



Swansea University
Prifysgol Abertawe



Cronfa - Swansea University Open Access Repository

This is an author produced version of a paper published in:
Journal of Water Process Engineering

Cronfa URL for this paper:

<http://cronfa.swan.ac.uk/Record/cronfa34952>

Paper:

Ainscough, T., Alagappan, P., Oatley-Radcliffe, D. & Barron, A. (2017). A hybrid super hydrophilic ceramic membrane and carbon nanotube adsorption process for clean water production and heavy metal removal and recovery in remote locations. *Journal of Water Process Engineering*, 19, 220-230.

<http://dx.doi.org/10.1016/j.jwpe.2017.08.006>

This item is brought to you by Swansea University. Any person downloading material is agreeing to abide by the terms of the repository licence. Copies of full text items may be used or reproduced in any format or medium, without prior permission for personal research or study, educational or non-commercial purposes only. The copyright for any work remains with the original author unless otherwise specified. The full-text must not be sold in any format or medium without the formal permission of the copyright holder.

Permission for multiple reproductions should be obtained from the original author.

Authors are personally responsible for adhering to copyright and publisher restrictions when uploading content to the repository.

<http://www.swansea.ac.uk/iss/researchsupport/cronfa-support/>

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**

4 Thomas J. Ainscough^a, Perry Alagappan^b, Darren L. Oatley-Radcliffe^{*ab}, Andrew R. Barron^{ac}

5
6 ^a Energy Safety Research Institute (ESRI), Swansea University, Bay Campus, Fabian Way,
7 Swansea, UK

8 ^b Centre for Water Advanced Technologies and Environmental Research (CWATER), Swansea
9 University, Bay Campus, Fabian Way, Swansea, UK

10 ^c Department of Chemistry, Rice University, Houston, USA

11
12 *to whom correspondence should be addressed

13 Tel: + 44 (0)1792 606668

14 Email address: d.l.oatley@swansea.ac.uk

15
16 **Abstract**

17 A novel hybrid membrane-adsorption process has been developed for the production of
18 clean water supplies. A 0.2 μ m 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

37 **Keywords**

38 Wastewater, filtration, adsorption, carbon nanotube, functionalised membrane

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 is 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

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

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

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

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 0.2m² 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 $\mu\text{g/L}$ can be filtered to meet the current
343 EPA Maximum Contaminant Level Goal of 1 $\mu\text{g/L}$. However, even in extreme cases, heavy
344 metal levels have not been found to exceed 100 $\mu\text{g/L}$ 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
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 0.66m², 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.

502 **5 Conclusions**

503 An experimental super-hydrophilic functionalised ceramic membrane was combined with a
504 carbon nanotube adsorption unit for the production of clean water. The benefits of this
505 novel unit are reduced fouling of the membrane and heavy metal removal. Thus, the unit is
506 capable of producing a clean water supply with little or no microbial contamination and
507 removal of heavy metals often found in waste and ground waters in various parts of the
508 world. Laboratory trials with the new unit showed that the initial high flux (~1400 LMH/bar)
509 of the membrane could be maintained over a period of time. However, when exposed to
510 severe contamination (spent engine oil/water mixtures) the initial flux declined rapidly (to
511 ~100 LMH/bar) but was then stable over a significant period of time (10 days). The rejection
512 of the membrane was shown to be >99.5% for general hydrocarbons. The carbon nanotube
513 adsorbent was shown to remove various heavy metals (Cd, Hg, Ni, Co and Pb) to a high
514 degree (>99.3% in all cases) and was easily regenerated to almost complete adsorptive
515 capacity using simple solutions of 50:50 acetic acid:water.

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

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

528 **6 Acknowledgements**

529 Financial support to T.J. Ainscough was provided by the Robert A. Welch Foundation and the
530 Welsh government Ser Cymru programme.

531 The authors would like to thank Jeff Lucas and the team from Millions from One for financial
532 and logistical support in Guatemala and Jonathan Powell from Trainer BMW Swansea (UK)
533 for kind supply of used motor oils.

534 **7 References**

535 Adelana, S. and MacDonald, A. eds., 2008. Applied groundwater studies in Africa: IAH
536 selected papers on hydrogeology (Vol. 13). CRC Press.

537 ASTM F838-15a, Standard Test Method for Determining Bacterial Retention of Membrane
538 Filters Utilized for Liquid Filtration, ASTM International, West Conshohocken, PA,
539 2015, www.astm.org

540 Barnes, D., Collin, C. and Ziff, S., 2009. The Biosand Filter, Siphon Filter, and Rainwater
541 Harvesting. Strategic recommendations for new water treatment technologies and
542 safe water storage to pure home water. Submitted in partial fulfilment of the
543 requirements for, 1, pp.25-27.

544

545 British Geological Survey, Department of Public Health Engineering (Bangladesh).

546 2001 *Arsenic contamination of groundwater in Bangladesh*. British Geological
547 Survey, 630pp. (WC/00/019) (Unpublished)

548 Chandel, S. S., Naik, M. N., & Chandel, R., 2015. Review of solar photovoltaic water pumping
549 system technology for irrigation and community drinking water supplies. *Renewable
550 and Sustainable Energy Reviews*, 49, 1084-1099.

551 Duke, W.F., Nordin, R.N., Baker, D. and Mazumder, A., 2006. The use and performance of
552 BioSand filters in the Artibonite Valley of Haiti: a field study of 107 households. *Rural
553 Remote Health*, 6(3), p.570.

554 Eltawil, M. A., Zhengming, Z., & Yuan, L., 2009. A review of renewable energy technologies
555 integrated with desalination systems. *Renewable and Sustainable Energy Reviews*,
556 13(9), 2245-2262.

557 Howard, G. and Bartram, J., 2003. Domestic water quantity, service level, and health (p. 33).
558 Geneva: World Health Organization.

559 Islam, M.A., Karim, M.R., Higuchi, T., Sakakibara, H. and Sekine, M., 2014. Comparison of the
560 trace metal concentration of drinking water supply options in southwest coastal
561 areas of Bangladesh. *Applied Water Science*, 4(2), pp.183-191.

562 Lance Energy Services, LLC, Votaw, W.R., Davis, J.L., Munson, E.E., Barron, A. and Maguire-
563 Boyle, S.J., 2013. Functionalized Ceramic Membranes for the Separation of Organics
564 from Raw Water and Methods of Filtration Using Functionalized Ceramic
565 Membranes. U.S. Patent Application 14/084,195.

566 Loo, S. L., Fane, A. G., Krantz, W. B., & Lim, T. T., 2012. Emergency water supply: A review of
567 potential technologies and selection criteria. *Water research*, 46(10), 3125-3151.

568 Meybeck, M., Chapman, D.V. and Helmer, R., 1990. Global freshwater quality; a first
569 assessment, Global Environment Monitoring System. OMS.

570 Mwabi, J.K., Adeyemo, F.E., Mahlangu, T.O., Mamba, B.B., Brouckaert, B.M., Swartz, C.D.,
571 Offringa, G., Mpenyana-Monyatsi, L. and Momba, M.N.B., 2011. Household water
572 treatment systems: a solution to the production of safe drinking water by the low-
573 income communities of Southern Africa. *Physics and Chemistry of the Earth, Parts*
574 *A/B/C*, 36(14), pp.1120-1128.

575 Orbaek, A.W., Aggarwal, N. and Barron, A.R., 2013. The development of a 'process map' for
576 the growth of carbon nanomaterials from ferrocene by injection CVD. *Journal of*
577 *Materials Chemistry A*,1(45), pp.14122-14132.

578 Pokhrel, D., Bhandari, B.S. and Viraraghavan, T., 2009. Arsenic contamination of
579 groundwater in the Terai region of Nepal: an overview of health concerns and
580 treatment options. *Environment International*, 35(1), pp.157-161.

581 Pritchard, M., Mkandawire, T. and O'neill, J.G., 2007. Biological, chemical and physical
582 drinking water quality from shallow wells in Malawi: Case study of Blantyre,
583 Chiradzulu and Mulanje. *Physics and Chemistry of the Earth, Parts A/B/C*, 32(15),
584 pp.1167-1177.

585 Pritchard, M., Mkandawire, T. and O'neill, J.G., 2008. Assessment of groundwater quality in
586 shallow wells within the southern districts of Malawi. *Physics and Chemistry of the*
587 *Earth, Parts A/B/C*, 33(8), pp.812-823.

588 Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Mariñas, B. J., & Mayes, A. M.,
589 2008. Science and technology for water purification in the coming decades. *Nature*,
590 452(7185), 301-310.

591 Stauber, C.E., Elliott, M.A., Koksai, F., Ortiz, G.M., DiGiano, F.A. and Sobsey, M.D., 2006.

592 Characterisation of the biosand filter for E. coli reductions from household drinking
593 water under controlled laboratory and field use conditions. *Water science and*
594 *technology*, 54(3), pp.1-7.

595 Stauber, C.E., Ortiz, G.M., Loomis, D.P. and Sobsey, M.D., 2009. A randomized controlled
596 trial of the concrete biosand filter and its impact on diarrheal disease in Bonao,
597 Dominican Republic. *The american journal of tropical medicine and hygiene*, 80(2),
598 pp.286-293.

599 Tellen, V., Nkeng, G. and Dentel, S., 2010. Improved filtration technology for pathogen
600 reduction in rural water supplies. *Water*, 2(2), pp.285-306.

601 UNEP (2008), *Vital Water Graphics - An Overview of the State of the World's Fresh and*
602 *Marine Waters*. 2nd Edition. UNEP, Nairobi, Kenya. ISBN: 92-807-2236-0

603 UNICEF/WHO., 2015. *Key Facts from JMP 2015*.

604 United Nations, Department of Economic and Social Affairs, Population Division
605 (2015). *World Population Prospects: The 2015 Revision, Key Findings and Advance*
606 *Tables*. Working Paper No. ESA/P/WP.241.

607 Williams, S.R., 2015. *Recovery of small organics from natural sources using membrane*
608 *technology* (Doctoral dissertation, Swansea University).

609 Winter, T.C., 1998. *Ground water and surface water: a single resource* (Vol. 1139). DIANE
610 *Publishing Inc.*.

611

612

613 **Figures**



614
615
616
617
618
619
620
621
622
623
624
625

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.

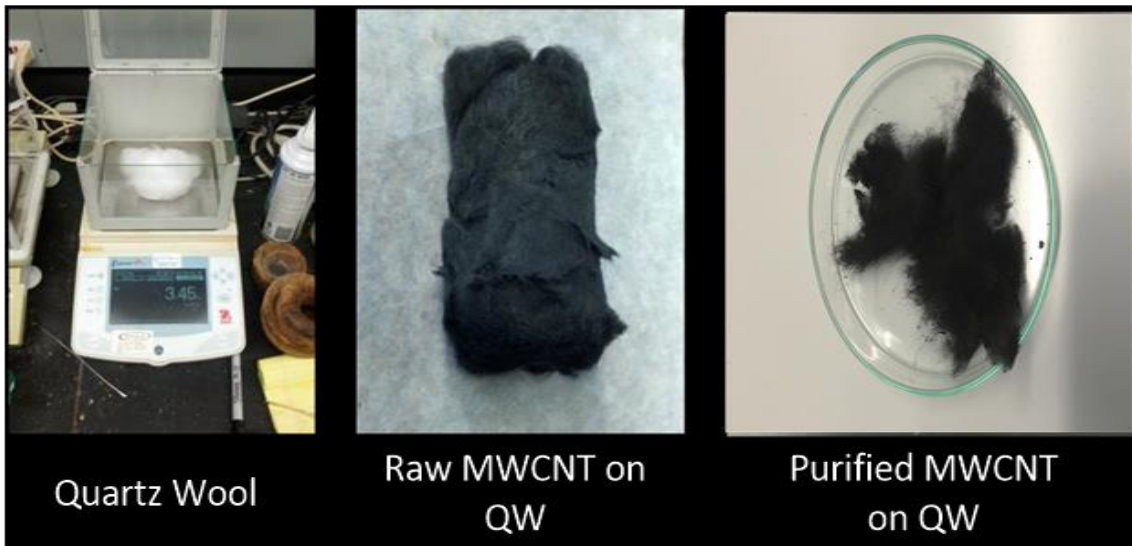


626

627

628

Figure 2: Ceramic membrane functionalisation equipment



629

630

631

Figure 3: Preparation stages for the novel adsorbent.



632

633

634

635

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



636

637

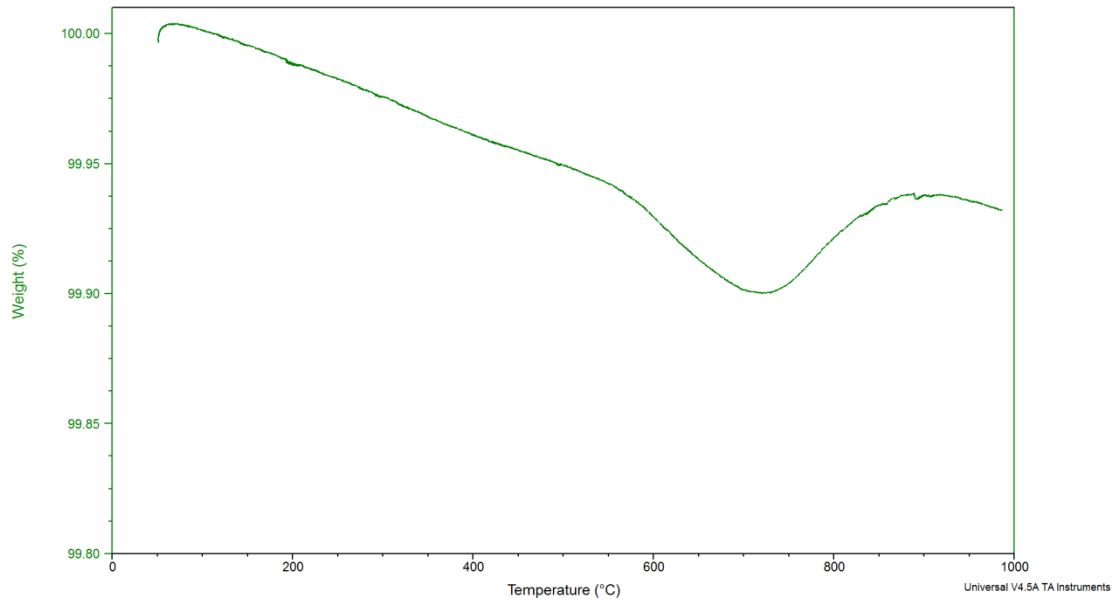
638

Figure 5: Modified Membranology filtration system during Guatemala trials

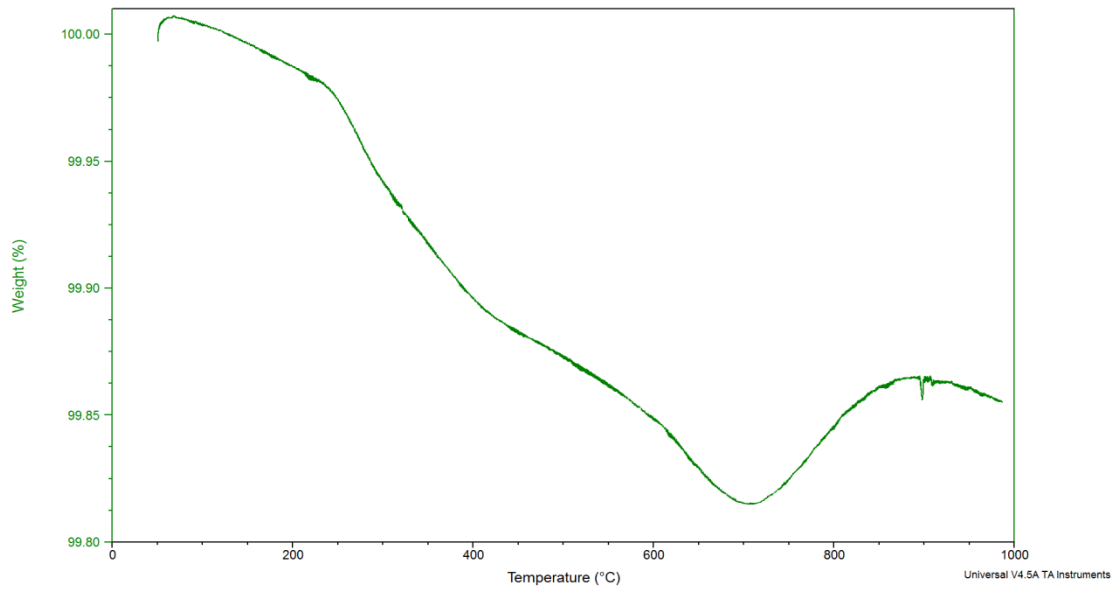


639
640
641

Figure 6: Original SENT adsorption pack as deployed in Guatemala



642



643

644 Figure 7: Total gravimetric analysis (TGA) of the ceramic membrane. Top, before
 645 functionalisation; Bottom, post functionalisation.

646

647

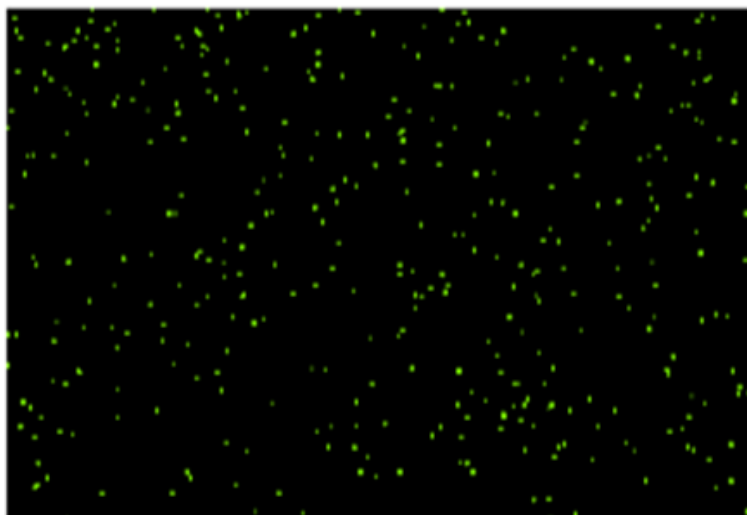
648

649

650

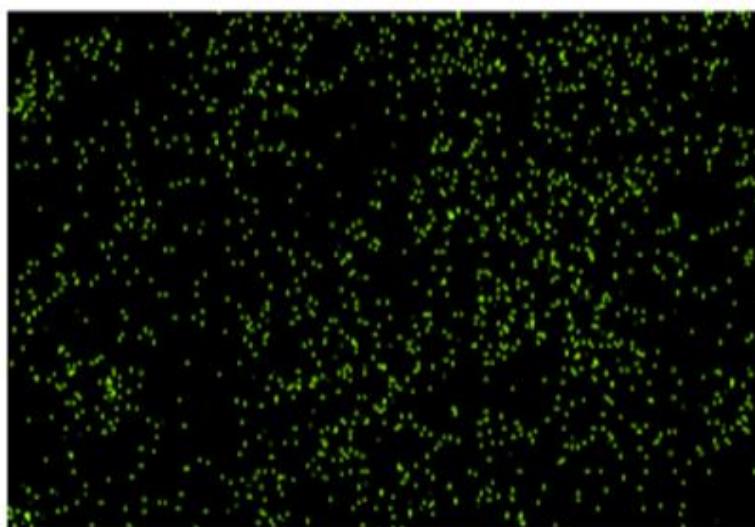
651

652



10µm

653



10µm

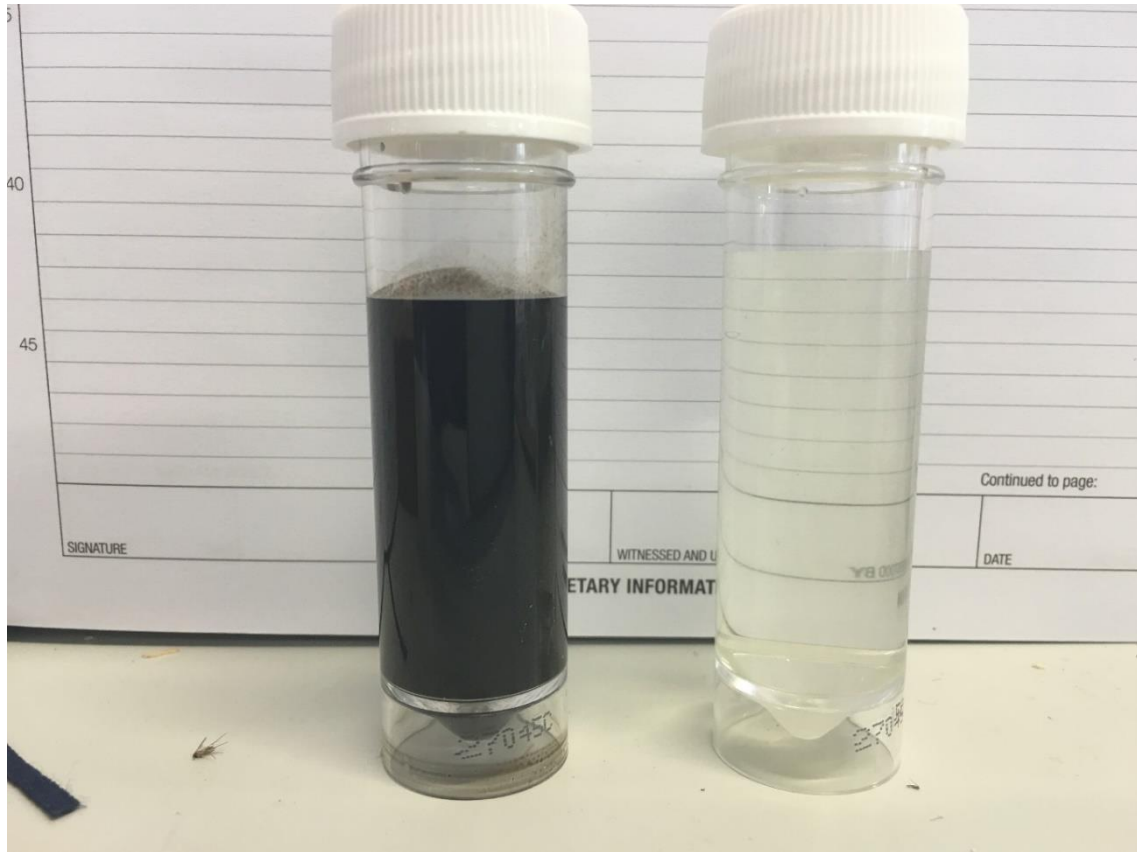
654

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.

658

659

660



661

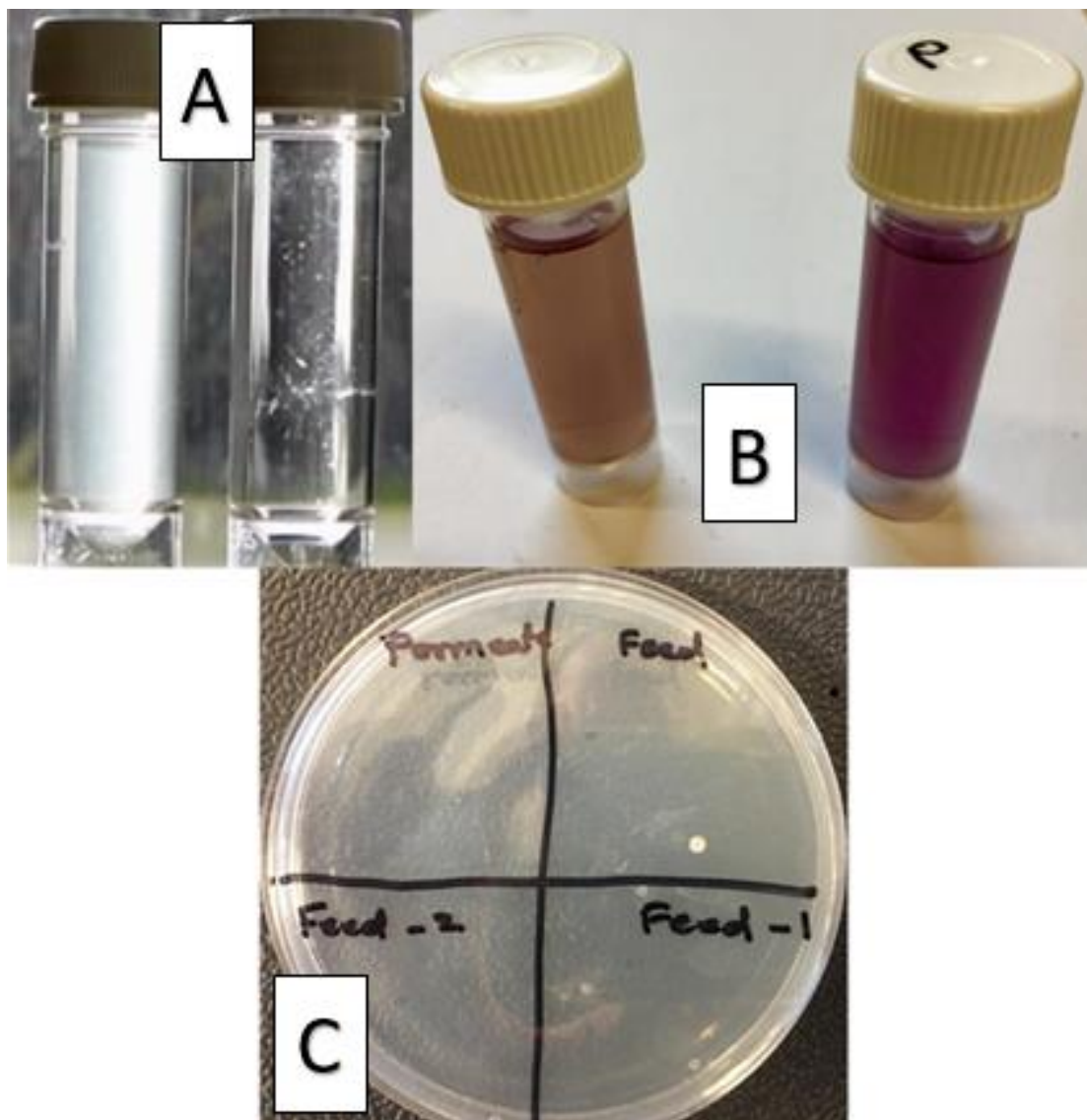
662

663

664

Figure 9: Visible comparison of oil-water feed (left) and functionalised 0.2 µm membrane permeate (right)

665



666

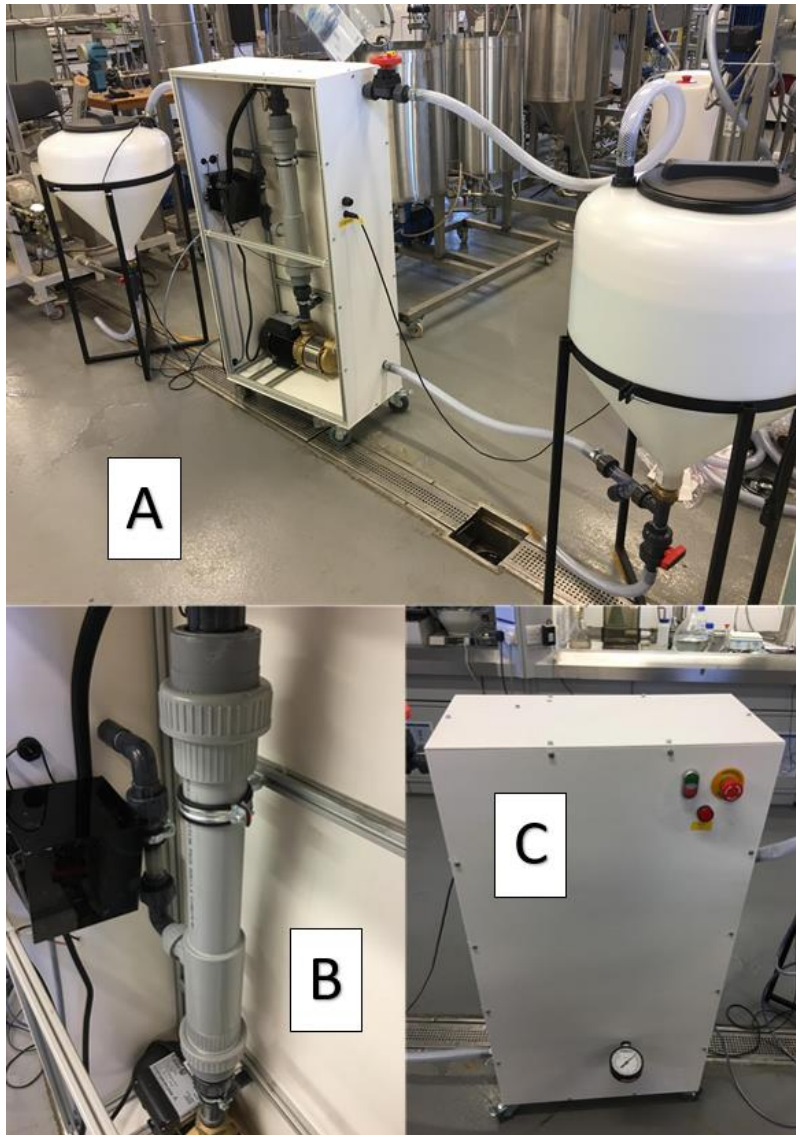
667 Figure 10: [A] Opacity difference between feed sample (left) and post SENTs filter (right), [B]

668 visual bacteria test of feed sample (left) and membrane permeate (right) after 1 day, [C]

669

bacterial growth on nutrient agar plate.

670



671
672
673
674
675
676

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.



677

678

Figure 12: Prototype SENT adsorption pack