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Towards new membrane-based technologies for water treatment and reuse in the textile industry

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Textile wastewater represents challenging feed streams to be treated by membrane separation due to the complex composition and presence of reactive components. Here we first briefly present some characteristics of textile wastewater remediation where a key issue is (bio)fouling. We then present Membrane Bioreactors (MBRs) and Forward Osmosis (FO) membranes as both technologies have attracted considerable interest due to the low fouling propensity of FO membranes. This makes them an intriguing supplement to existing method and we conclude this communication by highlighting some new developments and perspectives involving biomimetic aquaporin FO membranes and Osmotic Membrane Bioreactors (OMBRs).
Key words: *membranes, textile wastewater, forward osmosis, biomimetics*

1. Introduction

Textile processing is complex and includes sizing where various types of water soluble polymers also called textile sizing agents such as modified starch, polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and acrylates are used to increase the strength of the yarn, weaving, scouring (e.g. detergent treatment), bleaching, mercerising, where sodium hydroxide is added to provide lustrous appearance and strength to cotton, carbonising (adding acid followed by baking thereby removing (carbonized) impurities from wool, dyeing and finishing. Consequently wastewater pollutants arise both from the raw fabrics and a wide range of additives used to produce the finished product. In textile wastewater treatment one therefore has to deal with pollutants spanning a wide range including non-biodegradable highly persistent organic such as recalcitrant organics, colours, toxicants and inhibitory compounds, surfactants, chlorinated compounds (AOX), and even pesticides used in speciality textiles such as insect-proof fabrics [1].

Organic matter represents the main emission load for textile wastewater suggesting treatment based on biological processes. However, the introduction of effective and sustainable water recycling techniques in this branch of production is often prevented by recalcitrant organic compounds and remaining dyes. Surfactants generally constitute one of the major chemical oxygen demand fractions in textile wastewater, and non-ionic surfactants are commonly used in textile preparation stage (scouring, washing and mercerising), to remove impurities from the fabric and prepare them for the proceeding dyeing process [2]. They are applied at high doses and remain in the exhausted process effluent, contributing to at least 30% of the total COD load of the final dye-house effluent. In the environment surfactants may reveal harmful effects to organisms living there, mainly due to their toxicity and also due to enhancement of solubility of other toxic organic compounds (e.g. pesticides). The surfactants in aqueous solutions form micelles. Because of the poor biodegradability and sometimes even toxicity of the textile wastewater components, advanced treatment technologies are necessary. Especially if reuse of treated wastewater is the objec-

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tive, extensive removal of organic contents as well as almost complete decolourization is required.

When dyeing/printing textiles, water serves two purposes: first, it ensures the transmission of the colour onto the fibre and second, for washing out excess amounts of dyes from the treated fabrics. Of all dyed/printed textile fibres, cellulose fibres stands out as being the most prominent, and more than 50% of its production is dyed/printed with a special class of dyes the so-called reactive dyes. Over 80,000 tons of reactive dyes are produced and consumed each year, making it possible to estimate the total pollution caused by their use [3]. They are quite adsorptive to the cellulose fibres, and the hydrolysed dyestuff requires large amounts of water, preferably at high temperatures, to be properly washed out. Unfortunately, this class of dyes is also the most unfavourable from an ecological point of view, as the effluents produced are rather heavily coloured, and, in addition contain high concentrations of salt and exhibit high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values [3].

A particular problematic group of dyes is constituted by the so-called azo dyes (containing -N=N- bonds) as they and their metabolites may be mutagens and carcinogens [4-7]. Azo dyes commonly utilised in the textile industry include reactive, acid and direct dyes [8]. They are aromatic compounds that make up the largest and most diverse group of synthetic dyes found in the wastewaters of dye utilising industries, such as textile, paper printing, food and cosmetic industries.

2. Issues in textile wastewater remediation

The key factors affecting the remediation of treated wastewater are total suspended solids (TSS), turbidity, colour and non-biodegradable substances. Therefore, advanced treat-

ment processes are required to improve the quality of the treated wastewater up to re-use criteria [9, 10]. Many treatment methods for textile wastewater have been investigated including: 1) treatment using lime and alum, but this method generates large quantities of hazardous sludge and is generally ineffective in the removal of colour, TSS, BOD and COD; 2) biological treatment with aeration in order to reduce BOD and COD levels; 3) chlorination that successfully removes colour (e.g. as sodium hypochloride (NaOCl) based attack of dye molecule amino bonds). Although this method reduces BOD and COD, it produces chloro-organic compounds that are potentially carcinogenic and therefore not eco-friendly; 4) ozonation with or without ultraviolet irradiation; and 5) sorption using H_2O_2-Fe(II) salt and cucurbituril. Other methods include adsorption (e.g. via activated carbon, peat, wood chips, fly ash [11] and silica gels), ion-exchange (for cationic and anionic dyes), irradiation electron beams (combined with oxygenation), and electrokinetic coagulation (using added ferrous sulphate or ferric chloride), see [12] for a review of chemical and physical treatments. Results from literature indicate that membrane systems within treatment-recycling systems reduce the cost of wastewater treatment through the recovery and re-use of chemicals and water [13]. Membrane processes are categorised according to the pore size, molecular cut-off and pressure at which the membranes operate. These categories are interrelated, because as the pore size is reduced or the molecular cut-off decreases the pressure applied to the membrane, to maintain the same flux, increases [14]. Membrane separation processes in which water forms the permeate can be categorised into four groups based on the pore size of the membranes. These categories, arranged from smallest to largest pore size, are reverse osmosis (RO), nanofiltration (NF), ultrafiltra-

tion (UF) and microfiltration (MF), where the selection of membrane technologies for such effluent relies on costs based on the balance between water flux and solute retention [15-19].

3. Membrane filtration in textile wastewater treatment (NEW)

Processes using membranes provide possibilities for separating hydrolysed dyestuffs and auxiliaries, thus simultaneously reducing coloration. Over the last few years, technical and economical improvements have made the treatment of wastewater by membrane systems more and more advantageous over conventional treatment processes [20-22]. The most notable outcome of the membrane treatment is the superior quality of the produced water, which is attained with the addition of fewer chemicals, over conventional water treatment processes. Additionally, membrane plants can be much smaller than conventional wastewater treatment plants because of the modular configuration of the membranes, and the possible elimination of other processes (e.g. clarification). Ultrafiltration membranes have been successfully applied in many industries, but it has not been as widely accepted by the textile industry because it does not remove low molecular weight dyes. There are examples of micelle-enhanced use of UF membranes for dye removal [23-25] but in general the rejection range from 30 to 90% makes the direct use of UF membranes impossible and further filtration is required by either RO or NF membranes. In RO, problems with fouling are present which result in low fluxes due to the dense polymeric membrane used and poor separation. RO also becomes less effective when osmotic pressure, caused by high salt concentration in the feed wastewater, becomes too high to obtain a reasonable transmembrane permeate flux without applying

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excess transmembrane hydraulic pressure. In this situation NF provides a possible alternative, maintaining high dye rejections albeit with the cost of lower rejection of electrolytes.

NF membranes have been used in recovery of salt from used dyeing baths [26-31], where the principle is that electrolytes will pass through the membrane, as the dyes will be rejected. However, this principle requires the use of sufficiently small electrolytes. For example Na_2SO_4 which often is used as electrolyte is rejected by the NF membrane limiting the feasibility of this approach. Also standard electrolytes (such as NaCl) are not high-value products. An NF process for the treatment of mixed waste streams from reactive dyeing process has been developed using this principle where the retentate is further treated in a wet oxidation process. The effective desalination of the retentate by the NF membrane is desired as this diminishes electrolyte corrosion in the wet oxidation. NF based dye retention can be quite effective and retentions up to 99% with a permeate flux of 64 L/m2hr have been obtained [32].

RO membranes have also been used in textile wastewater treatment [33]. One example of this used a combination of RO membranes designed for brackish and seawater desalination [34]. Thus the brackish water RO membrane is used in the first stage and the sea water RO membrane is used in the second stage. In this way the retentate is recycled in the second stage in order to obtain high water recovery and the cross-flow velocity is kept high in order to minimise membrane fouling. Using this two-stage RO process water recovery is 85 to 95 % with a mean permeate flux of 15 L/m2hr.

In a comparative study [35] pilot plant tests with UF, NF, and RO treatment of wastewater from washing processes subsequent to reactive dyeing processes are described. UF membrane treatment leaves the permeate stream colorized; whereas NF membrane treatment results in efficient permeate decolourization with a flux of 70 L/m²hr at 10 bar. The RO membrane both decolourizes and desalinates the waste stream. Interestingly, the reactive dyes retention was somewhat lower than in the NF process despite the use of the denser RO membrane. Severe membrane fouling was observed if the waste stream containing dispersed dyes together with reactive dyes illustrating the important issue of membrane fouling when treating complex wastewaters.

4. Membrane bioreactor (MBR) technology

Dyes are generally resistant to fading on exposure to light, water and many chemicals. When decolourisation of water polluted with organic colorants occurs, it takes place by reduction of –C=C- and -N=N- bonds and heterocyclic/aromatic rings [36]. The azo (-N=N-) bonds (as well as sulfonic ($-SO_3$) groups) are electron withdrawing groups and this generates electron deficiency within the molecule, making the compound less susceptible to oxidative catabolism by aerobic bacteria [8]. Traditional aerobic/anaerobic activated sludge or aerobic biofilm processes are utilised worldwide for biodegradation due to simplicity and low cost. Disadvantages of this process include the following: 1) low biodegradability under aerobic conditions which limits the application of the aerobic biological process for the treatment of textile wastewater; and 2) longer hydraulic retention time or the requirement of a larger aerobic tank. Aromatic amines, metabolites, are more toxic than the dyes themselves; therefore a two-stage biological process is required for the treatment of textile wastewater, since the water contains reactive dyes. The two-stage biological process should consist of anaerobic and aerobic reactors in sequence, allowing the mineralisation of the xenobiotic azo-compounds [5-8].

In general membrane bioreactor (MBR) technology is a bio-treatment method involving a suspended growth activated sludge system and filtration on a porous-like membrane (i.e. microfiltration (MF) or UF) for solid/liquid separation. The use of MBRs technology in wastewater treatment was initially designed to achieve high organic matter removal (i.e. COD), since the MBR design in principle leads to total retention of the biomass and improved biological reactor operation [6, 9-12]. MBR systems have the potential to degrade residual organic matter and obtain high effluent quality, both for water re-use and additional purification steps [6]. The combination of activated sludge units and membrane filtration for biomass retention results in high effluent quality and compact plant configurations [9, 37-39]. MBR technology has demonstrated sustained performance over several years with a reliable product quality, providing a clear cost benefit [6]. The main drawback of MBR technology is the high cost associated with MBR systems, while membrane costs have decreased over the years since the commercialisation of submerged MBRs in 1990 [15, 43] leading to a decrease in capital costs, the energy demand associated with preventing and removing membrane fouling has become the main contributor to the overall operating costs [43].

The permeate stream from MBRs are normally free of bacteria [44, 45], since most of the micro-organisms are retained by the membranes within the bioreactor. The hydraulic retention time (HRT), then, becomes completely independent of the solids retention time (SRT) [46] and re-usable water can be recovered from the MBR permeate stream, thereby assisting industries producing wastewater in reducing water consumption and decreasing the amount of wastewater discharged [47-49]. In MBRs contact time between activated

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sludge and non-biodegradable pollutants present in wastewater is elongated, with increased contact time increasing the degrading efficiency of the bioreactor and providing an optimum environment for the treatment of textile wastewater, characterised by strong colour and low BOD5/COD ratio [47].

As mentioned earlier aerobic degradation is less effective when it comes to removal of dye stuff. However, anaerobic systems have been utilised to cleave azo bonds in the treatment of textile wastewater [50, 51], and many bacterial groups possess enzymes (i.e. azo-reductases) capable of disrupting the azo bonds under anaerobic conditions [3]. The anaerobic degradation product is colourless aromatic amines, which are carcinogenic, but these aromatic amines can then be readily degraded via aerobic digestion by non-specific enzymes through hydroxylation and ring opening of the aromatic compounds [52]. Mineralisation of the azo dyes is complete when the aromatic amines have been biodegraded to carbon dioxide (CO_2), water (H_2O) and ammonia (NH_3) 52, 53]. Thus, for complete mineralisation of azo dyes, a combination of reductive (anaerobic) and oxidative (aerobic) steps are required [54-56]. This can be realized in an AnMBR followed by aerobic degradation of metabolites from the MBR reaction.

A key issue in any form of MBR technology is to have an efficient membrane process. However, any membrane technology is prone to fouling – that is, the accumulation of unwanted material on the membrane surface, impeding, and in some cases completely block transport. In order to elucidate fouling effects, synthetic waste streams mimicking actual waste streams can be analysed [57]. This approach would in principle make it possible to relate the permeate flux decline to certain components or combination of component present in the actual waste stream. In general pressure driven membrane processes such as ultrafiltration (UF), nanofiltration (NF), and reverse os-

mosis (RO) are all prone to fouling typically caused by the presence of natural organic matter (NOM) [58] and biofouling [59]. With textile wastewater as a membrane feed stream this issue becomes particularly important and it is therefore necessary to address this issue. This can be done in principle by making no-go list of components (i.e. components with strong fouling propensity. Another more general strategy is to consider alternatives to pressure driven processes.

This has prompted new developments in using anaerobic bacteria and membrane technology where the concept of anaerobic membrane bioreactors (AnMBB) has attracted interest, see [37] for a review.

5. Forward osmosis membranes

In contrast to pressure-driven processes forward osmosis (FO) is less

prone to fouling and FO based systems are attracting increasing interest in water treatment/engineering applications Thus FO has been used to treat industrial wastewaters (at bench-scale), to concentrate landfill leachate (at pilot- and full-scale), and to treat liquid foods in the food industry (at bench-scale). FO is also being evaluated for reclaiming wastewater for potable reuse in life support systems (at demonstration-scale), for desalinating seawater, and for purifying water in emergency relief situations, for a detailed review see [60].

Forward osmosis (FO) is a membrane process that is increasingly attracting international interest as a novel technology for treatment of a wide variety of aqueous solutions [60-65] as well as energy production in pressure retarded osmosis (PRO) processes [66]. Forward osmosis
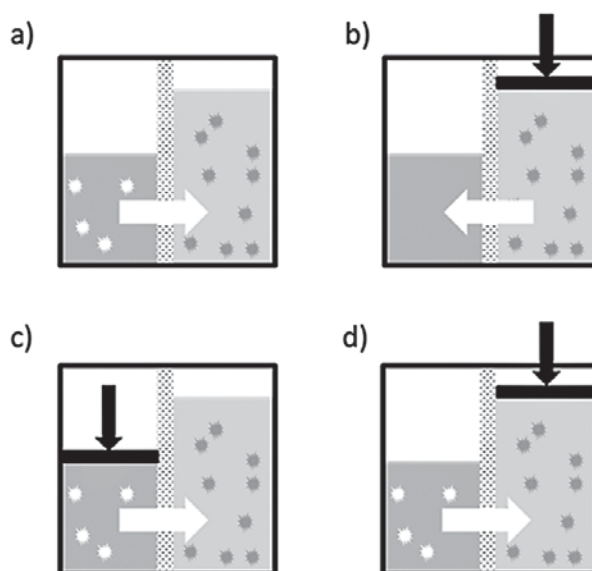

Fig.1 Osmotic processes. Flux (J) versus hydraulic pressure (ΔP) in a) forward osmosis (FO), b) reverse osmosis (RO), c) pressure assisted osmosis (PAO), and d) pressure retarded osmosis (PRO). For FO, there is no hydraulic pressure across the membrane. For RO, the applied hydraulic pressure must exceed the osmotic pressure and convectively drive the water from low to high water chemical potential. For PAO hydraulic pressure is applied in the same direction as the water flow. For PRO, the hydraulic pressure retards the FO process but the effective hydraulic pressure is still less than the osmotic pressure. In all cases the osmotic pressure difference across the membrane can be approximated as the difference in osmotic pressure of each solution. In ideal solutions the osmotic pressure π can be determined from the Morse equation: $\pi=iMRT$ where *i* is the van't Hoff factor, *M* is the molarity, *R* is the gas constant and *T* is temperature.

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takes advantage of the osmotic pressure gradient across a semi-permeable membrane. This is in contrast to the hydraulic gradient applied in RO extraction of clean water from impaired water, see Fig.1.

FO operates by concentrating a feed solution (FS) and diluting a highly concentrated aqueous solution – the draw solution (DS). The larger osmotic pressure of the DS compared to the FS constitutes the driving force for the separation process. Thus, FO is an osmotic concentration process which in principle can operate at zero hydrostatic pressure providing a sustainable water treatment solution.

FO is not getting implemented at a large-scale for several reasons. There are at least three 'must-win' battles to successfully overcome before FO becomes a large-scale technology comparable with established technologies such as RO. First, a new type of membrane is needed which has to be very thin in order to minimize internal concentration polarization. Second, good DS's are needed, the most studied currently are ammonium-bicarbonate-based DS [64] and their use poses several problems including unfavourable interactions with known (conventional) membrane materials. Third, a new system solution: an FO membrane cannot simply replace an RO membrane in conventional membrane modules [65, 66]. Until the prospect of winning battles one and two looks promising, no system-provider is likely to engage in the last challenge.

One way to increase water flux across the membrane, while preserving rejection of solutes is to enable facilitated water diffusion across the active layer. This has been studied intensively over the last couple of years where in particular the use of nature's own selective water channels – aquaporin proteins – have attracted considerable interest, for a recent review see [67] and for a general review of the biomimetic approach to membrane technology see [68]. Aquaporins constitute a large family of membrane spanning proteins, for recent reviews see [69-71]. Much has been revealed about this class of proteins since the purification of a red blood cell membrane protein and subsequent heterologous expression of this protein revealing rapid water diffusion along osmotic gradients, see Fig. 2.

The primary sequence of aquaporin reveals its general unit structure in the form of two tandem repeats each containing three transmembrane spanning segments. Biochemical analysis and later crystal structures revealed an hour-glass structure with pseudo two-fold symmetry where the six transmembrane segments surround a central pore. Each tandem repeat contains a loop between TM2 and TM3 with an asparagine-proline-alanine (NPA) signature motif. Each unit functions as a pore and the predominant unit-assembly in biological membranes is a four-unit arrangement see Fig.2.

The simplicity of the aquaporin structure as outlined above is only apparent. The structure is the basis of the remarkable ability to transport water molecules and simultaneously reject charged species including protons. Molecular dynamics (MD) simulations based on the experimental structure of the mammalian AQP1 show single-file transport of water molecules through a narrow <3Å pore (<0,3 nm) in which steric and electrostatic factors prevent electrolyte passage. The mechanism is not fully elucidated, however, it is clear that a delicate balance between hydrogen bonds in a hydrophobic narrow pore combined with electrostatic barriers [72, 73] and helical dipolar moments [74] result in a very efficient and highly selective transport of water (and rejection of other solutes), although various conducting states are likely to exist [75, 76].

Recently, a design was developed where vesicles are embedded in thin (<200 nm) films deposited on a porous support [77]. Briefly, a microporous polysulfone substrate was soaked with an m-phenylene-diamine (MPD) aqueous solution that contained aquaporin vesicles. The soaked substrate was subsequently exposed to trimesoyl chloride (TMC) to form a three-dimensionally crosslinked polyamide layer in which the aquaporin vesicles are embedded. The resulting membranes are made in sheets up to 600 cm^2 and are sufficiently stable to allow normal handling and shipping procedures.
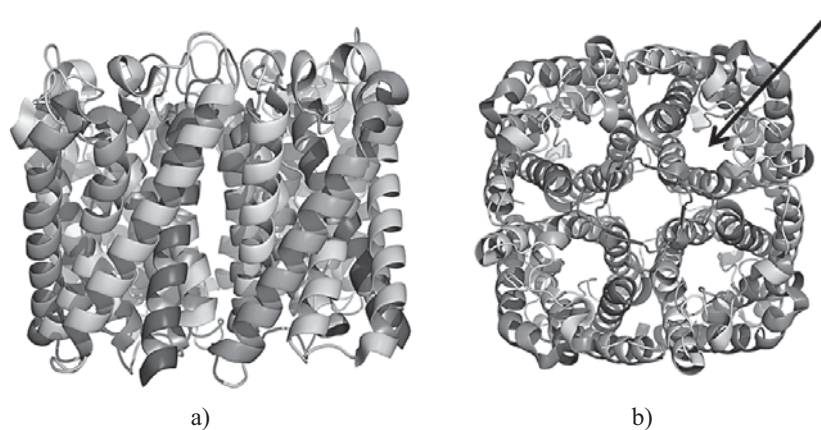

a)   b)

Fig.2 Aquaporin tetramer (AqpZ isoform, PDB coordinates 2ABM). Left: cross section; Right: top view. The four identical monomers are represented by their amino acid backbone structure. The top view shows the four water conducting pores – the pore in the top right monomer is indicated by the arrow. The apparent central pore is not real as only the protein backbone structure is shown. In reality the water conducting pores have very narrow (<0,3 nm) constriction regions allowing only single file transport of water molecules.

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The resulting thin film composite (TFC) membrane has been characterized in cross-flow set-ups. In FO the aquaporin membranes had >90% rejection of urea with a water flux of 10 L/m²h with 2M NaCl as draw solution. This clearly demonstrates the great potential of the aquaporin TFC membranes for industrial FO applications and from 2014 the Danish cleantech company Aquaporin A/S is commercializing membranes as Aquaporin Inside Membranes (AIM™) based on this design.

The configuration of an FO system can be very simple because only minimal hydraulic pressure is required in the FO process to overcome flow resistance in the membrane module. The use of FO for water and wastewater treatment has been evaluated in bench scale and pilot scale studies [60]. Full scale application of FO for landfill leachate treatment has also been reported [60]. In addition, FO has the potential to effectively remove a wide range of contaminants of concern in typical water and wastewater treatment applications, although this particular application is yet to be fully substantiated [78, 79]. Thus FO membranes could in principle be used to concentrate wastewater using for example seawater as draw solution, or, with suitable pretreatment, be used to directly up-concentrate dyes.

Perhaps the most interesting perspective is offered by the novel concept of combining activated sludge treatment and FO membrane separation for wastewater treatment has been recently explored by a few research groups [80-82]. This process is commonly referred to as an osmotic membrane bioreactor (OMBR). OMBR retains the inherent advantages of both MBR and FO. The high rejection capacity of the FO separation process can effectively retain small and persistent trace organic contaminants in the biological reactor, thus significantly prolonging their retention time in the reactor and subsequently facilitating their bio-

degradation. Limited evidence from three recent short term bench scale studies [80-82] available in the open literature indicates that OMBR may offer a simple and elegant technological solution for the production of high quality effluent for water reuse or for effluent discharge in environmentally sensitive areas. Although the OMBR concept is still in its infancy, the new developments in FO membrane technology hold interesting prospects for the future in terms of anaerobic OMBR treatment of textile wastewater.

6. Conclusions

In general wastewater represents a challenging feed streams to be treated by membrane separation. In particular, the large variability in composition and the presence of potentially reactive components makes textile industry wastewater a particularly difficult task for any remediation technology including membrane based methods. To date membrane technology for textile wastewater has been based on RO/NF/UF based systems but developments have been hampered by membrane fouling. Recent technological development of both MBR technology and FO membranes each has opened for the possibility to use this technology in industrial processes and wastewater treatment. The inherent low fouling propensity of FO membranes makes them an intriguing supplement to existing remediation methods. Thus FO can in principle be used to concentrate the wastewater – thereby reducing the hydraulic load on the wastewater treatment plant – with diluted seawater being the discharged water stream. FO potentially can also be used in up-concentration of dyes provided that dyes are the most prominent feed stream solute. Finally FO membranes may be used in anaerobic OMBR opening up for complete processing of textile wastewater.

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