# A contact angle study of different greywater sources with hydrophobic membranes

Mohammad Ramezanianpour, Muttucumaru Sivakumar, Natalie Osborn, Ying Zhang and Hakim Kawa

## ABSTRACT

The wetting phenomenon is a major problem in the membrane distillation (MD) process, and it is the main reason that limits MD being used in wastewater reclamation. Active surfactant in the detergents reduces the contact angle between the liquid and the hydrophobic membrane surface, which could result in wetting. Extensive laboratory research was conducted using commercial hydrophobic flat-sheet membranes to identify the impact of anionic surfactants and surface tension forces on these membranes. The aim of this paper is to find a suitable membrane for pure water production from greywater using MD, as well as to provide a relationship between surfactant concentration and the contact angle for different types of membrane. The absorbance of each sample was measured by a spectrophotometer prior to the contact angle test on four different types of hydrophobic membranes. It was concluded that the polypropylene membrane would be unsuitable for the treatment of greywater directly due to the loss of surface tension forces upon the addition of an anionic surfactant. However, the polytetrafluoroethylene membrane could be effective in this process while the concentration of surfactant in the feed source is kept constant. The results from the experimental tests proposed a relationship between the contact angle of a water droplet on the surface of a flat-sheet membrane and the concentration of surfactant in the solution.

**Key words** | contact angle, hydrophobicity, membrane distillation, wetting

**Mohammad Ramezanianpour** (corresponding author)
**Hakim Kawa**
Department of Engineering and Architectural Studies,
Ara Institute of Canterbury,
Christchurch,
New Zealand
E-mail: *matt.pour@ara.ac.nz*

**Muttucumaru Sivakumar**
**Natalie Osborn**
**Ying Zhang**
School of Civil, Mining and Environmental Engineering, Faculty of Engineering and Information Sciences,
University of Wollongong,
Wollongong, NSW,
Australia

## HIGHLIGHTS

- A comprehensive review of the contact angle test on hydrophobic membranes is required to specify its feasibility in the membrane distillation (MD) process.
- The characteristics of different polymer membranes, as well as recent data on contact angle measurement, classify membranes for greywater treatment.
- Surfactant is the main reason of reducing contact angle results in wetting phenomenon and is determined by measuring the linear alkylbenzene sulfonate (LAS) concentration.
- The relationship between the LAS concentration and the contact angle is provided.
- The PTFE membrane has the highest contact angle among the other types of membranes and is potential for greywater treatment using a suitable coating.

## INTRODUCTION

Growing demand of potable water has made municipal greywater reuse an attractive method to conserve available water supplies. The demand for water with quality lower than drinking water could account for over 50–80% of the water demand from domestic and industrial applications (Chin-Jung *et al.* 2005; Ramezanianpour *et al.* 2017). These

doi: 10.2166/wqrj.2020.021

can include use as process water, toilet flushing, garden water and car washing. Efforts to lower the overall water demand by increasing the efficiency of water supply systems and developing alternative water reuse systems including onsite greywater reuse have the potential to significantly impact mankind's dependency on potable water supplies (Friedler *et al.* 2005; Sivakumar & Ramezanianpour 2012).

Greywater refers to any domestic water generated from the shower, sink, bathtub, kitchen, hand basin and laundry with the exclusion of toilet water (Eriksson *et al.* 2002). The characteristics and physical parameters of greywater become important when assessing the potential for water reuse. For example, soap is an alkaline chemical generally present in greywater, and detergents such as linear alkylbenzene sulfonate (LAS) contain functional chemicals including surfactants. Domestic wastewater from baths, showers and hand basins contains soaps, shampoos, toothpaste, personal care products, skin residues, hair, hair dyes and body fats (Li *et al.* 2009). Thus, some odour, turbidity, bacteria, anionic surfactants including methylene blue active substances (MBAS) and high temperatures are present in these greywater sources. The range of water quality characteristics for different greywater sources is presented in Table 1. Laundry greywater is typically alkaline and contains a complex set of chemicals, elevated salinity levels, high concentration of bleaches, oils, paints, solvents and non-biodegradable fibres from clothing. Thus, the quantity of phosphates, nitrates, turbidity, oxygen demand and total suspended solids (TSS) needs to be considered for MD treatment.

LAS was introduced in 1964 as a 'readily biodegradable' replacement for the highly branched anionic surfactant (ABS) (Nimer *et al.* 2007). Being the major active surfactant in detergents, LAS is now the one with the single highest concentration in almost any detergent. By 2004, the production of LAS had reached 497 kton/year in Europe alone (Nimer *et al.* 2007). Close to 80% of this volume was produced for the intention of addition to household detergents, demonstrating the sheer volume of LAS that will be present in environmental wastewater discharge. LAS concentrations measured in a pilot study in urban sewers typically ranged between 2 and 5 mg/L (Whelan *et al.* 2007). A second monitoring study, using solid-phase extraction, was designed to track the behaviour of LAS in surface water streams which receive significant quantities of direct discharge wastewater. Aspects studied included in-channel solute transport using a pulse-injected tracer

**Table 1** | Range of typical greywater characteristics from different sources (Sivakumar & Ramezanianpour 2012)

| Parameter | Bathroom | Laundry | Kitchen | Mixed |
|---|---|---|---|---|
| Temperature (°C) | 29 | 28–32 | 27–38 | 18–38 |
| Turbidity (NTU) | 28–240 | 14–296 | 298 | 14–222 |
| pH | 6.4–8.1 | 8.1–10 | 6.3–7.4 | 5–8.7 |
| Total dissolved solids (TDS) (mg/L) | 126–218 | 504 | 873[a] | 135–368 |
| Total solids (TS) (mg/L) | 250–631 | 410–1,340 | 1,500–2,410 | 15.3–458 |
| TSS (mg/L) | 40–153 | 2.7–250 | 3.1–185 | 6.4–330 |
| Electrical conductivity (μS/cm) | 82–250 | 190–1,400 | – | 320–390 |
| COD (mg/L) | 24–633 | 12.8–725 | 3.8–1,380 | 13–590 |
| $BOD_5$ (mg/L) | 76–200 | 48–380 | 536–1,460 | 55–391 |
| TOC (mg/L) | 30–100 | 100–280 | 390–720 | 72.5–125 |
| TN (mg/L) | 5–17 | 0.28–21 | 0.31–74 | 0.54–18.1 |
| TP (mg/L) | 0.11–2 | 0.06–57 | 0.06–74 | 0.0064–0.6 |
| Total coliforms (cfu/100 mL) | $70–6 \times 10^6$ | $56–7 \times 10^5$ | $>2.4 \times 10^8$ | $7 \times 10^3–8 \times 10^7$ |
| Faecal coliforms (cfu/100 mL) | $1–6 \times 10^3$ | $9–1.6 \times 10^4$ | $1.3 \times 10^5–2.5 \times 10^8$ | $1–1.5 \times 10^8$ |

[a]Baskar *et al.* (2009).

and the collection of samples downstream. The study identified that LAS is rapidly removed from 513 ± 25 to 14 ± 2.9 μg/L, suggesting that the observed decrease in LAS concentration may result from in-stream degradation and sorption to sediment. The concentration of LAS in nature at different sources is shown in Table 2. High-performance liquid chromatography (HPLC) with fluorescence detection or a conductivity meter is the method used to record signals due to the presence of surfactants (Matthijs *et al.* 1999; Olsson *et al.* 2008).

Household greywater was characterised through the removal of organic matter and surfactants by direct nano- and microfiltration (Funamizu & Kikyo 2007). A variety of membrane pore sizes were investigated. It was concluded that the concentration of surfactant in the total volume of organic matter amounted to approximately 20–35% and that the total removal of anionic surfactants, classified as LAS, was significantly higher than the non-ionic surfactants at 92–98%. The LAS concentration was measured in terms of chemical oxygen demand (COD). It was determined through the measured mass concentration of LAS and the conversion factor from mass to COD unit. It was concluded that organic matter found in household wastewater is surfactant in its greatest percentage.

Pure water can be generated by evaporation and condensation from any water source as the process rejects all non-volatile constituents such as ions, dissolved non-volatile organics, colloids and pathogenic microorganisms. Based

**Table 2** | Concentration of LAS in different water sources

| Source | Concentration | Unit | Reference |
|---|---|---|---|
| Treated municipal sewage (effluent) Netherlands | 30–39 | μg/L | Olsson *et al.* (2008) |
| Raw and settled municipal sewage | 3 | mg/L | Olsson *et al.* (2008) |
| Influent sewage (average of individual plants) | 5.2 | mg/L | Olsson *et al.* (2008) |
| Wastewater treatment plant (WWTP) effluent | 19–71 | μg/L | Matthijs *et al.* (1999) |
| Urban and industrial WWTP-inlet stream | 8.7 | mg/L | Sanderson *et al.* (2006) |
| Effluent at downstream of the river | 740 | μg/L | Guckert *et al.* (1996) |

on simple physical principles, the natural process of evaporation and condensation can be engineered by creating a suitable vacuum at a lower feed temperature. Evaporation and condensation are employed in some distillation and desalination technologies. The process involved with the MD is driven by the temperature or pressure differences across a membrane. The creation of a certain pressure below the saturation pressure across the selected membrane allows the vapour molecules to evaporate from the feed solution (Santoro *et al.* 2017). The membrane is created in a way that would lead to a separation process through which only vapour molecules pass through a porous hydrophobic membrane to a permeate stream. Hydrophobic materials have no tendency to absorb water molecules, and the molecules tend to form discrete water droplets on the surface of the membrane. This property of the hydrophobic membrane materials leads to low wettability of the MD (Rezaei *et al.* 2017). On the feed side of the MD, the liquid feed, is in direct contact with a hydrophobic membrane at elevated temperatures (Eykens *et al.* 2017b). This principle can be applied to physical water treatment research in the form of vacuum MD (VMD). In VMD, a vacuum pump applies a pressure to the hollow fibre membrane module, lower than the saturation pressure of the influent.

During the MD process, the created membrane structure must be able to prevent the penetration of the liquid feed through the membrane (Lies *et al.* 2017). The penetration of feed solution into the membrane pores occurs if solutions with organic and/or inorganic compounds adsorb/deposit onto the membrane surface or if the transmembrane hydrostatic pressure surpasses the liquid entry pressure (LEP). While partial wetting of the membrane can lead to reduction in the permeate flux across the membrane, full wetting of the membrane can lead to the penetration of feed particles across the membrane resulting in the deterioration of permeate quality (Razmjou *et al.* 2012). Each membrane obtains a different LEP value which is established as a wetting criterion for the purpose of MD (Franken *et al.* 1987).

A number of polymeric and inorganic membranes are manufactured and can be used for the MD process which requires hydrophobicity characteristics of membranes. The polymeric membranes, however, have attracted more attention for MD use in different industries due to their low surface tension. Polytetrafluoroethylene (PTFE), polyvinylidenefluoride (PVDF) and polypropylene (PP) are the polymer membranes, which have been widely used in the MD process (Eykens *et al.* 2017b). Table 3 shows surface tension values for different polymer membranes. Among the common types of polymer, PTFE membranes are the most hydrophobic and show good thermal and chemical resistance (i.e. they have low solubility in most solvents). The main issue with PTFE membranes is the difficulty in processing, such as stretching and sintering during the manufacturing process. PP membranes have good solvent resistance, and they are also made through stretching or thermal-phase inversion. PVDF membranes exhibit efficient thermal and chemical resistance, but on the negative side they easily dissolve in most solvents (Eykens *et al.* 2017a).

A study of membrane characteristics is required for a practical application. The flux rate of permeate across the membrane is inversely proportional to the thickness of the membrane in the MD process. Very thin membranes, however, do lead to less stability and low thermal resistance in membranes. The optimum thickness for MD processing has been found to be within the ranges of 30–60 μm (Shirazi *et al.* 2014). Thermal conductivity of membranes in the MD applications should be as small as possible to avoid the transfer of heat across the membranes from the feed to the permeate side. Thermal conductivity of the polymer membrane used in the MD process is within the range of 0.15–0.45 $Wm^{-1} K^{\circ}$ (Charisiadis 2017). Also, the acceptable value of porosity for a membrane to work in MD processing is within 60–90% (Shirazi *et al.* 2014). A contact angle has less attention among the properties of the membrane.

The contact angle is defined as the angle at which the solvent molecule makes contact with the surface of the membranes or the angle formed between the solid/liquid interface. The contact angle can be used to measure the hydrophilic or hydrophobic capacity in a membrane. The higher the contact angle, the higher the resistance to wetting in a membrane. Measuring the advancing and receding liquid contact angles can determine the relative wettability of the membrane module. This is because perfect wetting and high wetting occur at the contact angle of 0° and below 90°, respectively. Membranes used in the MD process must have as high a contact angle as possible to achieve high hydrophobicity. Issues with the contact angle arise in the presence of strong surfactants such as those found in natural greywater, which significantly reduce the surface energy and therefore the contact angle (Lawson & Lloyd 1997). The contact angle values presented in Table 3 are reported in literature that have been measured using deionised water. The contact angle values for polysulfone (PS), polycarbonate (PC) and polyurethane (PU) membranes were reported as 144°, 91° and 136°, respectively, for the

**Table 3** | Membrane characteristics for different polymer membranes used in MD

| Polymer membrane | Thickness (μm) | Pore size (μm) | Porosity (%) | Surface tension (Dynes/cm) | Contact angle (°) | References |
|---|---|---|---|---|---|---|
| PTFE | 165–175 | 0.2–1.0 | 60–90 | 19 | 88–140 | Onsekizoglu (2012), Ramezanianpour & Sivakumar (2017) and Szczerbińska *et al.* (2017) |
| PVDF | 100–125 | 0.2–0.45 | 66–85 | 25 | 82–143 | Onsekizoglu (2012), Ramezanianpour & Sivakumar (2017), Szczerbińska *et al.* (2017) and Woo *et al.* (2017) |
| PP | 60–150 | 0.1–0.73 | 70–85 | 29–34 | 93–138 | Onsekizoglu (2012), Ramezanianpour & Sivakumar (2017) and Szczerbińska *et al.* (2017) |
| Polyethylene (PE) | 45–65 | 0.05–0.2 | 50–66 | 31 | 83–108 | Onsekizoglu (2012) and Zuo *et al.* (2016) |
| Polyvinyl alcohol (PVA) | 93–125 | 0.13–0.24 | 86–92 | 37 | 122–145 | Onsekizoglu (2012) and Woo *et al.* (2017) |
| PS | 30 | 0.6 | 48–64 | 41 | 144 | Huang & Yang (2006) and Onsekizoglu (2012) |
| PC | 24 | 0.2 | 10 | 45 | 91 | Onsekizoglu (2012) and Servi *et al.* (2017) |
| PU | 20 | 1.06 | 47–69 | 45 | 136 | Onsekizoglu (2012) and Gu *et al.* (2018) |

transition from hydrophilic to hydrophobic (Tian *et al.* 2015; Servi *et al.* 2017; Gu *et al.* 2018). A range of common detergents were tested to demonstrate the reproducibility and precision of a unique principle through which surfactant concentrations could be measured by comparison of contact angles (Kaufmann *et al.* 2006). This is a representation of the surface tension forces between the fluid and the membrane surface. A 20 μL droplet of detergent solution was deposited onto a slide of Parafilm M, and the side angles were recorded by two cameras. A comparison of the contact angle observed by the camera, with calibration curves of known detergent concentration, allowed the determination of the concentration of the detergent assessed.

Since some of these membrane modules were originally fabricated for use in microfiltration, their operational performance in MD is generally restricted due to porosity and pore size distribution. In light of these limitations, some researchers are focusing on the coating or chemical surface modification and fabrication of the flat-sheet hydrophobic membrane with a view to improving hydrophobicity beyond the commercial standard (Teoh & Chung 2009). Both asymmetric porous and symmetric dense polymeric membrane modules were considered when measuring the water contact angles of two flat-sheet hydrophobic membranes: PVDF and a copolymer of tetrafluoroethylene and vinylidene fluoride (Feng *et al.* 2004). The contact angle to distilled water was enhanced from 80.0° to 88.5° by the phase inversion process. With both membrane types, the permeate flux gradually increases with an increasing mean temperature difference, which is attributed to the water vapour pressure gradient across the membrane. The contact angles of two PVDF membranes with differing surface treatments were measured to achieve significantly varied results using a 8 μL water droplet (Peng *et al.* 2005). A smooth and dense PVDF membrane sample, manufactured using hot pressing, produced a contact angle of 82.0 ± 0.5°. A second PVDF sample, manufactured by the phase inversion technique and using deionised water in a soft precipitation bath, produced entry and exit contact angles of 85.2 ± 3.2° and 142.6 ± 1.3°, respectively. The greatly enhanced hydrophobicity is concluded to be the result of the asymmetric structure and the phase inversion technique preventing the formation of a dense skin layer on the membrane surface.

A pure PVDF hollow-fibre membrane was modified with the particle loading of PTFE to the polymer matrix (Teoh & Chung 2009). The contact angle for the original sample was found to be 88 ± 2°. The introduction of the PTFE particles in ratios of 30 and 50 wt.% increased the water contact angle to 93 ± 3° and 103 ± 3°, respectively. Lowering the surface tension as a result of the surface presence of PTFE particles (from 30.3 to 9.1 kN/m) may be the causative factor in increasing the contact angle. Although permeation flux across the membrane surface increased with feed temperature, the introduction of PTFE particles significantly reduced the flux performance of the membrane.

The performance of a laboratory-fabricated hollow-fibre PVDF sample prepared by the 'dry-jet wet phase inversion' process was assessed (Wang *et al.* 2008). The contact angle with distilled water was measured to be 112 ± 3°. This was used to specify the membrane's suitability for use in MD applications and is comparable to or superior to most of the PVDF hollow fibre membranes that are commercially available. The suitability of a commercially available PTFE membrane sample for DCMD application was investigated (Hwang *et al.* 2011). The contact angle was measured using the SV Sigma 701 Tensiometer from KSV Instruments Ltd (Helsinki, Finland). The reported contact angle was 122 ± 5° which was the average of three values. The membrane characteristics were studied to see the impacts on hydrophobicity as well as the rate of the permeate flux. These studies monitored the membrane characteristics in MD processes; however, the studies have not considered the impact of impurities in feed solution.

## MEMBRANE WETTING BY SURFACTANT

Over the last decade, the number of technical papers published on the application of MD systems in different industries has increased sharply; however, few have focused mainly on the wetting phenomenon (Figoli *et al.* 2017). Surfactants or oil traces existed in the feed stream reducing the surface tension and contact angle resulting in increased risk of membrane wetting in many wastewater treatment applications. The importance of water reuse by means of wastewater treatment through MD technologies has been emphasised since MD technology can recover useable water from wastewater (Shirazi *et al.* 2014). It is also concluded that the wetting in MD limits the use of MD in wastewater treatment industry. Wastewater mixtures include surfactants that increase the wettability of the membrane structure followed by membrane fouling.

Different techniques of membrane production were outlined in the research including stretching, phase inversion, nanofibers, carbon nanotubes, chemical modification of the membrane surface, plasma modification and surface-modifying macromolecules (De Sitter *et al.* 2014). In the case of membrane coating, the research concluded that all forms of surface modification with the use of coating resulted in a better performance of different types of MD technologies. The hydrophobicity of the membrane increased by coating in most cases; however, the stability of the coating materials on the surface of the membrane was noted as an issue. It was shown that the PTFE membranes coated with nanoparticles are more stable for treatment and are more reliable in terms of the wettability issue (Xu *et al.* 2017). The fabrication of a full-ceramic membrane was presented that would be suitable for different MD applications. A super-hydrophobic PP hollow fibre membrane was also prepared by the fabrication method (Xu *et al.* 2017). The coating was applied to the very smooth PP membrane surface using collosol mixed with silica particles and PP particles. The membrane was modified and tested for contact angle showing a static water contact angle of 157°.

The development of a coating method was studied to overcome the issue of wetting in MD for the treatment of sea water (Huang *et al.* 2016). The main aim of the research was to form a superhydrophobic solid layer on the surface of the membrane. The coating was formed by a silica/alumina nanoparticle. With the use of such a coating, a high flux of 29.3 L/$m^2$ h with a salt rejection rate of 99.9% was obtained at an operating temperature of 70 °C. In this study, a solid layer on a ceramic alumina substrate for vacuumed MD without sintering was created. A nanotype particle for the coating of the membrane surface was used to overcome wetting (Rezaei *et al.* 2017). The membrane wetting issue was improved with the use of $SiO_2$ nanoparticles on the surface of a PP membrane. The main objective of the coating in this study was to investigate how the coating of the PP membrane with $SiO_2$ would change the membrane surface roughness and the contact angle. Finally, it was described how the variation in these parameters would affect the wettability of the PP membrane. With the use of nanoparticles for the coating of the membrane, the roughness of the PP membrane surface increased from 126 to 160 nm. The water contact angle also increased from 139° to 154° accordingly. It was concluded that such an increase in water contact angle enhanced the liquid repelling property and therefore decreased wettability of the PP membrane. The inclusion of coating chemicals on the surface of membranes could be a challenging issue. Sometimes, the coating particles do not form good bonding with the membranes, and they are easily washed off with the feed solutions. Another problem with the coating is that the coating chemicals might not be chemically, or structurally strong enough to withstand the high temperature of the feed solvent, and the coating could therefore be easily damaged over time.

Electrospinning is used for super hydrophobicity on a PVDF–hexafluoropropene electrospun membrane which was fabricated by hybridising polydimethylsiloxane polymeric microspheres (An *et al.* 2017). The membrane presented a significant enhancement in the contact angle for the removal of dyes from industrial wastewater. The membrane roughness and contact angle increased to 1,285 nm and 155.4°, respectively. Stronger repulsive force between a dye and the membrane is the result of higher hydrophobicity of the membrane. Superhydrophobic PVDF membranes demonstrated strongly negative charges on the membrane surface (Chen *et al.* 2017). The MD performance was then stable in concentrating the anionic surfactant emulsified wastewater; however, the wetting phenomenon was observed when cationic surfactant was used. The cationic surfactant strongly adheres to the negative fabric surfaces. MD applications for wastewater treatment were impacted by the remaining surfactants or oil traces in the source. During the process, the concentration of surfactants would increase and result in major reduction in the contact angle. The VMD performance for greywater treatment requires a comprehensive study of greywater characteristics, membrane characteristics and data analysis in order to provide suitable solutions.

Previous studies show that it is necessary to measure the concentration of organic compound in the feed solution. More studies are required to create a membrane that would provide higher wettability resistance. Improvement in the membrane properties that would increase its resistance to wetting while maintaining membrane stability will drive the use of MD technology on a large scale in the future. Therefore, in this study, it is aimed to predict the relationship between LAS concentration and the contact angle. This research also aims to prevent the wetting of the membrane pores by selecting the most appropriate hydrophobic material for the treatment of greywater by the VMD process.

## MATERIALS AND METHODS

Membrane pore wetting is influenced primarily by pore size, surface tension and the contact angle between the absorption liquid and the membrane material, as calculated by the Laplace equation (Lv *et al.* 2010):

$$\Delta P = \frac{(-2\gamma \cos \theta)}{r} \qquad (1)$$

where $\Delta P$ (Pa) represents the pressure difference across the membrane pores, $\gamma$ (N/m) is the liquid surface tension, $\theta$ is the liquid–solid contact angle and $r$ (m) is the pore radius. From this equation, it is clear that for $\Delta P$ to be positive, $\theta$ must be above 90°. Equation (1) also illustrates that an increase in membrane pore size or a decrease in liquid surface tension or contact angle accelerates the wetting phenomenon.

The concentration of anionic surfactants in greywater and the impact of surface tension forces on the membrane surfaces have to be analysed in this research. LAS, being approximately 7.5% of the dry weight of detergent, is the surfactant found in highest concentrations in environmental streams (Olsson *et al.* 2008). To develop a relationship between the concentration of anionic surfactants and surface tension forces on the membrane, measurement of the contact angle between the surface of a number of flat-sheet hydrophobic membranes and solutions of a known concentration of the surfactant is necessary. Initially, the contact angle must be tested using pure, deionised water (Milli-Q) on the membrane surface.

A variety of standard methods is available for measuring detergents or quantifying the surfactants not reacting with colorimetric methods. An appropriate instrumental analysis such as HPLC or gas chromatography can be used for this purpose. The Standard Methods 5540 for surfactants details the procedure for analysing the concentration of anionic surfactants as a measure of MBAS, calculated as LAS (mol. wt.) (Eaton 2005). The acclaim surfactant column is mentioned as an automated and cost-effective way to determine LAS concentration in river and water streams, utilising the online solid-phase extraction (SPE) software combined with a specialty polar-embedded reverse-phase column (Liu & Pohl 2006). A two-step process for determining LAS concentrations in agricultural soil (ultrasound-assisted with methanol and preconcentration of the LAS by SPE on two adsorbent cartridges) has also been listed (Nimer *et al.* 2007). Separation and quantification from this process must be performed by liquid chromatography with fluorescence detection.

In this research, the standard method of MBAS is standardised by the LAS concentration which is diluted into distilled and Milli-Q water at a known concentration while the contact angle is measured. The disparity can be calculated as a percentage reduction in surface tension as a result of the presence of LAS and a calibration curve of contact angle versus LAS concentration produced. The colorimetric method (MBAS method) and a calibration curve are used to compare samples of synthetic and natural greywater from different sources to accurately determine their respective concentrations of LAS.

This research employs a sample of synthetic greywater modelled on the constituents outlined in the CSIRO's Greywater Technology Testing Protocol (Diaper 2001). For a litre sample of greywater, 15 mg of sunscreen, 32.5 mg of toothpaste, 10 mg of deodorant, 35 mg of $Na_2SO_4$, 25 mg of $NaHCO_3$, 39 mg of $Na_2PO_4$, 720 mg of shampoo and 150 mg of laundry powder were mixed in a 500 mL warm water. Then, 1.4 mg of boric acid, 28 mg of lactic acid, 7 mg of oil and 50 mg of clay were added and mixed for 24 h. Three samples were taken to measure the water quality parameters. The average of turbidity, COD, TSS, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and faecal coliform was 60.8 NTU, 664 mg/L, 180 mg/L, 54.5 mg/L, 2.67 mg/L, 39.4 mg/L and 700 cfu/100 mL.

A Ramè-Hart Goniometer (Model 200 Series F1) measures the left, right and mean contact angle (°) of a droplet on a surface using a camera and the computer software.

**Figure 1** | Goniometer components and water droplets on a surface of hydrophobic membrane.

The goniometer shown in Figure 1 calculates the advancing and receding contact angles by taking a two-dimensional measurement of the angle formed between the solid and the drop profile.

The static contact angle between Milli-Q water and four micro-porous, flat-sheet membranes was measured to evaluate the membrane hydrophobicity by the sessile drop method with a Ramè-Hart goniometer. Milli-Q water (3 μL) was carefully dropped on the membrane surface, and the contact angle was determined within 10 s of the water being dropped. The contact angle was measured 10 times at each of 10 various positions on one sample, and the mean values were reported. Four different types of membrane flat sheets were used in this research. The characteristics of the membranes are presented in Table 4. Nominal pore size between 0.1 and 0.45 μm was used which is applicable for MD systems. Different pore sizes were selected for the two PTFE membranes to monitor the impact of pore size. The contact angle for each membrane was tested using Milli-Q water sample.

A contact angle greater than 100° must be achieved before the membrane can be considered an appropriate material for VMD proceeded by the treatment of greywater (Qtaishat *et al.* 2009). Therefore, the same samples of household and synthetic greywater were collected and their contact angle was also measured. First, four calibration curves were graphed by measuring the contact angle of the LAS stock solutions on each of the flat-sheet membranes in concentrations of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 5.0 and 10 mg/L, respectively. The contact angle was plotted versus LAS concentration on a semi-log graph. Secondly, the contact angle of the natural and synthetic greywater samples was measured for each flat-sheet membrane and recorded.

**Table 4** | Membrane characteristics

| Name | GORE PTFE | Magna PVDF | Fluoropore (Millipore) | Microdyn PP 0.2 |
|---|---|---|---|---|
| Membrane material | PTFE | PVDF | PTFE | PP |
| Support material | Scrim/staple | PP | – | PP |
| Nominal pore size | 0.10 μm | 0.22 μm | 0.45 μm | 0.20 μm |
| Total thickness | 1.07 mm | 175 μm | 50 μm | 0.65 mm |
| Maximum operating temperature | 60 °C | – | 130 °C | 60 °C |
| Measured contact angle | 128.5° | 108.5° | 153.6° | 95.7° |

Once the MBAS absorbance tests have yielded the concentration of LAS (in mg/L) for each greywater sample, these values can be substituted into the logarithmic line equations for the contact angle, to give the expected contact angle for each sample. The purpose of this experiment is to determine the concentration of LAS in a number of natural, household greywater samples by infrared spectrometry; the purpose being to detect what impact it has on contact angle and therefore surface tension. LAS is the most widely used anionic surfactant and is used to standardise this method. Firstly, three successive extractions of methylene blue (cationic dye) with an anionic detergent in which the neutral compounds produced are extracted into chloroform ($CHCl_3$). Secondly, aqueous backwash and measurement of the blue colour in the $CHCl_3$ by spectrophotometry at 652 nm are carried out. This method can be applied to MBAS to a minimum of 0.025 mg/L (Seng *et al.* 2007).

The following natural, household greywater samples were prepared:

- Laundry: wastewater from each cycle of one full load and containing one regular scoop of 'Trimat' top loader washing powder.
- Shower: wastewater from one shower cycle.
- Kitchen (1): collected after hand washing only one or two dishes.
- Kitchen (2): collected on a separate day and after hand washing a full load of dishes.
- Mixed (1): mixed 30 mL each of laundry, shower and kitchen (1).
- Mixed (2) is the more accurate mixing of the natural greywater samples based on average household usage as kitchen (2) 12.25%, laundry 40.82% and shower 46.94%.
- Synthetic greywater was produced using the following procedure and based on the CSIRO's standard recipe as shown in Table 5 (Diaper *et al.* 2008).

**Table 5** | Recipe for 1 L of synthetic greywater

| Ingredient | Amount in 1 L (g) | Product Used |
|---|---|---|
| Sunscreen | 0.015 | UV Triple Guard |
| Toothpaste | 0.0351 | Colgate Maximum Cavity Protection (regular) |
| Deodorant | 0.015 | Mum |
| $Na_2SO_4$ | 0.0337 | Analytical Grade |
| $NaHCO_3$ | 0.0269 | Analytical Grade |
| $Na_2HPO_4$ | 0.0386 | Analytical Grade |
| Vegetable oil | 0.007 | Coles Own Brand |
| Shampoo and handwash | 0.72 | Palmolive |
| Laundry detergent | 0.1575 | Omo High Performance 2 × Concentrate |
| Boric acid | 0.0015 | Analytical Grade |
| Acetic acid | 0.028 | Analytical Grade |
| Secondary effluent | 20 mL | Treatment Plant at Coniston, Illawarra |

## RESULTS AND DISCUSSION

The results obtained within the scope of this research compared with those in previous literature reflect the fact that PTFE membranes are more effective material when considering suitability for VMD applications. When tested using Milli-Q water, the PTFE 0.45 μm (fluoropore) flat-sheet membranes were found to have the largest water contact angle at 153.64°. Second was the GORE PTFE 0.1 μm, having a mean contact angle of 128.5°, then MAGNA PVDF 0.22 μm having a mean angle of 108.5° and finally the Microdyn PP 0.2 μm membrane with a contact angle of 95.70°. Figure 2(a) represents the profile of a water droplet on the surface of the PTFE 0.45 μm membrane with a contact angle of 146.9° Figure 2(b) represents the profile of a water droplet on the surface of the GORE PTFE membrane with a contact angle of 117.9°. Figure 2(c) represents the profile of a water droplet on the surface of the PVDF membrane having a contact angle of 108°. Figure 2(d) represents the profile of a water droplet on the surface of the Microdyn PP 0.2 μm membrane having a contact angle of 94.0°.

A calibration curve was plotted for each flat-sheet membrane using data in Table 6 and is shown in Figures 3–6. Contact angle values are in accordance with the standard LAS solutions tested on each membrane. For the LAS concentration between 0 and 10 mg/L, PTFE 0.45 μm achieved the contact angle from 153.46° to 129.11°, GORE PTFE 0.1 μm achieved the contact angle from

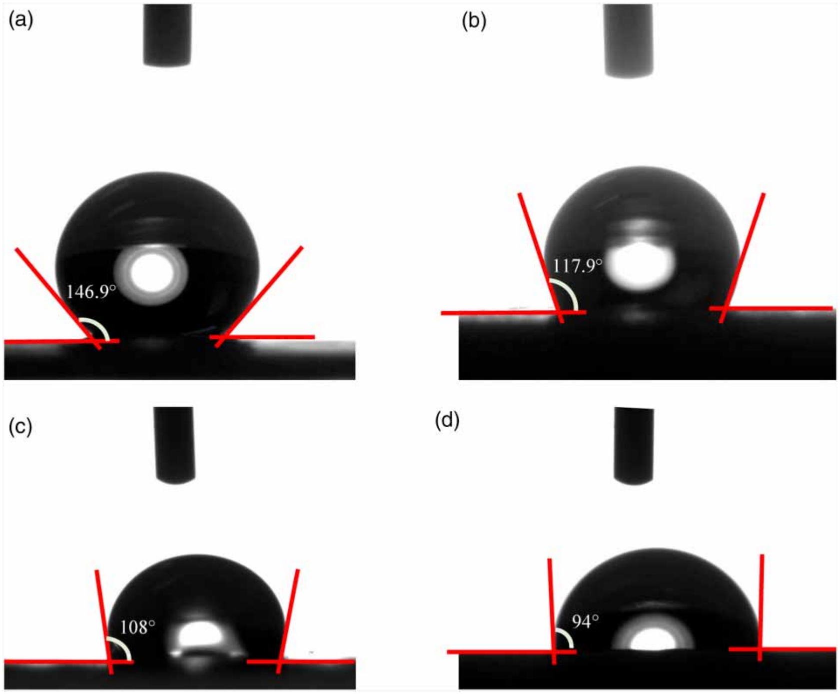


**Figure 2** | Water droplet on surface of (a) PTFE 0.45 μm membrane sheet, (b) PTFE 0.1 μm membrane sheet, (c) PVDF 0.22 μm membrane sheet and (d) PP 0.2 μm membrane sheet.

128.5° to 88.38°, MAGNA PVDF 0.22 μm achieved the contact angle from 108.5° to 85.4° and Microdyn PP 0.2 μm achieved the contact angle from 95.7° to 87.73°. A logarithmic trend line was added to the data series along with the equation of that line displayed along with an $R^2$ value describing the accuracy with which the trend line is fitted to the calibration data. The trend lines in the calibration curves all have $R^2$ values of at least 95%; therefore, the logarithmic equations can be considered to be an acceptable representation of the behaviour of the calibration curve and thus, the relationship between the contact angle and the concentration of LAS. It is clear that the increase in concentration of LAS will decrease the contact angle rapidly in a logarithmic approach. The rate of decrease in the contact angle is considerable in PTFE types of the membrane which is −2.602 and −4.381 in a log scale. Although the initial contact angle is high in PTFE types, however the presence of LAS can significantly reduce the angle. The PP membrane sample presented the lowest rate of decrease which is −0.825 in a log scale.

The LAS stock solutions were processed using the method outlined in methodology and their absorbance measured next to a blank of chloroform using a UV-1700 PharmaSpec visible spectrophotometer (Shimadzu) at 652 nm. The results of this experiment are presented in Table 7. The more absorbance is achieved for the higher concentration of LAS. Similarly, the absorbance of natural household and synthetic greywater samples was also tested for their respective absorbance using the same method. The results are shown in Table 8.

The results of this experiment, using the LAS stock solutions, were used to plot the calibration curve of *Absorbance versus LAS concentration*: The linear relationship between the absorbance and the LAS concertation was derived as shown in Figure 7. It is shown that for a 10 mg/L concentration increase, spectrophotometer rises 1.5 absorbance value. The absorbance of the greywater samples (Table 8) was substituted in the trend line formula to determine the concentration of LAS in their solutions. It was observed that the concentration of LAS in the greywater samples is between 10 and 20 mg/L. Most of the greywater samples including the synthetic one have the LAS concentration between 15 and 20 mg/L. Mixed greywater and synthetic sample represents average absorbance reading among all greywater sources. The final concentrations for each greywater sample are calculated in Table 9.

**Table 6** | Average contact angle for each LAS solution for different membranes

| Membrane | PTFE 0.45 μm | | | PTFE 0.1 μm | | |
|---|---|---|---|---|---|---|
| LAS (mg/L) | Contact angle (°) | Std. Deviation | Range (%) | Contact angle (°) | Std. Deviation | Range (%) |
| 0.00 | 153.64 | 4.032 | 5.467 | 128.5 | 1.042 | 2.957 |
| 0.01 | 147.67 | 4.807 | 7.178 | 125.21 | 1.444 | 3.115 |
| 0.02 | 142.35 | 3.983 | 6.393 | 119.81 | 1.95 | 4.090 |
| 0.05 | 140.12 | 3.123 | 5.567 | 116.11 | 1.048 | 1.895 |
| 0.1 | 139.11 | 3.003 | 5.320 | 114.43 | 2.868 | 5.942 |
| 0.2 | 137.78 | 0.038 | 0.073 | 113.23 | 0.117 | 0.265 |
| 0.5 | 135.87 | 3.384 | 5.962 | 110.73 | 2.439 | 4.515 |
| 1 | 133.07 | 2.99 | 5.411 | 104.36 | 1.6899 | 3.737 |
| 2 | 132.27 | 4.467 | 8.468 | 99.35 | 0.069 | 0.302 |
| 5 | 130.97 | 3.910 | 8.323 | 93.98 | 0.4782 | 1.064 |
| 10 | 129.11 | 3.492 | 6.351 | 88.38 | 1.756 | 0.453 |
| | | Average | 5.865 | | Average | 2.576 |
| **Membrane** | **PVDF 0.22 μm** | | | **PP 0.2 μm** | | |
| **LAS (mg/L)** | **Contact angle (°)** | **Sth. Deviation** | **Range (%)** | **Contact angle (°)** | **Sth. Deviation** | **Range (%)** |
| 0.00 | 108.5 | 0.281 | 0.737 | 95.7 | 0.067 | 0.209 |
| 0.01 | 100.1 | 4.508 | 11.089 | 94.08 | 0.084 | 0.213 |
| 0.02 | 97.71 | 2.91 | 5.936 | 93.38 | 0.084 | 0.214 |
| 0.05 | 97.01 | 3.530 | 8.247 | 92.96 | 1.19 | 3.012 |
| 0.1 | 95.43 | 5.492 | 12.994 | 91.46 | 0.084 | 0.219 |
| 0.2 | 94.9 | 0.498 | 1.475 | 91.12 | 0.053 | 0.219 |
| 0.5 | 93.01 | 1.226 | 2.795 | 90.94 | 0.071 | 0.330 |
| 1 | 92.21 | 0.7108 | 1.735 | 90.6 | 0.041 | 0.221 |
| 2 | 91.74 | 1.320 | 3.379 | 90.1 | 0.065 | 0.222 |
| 5 | 87.46 | 0.0719 | 0.229 | 89.165 | 0.0595 | 0.224 |
| 10 | 85.4 | 2.073 | 4.918 | 87.73 | 0.078 | 0.342 |
| | | Average | 4.867 | | Average | 0.493 |

Finally, the contact angle for a particular greywater sample can be determined using the formula derived from the contact angle calibration curve and the concentration of LAS from the absorbance calibration curve. Both the experimental and calculated contact angles for PTFE 0.45 μm, PVDF 0.22 μm, PTFE 0.1 μm and PP 0.2 μm flat-sheet membranes are presented in Figure 8. The PTFE 0.45 μm membrane achieved contact angles between 121.5° and 134.32° for all greywater samples with the LAS concentration between 15 and 20 mg/L. For the same samples, the PTFE 0.1 μm could achieve contact angles between 87.4° and 98.7°, while the range of contact angles for PVDF 0.22 μm was between 82° and 95.8°. The lowest contact angle for greywater samples with the PP 0.2 μm was 81.2°–90.4°. The expected contact angle obtained from the calibration curve is not varying for a small change in LAS concentration. However, the range of experimental data varies between 1 and 11% from the calculated data. This discrepancy has been noted in contact angle measurement for the standard LAS concentrations. There is relatively good agreement between the expected contact angle, calculated from the calibration curves, and the measured contact angles determined using

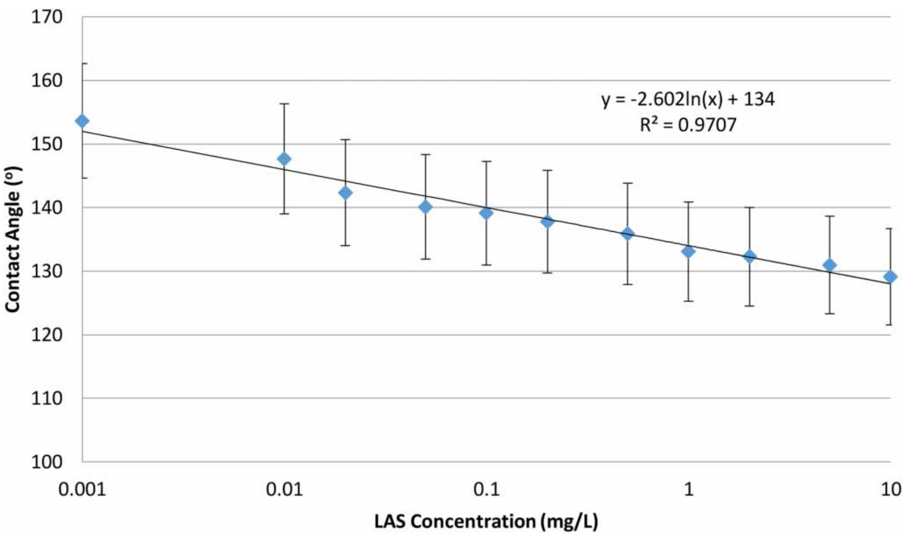


**Figure 3** | Calibration curve for the contact angle of different LAS concentrations with the PTFE 0.45 μm membrane.

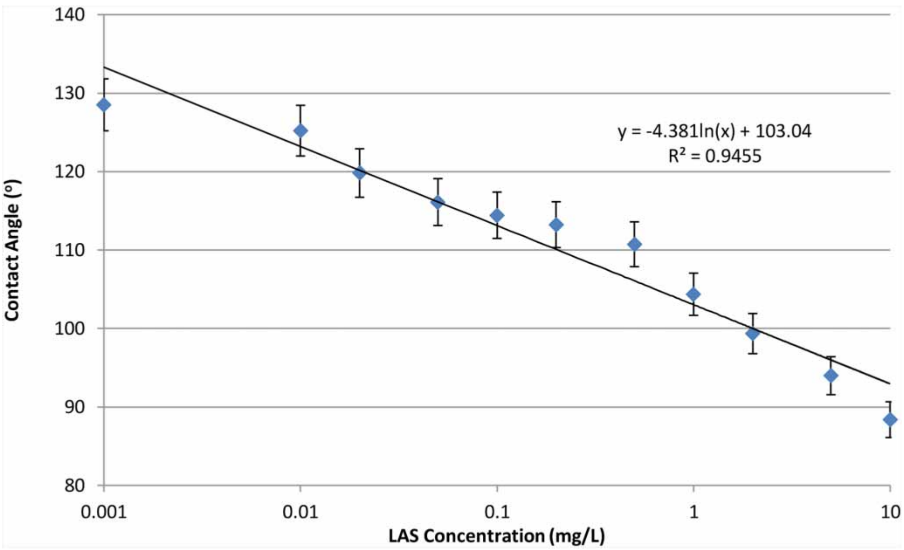


**Figure 4** | Calibration curve for the contact angle of different LAS concentrations with the PTFE 0.1 μm membrane.

the goniometer. This result demonstrates that, should the availability of a goniometer or other contact angle-measuring device be limited, the absorbance method is a suitable alternative for finding the expected contact angle for a given membrane material and acting as a guide as to the suitability for use in VMD.

Minimal discrepancies encountered when testing for contact angle could occur in a number of instances including the quality of lab equipment like a Rame-Hart goniometer, sensitivity of apparatus to ambient temperature, reaction time of the operator and deviations in the exact volume of water being expelled from the syringe. There is always a possibility of experimental interference which can be caused by the presence of surfactants in solvents, reagents, glassware and other sample processing equipment. These interferences were minimised where possible, by thoroughly rinsing all glassware and equipment with Milli-Q water and using high purity reagents where necessary.

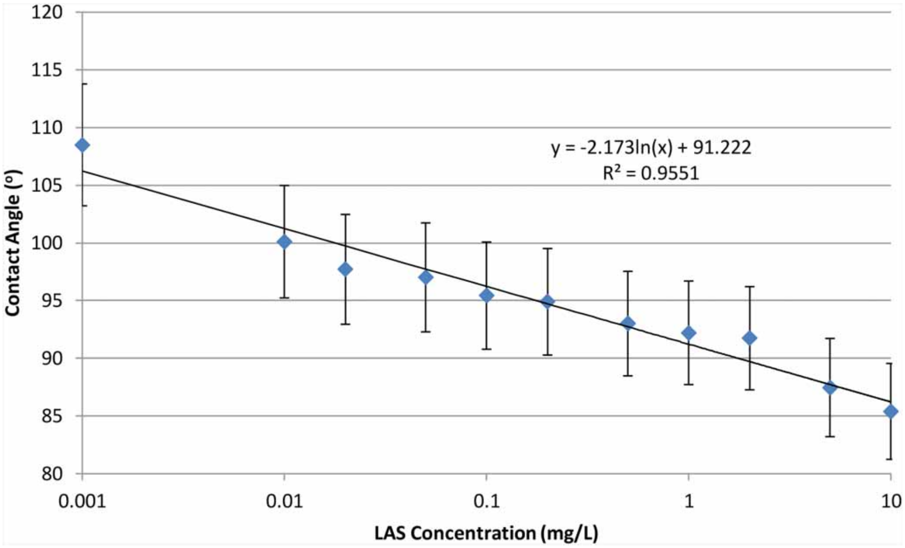


**Figure 5** | Calibration curve for the contact angle of different LAS concentrations with the PVDF 0.22 μm membrane.

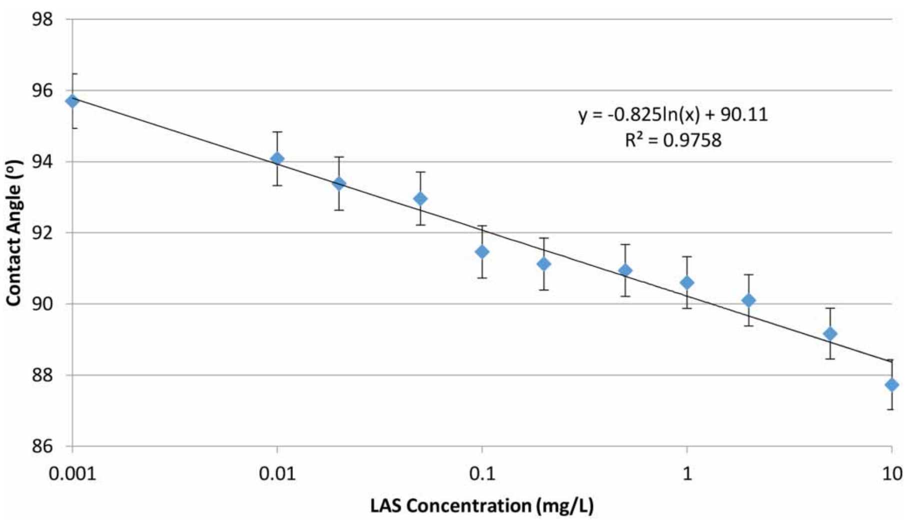


**Figure 6** | Calibration curve for the contact angle of different LAS concentrations with the PP 0.2 μm membrane.

**Table 7** | Results of absorbance for LAS stock solutions from 0 to 20 mg/L

| LAS concentration (mg/L) | 0.00 | 0.01 | 0.1 | 1 | 10 | 12 | 15 | 20 |
|---|---|---|---|---|---|---|---|---|
| Absorbance at 652 nm | 0.002 | 0.027 | 0.04 | 0.27 | 2.533 | 2.960 | 3.068 | 4.102 |

**Table 8** | Results of absorbance for natural and synthetic greywater solutions

| Greywater sample | Laundry | Shower | Mixed (1) | Mixed (2) | Kitchen (1) | Kitchen (2) | Synthetic |
|---|---|---|---|---|---|---|---|
| Absorbance at 652 nm | 3.215 | 3.311 | 3.412 | 3.231 | 3.913 | 2.977 | 3.651 |

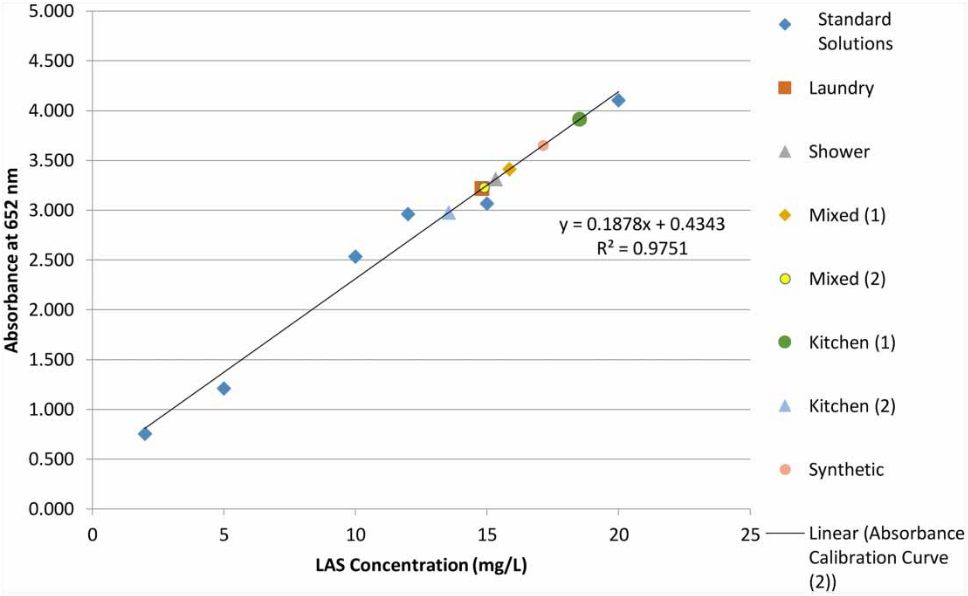


**Figure 7** | Calibration curve for the absorbance of LAS stock solutions.

**Table 9** | Concentration of LAS for each greywater sample as determined by the calibration curve

| Greywater sample | Laundry | Shower | Mixed (1) | Mixed (2) | Kitchen (1) | Kitchen (2) | Synthetic |
|---|---|---|---|---|---|---|---|
| LAS concentration (mg/L) | 14.81 | 15.32 | 15.86 | 14.89 | 18.52 | 13.54 | 17.13 |

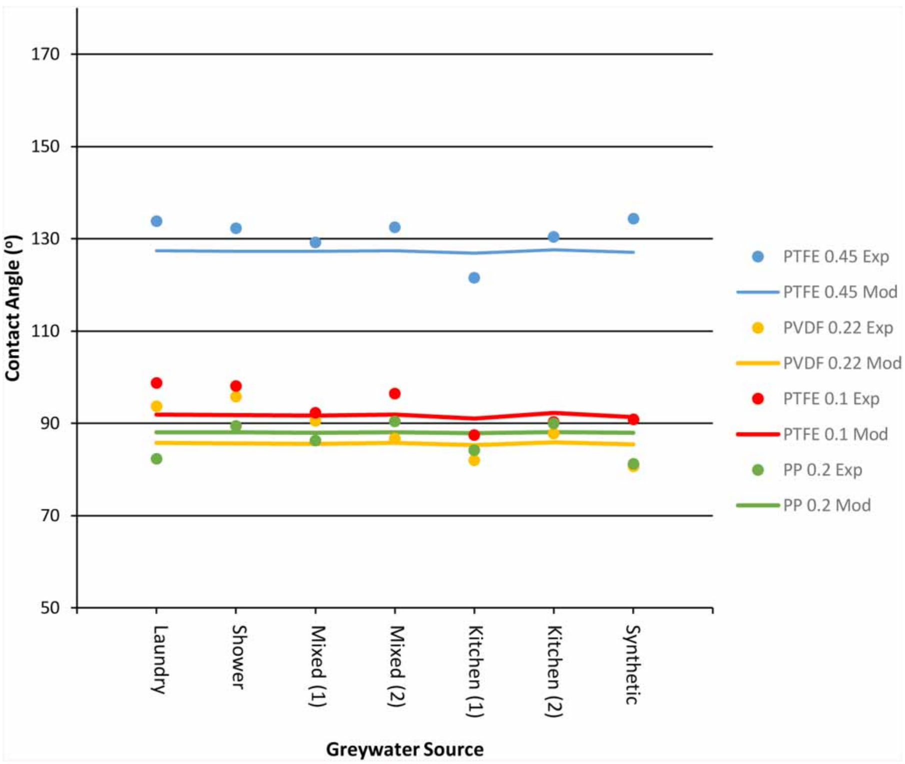


**Figure 8** | Comparison of measured and the calculated contact angle for different flat-sheet membranes.

Surface tension is reduced by the adsorption of surfactant molecules to the liquid–vapour interface, disturbing the ordering of the water molecules (Kaufmann 2006). This favours the spreading of the water molecule, as well as surfactant adsorption to the solid–liquid interface which exposes the hydrophilic head group on the hydrophobic substrate.

From the results, it can be identified that the PTFE material has a larger contact angle than the PVDF and PP, and these results show that the 0.45 μm pore size produced significantly higher contact angles overall than the 0.1 μm of the same material. By visual inspection, it is thought that the surface properties of the 0.1 μm membrane, the inconsistencies caused by the roughness of the felt support material and the manufacturing technique may have negatively impacted the surface tension forces in these experiments, causing the spread of droplets on its surface. From the contact angle results, it can be shown that overall $\theta_{PP} < \theta_{PVDF}$; therefore, it can be concluded that $\Delta P_{PP} < \Delta P_{PVDF}$. The pressure difference required across a PP membrane is less than that required by a PVDF membrane; similarly, $\Delta P_{PVDF} < \Delta P_{PTFE}$. It can be concluded that if the same pressure difference is applied to each membrane, or indeed the same contact angle is observed on the membrane surface, a higher flux can be attained by the PP membrane than PVDF and PTFE.

## CONCLUSION

The wetting issue in membranes is one of the main challenges of the MD process. Although a large variety of both inorganic and polymer membranes is available, the use of membranes in the MD process has not become that popular across different industries. To prevent membrane wetting, either contact angle or the concentration level of surfactants is required. Calibration curves which show the comparison between the contact angle and the concentration of MBAS were developed in this research for four different commercial flat-sheet membranes. Similarly, a calibration curve comparing the absorbance of solutions at 652 nm with the concentration of MBAS has been plotted. Therefore, the absorbance for a given greywater sample can be used to find the expected contact angle for any substance for the membrane surfaces. This information can be used as a guide to determine whether the membrane material is appropriate for use in treating the particular greywater using VMD.

Of the three common types of polymer membranes (PP, PVDF and PTFE), PTFE has low thermal conductivity and a high contact angle, which explains that PTFE has higher hydrophobicity. The maximum contact angle measured when testing using greywater samples was less than 100° for the PP flat-sheet membrane, so it is deemed to be unsuitable for the distillation and treatment of greywater by VMD. A pre-treatment unit is required to reduce the LAS concentration to overcome the wetting phenomenon when PP is used. This is a key point to the success of VMD, as the LEP of the hollow-fibre membrane must not be overcome by the surface tension forces impacted by greywater. This is true of both the PVDF 0.22 μm and PTFE 0.1 μm flat-sheet membranes. The fluoropore PTFE 0.45 μm membrane consistently achieved contact angles above 100° for every greywater sample tested and based on the expected contact angles generated, it can be proposed as a suitable material, in a hollow-fibre form, for VMD applications using greywater. This is based on the assumption that flat-sheet membranes will behave in the same way as hollow-fibre membranes of the same type and material. It has to be noted that the LAS concentration of feed solution must be kept constant; otherwise due to the extraction of pure water from feed solution, the LAS concentration will increase resulting in contact angle reduction.

## ACKNOWLEDGEMENTS

The authors thank Mrs Anne Scragg for proofreading the manuscript.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## REFERENCES

An, A. K., Guo, J., Lee, E.-J., Jeong, S., Zhao, Y., Wang, Z. & Leiknes, T. 2017 PDMS/PVDF hybrid electrospun membrane with superhydrophobic property and drop impact dynamics for dyeing wastewater treatment using membrane distillation. *Journal of Membrane Science* **525**, 57–67.

Baskar, G., Deeptha, V. T. & Rahman, A. A. 2009 Treatment of wastewater from kitchen in an institution hostel mess using constructed wetland. *International Journal of Recent Trends in Engineering* **1** (6), 54–58.

Charisiadis, C. 2017 *Membrane Distillation and Treatment of Reverse Osmosis Reject*. Leibniz Universitat Hannover, Hanover.

Chen, Y., Tian, M., Li, X., Wang, Y., An, A. K., Fang, J. & He, T. 2017 Anti-wetting behavior of negatively charged superhydrophobic PVDF membranes in direct contact membrane distillation of emulsified wastewaters. *Journal of Membrane Science* **535**, 230–238.

Chin-Jung, L., Shang-Lien, L., Chao-Yin, K. & Chung-Hsin, W. 2005 Pilot-scale electrocoagulation with bipolar aluminum electrodes for on-site domestic greywater reuse. *Journal of Environmental Engineering* **131** (3), 491–495.

De Sitter, K., Dotremont, C., Genné, I. & Stoops, L. 2014 The use of nanoparticles as alternative pore former for the production of more sustainable polyethersulfone ultrafiltration membranes. *Journal of Membrane Science* **471**, 168–178.

Diaper, C. 2001 Small scale water recycling systems-risk assessment. *Water Science and Technology* **10**, 83–90.

Diaper, C., Toifl, M. & Storey, M. 2008 Greywater technology testing protocol. In: *CSIRO: Water for a Healthy Country National Research Flagship*. CSIRO, Clayton, Australia.

Eaton, A. D. 2005 *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC.

Eriksson, E., Auffarth, K., Henze, M. & Ledin, A. 2002 Characteristics of grey wastewater. *Urban Water* **4** (1), 85–104.

Eykens, L., De Sitter, K., Dotremont, C., De Schepper, W., Pinoy, L. & Van Der Bruggen, B. 2017a Wetting resistance of commercial membrane distillation membranes in waste streams containing surfactants and oil. *Applied Sciences* **7** (2), 118.

Eykens, L., De Sitter, K., Dotremont, C., Pinoy, L. & Van der Bruggen, B. 2017b Review: membrane synthesis for membrane distillation: a review. *Separation and Purification Technology* **182**, 36–51.

Feng, C., Shi, B., Li, G. & Wu, Y. 2004 Preliminary research on microporous membrane from F2.4 for membrane distillation. *Separation and Purification Technology* **39**, 221–228.

Figoli, A., Ursino, C., Galiano, F., Di Nicolò, E., Campanelli, P., Carnevale, M. C. & Criscuoli, A. 2017 Innovative hydrophobic coating of perfluoropolyether (PFPE) on commercial hydrophilic membranes for DCMD application. *Journal of Membrane Science* **522**, 192–201.

Franken, A. C. M., Nolten, J. A. M., Mulder, M. H. V., Bargeman, D. & Smolders, C. A. 1987 Wetting criteria for the applicability of membrane distillation. *Journal of Membrane Science* **33** (3), 315–328.

Friedler, E., Kovalio, R. & Galil, N. I. 2005 On-site greywater treatment and reuse in multi-storey buildings. *Water Science and Technology* **51** (10), 187–194.

Funamizu, N. & Kikyo, Y. 2007 Direct filtration of wastewater from washing machine. Proceeding of Advanced Sanitation Conference, March 2007, Aachen, Germany. J. Pinnekamp, ed. pp. 35/1–35/8.

Gu, J., Gu, H., Zhang, Q., Zhao, Y., Li, N. & Xiong, J. 2018 Sandwich-structured composite fibrous membranes with tunable porous structure for waterproof, breathable, and oil-water separation applications. *Journal of Colloid and Interface Science* **514**, 386–395.

Guckert, J. B., Walker, D. D. & Belanger, S. E. 1996 Environmental chemistry for a surfactant ecotoxicology study supports rapid degradation of C12-alkyl sulfate in a continuous-flow stream mesocosm. *Environmental Toxicology and Chemistry* **15** (3), 262–269.

Huang, H.-L. & Yang, S. 2006 Filtration characteristics of polysulfone membrane filters. *Journal of Aerosol Science* **37** (10), 1198–1208.

Huang, C.-Y., Ko, C.-C., Chen, L.-H., Huang, C.-T., Tung, K.-L. & Liao, Y.-C. 2016 A simple coating method to prepare superhydrophobic layers on ceramic alumina for vacuum membrane distillation. *Separation and Purification Technology* **198** (8), 79–86.

Hwang, H. J., He, K., Gray, S., Zhang, J. & Moon, I. S. 2011 Direct contact membrane distillation (DCMD): experimental study on the commercial PTFE membrane and modeling. *Journal of Membrane Science* **371**, 90–98.

Kaufmann, T. 2006 A novel method for detergent concentration determination. *Biophysical Journal* **90**, 310–317.

Kaufmann, T. C., Engel, A. & Rémigy, H. W. 2006 A novel method for detergent concentration determination. *Biophysics* **90** (1), 310–317.

Lawson, K. W. & Lloyd, D. R. 1997 Membrane distillation. *Journal of MEMBRANE Science* **124**, 1–25.

Li, F., Wichmann, K. & Otterpohl, R. 2009 Evaluation of appropriate technologies for grey water treatments and reuses. *Water Science and Technology* **59** (2), 249–260.

Lies, E., Kristien De, S., Chris, D., Wim De, S., Luc, P. & Bart Van Der, B. 2017 Wetting resistance of commercial membrane distillation membranes in waste streams containing surfactants and oil. *Applied Sciences* **7** (2), 118–130.

Liu, X. & Pohl, C. 2006 Analysis of cationic surfactants using the acclaim surfactant column. *LC GC Europe* **24**, 17.

Lv, Y., Yu, X., Tu, S.-T., Yan, J. & Dahlquist, E. 2010 Wetting of polypropylene hollow fiber membrane contactors. *Journal of Membrane Science* **362** (1–2), 444–452.

Matthijs, E., Holt, M. S., Kiewiet, A. & Rijs, G. B. J. 1999 Environmental monitoring for linear alkylbenzene sulfonate, alcohol ethoxylate, alcohol ethoxy sulfate, alcohol sulfate, and soap. *Environmental Toxicology and Chemistry* **18** (11), 2634–2644.

Nimer, M., Ballesteros, O., Navalón, A., Crovetto, G., Verge, C., López, I., Berna, J. L. & Vílchez, J. L. 2007 New sample treatment for determination of linear alkylbenzene sulfonate (LAS) in agricultural soils by liquid chromatography with fluorescence detection. *Analytical and Bioanalytical Chemistry* **387** (6), 2175–2184.

Olsson, J., Ivarsson, P. & Winquist, F. 2008 Determination of detergents in washing machine wastewater with a voltammetric electronic tongue. *Talanta* **76** (1), 91–95.

Onsekizoglu, P. 2012 Membrane distillation: principle, advances, limitations and future prospects in food industry, distillation. In: *Distillation, Advances from Modeling to Applications* (S. Zereshki ed.). IntechOpen, Trakya University Department of Food Engineering, Edirne, Turkey.

Peng, M., Li, H. B., Wu, L. J., Zheng, Q., Chen, Y. & Gu, W. F. 2005 Porous poly(vinylidene fluoride) membrane with highly hydrophobic surface. *Journal of Applied Polymer Science* **98** (3), 1358–1363.

Qtaishat, M., Khayet, M. & Matsuura, T. 2009 Guidelines for preparation of higher flux hydrophobic/hydrophilic composite membranes for membrane distillation. *Journal of Membrane Science* **329**, 193–200.

Ramezanianpour, M. & Sivakumar, M. 2017 Fouling and wetting studies relating to the vacuum membrane distillation process for brackish and grey water treatment. *Journal of Porous Media* **20** (6), 531–547.

Ramezanianpour, M., Sivakumar, M. & Stojanovski, A. G. 2017 Grey water treatment using a solar powered electro-coagulator and vacuum membrane distillation system. *Desalination and Water Treatment* **85**, 46–54.

Razmjou, A., Arifin, E., Dong, G., Mansouri, J. & Chen, V. 2012 Superhydrophobic modification of $TiO_2$ nanocomposite PVDF membranes for applications in membrane distillation. *Journal of Membrane Science* **415–416**, 850–863.

Rezaei, M., Warsinger, D. M., Lienhard V, J. H. & Samhaber, W. M. 2017 Wetting prevention in membrane distillation through superhydrophobicity and recharging an air layer on the membrane surface. *Journal of Membrane Science* **530**, 42–52.

Sanderson, H., Price, B. B., Dyer, S. D., DeCarvalho, A. J., Robaugh, D., Waite, S. W., Morrall, S. W., Nielsen, A. M., Cano, M. L. & Evans, K. A. 2006 Occurrence and hazard screening of alkyl sulfates and alkyl ethoxysulfates in river sediments. *Science of the Total Environment* **367** (1), 312–323.

Santoro, S., Vidorreta, I. M., Sebastian, V., Moro, A., Coelhoso, I. M., Portugal, C. A. M., Lima, J. C., Desiderio, G., Lombardo, G., Drioli, E., Mallada, R., Crespo, J. G., Criscuoli, A. & Figoli, A. 2017 A non-invasive optical method for mapping temperature polarization in direct contact membrane distillation. *Journal of Membrane Science* **536**, 156–166.

Seng, S., Kita, M. & Sugihara, R. 2007 New analytical method for the determination of detergent concentration in water by fabric dyeing. *Journal of Chemical Education* **84** (11), 1903–1805.

Servi, A. T., Guillen-Burrieza, E., Warsinger, D. M., Livernois, W., Notarangelo, K., Kharraz, J., Lienhard V, J. H., Arafat, H. A. & Gleason, K. K. 2017 The effects of iCVD film thickness and conformality on the permeability and wetting of MD membranes. *Journal of Membrane Science* **523**, 470–479.

Shirazi, M. M. A., Kargari, A. & Tabatabaei, M. 2014 Evaluation of commercial PTFE membranes in desalination by direct contact membrane distillation. *Chemical Engineering and Processing: Process Intensification* **76**, 16–25.

Sivakumar, M. & Ramezanianpour, M. 2012 *Green Technology Options for Greywater Treatment*. National Convention of Environmental Engineers Mangalore Local Centre, Karnataka, India.

Szczerbińska, J., Kujawski, W., Arszyńska, J. M. & Kujawa, J. 2017 Assessment of air-gap membrane distillation with hydrophobic porous membranes utilized for damaged paintings humidification. *Journal of Membrane Science* **538**, 1–8.

Teoh, M. M. & Chung, T.-S. 2009 Membrane distillation with hydrophobic macrovoid-free PVDF–PTFE hollow fiber membranes. *Separation and Purification Technology* **66**, 229–236.

Tian, M., Yin, Y., Yang, C., Zhao, B., Song, J., Liu, J., Li, X.-M. & He, T. 2015 CF4 plasma modified highly interconnective porous polysulfone membranes for direct contact membrane distillation (DCMD). *Desalination* **369**, 105–114.

Wang, K. Y., Chung, T.-S. & Gryta, M. 2008 Hydrophobic PVDF hollow fiber membranes with narrow pore size distribution and ultra-thin skin for the fresh water production through membrane distillation. *Chemical Engineering Science* **63** (9), 2587–2594.

Whelan, M. J., Van Egmond, R., Guymer, I., Lacoursière, J. O., Vought, L. M. B., Finnegan, C., Fox, K. K., Sparham, C., O'Connor, S., Vaughan, M. & Pearson, J. M. 2007 The behaviour of linear alkyl benzene sulphonate under direct discharge conditions in Vientiane, Lao PDR. *Water Research* **41**, 4730–4740.

Woo, Y. C., Tijing, L. D., Park, M. J., Yao, M., Choi, J.-S., Lee, S., Kim, S.-H., An, K.-J. & Shon, H. K. 2017 Electrospun dual-layer nonwoven membrane for desalination by air gap membrane distillation. *Desalination* **403**, 187–198.

Xu, Z., Liu, Z., Song, P. & Xiao, C. 2017 Fabrication of super-hydrophobic polypropylene hollow fiber membrane and its application in membrane distillation. *Desalination* **414**, 10–17.

Zuo, J., Bonyadi, S. & Chung, T.-S. 2016 Exploring the potential of commercial polyethylene membranes for desalination by membrane distillation. *Journal of Membrane Science* **497**, 239–247.

First received 26 September 2019; accepted in revised form 10 June 2020. Available online 16 July 2020