Membrane Society of Australasia

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Feature:
Membrane filtration for the food industry at CSIRO

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The global food industry is facing many challenges, including an expanding population, increasing consumer demands for healthier, more nutritious and better quality food, the consequences of climate change and limited natural resources. As such, technology innovations underpinned by scientific engineering research are vital to food, water and energy security.

The Separation Science team at CSIRO is striving to address these challenges by developing sustainable and innovative processes, improving the environmental sustainability of the food supply chain, providing innovative separation technologies to add value to waste streams and designing new food ingredients and products.

The Separation Science team led by Mr Kirthi De Silva is based at CSIRO's site in Werribee. The team is developing advanced separation technologies to extract valuable molecules from plant and animal products in an environmentally friendly manner. The technologies are initially developed at laboratory scale and followed up with scale-up and testing at pilot scale prior to commercialisation with industry partners.

Technologies currently being investigated by CSIRO and collaborators include novel membrane systems (eg. membrane filtration cascade, and microsieve membranes) and stimuli responsive materials for membranes and resins.

Membrane filtration cascade systems offer new possibilities for fractionation of molecules from food and pharmaceutical streams while membrane microsieves posses well defined pores and may allow fractionation of particles by molecular size. These novel membrane materials and process design concepts will improve molecular separation and may overcome some of the problems associated with concentration polarization, and membrane fouling. This will result in an extension of the useful life of the membranes, thus making the processes more reliable and economical for the

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food industry. Stimuli responsive materials can be used to functionalise membranes allowing selectivity and permeability to be controlled by external on-off triggers. These materials may be used to isolate molecules from food streams.

Research at CSIRO, Werribee, is focused on food processing research and consists of five food grade factory modules and research laboratories with both bench and pilot scale equipment, valued at over $40M. There are several bench scale filtration systems (spiral, cassette type, and tubular) capable of processing small batches of samples (1-20L) and large scale filtration units which can be used for large scale process development. These large systems include spiral wound, tubular, hollow fibre and plate and frame designs with a variety of membrane materials including polymeric, ceramic and stainless steel. This is supported by a variety of modern analytical equipment including spectrophotometers, HPLC systems, capillary electrophoresis, an FTIR lactoscope, and a confocal microscope which enable real-time analysis and characterisation of samples.

Some recent projects have involved microfiltration in fruit juice processing, and separation of whey and casein proteins from skim milk using organic and inorganic membrane materials.

Microfiltration in fruit juice processing

During the processing of fruit, fruit skins and stones are removed resulting in the loss of significant amount of fibre and other phytonutrients from the product. Processing not only removes these nutrients, but also results in the generation of a significant amount of waste material.

Fruit processing waste streams are likely to be rich in fruit fibre of which there are two broad categories: soluble and insoluble dietary fibre. Soluble dietary fibre contains pectic substance and hydrocolloid components, which are soluble in water and not digestible by humans. However, they are digestible by the microflora in the large intestine of the human digestive tract, having prebiotic activity and promoting the growth of healthy bacteria in the colon. Insoluble dietary

Figure 1. Pilot scale filtration equipment at CSIRO including a membrane filtration pilot plant flexible to perform pilot studies on the full range of membrane filtration technologies (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) under a wide range of operating conditions and a ceramic microfiltration pilot plant.

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fibre includes cellulose, hemicellulose (some hemicellulose are soluble) and lignin components Whole grain cereals and fruits are good sources of insoluble fibres.

The US Federal Drug Administration reports that Americans consume only 15 grams of fibre per day on average, compared to the recommended dietary reference intake of 28 to 35 grams per day. Numerous studies have demonstrated the beneficial health effects of fibre consumption. For example, increased fibre consumption can help protect against heart disease and cancer, normalize blood lipids, regulate glucose absorption and insulin secretion and prevent constipation and diverticular disease (Aldoori *et al*, 1998; Jenkins *et al*, 1998; Salmeron *et al*, 1997 and Kritchevsky *et al*, 1997).

Fruit processing waste streams are also likely to be a rich source of phenolic

materials. These components have recently attracted considerable attention due to their antioxidant properties and potential health benefits. For example, fruit phenolics are reported to play a role in the prevention of heart disease, improve blood circulation, maintenance and support of heart function, prevention of osteoporosis, cancer, neurodegenerative diseases, and diabetes.

Research conducted by the Separation Science Team suggests that significant amounts of the total polyphenols (measured using the Folin-Ciocalteu assay & Oxygen Radical Absorbance Capacity method) available in the fresh fruit can be lost during fruit juice manufacturing.

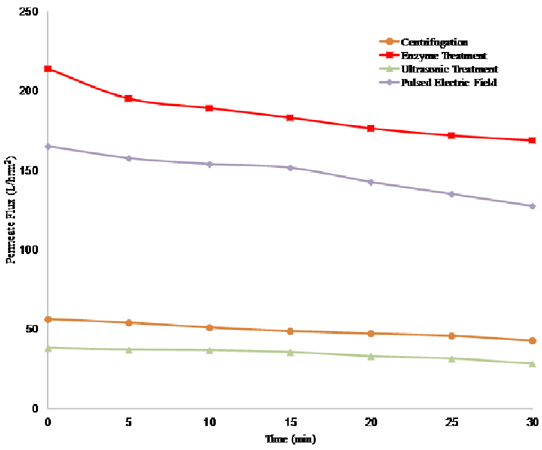

Figure 2. Microfiltration membrane performance characteristics (permeate flux rate versus time) compared with different pre-treatment methods.

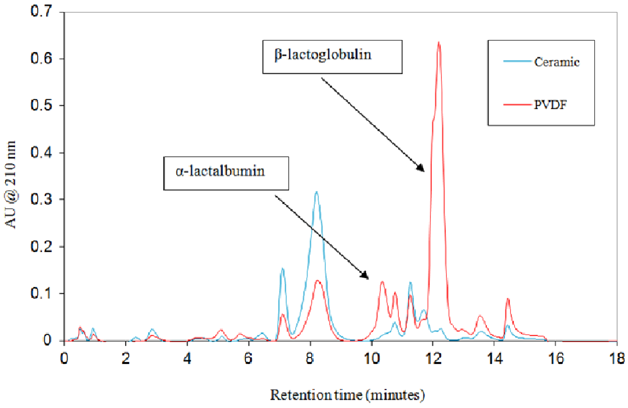

Figure 3. HPLC chromatogram showing the major whey proteins a-lactalbumin and b-lactoglobulin present in MF retentate samples using ceramic and polymeric (PVDF) membranes.

Ultrafiltration has previously been applied to the filtration of fruit juices and especially in the production of clear juices. However, in order to prevent membrane fouling and flux decline, fruit juices are generally treated with a combination of enzymes designed to degrade pectin, cellulose, hemicellulose, starch and protein. The use of enzymes comes at a high economic cost and leads to the degradation of the nutritionally valuable components.

Studies carried out using an inorganic microfiltration membrane compared the effect of different treatment methods (centrifugation, ultrasonics, pulsed electric field (PEF), and enzyme treatment methods) on the permeate flux rate.

The results in Figure 2 show a typical flux decline over time for all treatment conditions using the inorganic membrane. The fruit juices treated with enzymes produced the highest flux rates. However, the permeate flux rate for the PEF treated samples was comparable to that of the enzymatic treatment. In addition, samples treated by the non-enzymatic methods (ultrasonics, PEF and centrifugation) also contained significantly higher soluble fibre in the microfiltered (MF) permeate.

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Separation of whey and casein proteins using organic and inorganic membranes

Microfiltration is widely used in the dairy industry to remove bacteria and spores thus reducing microbial load in milk. More recently microfiltration has been considered for the separation of casein micelles from whey proteins by processing skim milk using various membrane materials and different configurations (Brans *et al*, 2004). The MF separation process, unlike the traditional methods such as acidification and coagulation, does not change the casein micelles structure and retains their valuable physicochemical properties (Al-Akoum *et al*, 2002).

Pilot scale studies were carried out to evaluate the performance of ceramic, polymeric and stainless steel MF membranes when used for filtration of skim milk at the temperature of 5°C. The performance of the membranes at different cross flow rates and trans membrane pressures was evaluated.

Results in Figure 3 below showed the retention of two major whey proteins (β-lactoglobulin and α-lactalbumin) by ceramic and polymeric (PVDF) membranes. The MF retentate from the polymeric membrane contained higher concentrations of β-lactoglobulin and α-lactalbumin compared to the concentrate from the ceramic membrane.

The different separation characteristics of the two types of membrane material suggests that the hydrodynamic properties (charge, size, shape) of the whey and casein proteins as well as their interaction with different membrane materials need to be understood to efficiently separate these components from each other.

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Up coming events:

- 7th Conference of the Aseanian Membrane Society — Korea, July 4-6, 2012
- 12th International Conference on Inorganic Membranes (ICIM) - Enschede, The Netherlands, July 9 - 13, 2012
- North American Membrane Society (NAMS) Conference - New Orleans, Louisiana, June 9-13, 2012
- Euromembrane - London, UK, September 23-27, 2012
- MSA Early Career Researcher Symposium — Brisbane, November 28-30, 2012

Challenges of Working with Inorganic Membranes

Inorganic membranes are commonly defined as membranes made from materials such as metals, a wide variety of oxides and silicates and elemental carbon, in other words – materials that are not polymers. They offer a vast array of benefits including greatly enhanced chemical and thermal stability; and exceptional selectivity and permeability for specific molecules. This has seen them investigated for the separation of H_2 from syngas, CO_2 from natural gas or flue gases, O_2 from air, water from reaction mixtures and dissolved salts or contaminants from water. Over the last three decades research into inorganic membranes has dramatically increased and a multitude of high performance membranes have been reported in the literature; yet few industrial processes outside niche liquid or filtration applications have seen inorganic membranes commercially deployed. Indeed, polymeric membranes have long held sway in the industrial arena, being used commercially for both desalination and natural gas purification since the 1970's.

The primary factors behind the lack of commercial deployment has been both the high cost of membrane materials in the case of metallic membranes (such as palladium based alloys for H_2 production) and the long timeframes and high defect rates associated with traditional thin-film membrane fabrication techniques. Much of the research work has focussed on reducing these costs through the continued development of low cost, high performance materials and application rapid thermal processing techniques such as those employed in the semi-conductor industry. Working At the Films and Inorganic Membrane Laboratory (FIMLab) in the School of Chemical Engineering at The University of Queensland, has afforded the opportunity to not only develop novel, high performance inorganic membranes for wide range of gas and liquid separations, but also to identify a number of smaller but nonetheless important challenges that must be met in order to successfully take inorganic membranes to their chosen markets.

Two of the most important of these challenges spring from the traditional, layered structure of inorganic membranes which most commonly features the ultra-thin (<500nm) membrane layer, intermediate layers of graded porosity and smoothness, on top of a porous support for mechanical strength. This structure allows for the thinnest membrane possible whilst still retaining the strength and robustness required for industrial applications. The porous support is most commonly made from ceramic materials which have high compressive strengths but at the cost of toughness and most are brittle, prone to cracking and susceptible to thermal shock. This is particularly problematic when considering that the higher cost of inorganic membranes means they will need to demonstrate significantly longer working lives than their polymeric counterparts. This includes not only maintaining high flux and product purity but also being robust enough to endure the high flow rates, pressures, vibrations, and thermal cycles associated with process start-up, normal operation and shut down. Recent advances in the development of porous metallic supports is promising and several research groups are have successfully made the shift. The mechanical stability of the membrane layer itself has received little attention from the research community. If the supports remain stable whilst the membrane layer cracks, or develops defects, the entire membrane module will suffer from reduced performance. Of most interest is the ability to withstand exposure to particulates in the feed stream under high temperature, high pressure processing conditions, without compromising membrane integrity.

Secondly, for a membrane module to efficiently separate gases, it goes without saying that the sealing of the membranes into the module must be gas tight. However, sealing inorganic membranes into steel process units is not a trivial task even at low temperatures. The geometry and strength of the membrane and its support along with the ease of assembly for repair and replacement must all be taken into consideration. Inorganic membranes are conventionally fabricated on porous ceramic supports which are brittle and highly

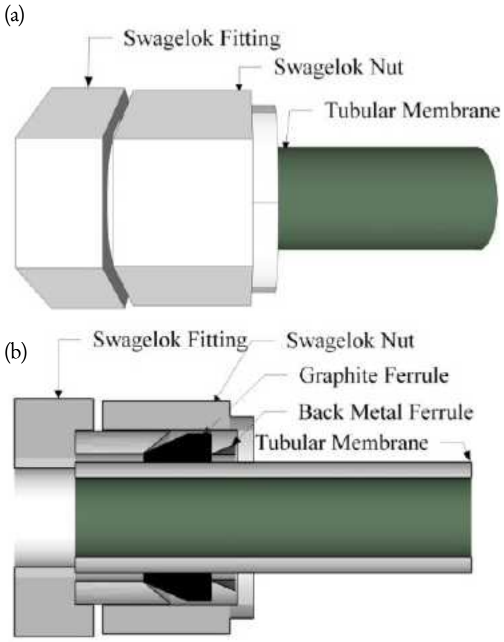

Fig. 1 Membrane sealing design (a) assembled membrane (b) cut-away of assembled membrane showing graphite ferrule and back metal ferrule in place (adapted from - C. Yacou, S. Smart and J. C. Diniz da Costa, Energy Environ. Sci., 2012, 5, 5820-5832)

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Challenges of Working with Inorganic Membranes cont.

susceptible to failure. Research groups often employ soft polymeric o-rings in compression, but at the high temperatures required for many of the gas separation applications, these seals will melt or burn away.

The first option is to design the membrane module so as to isolate the seals from the hot feed gas and primary heating zone of the module, but this requires complex mechanical design and extra cooling requirements. The second option is to replace the conventional o-rings with ones that can withstand the operating environments. There are several materials worth consideration including graphitic, silicate and metallic materials. As an example FIMLab has utilised novel graphite based sealing designs (Fig. 1) up to 500°C without leaks. The final option is to alter the membrane support from a porous ceramic substrate to a porous metallic substrate with dense metal ends that can be conveniently welded into a module, bypassing the sealing limitations experienced with ceramic supports.

These are a few of the challenges of working with inorganic membranes and they are presented in an effort to not only balance their enormous potential against the industrial reality; but also to highlight the remaining areas of research potential and to challenge membrane researchers, technologists and industrial operators alike to identify new ways of solving them.

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Message from the President

Thanks you for reading our second newsletter for 2012. I am pleased to say that our third Annual General Meeting and election of the board of directors on the 23rd May has passed with success. Please welcome Dr Matthew Hill, CSIRO, and Peter Macintosh, who together bring extensive experiences to the board in membrane sciences and industry. The MSA welcomes their involvement with the direction of the MSA. The election also saw the departure of the two directors, Dr Aaron Thornton, CSIRO, and Prof Vicki Chen, UNSW. Aaron and Vicki's active involvement in the MSA will be missed, but we look forward to their continued partnership with the MSA regardless.

The MSA was honoured to have Prof Hans Coster, (FAIP, MIP (UK), CPhys (UK), CSci (UK), FTSE) from the Department of Chemical and Biomolecular Engineering, The University of Sydney, give the invited talk at the AGM. Prof Coster gave us a very interesting talk on piezo-electric membranes, whilst also giving great insight into the future directions of the MSA in the meeting.

This year, the MSA board and committees will be mostly working on the upcoming Early Career Researchers Membrane Symposium 2012, and the 2013 International Membrane Science and Technology Conference (IMSTEC 2013). So the next key event to mark in your diaries is the ECR Researchers Membrane Symposium, which will be held at the University of Queensland, Brisbane, from November 28 to 30. Abstracts are due 31st August 2012! So far, the symposium has confirmed sponsorship from Siemens Water Technologies and Hatch. I would like to thank the commitment from the initial sponsors and the hard work so far from the chair, Dr Simon Smart, and the committee. It's certainly looking to carry on the tradition of success from the previous two student/ECR conferences. I look forward to seeing you there.

While all this is going on, I am also undergoing negotiations with our partner societies, in particular the European Membrane Society and the North American Membrane Society, to arrange conference discounts for MSA members to attend their conferences. Early discussions on this are looking positive, and I hope to be able to establish a formal arrangement which will benefit MSA members attending the conferences of our international partners.

Finally, I would like to congratulate Ms Zongli Xie, CSIRO and Victoria University, for receiving the MSA – AMS7 student travel award! PhD students attending the 7th Conference of the Aseanian Membrane Society (AMS7) were invited to apply for award, and the winner was selected by the judging panel based on the quality of the abstract and need for financial assistance to travel to AMS7. Congratulations to Zongli and thanks to all the applicants and judging panel. We look forward to bringing more such awards to MSA student members for future overseas conferences.

Mikel Duke

President, MSA

MSA AGM and Board of Directors

The Membrane Society of Australiasia Annual General Meeting was held on Wednesday 23 May 2012 at the University of New South Wales, Sydney.

The new board as of the AGM on 23, May, 2012 is:

President - Mikel Duke,
(Victoria University)
Vice President - Long Nghiem
(University of Wollongong)
Secretary - Simon Smart
(University of Queensland)
Acting Treasurer - Aaron Thornton (CSIRO)

General Board

Andrew Groth (Siemens)
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New

Peter Macintosh (Private Consultant)
Matthew Hill (CSIRO)

Membrane Society of Australasia
Early Career Researcher's Symposium 2012

Brisbane 28 – 30th November

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