*

468   The SENT adsorption pack will require regular regeneration (estimated as 3-4 times per

469   year), currently the design allows the pack to be removed from the system and flushed with

470   acetic acid. With some minor pipework and valve additions this could be completed in-situ

471   with minimal effort. A system with zero operator input would require a sophisticated

472 automated cleaning procedure for the adsorption pack and membrane backwashing which

473 would add significant cost.

474 *4.3   SENT Adsorption Pack*

475 Currently the SENTs are layered between PP beads to improve water permeability through

476 the adsorption pack, they are necessary due to the compressibility of the quartz wool

477 support. This compaction results in declining flow rates and potential flow paths being

478 formed through the pack leading to minimal contact time between the water and SENTs

479 causing poor metal removal. The preferred option would be to incorporate the beads and

480 SENTs as one entity, this requires further research into the possibility of growing the

481 MWCNTs directly on quartz beads rather than quartz wool.

482 *4.4   Unit Redesign*

483 As previously alluded to, an increase in production capacity requires the unit to be

484 redesigned to contain larger or additional membranes and adsorption packs. The envisaged

485 final product will be constructed entirely from injection moulded plastic excluding the

486 pump, membrane and SENTs. The design philosophy is to utilise a no tool hand tightening

487 installation procedure; the membranes in particular will be transported separately in

488 protected packages to avoid damage. The membranes can be easily fitted inside the custom

489 membrane housings and then installed using unions into the unit in the same manner as the

490 current prototype. The SENT adsorption packs would work from the same principle, should

491 they require replacing, they can be removed and replaced easily.

492 *4.5   Power*

493 The system currently operates from a 230 VAC mains power supply, with a suitable dual

494 voltage pump then 110 VAC is also compatible. The research group has been contacted by

495 another charity who would be interested in using this system in a disaster relief capacity for

496 supplying clean drinking water in an emergency situation. The main issue with this type of

497 deployment would be a secure and reliable source of power. In the event of a severe natural

498 disaster it would be prudent to assume that mains electricity is not available. Also diesel or

499 petrol may be in short supply to run a generator, the fuel would also be vulnerable to theft

500 in times of fuel shortages. Therefore, a hybrid solar-battery operated unit is currently being

501 investigated within the research group to determine feasibility.

5 Conclusions

An experimental super-hydrophilic functionalised ceramic membrane was combined with a carbon nanotube adsorption unit for the production of clean water. The benefits of this novel unit are reduced fouling of the membrane and heavy metal removal. Thus, the unit is capable of producing a clean water supply with little or no microbial contamination and removal of heavy metals often found in waste and ground waters in various parts of the world. Laboratory trials with the new unit showed that the initial high flux (~1400 LMH/bar) of the membrane could be maintained over a period of time. However, when exposed to severe contamination (spent engine oil/water mixtures) the initial flux declined rapidly (to ~100 LMH/bar) but was then stable over a significant period of time (10 days). The rejection of the membrane was shown to be >99.5% for general hydrocarbons. The carbon nanotube adsorbent was shown to remove various heavy metals (Cd, Hg, Ni, Co and Pb) to a high degree (>99.3% in all cases) and was easily regenerated to almost complete adsorptive capacity using simple solutions of 50:50 acetic acid:water.

The experimental unit was deployed for a basic feasibility study to treat contaminated river water from the Rio Las Vacas (Guatemala City). The river is an example of a water source with a high degree of organic and inorganic pollutants. The feasibility trial lasted only 3 days, but served to demonstrate the effectiveness of the novel treatment platform to produce a clean water, suitable for drinking, from an otherwise non-potable source. The basic chemical analysis performed onsite suggests that the permeate supply produced was free from microbial contamination and the flux rates were approximately 33% of the clean water flux observed in the laboratory. No metals analysis for the trial was available.

Based on the brief feasibility trial in Guatemala, a prototype unit is currently in construction and is being developed for long term deployment to formally validate this new technology. Our hope is that this technology can act as a source of clean water in remote locations, disaster relief zones and for humanitarian use.

6 Acknowledgements

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Figures

Figure 1: [A] Tributary of Rio Las Vacas river running through Guatemala City dump, [B] observed dumping of unknown material directly into the water course.
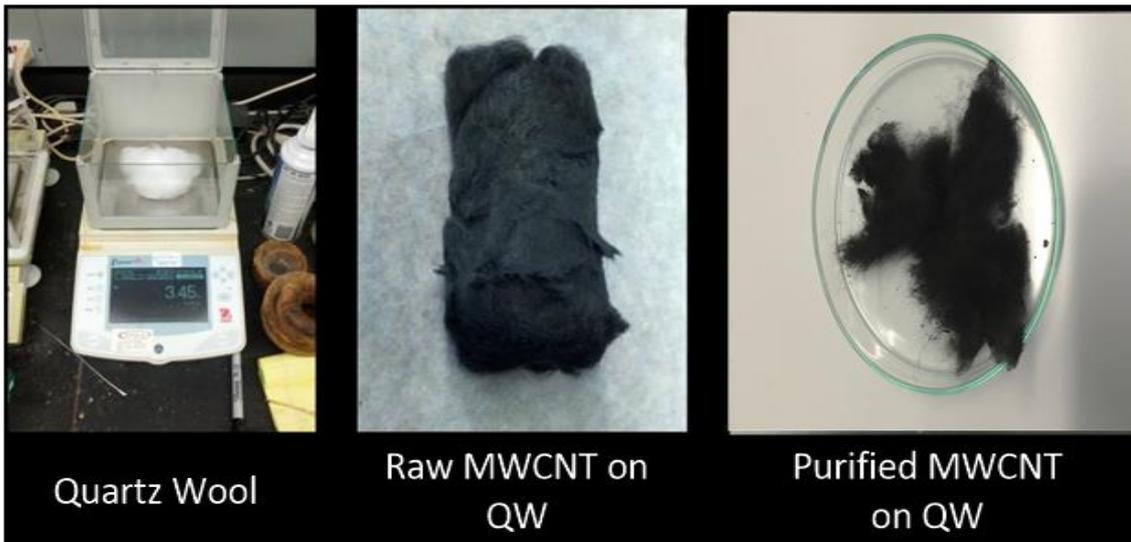
626

627 Figure 2: Ceramic membrane functionalisation equipment

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Figure 3: Preparation stages for the novel adsorbent.

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633   Figure 4: Swansea University microfiltration pilot system (the membrane, yellow housing,
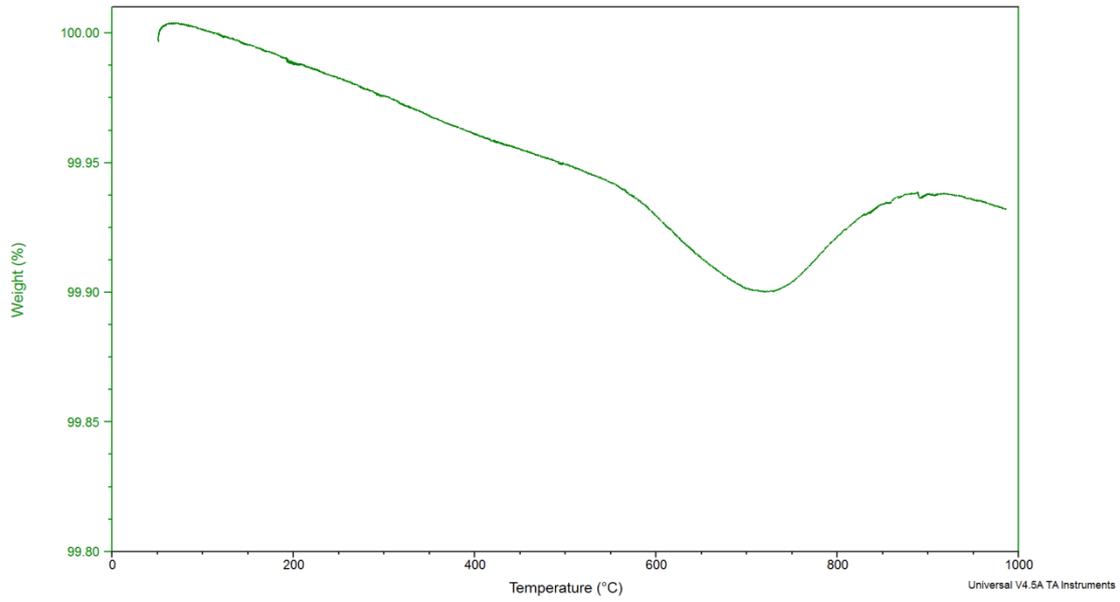
634   was replaced with the novel ceramic for this study)

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637   Figure 5: Modified Membranology filtration system during Guatemala trials

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Figure 6: Original SENT adsorption pack as deployed in Guatemala

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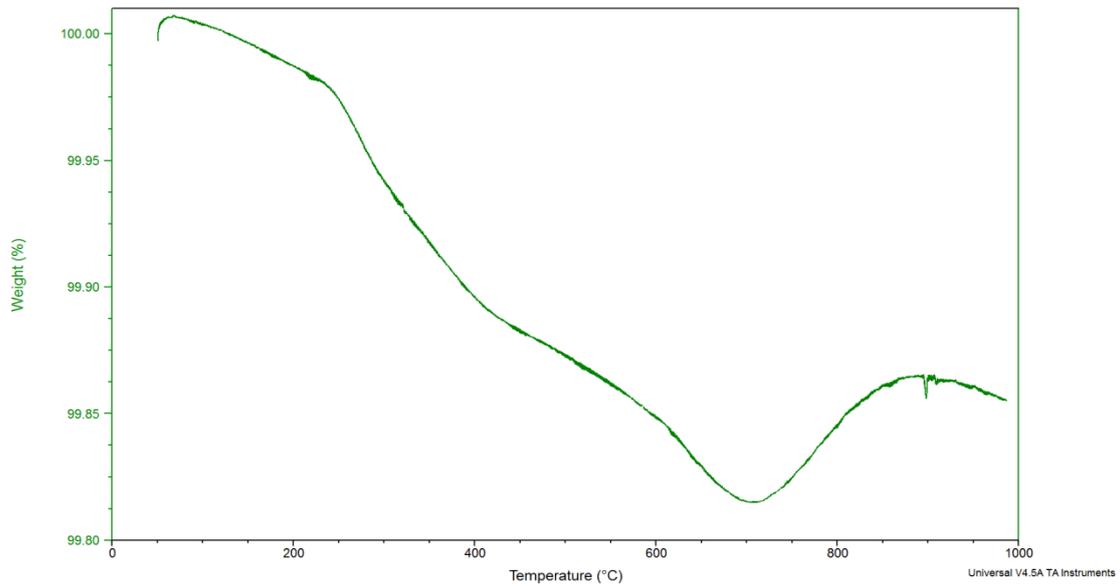
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644 Figure 7: Total gravimetric analysis (TGA) of the ceramic membrane. Top, before
645 functionalisation; Bottom, post functionalisation.
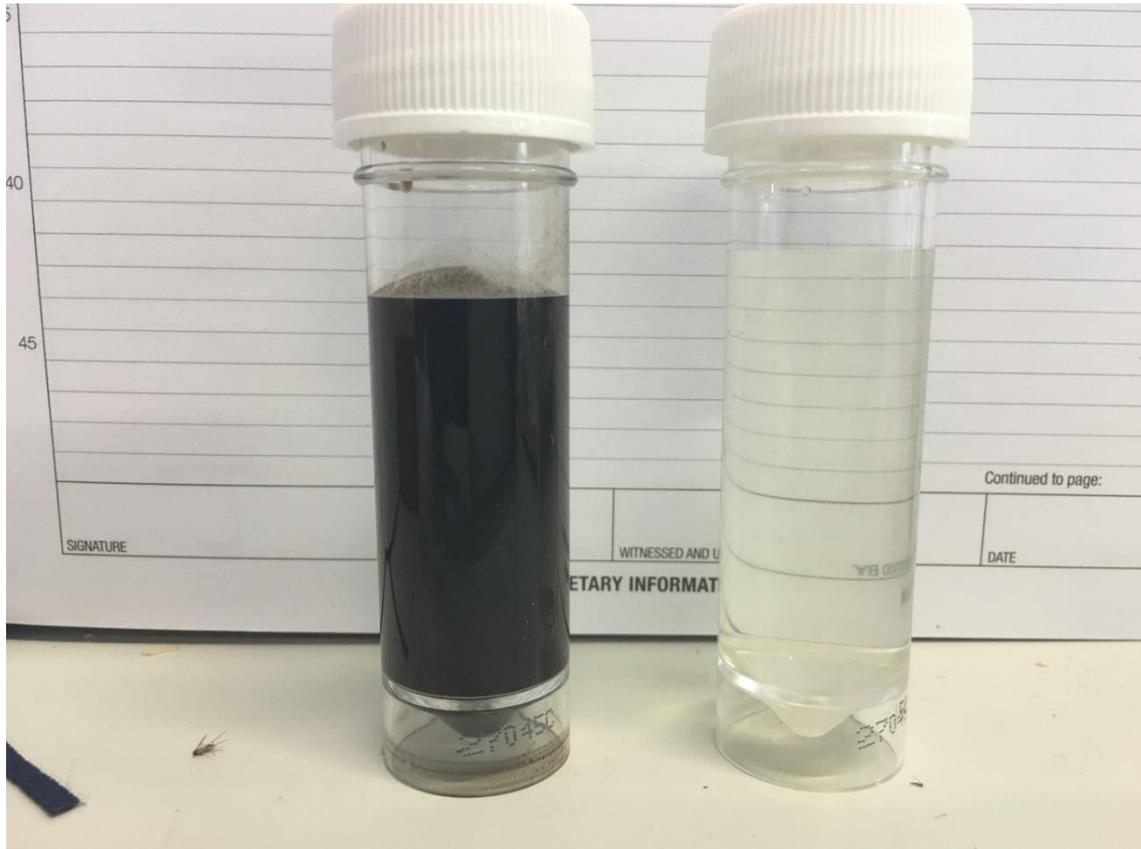
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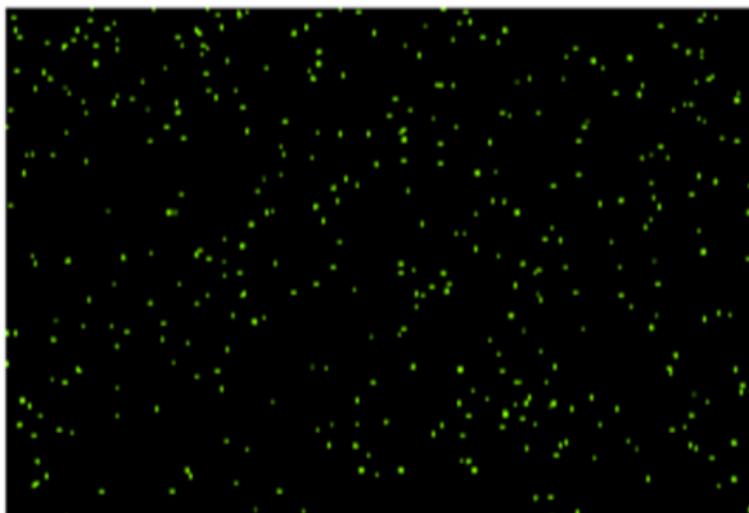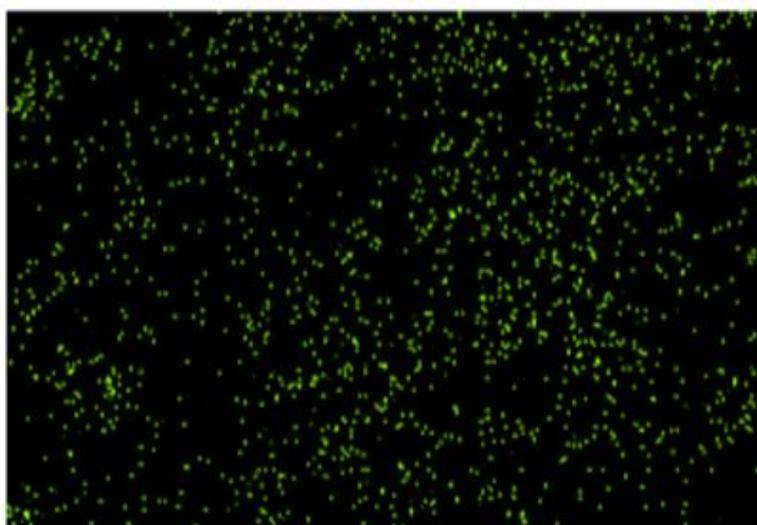
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655 Figure 8: An X-ray dispersive spectroscopy (EDX) image for sulphur obtained using the
656 scanning electron microscope (SEM) for the ceramic membrane. Top, prior to
657 functionalisation; Bottom, following 96 hour functionalisation process.
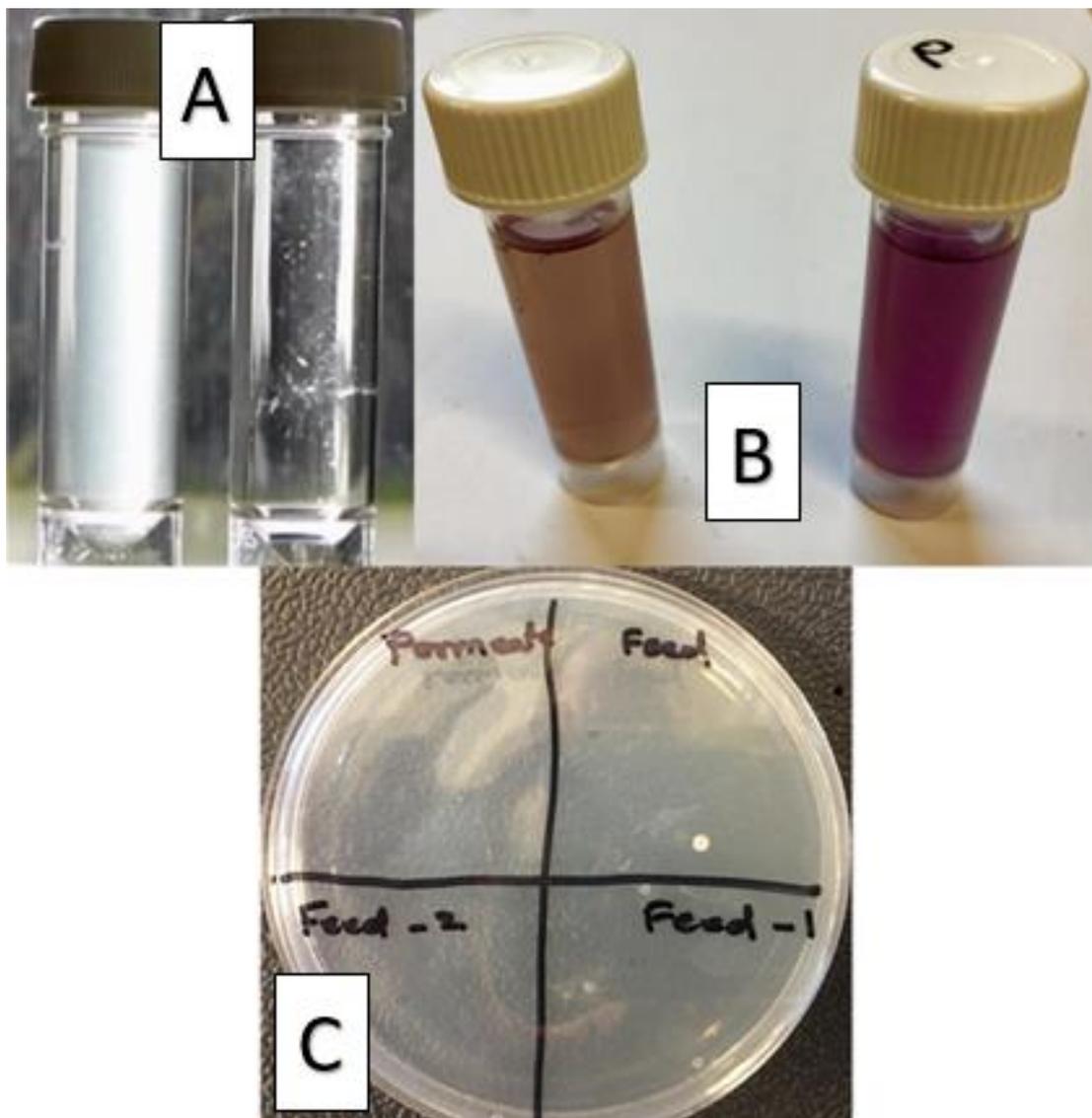
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Figure 9: Visible comparison of oil-water feed (left) and functionalised 0.2 μm membrane

663   permeate (right)

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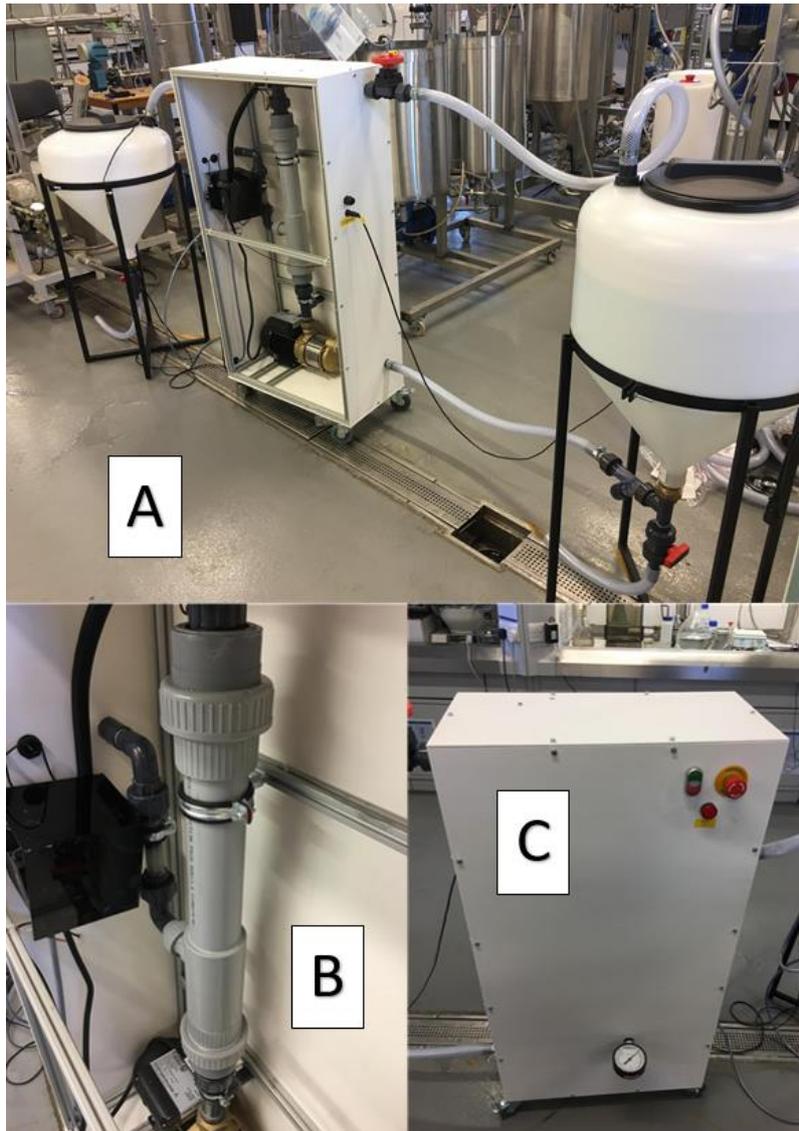
Figure 10: [A] Opacity difference between feed sample (left) and post SENTs filter (right), [B] visual bacteria test of feed sample (left) and membrane permeate (right) after 1 day, [C] bacterial growth on nutrient agar plate.

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Figure 11: [A] Rear view of prototype filtration system with back panel removed, feed tank

(right), system housing including membrane and adsorption pack (centre) and clean water

tank (left), [B] membrane and SENT adsorption pack close up, [C] front view of prototype

filtration system showing power control and pressure gauge.

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678   Figure 12: Prototype SENT adsorption pack