

Forward osmosis: dyeing draw solutions for water reclamation from feed water resources

Estella Z. Jingxi, Debbie De Jager, Robyn Augustine, Irena Petrinic, Claus Helix-Nielsen and Marshall S. Sheldon

ABSTRACT

Reactive Black 5 and Basic Blue 41 GRL dyeing solutions (dye-to-salt mixture in a 1:10 dye-to-salt mass ratio) were investigated as draw solutions (DS) in a forward osmosis (FO) system with a biomimetic membrane. Synthetic seawater (SSW) and textile wastewater (TWW1 and TWW2) were evaluated as feed solutions (FS) for water reclamation. Reactive Black 5 and Basic Blue 41 GRL were diluted from 0.02 M to concentrations of 0.002 and 0.004 M, respectively. With Reactive Black 5 as DS and SSW as FS, an initial flux of 20.24 L/m² h and water recovery of 75% was achieved. Using TWW1 and TWW2, initial water fluxes of 19.51 and 13.43 L/m² h were achieved, respectively, with a 30% water recovery. Using Basic Blue 41 GRL, initial water fluxes of 18.72, 15.13 and 13.42 L/m² h were achieved with SSW, TWW1, and TWW2 as FS with water recoveries of 50%, 20% and 20%, respectively. The average reverse solute fluxes for Reactive Black 5 and Basic Blue 41 GRL were 0.06 to 0.34 g/m² h, respectively. Diluted dyeing solutions were produced, with simultaneous water reclamation from SSW and TWW resulting in similar or higher water fluxes and lower reverse solute fluxes compared with other commercially available membranes.

Key words | biomimetic membranes, draw solutions, feed solutions, forward osmosis, textile wastewater

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INTRODUCTION

One of the main industries that utilise water resources extensively is the textile industry. The consumption of fresh water varies from 200 to 400 m³ to produce 1 ton of finished fabric products, resulting in the generation of a large amount of textile wastewater (Lin *et al.* 2015; Güyer *et al.* 2016). This results in an annual discharge of around 280,000 tons of dyes to receiving water bodies, which poses a detrimental impact on public health and ecological systems (Jiang *et al.* 2018). Dyeing solutions used in the dyeing process contain among other auxiliary chemicals inorganic salts that act as catalysts and co-solubilisers. Salts are utilised in the textile dyeing industry for several reasons including: (i) increasing dye affinity for the fibre;

(ii) promoting full exhaustion of dye molecules during the dyeing process; and (iii) acting as an electrolyte for movement, adsorption and fixation of the dyestuff to the cellulose material (Samanta *et al.* 2015; Talukder *et al.* 2017). The dyeing wastewater is characterised by high pH, high turbidity, poor bio-degradability, complex composition, high chrominance, and is discharged in large amounts (Yang *et al.* 2018). Such wastewater must be treated prior to discharge into water bodies to prevent contamination of water resources and environmental deterioration. Membrane-based technology such as reverse osmosis (RO) and nano-filtration (NF) has drawn growing interest in the treatment of textile wastewaters due to the high membrane rejection and lower production of secondary pollutants. However, membrane fouling and high energy-cost remain limiting factors (Van der Bruggen *et al.* 2004; De Jager *et al.* 2012, 2014). The need for the development of technologies that use alternative water resources, such as seawater and brackish water (Phuntsho *et al.* 2011, 2012) and

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wastewater recovery has gained worldwide attention. Forward osmosis (FO) is attracting attention as a potential technology to augment water supplies using seawater and wastewater (Achilli *et al.* 2009; Garcia-Castello *et al.* 2009; Chekli *et al.* 2012; Lambrechts & Sheldon 2019). FO is recognised as an emerging membrane separation technology, which has potential use to treat complex highly concentrated organic wastewater, such as landfill leachate, dyeing wastewater, anaerobic digester concentrates and liquid foods in the food industry (Sant'Anna *et al.* 2012; Xie *et al.* 2014; Heikkinen *et al.* 2017; Huang *et al.* 2017).

FO operates on the basis that the osmotic pressure gradient (ΔOP) between the feed solution (FS) and the more concentrated draw solution (DS) spontaneously allows water flow across a semi-permeable membrane (Wang *et al.* 2012; Zaviscka & Zou 2014). In comparison with pressure-driven NF and RO, FO demonstrates the advantages of lower energy consumption, superior separation efficiency, potentially lower fouling tendency and higher recovery due to the lack of hydraulic pressure (Zhang *et al.* 2014). With the use of appropriate draw solutes, FO has the potential to be economically feasible and technically sound. In certain applications, the diluted DS can be used directly without any further treatment. Therefore, FO can be applied as a standalone process, not requiring any regeneration process (Nasirabadi *et al.* 2016). Several materials have been investigated for FO membrane fabrication including cellulose, polyamide (and other polymers), and polyelectrolytes. Also, so-called mixed matrix membranes have been investigated. A special case is the concept of biomimetic FO membranes, where aquaporin proteins (AQPs) are incorporated in the membrane, enhancing water flux while preserving high solute rejection. One remarkable property of AQPs is an effective water conductance at rates close to 10^9 molecules per second and an excellent exclusion of solutes (Tajkhorshid *et al.* 2002). The fascinating properties of AQPs present aquaporin-based membranes as potential alternatives to membranes made from conventional materials (e.g. polymers) (Tang *et al.* 2015; Giwa *et al.* 2017). There is limited research on the application of FO technology in the textile industry although recent research has demonstrated the feasibility of FO in treating textile wastewater (Zhao *et al.* 2015; Han *et al.* 2016; Korenak *et al.* 2019; KoSint & Ratanatamskul 2019). Li *et al.* (2018) conducted a study on the anaerobic biodegradation and decolourisation of a refractory acid dye using an FO membrane bioreactor (FOMBR). Using a cellulose triacetate (CTA) membrane (supplied by Hydration Technology Innovations, i.e. HTI-CTA) the water flux (J_w) of the

membrane was found to be $22 \text{ L/m}^2 \text{ h}$ using 2 mol/L MgCl_2 as the DS and DI water as FS. Recently, Li *et al.* (2019) presented a self-standing, support-free FO membrane using a novel poly-(triazole-co-oxadiazole-co-hydrazine) (PTAODH) skeleton for the concentration of artificial textile wastewater effluent (Congo Red was used as a model dye FS). Its superior antifouling performance was compared with two state-of-the-art commercial FO membranes, i.e. HTI-CTA and a polyamide thin film composite membrane (CSM-TFC) supplied by Toray Chemical Korea. Li *et al.* (2019) reported a J_w of $11.7 \pm 0.7 \text{ L/m}^2 \text{ h}$ for the PTAODH membrane using 1.5 M Na_2SO_4 as the DS, and for the HTI-CTA and CSM-TFC membranes in FO mode J_w was 8.5 ± 0.2 and $21.0 \pm 2.5 \text{ L/m}^2 \text{ h}$, respectively.

This study was aimed at evaluating FO using dyeing solutions as the DS and alternative water resources as the FS, allowing for water reclamation and production of diluted dye solutions. This is a follow-up article to Sheldon *et al.* (2018) that demonstrated the potential of dyes as draw solutes. The novel aspects of this study are: (i) the production of diluted reactive and basic dyeing solutions at specific concentrations for direct use within the textile dyeing processes, therefore not requiring a regeneration step; (ii) simultaneous reclamation of water from synthetic seawater (SSW) and textile wastewater (TWW); and (iii) the utilisation of a biomimetic membrane in a dyeing solution drawn FO system. As far as the authors could determine, these novel aspects have not been demonstrated previously.

MATERIALS AND METHODS

Materials and chemicals

In Sheldon *et al.* (2018), previously, three reactive dyes (i.e. Reactive Black 5, Remazol Red, and Levifix Olive Ca) and three basic dyes (i.e. Maxilon Blue 5G, Maxilon Red GRL and Basic Blue 41 GRL) were selected based on their common use in the South African textile industry and tested for osmotic potential (OP), with and without the addition of salt. The dye samples were prepared at different concentrations and dye-to-salt mass ratios (1:10 to 1:60) and assessed for OP , using a freezing point Gonotec Osmomat 3000 Osmometer (Scientific Group, Germany). Sheldon *et al.* (2018) concluded that dye solutions without salt could not be considered as suitable DS as they generated a lower OP , and the addition of salt was necessary to increase the OP .

The Reactive Black 5 and Basic Blue 41 GRL dyeing solutions (meaning dyes and salts) generated a higher *OP* compared with the other dyes evaluated and were therefore selected as DS at an initial concentration of 0.02 M for this study. Sodium chloride (NaCl) (Merck, Germany) was mixed with the dyes in a 1:10 dye-to-salt mass ratio. The 1:10 dye-to-salt mass ratio was selected based on recipes received from the textile industry used in their dyeing processes. Table 1 provides information on the two dyes used. The Reactive Black 5 and Basic Blue 41 GRL dyeing solutions mixed in a 1:10 NaCl mass ratio (hereafter referred to as the dyeing solution) both at an initial dye concentration of 0.02 M generated initial *OP*s of 166 and 98 bar, respectively. The production of the diluted Reactive Black 5 and Basic Blue 41 GRL dyeing solutions required dilution to target concentrations of

0.002 M and 0.004 M, respectively, based on dye recipes received from the textile industry. From the previous *OP* and concentration studies conducted, these diluted target concentrations corresponded to an *OP* of 86 and 89 bar for the respective Reactive Black 5 and Basic Blue 41 GRL dyeing solutions.

The aquaporin (AQP) biomimetic membrane used in this study was sourced as a flat sheet prototype from Aquaporin A/S (Kongens Lyngby, Denmark). Figure 1 illustrates scanning electronic microscope (SEM) images of the cross-section (Figure 1(a)) at 2,500× magnification, active and support layers (Figure 1(b) and 1(c)) at 5,000× magnification, respectively. The membrane thickness was $110 \pm 15 \mu\text{m}$ (as determined from SEM) and had reverse flux of $2 \text{ g/m}^2 \text{ h}$ (DI water as the FS and 1 M NaCl as the DS as provided by the supplier) (Aquaporin Inside™, FO Flat Sheet Test Membrane, data sheet 1.8).

Table 1 | Parameters used in the production of the dyeing solutions

Parameter	Reactive Black 5 dyeing solution	Basic Blue 41 GRL dyeing solution
Chemical formula	$\text{C}_{26}\text{H}_{21}\text{N}_5\text{Na}_4\text{O}_{19}\text{S}_6$	$\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_6\text{S}_2$
Molecular weight (M_w) (g/mol)	991	482
Diluted target concentration (M)	0.002	0.004
<i>OP</i> at target concentration (bar) (Sheldon <i>et al.</i> 2018)	86	89
pH – initial	4.16	4.22
pH – final	6.34	9.07
<i>EC</i> (mS/cm) – initial	188	140
<i>EC</i> (mS/cm) – final	130	78.7
Temperature (°C)	22 ± 0.5	22 ± 0.5

Forward osmosis tests for the production of a dyeing solution

A bench-scale FO unit (Figure 2) was utilised for the production of a target concentration dyeing solution using dye solutes as DS and alternative water resources as FS. The main unit consisted of a CF042D FO cell (Sterlitech Corporation, USA) with outer dimensions ($12.7 \times 10 \times 8.3 \text{ cm}$) and an effective membrane area of 42 cm^2 . The FS included DI water as the control solution, synthetic seawater (SSW) with $35,000 \text{ mg/L NaCl}$ (Akther *et al.* 2015) and textile wastewater (TWW) collected from the textile industry (TWW1 and TWW2), both using a reactive dye in the dyeing process. Two identical variable speed Watson Marlow 323S peristaltic pumps (Dune Engineering, South Africa) were used for the circulation of the FS and DS

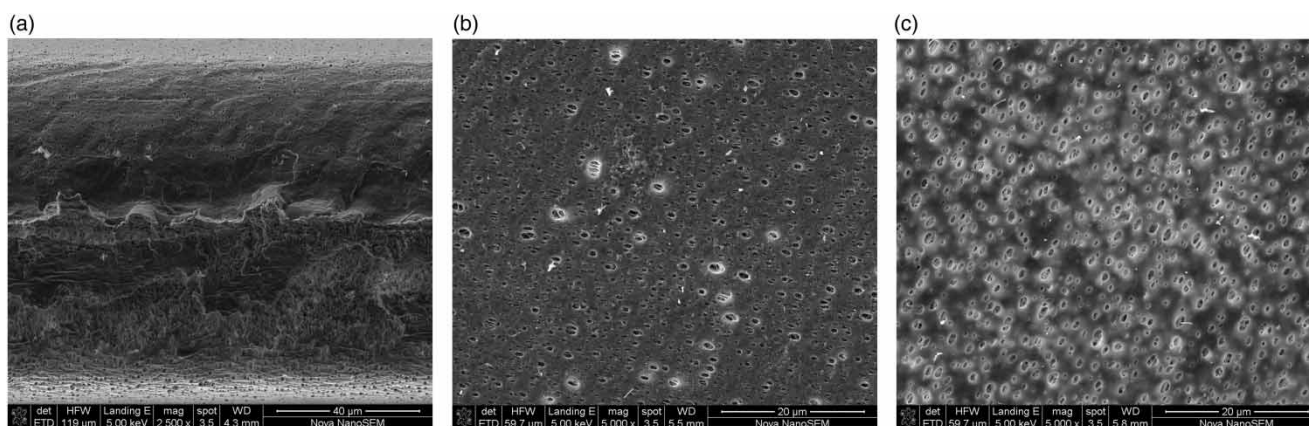


Figure 1 | SEM images of the AQP biomimetic membrane: (a) cross-section (2,500× magnification); (b) active layer (5,000× magnification); and (c) support layer (5,000× magnification).

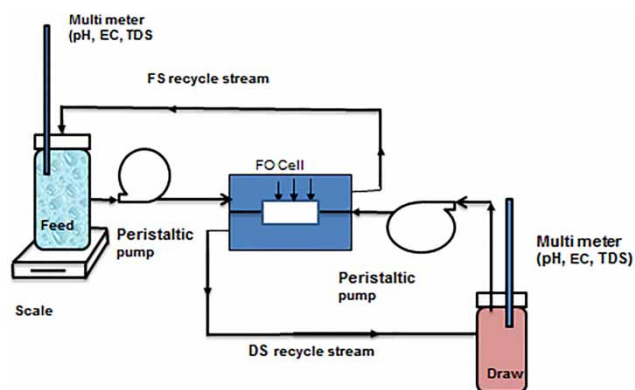


Figure 2 | Process flow diagram (PFD) of the laboratory bench-scale FO process.

through the membrane cell, counter-currently. A volumetric flow-rate of 600 mL/min was selected based on membrane integrity tests that were performed at varying flow rates.

Bench-scale experiments were conducted at room temperature ($22 \pm 0.5^\circ\text{C}$). The initial volume of the FS and DS was 2 L and 1 L, respectively, and the initial dye DS concentration was 0.02 M for both reactive and basic dyeing solutions. During experimentation, the weight change of the FS was recorded manually using a Labex WA606 mass balance (Labex, South Africa) at 1 h intervals. Control experiments were run with DI water to evaluate the maximum feed water recovery rate at the end of a 30 h filtration. Each experiment was conducted in duplicate and a new FO membrane was utilised for each experiment. The membrane was placed in the FO mode orientation, i.e. the active layer facing the FS side and the support layer facing the DS side. All experiments were conducted for 30 h except for the experiment conducted with SSW as the FS and Reactive Black 5 dyeing solution as the DS, which took 44 h due to the time required to achieve the target concentration.

The physicochemical parameters, pH and electrical conductivity (EC), were measured at 1 h intervals using a Lovibond Sensor direct multipurpose meter (Seletech, South Africa). *OP* analysis was conducted at 2 h intervals using the Gonotec Osmomat 3000 Osmometer (Scientific Group, Germany). Colour Hazen analysis was performed at the initial and final stage of the experiment only. Samples for Colour Hazen were analysed by a South African National Accreditation System accredited laboratory. Data for the dye drawn FO system was recorded manually. The system was run continuously and left running overnight therefore some figures in the results sections are presented with the omission of recorded data. The experimental water flux (J_w) across the FO membrane was calculated

using Equation (1) (Han et al. 2016):

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

where J_w is the water flux ($\text{L}/\text{m}^2 \text{ h}$); ΔV (L) is the permeate water over a predetermined time interval Δt (h); and A_m is the effective membrane surface area (m^2) (Han et al. 2016).

The reverse permeation of draw solutes in osmotically driven membrane processes is a direct result of the solute concentration difference across the membrane. This reverse solute flux (J_s) reduces the effective *OP* difference across the membrane and thus the efficiency of the FO system (Yong et al. 2012). J_s was calculated using control experiments with DI water as the FS and Equation (2) (Han et al. 2016):

$$J_s = \frac{(C_{f,t}V_{f,t} - C_{f,i}V_{f,i})}{A_m \Delta t} \quad (2)$$

where J_s is the reverse solute flux ($\text{g}/\text{m}^2 \text{ h}$); $C_{f,t}V_{f,t}$ are the salt concentration (g/L) and feed volume (L) at the end of the experiment, respectively; $C_{f,i}V_{f,i}$ are the initial salt concentration (g/L) and total feed volume (L) at the start, respectively; and Δt is the change in time (h) (Han et al. 2016).

J_s was only calculated for experiments with DI water as the controlled FS. C_f was determined from a standard conductivity curve relating *EC* to the respective dyeing solution concentrations. When TWW was used as the FS, the reverse permeation of the dyeing solution solutes was monitored by monitoring the feed *EC*.

The feed water recovery rate, R_e (%), is the amount of water permeated per unit time and was calculated using Equation (3) (Han et al. 2016):

$$R_e = \frac{\Delta V}{V_{f,i}} \times 100 \% \quad (3)$$

where R_e is the feed water recovery rate (%), $V_{f,i}$ is the initial volume (L) of the FS and ΔV is the change in volume (L) (Han et al. 2016).

RESULTS AND DISCUSSION

Control experiments

Control experiments were conducted using DI water as the FS and Reactive Black 5 and Basic Blue 41 GRL mixed

with NaCl in a 1:10 mass ratio as the dyeing DS, respectively. These experiments were conducted to evaluate the maximum feed water recovery (R_e) after a 30 h filtration period, and the reverse solute flux (J_s), while producing a dyeing solution that can be used directly for dyeing processes. Figure 3 illustrates the water flux profiles for both the Reactive Black 5 and Basic Blue 41 GRL dyeing solutions control experiments.

The initial osmotic pressure gradients (ΔOP) for the Reactive Black 5 and Basic Blue 41 GRL controls were 166 and 98 bar, respectively. The difference between the initial ΔOP for the Reactive Black 5 dyeing solution and Basic Blue 41 GRL dyeing solution controls was explained in Sheldon et al. (2018) and was as a result of the dye chemistry and molecular weight (M_w) of the Reactive Black 5 and Basic Blue 41 GRL dyeing solutions, rather than the type of dye used. The Reactive Black 5 dyeing solution with an M_w of 991 g/mol required more sodium chloride (NaCl) than the Basic Blue 41 GRL dyeing solution with an M_w of 482 g/mol at a dye-to-salt mass ratio of 1:10. The initial water flux (J_w) for the controls with Reactive Black 5 and Basic Blue 41 GRL dyeing solutions was 19.01 and 16.73 L/m² h and decreased to 18.17 and 14.65 L/m² h, respectively, an initial decline of 10% and 22% after 2 h, respectively.

The J_w obtained in this study, using an AQP biomimetic membrane, was higher than and comparable to the flux of 18.95 L/m² h, using a thin-film composite (TFC) FO membrane, reported in Phuntsho (2012) for a fertiliser drawn FO process. The J_w was also comparable to the 22 L/m² h obtained by Li et al. (2018), using the HTI-CTA membrane. This was higher than the 11.7 L/m² h by Li et al. (2019), using the PTAODH membrane, and found to be higher than fluxes reported by Zhao et al. (2015) ranging from 8 to 14 L/m² h, using a TFC FO membrane, in a polyelectrolyte-promoted FO process for dye wastewater. The decrease in the J_w profiles in Figure 3 was as a result of a

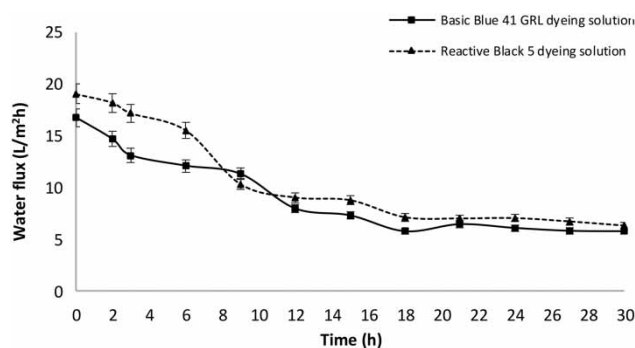


Figure 3 | Water flux profiles for the Reactive Black 5 and Basic Blue 41 GRL dyeing solution controls with DI as the FS.

decreased ΔOP which occurs due to the dilution of the dyeing solutions, as well as the J_s of the dyeing solution. The average initial J_s for the Reactive Black 5 and Basic Blue 41 GRL dyeing solution controls were 0.34 and 0.06 g/m² h, respectively. This J_s was well below the manufacturer specification of 2 g/m² h for the AQP biomimetic FO membrane when using a 1 M NaCl solution as a DS. The higher J_s achieved using the Reactive Black 5 compared with the Basic Blue 41 GRL dyeing solution was postulated to be as a result of several factors which may include: (i) the dye chemistry and the M_w of the dye in the dyeing solution (Sheldon et al. 2018); and the (ii) ionic charges of dyes in the dyeing DS, as dye had a tendency to adhere to the surface of the membrane, observed by a colour-stained membrane at the end of the filtration period. The absence of colour in the DI water at the end of the filtration period for both controls, using Reactive Black 5 and Basic Blue 41 GRL dyeing solutions, was an indication that the J_s obtained was the result of NaCl penetration through the AQP biomimetic membrane from the respective dyeing solutions. Korenak et al. (2019) tested a flat sheet AQP membrane for concentrating real textile wastewater as the FS and reported higher J_s of 0.04 and 2.9 g/m² h when using 1 M MgCl₂ and 1 M NaCl as the DS, respectively.

Feed water recovery rates (R_e) of 82% and 67% were achieved after a 30 h filtration period for the Reactive Black 5 and Basic Blue 41 GRL dyeing solution controls, respectively.

Production of a Reactive Black 5 dyeing solution

A Reactive Black 5 dyeing solution, at an initial concentration of 0.02 M and a dye-to-salt ratio of 1:10, was used as a DS with SSW and textile wastewaters from two textile factories (TWW1 and TWW2) as FS. As indicated previously the target concentration for the Reactive Black 5 dyeing solution was 0.002 M, corresponding to an OP of 86 bar. Table 2 illustrates the average water fluxes and feed water recovery rates of duplicate FO mode experiments under these conditions.

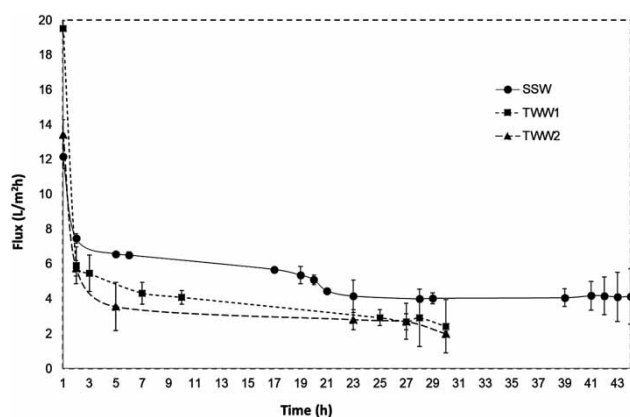
The Reactive Black 5 control reached the target concentration at approximately 3.6 h with a corresponding J_w of 17.1 L/m² h. The initial ΔOP was 136, 150 and 130 bar, with SSW, TWW1, and TWW2 as the FS, respectively.

As shown in Table 2 and illustrated by Figure 4, the decrease in flux could be divided into two stages. Stage 1: a sharp decline within the first 2 h (with SSW as FS, a 58% decrease in J_w was observed from an initial 20.2 to 8.6 L/m² h, while for the TWW1 and TWW2 flux declines

Table 2 | Average water flux (J_w) and feed water recovery rates (R_e) with Reactive Black 5 dyeing DS and alternative FS (DI, SSW, TWW1 and TWW2)

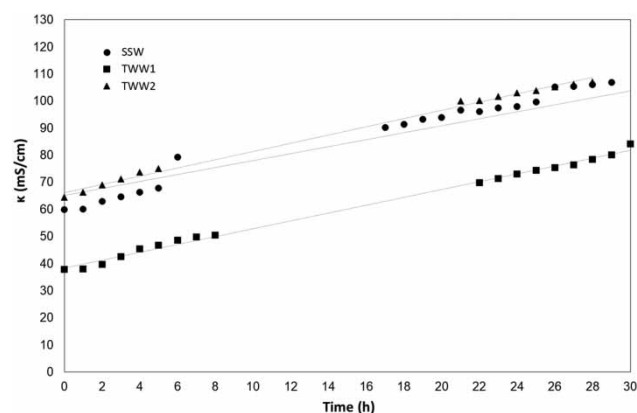
Draw solution		Reactive Black 5 dyeing solution			
Feed solutions		DI	SSW	TWW1	TWW2
Parameters	Units				
ΔOP	bar	166	136	150	130
Initial flux (J_w)	L/m ² h	19.0	20.2	19.5	13.4
J_w @ 2 h	L/m ² h	18.2	8.6	5.9	5.7
J_w @ target concentration	L/m ² h	17.1	5.2	4.1	4.2
J_w @ 30 h	L/m ² h	6.3	5.7	0.76	0.98
R_e @ target concentration	(%)	21	75	30	30
R_e @ 30 h	(%)	82	65	65	65

Note: DI, deionised water; FS, feed solution; DS, draw solution; SSW, synthetic seawater; TWW1, textile wastewater 1; TWW2, textile wastewater 2.

**Figure 4** | Water flux (J_w) profiles with Reactive Black 5 as a DS and different FS (SSW, TWW1, and TWW2).

of 67% and 58% were observed from initial fluxes of 19.5 and 13.4 to 5.9 and 5.7 L/m² h, respectively) suggested that concentration polarisation (CP) and membrane fouling occurred and developed fast. Stage 2: after 2 h, the J_w declined slower for SSW than for TWW1 and TWW2 as FS. The slower decline of flux indicated a slower developing fouling process. With the development of fouling, the foulants increased the resistance through the membrane from the FS to the DS. The enhanced OP on the FS side reduced the effective OP of the membrane on both sides, thereby a decrease in water flux occurred (Boo *et al.* 2012).

Figure 5 illustrates the increase in EC of the different FS. The EC of SSW increased from ± 60 to 117 mS/cm over a 44 h filtration period (the period to reach the target dye concentration of 0.002 M), while that of the TWW1 and TWW2 increased from ± 38 to 60 mS/cm and 65 to 90 mS/cm,

**Figure 5** | Electrical conductivity (EC) of different FS with Reactive Black 5 dyeing solution as the DS, after 30 h.

respectively, over approximately 22 h (target dye concentration of 0.002 M reached). The increase in the feed EC over time was due to reverse solute flux of dissolved solutes of the reactive dyeing solution from the DS, as well as being due to the increased concentration of the FS.

The concentration of the DS (dye-to-salt mixture) was kept constant at 0.02 M. We can assume that a higher contribution of CP can be observed when SSW was used due to its composition (35,000 mg/L NaCl) compared with TWW1 and TWW2. Beyond this increased CP, the concentration of solutes (mostly Na⁺ and Cl⁻ ions) in the DS should not affect the flux of the solutes from the FS (Irvine *et al.* 2013). However, the more pronounced effect of CP, when using SSW as a feed, resulted in longer time needed to reach the DS target concentration due to the solution-diffusion mechanism where anions from the DS permeate across the membrane with cations from the FS in order to maintain electro-neutrality.

Besides the solution-diffusion mechanism, an ion exchange mechanism occurred when TWW1 and TWW2 were used. Pristine AQP membranes are negatively charged (Singh *et al.* 2018) below the isoelectric point at approximately 2.9 pH. The adsorption of reactive dye molecules onto the surface of the charged membrane is influenced by the electrostatic interaction between the reactive dye molecules and the membrane surface that also contributed to the initial sharp decline in water flux in the first 2 h. Studies by Koyuncu & Topacik (2003) and Zahrim *et al.* (2011) illustrated that dye molecules deposited on the membrane surface had a profound effect on the membrane J_w and fouling propensity due to the physicochemical interactions (i.e. charge transfer). The high pH of the TWW signified that they were alkaline. Koyuncu & Topacik (2003) stated that under alkaline conditions the formation of strong and

stable dye-to-salt complexes would result in increasing hydrophobicity consequently increasing the absorption of dye molecules on the membrane surface. Therefore, when an ion exchange mechanism occurs, dye molecules covalently bond on the membrane surface and anions from the FS are exchanged with the anions from the DS.

When TWW1 and TWW2 were used as the FS, the target concentration was reached after approximately 22 h with corresponding J_w of 4.05 and 4.15, respectively. The J_w achieved for the TWW1 and TWW2 experiments were comparable since both were of reactive dye origin. The time required for TWW1 and TWW2 solutions to reach the target concentration was further attributed to the decreased water flux over time, a consequence of high-rate fouling on the active layer of the AQP membrane (Zhao et al. 2015; Li et al. 2018). Therefore, there was also a contribution to the EC from the reverse solute flux of dye molecules from the Reactive Black 5 dyeing solution, corroborated by Colour Hazen analysis performed at the initial and final stage of the filtration period. SSW had an initial colour concentration of 0 mg/L Pt that increased to 496 mg/L Pt after 30 h. TWW1 and TWW2 with initial colour concentrations of 288 and 200 mg/L Pt, respectively, both doubled to 500 mg/L Pt after 30 h. Regardless of the CP and membrane fouling (adsorption) that occurred on the membrane surface, the EC in the FS with time is linear, therefore, the same amount of solutes is diffusing from the draw to the feed side.

The R_e at the target concentration of 0.002 M was 75%, 30% and 30% for SSW, TWW1, and TWW2, respectively. It was noted that after 30 h, although the J_w had declined for all the respective FS, the R_e was constant at 65% for SSW, TWW1, and TWW2, respectively.

Production of a Basic Blue 41 GRL dye solution

Basic Blue 41 GRL dyeing solution at an initial concentration of 0.02 M and a dye-to-salt ratio of 1:10 was used as a DS with alternative FS (SSW, TWW1, and TWW2) for the production of a diluted 0.004 M dyeing solution with a corresponding OP of 89 bar. Table 3 illustrates the average J_w and R_e while Figure 6 illustrates the J_w profiles.

The Basic Blue 41 GRL control reached the target concentration of 0.004 M at approximately 3 h with a water flux of 13.10 L/m² h. Using SSW, TWW1, and TWW2 the initial ΔOP was 70, 83 and 65 bar, resulting in initial J_w of 18.7, 15.1 and 13.4 L/m² h, respectively. The initial fluxes using an AQP biomimetic membrane were comparable to fluxes previously obtained in the literature as demonstrated earlier.

Table 3 | Average water flux (J_w) and feed water recovery rates (R_e) with Basic Blue 41 GRL dyeing DS and alternative FS (DI, SSW, TWW1 and TWW2)

Draw solution		Basic Blue 41 GRL dyeing solution			
		DI	SSW	TWW1	TWW2
Feed solutions					
Parameters	Units				
ΔOP	bar	97	70	83	65
Initial flux (J_w)	L/m ² h	16.7	18.7	15.1	13.4
J_w @ 2 h	L/m ² h	14.6	3.2	3.2	4.6
J_w @ target concentration	L/m ² h	13.1	2.8	3.5	3.2
J_w @ 30 h	L/m ² h	5.8	2.2	1.5	2.6
R_e @ target concentration	(%)	20	50	20	20
R_e @ 30 h	(%)	67	75	50	65

Note: DI, deionised water; FS, feed solution; DS, draw solution; SSW, synthetic seawater; TWW1, textile wastewater 1; TWW2, textile wastewater 2.

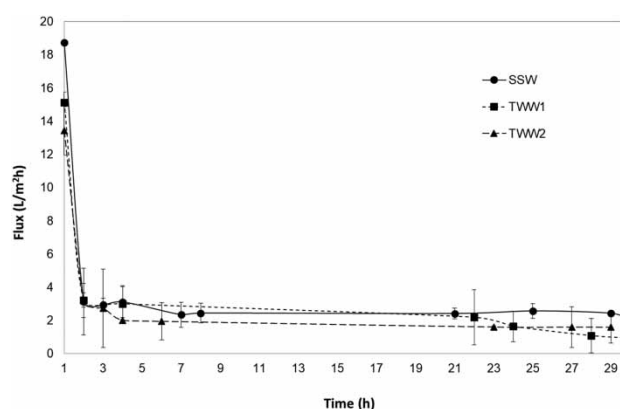


Figure 6 | Water flux (J_w) profiles for FO experiments with Basic Blue 41 GRL dyeing solution as DS and different FS (SSW, TWW1, and TWW2).

With SSW, TWW1, and TWW2 as FS, the system target concentration was reached after approximately 20 h, with a corresponding water flux of 2.8 L/m² h for SSW and after 4 h for both TWW1 and TWW2 with corresponding water fluxes of 3.5 and 3.2 L/m² h, respectively. The initial declines in J_w of 83%, 79% and 65% after 2 h for FS – SSW, TWW1, and TWW2, respectively – indicated in Table 3 and illustrated in Figure 6 were similar as seen and explained when Reactive Black 5 solution was used as a DS (Figure 4). The declines in J_w were also associated with the effect of the dyeing solution J_s and the deposition of the Basic Blue 41 GRL dye molecules on the membrane surface (evidenced by the observed staining of the membrane) that was more pronounced than with the Reactive Black 5 dyeing solution.

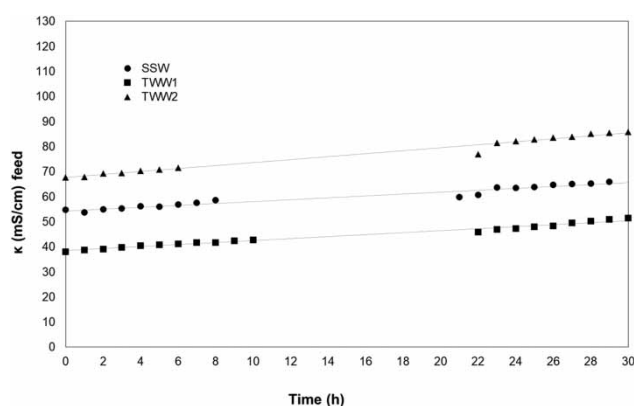


Figure 7 | Electrical conductivity (EC) of different FS with Basic Blue 41 GRL as the DS.

Basic Blue 41 GRL is a cationic dye in nature, and the positive charges of the Basic Blue 41 GRL dyeing DS induced a strong attraction between the dye molecules and the negatively charged polysulfone support layer (Yu *et al.* 2010; Motsa *et al.* 2014; Han *et al.* 2016) of the AQP biomimetic membrane. Because of the strong electrostatic interaction between the Basic Blue 41 GRL dye molecules and the AQP biomimetic membrane, fouling was accelerated. This accelerated fouling reduced the water flux of the membrane. The R_e after 30 h were 75%, 50% and 65% for the SSW, TWW1, and TWW2, respectively.

Figure 7 illustrates the increase in EC of the different FS (SSW, TWW1, and TWW2). The EC of SSW increased from ± 55 to 66 mS/cm while the EC for TWW1 and TWW2 increased from ± 38 to 51 mS/cm and from 68 to 86 mS/cm, respectively, over 30 h.

The increase in EC was the result of ion transport through the membrane (explained previously), evidenced by the colour change of the FS from an initial colour concentration of 0 mg/L Pt, to a final colour concentration of 24 mg/L Pt for SSW. The feed colour concentrations increased from 200 to 256 mg/L Pt for TWW1 and from 288 to 383 mg/L Pt for TWW2. The substantially lower J_s of 0.09 g/m² h observed for the Basic Blue 41 GRL control was substantiated by the considerably lower increase in EC and colour concentration observed for various alternative FS when Basic Blue 41 GRL dyeing solution was used as a DS.

CONCLUSIONS

This study encompassed the assessment of an AQP biomimetic membrane FO system for the production of Reactive

Black 5 and Basic Blue 41 GRL direct dyeing solutions at target concentrations of 0.002 and 0.004 M, respectively, using alternative feed water resources. The selectivity of the AQP biomimetic membrane was excellent and enhanced the water flux, as suggested in theory while preserving high solute rejection. The water fluxes obtained with the use of the AQP biomimetic membrane were comparable to and in some instances higher than other commercially available FO membranes. The production of diluted reactive and basic dyeing solutions ready for direct application in the textile dyeing industry was achieved at 0.002 and 0.004 M, respectively. It was concluded that the target concentrations were reached at various times depending on the FS used. The use of dyeing solutions as DS to reclaim water from SSW and TWW were successfully demonstrated. The decline in water flux over time was found to be associated with the DS being slowly diluted, and the increase in EC of the FS which led to the decrease of the transmembrane driving force (i.e. the bulk ΔOP). The production of direct dyeing solutions resulted in feed water recovery rates ranging from 20% to 75%.

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