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Potential large-scale applications of track-etched ultrafiltration polymer membranes*

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Abstract

Track-etched membranes (TEMs) can be produced with precisely determined pore size, shape and distribution, but only find niche applications from industrial and biomedical separations processes to nanotemplating because their conventional production is too expensive for large-scale separation processes. We developed recently new technology for the cost-effective production of TEMs. The commercial viability of this new class of thin polymer membranes hinges on inexpensive production, suitable chemistries, scalable processing methods and efficacy demonstration in real separation environments. This paper outlines their potential large-scale applications: drinking water treatment, extractive industrial water processes and effluent treatment, industrial gas separation, domestic air filtration, and biochemical sensing. Modern membrane filtration technology utilising ultrafiltration TEMs is an attractive complete or partial solution to these areas, and could be used in preference to conventional separation methods

Keywords: Energy Saving, Ultrafiltration Membrane, Nanostructure Morphology, Water Treatment, Gas Treatment, Sustainability

1 INTRODUCTION

We developed recently a new class of ultrafiltration (UF) membranes for water treatment and gas separation processes. The industrial, commercial or municipal viability of this new class of thin polymer membranes hinges on inexpensive production, suitable chemistries, scalable processing methods and efficacy demonstration in real separation environments.

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UF membranes have very narrow pores (1–100 nm) and are attractive due to their ability to purify, separate, and concentrate target molecules in continuous systems. Commercial UF membranes are produced by phase-inversion processes that are time consuming and need careful control, and so are expensive, have poor structural definition and decreased separation selectivity. A more suitable alternative to phase-inversion produced membranes are highly-defined nanostructured track etch membranes (TEMs) which could maximize the full efficiency of UF modules tailored to exact separation processes. Of all membrane production methods that can control precisely the size of nano- to microscale pores produced, track etching has one unique and very attractive property: it is scalable up to the dimensions demanded by industrial and municipal separation processes.

Although TEMs (i) can be produced with precisely determined pore size, shape and distribution (Apel, Spohr 2001), (ii) find many niche applications from industrial and biomedical separations processes to nanotemplates (Belkova et al. 2009, Ferain, Legras 2009, Xavier et al. 2008, Koshikawa, Usui & Maekawa 2009, Hanot, Ferain 2009), and (iii) can be surface functionalised to improve chemical selectivity or permit stimuli-response (Ulbricht 2006, Cuscito et al. 2007, Geismann, Yaroshchuk & Ulbricht 2007, Friebe, Ulbricht 2007, Friebe, Ulbricht 2009, He et al. 2009, Kuroki et al. 2010), their conventional production is too expensive for large-scale separation processes. The key initial manufacturing stage of TEMs is typically heavy ion irradiation of thin polymer films at a nuclear reactor or large accelerator facility with large costs and lead times (Wanichapicharta et al. 2000, Apel 2003). It is this stage that alone incurs costs prohibitive to nearly all industrial UF system consumers.

The accepted paradigm was that continuous etchable tracks are the preserve of irradiation by energetic heavy ions (Trautmann 1995, Trautmann, Bouffard & Spohr 1996, Yamauchi et al. 2012). Light ions used by our group impart a comparatively small amount of energy and are typically regarded as insufficient. We investigated this issue intensively only to confirm the validity of published results when using conventional techniques. Motivated by the desire to substantially reduce production costs, we explored unusual combinations of conventional techniques. In 2013 we developed a completely novel etching technique that started to yield the first ever TEMs produced by light ion irradiation (Heikkilä 2013, Paronen 2013). Irradiation instead by light ions significantly reduces investment production costs because it only requires a common type of small accelerator than has low running costs, frequently available beamtime and capacity for high membrane production volume. The estimated costs for UF-TEM production using our method are significantly lower those currently marketed, and thus competitive with phase-inversion UF membranes currently employed for industrial water treatment.

The initial motivation for our research was to develop a membrane production method that would be acceptable to industry in terms of outlay cost, and create membranes that would reduce substantially their process energy consumption and the release of environmentally harmful effluents. Our work is evolving from the fundamental scientific proof-of-concept stage to initial validation of the novel technology in the laboratory. The near-term desire is to scale-up the production process to the mini-pilot scale and progress to validation and demonstration of the technology in relevant environments in order to build industrial and academic collaborations.

Our new membranes are very versatile and can be applied to potentially many different types of separation processes. We have chosen to focus in the near-future on two applications to investigate and demonstrate their viability, both of which could have major industrial or societal impacts: selective removal of (i) metal ions from process water and effluent typical to the Finnish mining industry and (ii) natural organic matter (NOM) from peat production runoff. Both these applications and other potential applications are described below in this paper.

2 MEMBRANES FOR MODERN WATER AND GAS TREATMENTS

There are solid indicators that conventional treatment processes for industrial water are no longer sufficient to cope with current demands (Kroiss 2014). Industries face increasing pressure to optimise costs, minimise water usage and comply with ever more stringent environmental regulations, and are driving the mining, pulp and metallurgical industries to treat and reuse the vast volumes of water they consume (Shao et al. 2009, Jönsson 2013, Mänttäri, Nyström 2010, Katsou et al. 2010, Li et al. 2009, Katsou et al. 2012) and the development and testing of innovative materials, process technologies and tools for integrated water management. The chemical industry too in Europe is overhauling its process water loops into more sustainable systems through major project initiatives and activities in industrial water technology, e.g. E4Water and ChemWater (Lyko 2014). Their water treatment is a challenging process due to the typically high content levels of NOM, organics, salts, large variations in composition, cost limitations and reliability specifications.

In recent years interest has grown in the integration of UF into a multi-stage separation processes in these industries to remove suspended solids, bacteria and colloids effectively. Such reuse leads to reduction in water consumption, cleaner and less effluent, which is especially important in environmentally sensitive and water-stressed locations. Fortunately science and technology can mitigate environmental impacts and increase efficiency because current treatment methods are still far from natural-law limits in their ability to separate compounds, deactivate or remove deleterious chemical agents, transport water molecules, and move ions against concentration gradients (Shannon et al. 2008, Craig, Gardner & Meares 1975b, Craig, Gardner & Meares 1975a).

The use of modern membranes to filter out compounds from water continues to gain acceptance in the water treatment industry. The technology is an attractive and alternative approach to established separation methods due to its fast and energy-efficient process and its lack of need for a phase change (Mehrparvar, Rahimpour & Jahanshahi 2014). Membranes have the advantage over other chemical and physical treatment methods in their capability to remove both suspended and dissolved solids and many pathogens. Membrane technology can shorten and simplify the long water treatment chains of physiochemical and biological unit processes needed to satisfy stringent water quality criteria (Metsämuuronen et al. 2014).

Membrane filtration will increasingly be used in preference to conventional treatment, offering capital cost savings, ease of construction, and the production of high quality water (Binnie, Kimber 2013). The WIPO reports that the membrane-based water treatment field is currently seeing a high level of innovation, and of all the water treatment technologies, innovation in membrane filtration was voted to be having by far the highest impact (World Intellectual Property Organization (WIPO) 2012). Several market reports estimate the global market for membrane technologies is approximately 12.5 billion € with a 9% annual growth rate.

UF systems for industrial water treatment are most attractive in a modular configuration. The design should allow variable operation of hydraulic load changes throughout the day, handle changing levels of fluid properties (e.g. turbidity) by adjusting the trans-membrane-pressure be easily scaled up to meet future demands.

UF membranes could also be used to selectively separate different gases and remove small airborne particles using the size exclusion principle. Thus they could also enter the field of industrial gas separation and purification of air from bacteria and fine particulate matter (PM).

3 POTENTIAL LARGE-SCALE APPLICATIONS

3.1 Treatment of surface water for safe potable use

Lack of access to clean water is an urgent health and economic issue that affects a large proportion of the world’s population. Although many have gained access to improved drinking water sources, many rural and poor populations miss out on improvements – the burden of poor water supply falling most heavily on girls and women. The WHO reports that 768 million people, or 11% of the global population, are currently without access to clean drinking water, persisting at an estimated 605 million people in 2015 (World Health Organization (WHO) and UNICEF 2012, World Health Organization (WHO) and UNICEF 2013). This is particularly dramatic in developing countries where the combined growth of industrial chemical release into the environment, population numbers, climate change and unregulated urbanization contribute heavily to the severe pollution of water and soils (Li 499, Intergovernmental Panel on Climate Change (IPCC) 2014).

A significant proportion of the populations in Oceania and sub-Saharan Africa still use surface water. Left untreated the water contains unsafe levels of microbes such as bacteria and protozoa, and also viruses and solid and dissolved compounds, and its consumption contributes directly to the 1.8 million annual deaths caused by diarrhoeal diseases, especially among children aged under 5 years, and rates as one of the highest causes of global burdens of disease (World Health Organization (WHO) 2007, World Health Organization (WHO) 2014).

Nearly all cases of diarrhoeal disease in developing countries are preventable by interventions in clean water access and improvements in sanitation and hygiene (Fewtrell et al. 0201). To achieve significant health impacts a purification technology must be effective in removing pathogens, available at a reasonable cost and scalable to widespread sustained use (World Health Organization (WHO) 2007). A number of physical, biological, chemical and radiative technologies exist that have varying degrees of efficacy in treating freshwater to generate safe potable water. Many, however, are far too expensive for developing countries, and so will not be implemented in the rural areas where they are most needed, or are affordable by uptake by communities has not been widespread because of technical and other reasons.

Among all the possible technological solutions to drinking water purification, low cost and highly efficient UF might be the most promising (Hillie, Hlophe 2007, Han, Xu & Gao 2013). UF is presented as an alternative to chemical disinfection to obtain safe drinking water because of its ability to remove microbiological contamination (Iannelli et al. 2014). Large contaminants are first removed with coarse filters before the water passes through a finer UF membrane to remove smaller pathogens. Suitable advanced membranes, however, typically cost thousands of euros per square metre or simply cannot be produced on a large scale. This issue must be addressed on two fronts: (i) as above, developing an affordable, high selectivity UF membrane; (ii) development of a low-cost, modular portable water filtration device suitable for use at the household level. The most applicable end users will be rural populations in developing countries that do not have access to clean communal water, but need to rely upon household or small community level purification of dirty surface water.

3.2 Municipal drinking water treatment

The integration of UF into current municipal water treatment systems in developed countries is increasing in pace and the trend is expected to continue for the reasons described above. TEMs are well suited to such purposes, especially with regard to the removal of NOM (described below) and pathogens. Here, however, attention is drawn to a region where municipal water treatment is currently under a phase of rapid and extensive improvements due to massive urban expansion.

In regions in China where the water quality is poor, 190 million fall ill and 60 000 die annually from diseases such as liver and gastric cancers caused water pollution (Qiu 2011). One quarter of China’s 4000 urban water treatment plants surveyed in 2009 did not comply with quality controls, and despite a national program to deliver safe drinking water by upgrading pipes and treatment plants, urban expansion will continue to outpace such improvements (Tao, Xin 2014). An alternative to treating the vast volumes of polluted water is to prioritize the drinking water which accounts for only 2% of total water use (most water is consumed by industry, agriculture and non-drinking domestic). Cheaper technologies at the point of use, such as purifiers on taps, would be enough to deliver clean drinking water to most of China’s population (Tao, Xin 2014). In Kenya, Bolivia and Zambia water purifiers at the point of use have been shown to reduce diarrhoeal disease by 30–40% (Fewtrell et al. 2005, Sobsey et al. 2008), but less than

5% of Chinese homes have such devices (most still boil water) although China's water purification industry is growing by about 40% annually (Tao, Xin 2014).

3.3 Mining industry

The Finnish mining industry has recently experienced increased demand for metals and certain industrial minerals, stimulating technological developments while at the same time increasing environmental conflicts of which half are water related (Wessman et al. 2014). While the major wastes generated by mines are waste rock, tailings and overburden, more than 70% of all pollutants from the mining industry are found in discharged mine water (Doll 2012). Thus it is critical to avoid a discharge of toxic components into the environment and subsequently back to the food-chain. Because of this, regional discharge requirements are becoming more stringent, while non-compliance is being penalized more frequently and more heavily. Water and wastewater treatment is thus becoming a major focus of mine operations, which is changing the landscape of site water management and treatment. Hence, there is a trend towards sustainable mining under the Green Mining paradigm. Development and implementation of new technologies in the Finnish mining sector have not satisfied demand, especially with regard to water treatment technology (Kohl et al. 2013).

In any mining project water is a critical element in understanding sustainability. Metal mines in Finland consume typically 2 m^3 water/ton ore (1–6 million m^3 water/year) of which over half is recycled (Wessman et al. 2014). While the total consumption is relatively low, on a local scale mining operators are generally the highest water consumers/dischargers in the immediate are. Ensuring a social licence to operate, the mining industry strives to manage their waters in an ecological and efficient manner. Unlike many water-stressed regions, mining operations in Finland endure excess water from heavy rainfall and melting snow consequently increasing the risk of accidental discharges into the environment. Furthermore, ice cover limits chemical degradation of pollutants leading to oxygen depletion in aquatic systems (Kauppi 2013).

Replacing fresh water with lower quality water at the mine and recycle more water often reduces overall consumption of water and process chemicals, but is very case specific as water quality impacts on process performance (Wessman et al. 2014). New cost-efficient water treatment technologies should be developed to attain this need for recycling water that meets the quality standards of specific extraction industrial processes. Sustainable mining requires innovative, energy-efficient, modular solutions for treating raw, process, recycled and waste waters and for rejection concentration and recovery of metals (Kankkunen 2013).

Advanced membrane systems have already proven to be robust, reliable and economic when applied to underground mine drainage water, open pit mine intrusion water and excess water from tailing storage facilities (Doll 2012). For example, GE developed its ZeeWeed UF technology and applied successfully in the Buchanan No. 1 coal mine (GE 2010). The advanced filtration membranes and thermal water treatment technology treat mine water, enabling about 99% of the water to be reused in other mining operations throughout the plant. The system incorporates UF hollow fibre membrane technology to separate particulates from water, and reverse osmosis technology to remove dissolved impurities. The concentrated brine is then treated by thermal evaporation, crystallization and drying to achieve zero liquid discharge.

TEMs may offer further opportunities for improved contaminant retention or recovery of valuable constituents from wastewaters, without intensive chemical treatment and while reducing the need for subsequent decontamination. However, advanced filtration processes require membranes with much narrower pore size distributions than those derived from immersion precipitation (Shannon et al. 2008). TEMs can be produced with extremely narrow pore size distributions – the highest of any polymer membranes. Pore size alone may not be sufficient nor the optimal membrane property in the selective separation of ions. Often the selective separation of a particular metal ion in the presence of similarly-sized competing ions will only be afforded with appropriate membrane surface chemistry that exploits a difference such as ion oxidation state. So, chemical functionalization of TEM surfaces/pores would need to be developed accordingly.

A technological barrier that needs to be addressed for application of membrane technology in mining water treatment is the capacity of a membrane material to tolerate high temperatures and low pH environments. Process waters in the metal industry often exceed 80°C, whereas most commercial polymer membranes operate preferably below 50°C. Ceramic membranes are heat and acid resistant, but expensive and not so selective for dissolved metals (Tanninen 2011). However, our TEMs are produced from polyarylate, an advanced polymer product from the polycondensation of phenolphthaleine and terephthalic acid, that has robust mechanical properties and withstands temperatures up to 175°C. It is resistant to most acids and salts, but less so to alkalis and organic solvents. Importantly it has low water absorption, max. 0.25%, and thus is dimensionally stable.

3.4 Removal of NOM from peat extraction runoff

Peat production activities such as drainage of the peatland area and the exposal of peat layers are known to cause an increase on the runoff water discharging from the production sites and an increase on the leaching of pollutant substances into water bodies located downstream. The leaching of pollutant substances such as suspended solids, nutrients, toxic metals and natural organic matter (NOM) may result in the eutrophication and siltation of the receiving water bodies causing water quality deterioration and a series of negative impacts to the local aquatic ecosystem (Heiderscheidt 2011).

Several treatment methods have been developed and are now applied in the purification of peat harvesting runoff water (Turveteollisuusliitto ry 2009). Improvements to the different methods surfaced from the increasing awareness within the industry regarding the environmental impacts of the imposed loads and from stricter emission limits imposed by Finnish authorities. Nevertheless, due to factors such as load concentration and volumetric discharge variations, the purification levels achieved by the applied treatment methods do not reach in all production sites the requirements set by Finnish legislation (Silvan, Silvan & Laine 2010). Further developments to all peat harvesting water treatment methods are required to ensure the appropriate level of load reduction and the protection of water resources surrounding peat production sites (Heiderscheidt 2011).

NOM is a complex heterogeneous mixture of organic compounds, typically humic acids, which cause problems in water treatment plants and for consumers (Metsämuuronen et al. 2014). All surface waters contain NOM from the chemical and biological degradation of plant and animal residues. However, it is the high concentration and composition variations of NOM in peatland runoff waters that make it challenging to remove totally.

For drinking water consumers the main concern with NOM comes from toxic disinfection byproducts: NOM can react with chlorine to form carcinogenic compounds such as trihalomethanes (THM) and haloacetic acids (HAA) (Metsämuuronen et al. 2014). Other reasons to remove NOM from drinking and process water summarized elsewhere (Odegaard et al. 2010) include: a) affects organoleptic properties of water (colour, taste and odour); b) reacts with disinfectants used in water treatment, thus reducing their disinfection power; c) influences disinfectant demand and – process design, operation and maintenance; d) affects stability and removal of inorganic particles; e) influences heavily on coagulant demand; f) may control coagulation conditions and coagulation performance; g) affects corrosion processes; h) affects biostability and biological regrowth in distribution systems; i) forms complexes with and increases mobility of chemical substances found in nature; j) fouls membranes; k) reduces adsorption capacity of granular or powdered activated carbon (GAC/PAC) by pore blocking, l) competes with taste and odour compounds for adsorption sites in GAC/PAC.

The use of membranes to treat soft peaty waters has become common (Binnie, Kimber 2013). Microfiltration (MF) membranes have large pores and are able to exclude NOM compounds only if they are first chemically coagulated into larger flocks. Ultrafiltration (UF) membranes with smaller pores can efficiently remove larger NOM fractions (Lowe, Hossain 2008). However, it requires the combination of MF/UF with other processes (coagulation, adsorption, oxidation or nanofiltration) to remove the smaller NOM compounds that would otherwise cause bacterial growth and biofilm formation in water distribution systems.

The attractiveness of using UF to remove NOMs is the good property of high-flux filtration. However, such efficient water treatment does not usually meet the needs of industrial processes. Fouling of the membrane surface or pores reduces the flux and makes frequent membrane cleaning unavoidable, which adds to operating costs (Mehrparvar, Rahimpour & Jahanshahi 2014, Shao, Hou & Song 2011). Membranes typically need to recovery their near-initial permeability with appropriate cleaning protocols to remove fouling. Better fouling resistance occurs when membrane hydrophilicity increases, because a more hydrophilic surface absorbs water molecules to make a layer between the membrane surface and organic molecules (Mehrparvar, Rahimpour & Jahanshahi 2014). Many foulants are hydrophobic and so will have a lower tendency to absorb to a hydrophobic surface. So, while the main advantage over chemical disinfection is the drastic reduction of disinfection-by-product formation, some chemicals are still required to control fouling (Iannelli et al. 2014) depending on the membrane surface/pore chemistries.

3.5 Industrial gas separation and domestic air filtration

Membrane processes for gas separation are gaining a larger acceptance in industry and in the market are competing with consolidated operations such as pressure swing absorption and cryogenic distillation. The key for new applications of membranes in challenging and harsh environments (e.g. petrochemistry) is the development of new tough, high performance materials, such as the high technology polymer we use in membrane production. The modular nature of membrane operations is intrinsically fit for process intensification, and this versatility might be a decisive factor to impose membrane processes in most gas separation fields, in a similar way as today membranes represent the main technology for water treatment.

The motivation to implement membranes in industrial gas separations is due to (i) the increasing need to separate out high-value products and contaminants from industrial water and gas streams to enhance profitability and compliance with environmental regulations, (ii) the recent development of membrane gas separation technology to stage where it can outperform conventional units on the basis of overall economics, safety, environmental and technical aspects, and (iii) the compliance with sustainable development of modern industrial processes.

Indoor air pollution in some developing regions is a major cause of disease burden or deadly risk, especially from the inhalation of small particulate matter. The demand for improved air filtration is being driven by high levels of coal, fuelwood, biomass and crop residue burning releasing particulate matter near large urban areas, and increasing vehicle emissions and traffic congestion. Air quality is further degraded by seasonal dust clouds due to intensified desertification

3.6 Biochemical sensors

While the potential applications described above are large scale, either in terms of the dimensions or quantity of UF units, there is another interesting future application for TEMs as biochemical sensors due to ability to control pore size and, crucially, the capacity to generate them with conical or biconical nanopores. This technology is still at a nascent stage, so the scale of any uptake would be only speculative.

Several leading international TEM research groups have targeted nanopores as templates for biological sensors as well as model to understand transport phenomena at the nanoscale (Pietschmann et al. 2013). This interest stems from the crucial role that transport phenomena through biological channels and pores play in many physiological processes in living organisms (Siwy 2006). Biological cells use protein nanopores and channels embedded within the cellular membranes to communicate chemically and electrically with the extracellular environment. The protein channels open and close in response to stimuli such as a change in the transmembrane potential difference, the presence of a specific small-molecule ligand, or a mechanical stress on the cell (Choi et al. 2006, Apel et al. 2009). Recently, significant interest exists in developing abiotic analogues of such biological nanopores as sensing elements for chemical and biochemical sensors, often by creating synthetic polymer nanopores using the track etch method (Apel et al. 2009, Cao, Wang 2009, Sartowska et al. 2012, Davenport, Healy & Siwy 2011). Careful control of conical pore geometry enhances ion current rectification so that the pores can act as ion switches, which will be the key component of ionic circuits, lab-on-a-chip systems, and for manipulation and signal amplification of proteins and DNA (Pevarnik et al. 2012, Vlassiouk, Smirnov & Siwy 2008).

4 CONCLUSIONS

Making industries environmentally sustainable requires innovative, energy-efficient, modular solutions for treating raw, process, recycled and waste waters and for rejection concentration and recovery of metals. Producing safe drinking water from surface water or from low quality municipal water demands careful, selective removal of natural organic matter and pathogens. Modern membrane filtration technology utilising UF TEMs is an attractive complete or partial solution to these areas, and could be used in preference to conventional separation methods: it reduces the dependence on chemical treatments, reduces energy consumption, reduces consumption of natural resources and can more efficiently reduce environmental contamination.

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