

## **Recent Trends in Membranes Technology:**

Emerging Opportunities and Solutions for Desalination and Wastewater Treatment

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## Introduction to AMTEC



## **AMTEC in Brief**



## **Research Niche and Pillars**

## **3** Research Niche





## **Research Area**



## **Research Activities**





Innovative • Entrepreneurial • Global

10,000 victims of earthquake in Ranau, Sabah.
6,000 victims of floods & droughts in Kelantan (> 12,000 estimated population in Malaysia).
3,000 people water shortage problem in Bachok, Kelantan.
2,000 people in Kiulu, Sabah for the supply of treated clean water.
1,000 people water shortage problem in Mersing Johor

COMMUNITY & SOCIAL

MPAL

INDUSTRY

ECONO

5 National Collaboration1 International Collaboration

Income Generated Worth **RM6.04 million** Spin off Company 1 Malaysia Patent 27

Academic Staff Ph.D. Graduated MSc. Graduated Index Paper

NATION

## **Presentation Outline**

- **1.** Introduction-Desalination and Water Treatment
- 2. Current Trend of Membrane Technology
- **3. Performance Evaluation**
- 4. Translational Research and Commercialization
- **5** Future Outlook and Concluding Remark

## 1. Membrane Technology

#### MEMBRANE

- 'Membrana', a Latin word defined as skin or thin film.
- Act as boundary or selective barrier between two phases. It is semipermeable.
- Examples: human skin, animals and plants cell

## The history of MEMBRANES dates back to the 18th century...



## 1748

#### Jean-Antoine Nollet

(1700-1770) coined the term **"osmosis"** 



Diffusion of molecules from a place of higher concentration to a place of lower concentration until the concentration on both sides is equal.

#### 0 -0-20 J. 3 3 **Adolf Fick** postulated the law of diffusion across concentration gradient. 0 Gr. 1860 1831 1855 J.K. Mitchell **Thomas Graham** reported semipermeable described the solutionfilms allow permeation of diffusion mechanism of gases at different rates. gases through dense films.

2.

- During the following century, osmosis was of special interest to practitioners in the biological and medical sciences.
- Early membrane investigators experimented with every type of diaphragm available to them, such as bladders of pigs, cattle or fish and sausage casings made of animal gut.





#### Elford, Zsigmondy and Bachmann and Ferry

Improved Bechhold technique, which made microporous collodion membranes commercially available.

1907

## 1930

## 1950

#### Bechhold (1907)

devised a technique to prepare nitro-cellulose membranes of graded pore size. Membranes found their first significant application in the testing of drinking water at the end of World War II. The research effort was sponsored by US Army, which later exploited by Millipore Corp., the first and still the largest US microfiltration membrane producer.

- By 1960, membranes were used in only a few laboratory and small, specialized industrial applications.
- Membranes suffered from four problems that prohibited their widespread use as a separation process: They were too unreliable, too slow, too unselective, and too expensive.

## 1900-1960

 The seminal discovery that transformed membrane separation technology from a laboratory to an industrial process started from the early 1960s.







#### Sidney Loeb & Srinivasa Sourirajan (1962)

A "skin type" membrane with porous sublayer in a single step which involved quenching in a non-solvent coagulant known as the "phase inversion" technique.

#### **General Atomics (1963)**

Produced the first spiral-wound Module for reverse osmosis.



## 1960-1980



#### Du Pont (1967)

Produced the first hollow fiber module for reverse osmosis.

#### Henis and Tripodi (1980)

Invented a coating technique which made separating gas by membranes practical on larger scale.

#### Monsanto (1980)

Launched the first hydrogen separating-membrane (Prism<sup>®</sup>).

## 1980-1990

#### **Cynara and Separex**

Produced systems to separate carbon dioxide from natural gas.

H<sub>2</sub>O He H<sub>2</sub> NH<sub>3</sub> CO<sub>2</sub> O<sub>2</sub> CO Ar N<sub>2</sub> C<sub>4</sub>H C<sub>2</sub>H<sub>8</sub> C<sub>3</sub>H

#### Dow

Produced systems to separate nitrogen from air.



- Progresses in membrane technology is growing rapidly.
- State-of-the-art researches are conducted globally to expand the application of membrane technology into every aspect of our lives.

## PRESENT

 Can be applied in heavy duty industrial sectors, energy storage and production, food processing industry, waste treatment for environmental control, providing clean and save daily needs of water supplies, pharmaceuticals, lifesaving devices, etc.





## APPLICATIONS OF MEMBRANE TECHNOLOGY

Flood



By 2020, the global membranes market is projected to grow at a \*CAGR of 9.47% from 2015 to reach a value of -

\*Compound Annual Growth Rate (CAGR)

Membranes Market by Type (Polymeric membranes, Ceramic membranes, and others), by Technology (MF, RO, UF, Pervaporation, Gas Separation, Dialysis, NF, and Others), by Region and by Application - Global Forecast to 2020, October 2015

**USD 32.14** 

**Billion** 

Asia-Pacific and North America are the key markets for membranes, whereas the developing economies such as the Middle East & Africa and Latin America are projected to witness high growth rates between 2015 and 2020.

Membranes Market by Type (Polymeric membranes, Ceramic membranes, and others), by Technology (MF, RO, UF, Pervaporation, Gas Separation, Dialysis, NF, and Others), by Region and by Application - Global Forecast to 2020, October 2015

Water & wastewater treatment, pharmaceuticals & medical uses, and food & beverages are the topmost segments in terms of market share, whereas the *industrial oil* & gas processing segment is projected to witness the highest growth rate.

Membranes Market by Type (Polymeric membranes, Ceramic membranes, and others), by Technology (MF, RO, UF, Pervaporation, Gas Separation, Dialysis, NF, and Others), by Region and by Application - Global Forecast to 2020, October 2015

## Water Scarcity: The FACTS

By 2025, an estimated 1.8 billion people will live in areas plagued by water scarcity, with two-thirds of the world's population living in water-stressed regions.

Water demand is projected to grow by 55 percent by 2050 (including a 400-percent rise in manufacturing water demand)

By 2050, 1 in 5 developing countries will face water shortages.

By 2030 humanity's "annual global water requirements" will exceed "current sustainable water supplies" by 40%.

Source: http://www.seametrics.com/blog/global-water-crisis-facts/

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## Water Scarcity: The Factors



## **Availability of Freshwater**



## **Engineering Solutions**



#### **Wastewater Treatment**



**Desalination** 

The total number of desalination plants worldwide ~18,500

The global capacity of commissioned desalination plants >86.8 million cubic meters per day

The number of countries where desalination is practiced >150

The number of people around the world who rely on >300 million desalinated water for some or all their daily needs

Source: http://idadesal.org/desalination-101/desalination-by-the-numbers/

## How Membrane Technology HELPS?



## Membrane in Water Treatment



## **R&D&C of Membrane Technology**



## **Multidisciplinary in Membrane Technology**



2. Current Trends in Membrane Technology for Wastewater treatment and Desalination

## Nanocomposite Membranes



Energy-Efficient Membrane Processes



## Nanocomposite Membranes

## Membrane Design

#### Nanotube

- Halloysite Nanotube
- Carbon Nanotube
- Titanium Nanotube

Changing the chemical composition at the opening of nanotube so that It can have charged or possess some functional groups



The charge at the opening of nanotube act as gate to repel salt ion and only allow water molecule to pass through.



## Nanocomposite Membranes

### **Membrane Design**

#### Nanoparticles

- Titanium Dioxide, TiO<sub>2</sub>
- Silver, Ag
- Calcium carbonate
- Silver Phosphate, Ag<sub>3</sub>PO<sub>4</sub>







Most of the nanoparticle are metal oxide which could be easily hydrolyzed to form hydroxides. Eg: When TiO<sub>2</sub> or Ag nanoparticle are incorporated in a membrane, photocatalytic antibacteria and antivirus activities of TiO<sub>2</sub> occur simultaneously.

## Photocatalytic Nanocomposite Membranes

#### Photocatalytic nanocomposite membrane development

Flat sheet membrane



#### Dual layer hollow fiber





## **Photocatalytic Membrane Reactors**

#### Membrane: Flat sheet membrane Membrane: Dual layer hollow fiber membrane Pollutant: Nonylphenol (NP) Pollutant: Biphenol A (BPA) Connect to UV power suppl $\mathbb{T}$ UV/Visible Lamp UV lamp Stainless steel UVA lamp reactor body frame Membrane The state filtration cell Glass tank Membrane module Peristaltic pump Dual layer hollow Flow meter fibre membranes 32.5 Measuring Pressure gauge Connect to air compressor cylinder Connect to peristaltic pump-Tubing Air diffuser 4 Air bubble PVC adapter tube Nanocomposite Membran **Discharge outlet** Clean water

Membrane: Single layer hollow fiber membrane Pollutant: Oily wastewater

## **Adsorptive Nanocomposite Membranes**



## **Energy-Efficient Membrane Processes**



Forward osmosis (FO) is an **osmotically driven membrane process** that takes advantage of the osmotic pressure gradient to drive water across the semipermeable membrane from the **feed solution** (low osmotic pressure) side to the draw solution (high osmotic pressure) side.

Image: Oasys Water

## **Energy-Efficient Forward Osmosis**

#### The potential benefits of FO used in water treatment

- Due to the very low hydraulic pressure required, FO delivers many potential advantages over conventional pressure driven membrane processes, such as:
  - less energy input
  - lower fouling tendency
  - easier fouling removal
  - higher water recovery



Zhao et al. Journal of Membrane Science 396 (2012) 1-21

## **Energy-Efficient Hybrid System: FO-RO**



The key benefits include

- (i) Energy saving
- (ii) Chemical storage and feed systems may be reduced for capital and operations and maintenance cost savings,
- (iii) Water quality is improved for increased consumer confidence and reduced process piping costs
- (iv) The overall sustainability of the desalination process is improved.



Specific energy consumption (SEC) and total membrane area of an integrated FO-RO seawater desalination process compared to a two-pass RO process.

Chung et al. Separation and Purification Technology 156 (2015) 856-860, Shaffer et al. Journal of Membrane Science 415–416 (2012) 1–8

## **Energy-Harvesting through Salinity Gradient**

- Salinity gradient energy SGE is a zero-emission and sustainable technology that can be practically applied worldwide to harvest Blue Energy.
- When the two mediums are mixed, the SGE can be generated based on the Gibbs free energy.
- Pressure retarded osmosis (PRO) and reverse electrodialysis (RED) are the two most commonly known SGE methods that based on membrane technology.



## PRO & RED



Logan and Elimelech Nature 488 (2012) 313

## **PRO – Current Development and Challenges**



PRO technology generates power by using an **osmotic pressure difference** across a semipermeable membrane to produce a flux of water from a low concentration feed solution to a high concentration draw solution.

Image: Pressure retarded osmosis (PRO) system for salt water adopted by Statkraft (2014) (Water Research, 2014, 66, 122-139)

Theoretically, the maximum extractable energy during the reversible mixing of a dilute stream with saline draw solutions ranging from 0.75 -14.1 kWh/ cubic metre of the low-concentration stream. The actual energy extracted will always be lower because of inherent, irreversible energy losses.

#### Challenges

- low-cost and robust membranes that have minimal ICP and fouling
- Reverse salt flux in the PRO subsystem

#### Way forward

- Designing highly selective PRO membranes with a minimal salt permeability
- Employing a novel draw solute that possesses a large molecule size and negligible leakage (Enviro

(Environ. Sci. Technol., 2015, 49, 13050-13058)

## **RED – Current Development and Challenges**

In RED, the energy generated by the mixing of fresh and salt water based on alternating cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs), with low- and high-concentration solution flowing through each alternate channel. The difference in electrochemical potential as a result of the positive ions moving one way and the negative ions moving the other is turned into an electrical current at the electrodes.



#### Challenges

- The cost of ion-exchange membranes
- At least 20 pairs of membranes are needed to overcome energy losses at the electrodes
- Safety concern: Water splitting releases oxygen and, from seawater, toxic chlorine gas from the anode, and potentially explosive hydrogen gas at the cathode

#### Way forward

- Improvement of membrane materials, membrane spacing and architecture.
- Introducing ridges and flow patterns into the membrane material to avoid using to reduce the size of RED systems 50 and increasing power generation.

## PERFORMANCE EVALUATIONS

## **GO/TFN for Nanofiltration**



Synthesized GO is single flake form in nature. The sp2 hybridization state of carbon in graphene changed into sp3 hybridization state in GO, resulting in the disruption of the original planar structure of graphene into a wrinkled structured in GO

#### **TFN Formation**



GO incorporated into PSf membrane



- 0.3wt% GO incorporated TFN showed high rejection towards multivalent salts i.e. Na2SO4 rejection: 95.2% and MgSO4 rejection 91.1%.
- GO nanosheets has potential to overcome trade-off effect encountered by typical TFC membrane i.e. increasing both membrane water permeability and salt rejection.
- The improvements were due to unique characteristics of GO nanosheets, i.e. highly charged and hydrophilic surfaces.

## **TiO2/TFN for Forward Osmosis**

## Nanocomposite Membrane: TiO<sub>2</sub> TFN for FO

#### Polyamide TFN with PSf–TiO2 nanocomposite substrate



- The hydrophilicity and porosity of the PSf– TiO2 nanocomposite substrate was improved upon addition of TiO2.
- TFN prepared from PSf substrate embedded with 0.5 wt% TiO2 was found to be the best performing FO membrane for water desalination process owing to its high water permeability and low reverse solute flux, without compromising rejection
- The increase in water permeability can be attributed to decrease in structural parameter which resulted in decreased internal concentration polarization (ICP).
   A.F. Ismail et al. / Chemical Engineering Journal 237 (2014) 70–80

## Nanoporous Titanate/TFN Antifouling Membranes



Hydrophilic nanoporous titanate senhanced miscibility of the organic and aqueous phases during interfacial polymerization- Enhanced the interfacial polymerization rate.

The existence of large number of hydroxylgroups (-OH) on the surface of nanoporous titanate improved membrane hydrophilicity

Ismail et al. Materials Science and Engineering C 75 (2017) 463

The presence of strongly hydrated layer at the hydrophilic polyamide surface tends to reduce the adsorption of combined BSA and SiO<sub>2</sub> to the membrane surface



#### Thin film nanocomposite membrane

## Hydrous Ferric oxide MMM adsorptive Membrane

#### Polysulfone/hydrous ferric oxide ultrafiltration mixed matrix membrane for adsorptive removal of Pb(II)



- ✓ Hydrous ferric oxide (HFO) is known to have excellent properties against Pb ions
- ✓ This is due to its high specific surface area to volume ratio, fast kinetic rate, environmental friendly and widely available

A.F. Ismail et al. Chemical Engineering Journal 289 (2016) 28-37

## Titania Nanotube/PVDF Membrane



Unique properties of TNT:

- High surface area due to tubular structure
- Highly hydrophilic for anti-fouling properties

PVDF-TNT 0.5% TNT exhibited the most promising result in terms of AT-POME flux, AT-POME colour removal and fouling stability and recovery (90% flux recovery and >95% rejection recovery rate) after 5 cycles of filtration.

A.F. Ismail et al. Chemical Engineering Journal 316 (2017) 101-110

#### PVDF/TNT Hollow fiber mixed matrix membrane for decolourization of AT-POME





# Translational Research & Commercialization

## **Route to Translational Research**



## **Desalination Plant@Pantai Senok, Kelantan, MALAYSIA**



- No natural supply of potable water- over dependent on tube well supply
- Yellowish and poor water quality supply

#### **The Necessity & Societal Benefits**

<image>

#### Water Quality Analysis Before and After Treatment

esults of Analysis			Seawater	SWRO	I Dormiti
Parameter	Unit	Method			Level
Physical standard			10.110		
pH		APHA 4500 H' B	7.6	6.5	6.5 - 8.5
Colour	TCU	APHA 2120 B	10 *	<5	15
Turbidity	NTU	APHA 2130 B	2.7 *	0.30	2
Chemical standard		- new state of the second	And States	a series and the series	
Aluminium as Al	mg/L	APHA 3030 F / USEPA 6010 B	0.05	ND (< 0.02)	0.2
Barium as Ba	mg/1,	APHA 3030 F / USEPA 6010 B	0.08	ND (< 0.02)	0,7
Biocides (Total)	mg/L	USEPA 8270 B	ND	ND	0.1
Boron as B	mg/L	APHA 3030 F / USEPA 6010 B	2.7 *	0.5	0.5
Cadmium as Cd	mg/L	APHA 3030 F / USEPA 6010 B	ND (< 0.002)	ND (< 0.002)	0.003
Carbon Chloroform Extract	mg/L	GC - In House	ND	ND	0.5
Chloride as CT	mg/L	APHA 4500-CT B	14,120 *	110	250
Fluoride as F	mg/L	APHA 4500-F D	< 0.1	< 0.1	0.6
Hardness as CaCO <sub>3</sub>	mg/L	APHA 2340 C	4,300 *	4	500
Iron as Fe	mg/L	APHA 3030 F / USEPA 6010 B	0.19	ND (< 0.02)	0.3
Lead as Pb	mg/L	APHA 3030 F / USEPA 6010 B	ND (< 0.01)	ND (< 0.01)	0.01
Magnesium as Mg	mg/L	APHA 3030 F / USEPA 6010 B	871 *	0.8	150
Manganese as Mn	mg/L	APHA 3030 F / USEPA 6010 B	0.05	ND (< 0.02)	0.1
Mercury as Hg	mg/L	APHA 4500 Hg / APHA 3112 B	ND (< 0.001)	ND (< 0.001)	0.001
Mineral Oil	mg/L	AOAC 945.102 (Mod.)	ND	ND	0.3
Nickel as Ni	mg/L	APHA 3030 F / USEPA 6010 B	ND (< 0.02)	ND (< 0.02)	0.02
Nitrite as NO2	mg/L	APHA 4140 B	< 0.1	< 0.1	0.2
Nitrate as NO3"	mg/L	HACH Nitrate Test Kit	< 0.1	0.1	50
Nitrate as N	mg/L	HACH Nitrate Test Kit	< 0.1	< 0.1	10
Phenol as C6H3OH	mg/L	HACH Method 8047	ND (< 0.002)	ND (< 0.002)	0.002
Residual Chlorine (Free) as Cl <sub>2</sub>	mg/L	APHA 4500-C1 G	0.13	0.05	≥ 0.2
Sodium as Na	mg/L	APHA 3030 F / USEPA 6010 B	3,793 *	54	200
Styrene	mg/L	USEPA 8260 B	ND	ND	0.2
Sulphate as SO42	mg/L	APHA 4500-SO42. E	180 *	4	250
Zinc as Zn	mg/L	APHA 3030 F / USEPA 6010 B	0.06	0.15	3
Total Dissolved Solids	mg/L	APHA 2540 C	17,100 *	150	

\*Standard for Water, 25th A Schedule of Malaysian Food 1983 (Act 281) & Regulation (Subregulation 394 (1)) as at ubregulation 394 (1)) as at 1th March 2013.

- SWRO DESAL with max. capacity of 0.5 MLD can benefit 3,300 residents (150 Litre/person) for sustainable daily freshwater supply.
- The clean and sustainable water supply is the catalyst to revive the tourisms industry

SWRO Plant Location

111 Contraction of a second

1.5

1.0. 23

RESERVENCES

#### **Site Location of Desalination System Installation**







## **FLOOD RELIEF**

Home-grown portable membrane water filtration system

Tube Well Seawater River Water Water Sources

Integrated mobile reverse osmosis (RO) water purification system (UTM Membrane)

Clean water support without committing large water production assets from the logistics support structure.

#### Innovative • Entrepreneurial • Global

Estimated population in Malaysia





## **Our Experiences**

## Membrane system for surface water/ river water treatment

#### **Features:**

- Portable system
- Beneficial to 2,000 users (20,000 litre/day)
- High water quality <0.1 NTU
- 99.9 % bacteria and viruses removal
- 100% colloidal removal
- Low cost and maintenance
- No chemicals are required
- Includes back flushing system for cleaning purpose



## **Our Experiences**

## Membrane system for brackish/sea water treatment

#### **Features:**

- Portable system
- Beneficial to 300-500 users (6000 litre/day)
- High water quality < 0.1 NTU
- 99.9 % bacteria and viruses removal
- 100% colloidal removal
- Low cost and maintenance
- No chemicals are required
- Includes back flushing system for cleaning purpose



## **AMTEC-AIRB JOINT VENTURE**



Main Design Parameters					
Feed Water Capacity (treated WW)	:	1,600 m³⁄ day			
Recycled Water Capacity	:	1,000 m³⁄ day			
Operating Hours	:	21 Hours			
System Design Configuration	:	2 x 50%			
Treated Water Quality					
Temperature	:	30-36 Celsius			
рН	:	6.0 - 8.5			
Conductivity	:	< 200 ppm			

30%

Cost Saving on water treatment

50%

Reduction in raw water procurement



Extra **50%** of raw water supply can be rechannelled to approx. **3300** people!

#### **Major TRANSLATIONAL RESEARCH Output**



## **Future Outlook**

Exploration of more functional and advanced materials/ nanomaterials Membrane improvement based on emerging materials and membrane design Integrated system of pressure driven + osmotically driven processes for desalination and wastewater treatment Membranes and membrane systems for wider emerging treatment applications and commercialization



## **Concluding Remarks**

- Membrane technology is a promising technology to address water shortage issues through wastewater treatment and desalination
- Innovation focused on improved membrane materials and system configurations to reduce equipment and operating costs.
- The current trend of membrane science and technology involves the development of high performance nanocomposite membrane, energy-efficient membrane processes and blue energy harvesting
- Membrane technology holds tremendous potential for translational research and global market opportunity.

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# THANK YOU!

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