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MEMBRANES AND MEMBRANE SYSTEMS TO PROVIDE CLEAN WATER AND ENERGY AND ENVIRONMENTAL PROBLEMS

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Abstract

Membrane applications are practiced in industries to produce materials and treat waste effluents. As such, membranes and related processes are not to be neglected. In this paper, different membrane systems are described with the appropriate membrane types. Their application to treat brackish and sea water as well as some industrial effluents are described to produce clean water for human consumption. Role of membranes for the possible recovery of precious metals, like, gold and silver, are also described for their applicability in Pakistan. Membranes are built in humans and plants. Theories of water and ions transport are similar to understand the natural and artificial chemical processes in their bodies. The present article intends to press a need for adopting the membrane processes for attracting attention of policy-making authorities in Pakistan. These membrane processes and applications could be used to bring Pakistan out of the current energy and water crises. This will result in better economic achievements, as all the membranes processes are less energy-consuming than the classical and old techniques.

Keywords: Membranes, Membrane systems**,** Water treatment

Introduction

Membranes and membrane processes are gaining importance due to their simple configuration, low energy consumption in the related unit processes, less space requirement and simplicity (Koros et al., 1996, Rautenbech and Albrecht, 2008. Most of the new and environment-friendly industries which produce chemicals and energy are now being shifted or have been shifted on membrane based systems. The sale of membranes and membrane-related systems is in the order of nearly 200 billion Yuan in China alone in the year 2005 and in the tune of 300 billion Yuan in the year 2008 (Aqucell Membrane Technology, home page). According to the industrial experts, the membranes and membrane-related system market is going to expand continuously at a growth rate of 20 to 30% per year. The sewerage water volume in all the countries of the world is very large. To illustrate, if water consumption of 20 liters per person per day is considered and it is supposed that 25% of the Pakistan receive benefits from this facility, the sewerage water effluents in Pakistan are estimated to be 3.4 to 4.0 trillion liters. As such, it can be seen that if this water is to be recycled to overcome the visualised water shortage, then some simple and energy efficient systems are to be used. Membrane-based systems meet this challenge.

There are large volumes of the gaseous effluents emitted from power sector and from fertiliser, brick, steel and industries which are harmful to health These effluents are to be stopped or stripped off to contain them for useful purpose. Gaseous separation by membranes is an economic and energy-efficient alternative. In this article, use of membrane processes for water treatment, application in gaseous separation and use in fuel cells in electricity production are also discussed.

Membranes

Membranes are the barriers to select or reject the constituents of a mixture of gases and liquid solutions selectively. There are the following membranes types: symmetric, asymmetric, and based on charged groups, ion-exchange membranes. Membranes are organic and

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inorganic in nature. Different types of membranes are used for different purposes. Membranes are also of supported and emulsion types as well, described in the later part of this article.

Membrane Systems

A number of membrane systems have been developed. These systems do have applications in water treatment, material production and their separation. Some of these are mentioned below. More detail about these and other membrane processes is reported by Chaudry, 1997; Chaudry, 1982; Chaudry, 1980; Mulder, 1996; Kruer, 2001 and Gerald, 2007.

- Supported liquid membranes systems (SLM)
- Emulsion liquid membrane (ELM) systems
- Reverse osmosis (RO)
- Electro dialysis (ED)
- Ultrafilteration (UF)
- Supported liquid membrane (SLM) systems
- Microfiltration (MF)
- Pervaporation (PV)
- Fuel cells

Applications of a few of the above membrane systems are discussed in the following sections.

Membrane Systems to Clean Water in Pakistan

Water is available in sea and underground. The concentration of salts in sea is very high and a large portion of underground water is brackish, as mentioned in Table 1, and not suitable for human consumption. A large volume of industrial effluents is added to water bodies to contaminate these. A huge volume of sewerage water is available for recycling for municipal communities use and to overcome water shortage in the cities.

Table 1. Zone areas and quality of water in Pakistan (Chaudry, 1979) (Million hectares of development CCA)

Salinity	<1,000ppm	1,000-3,000ppm	>3,000ppm	Total
Upper Indus Plain	5.02	1.66	1.57	8.25
Lower Indus Plains	0.73	0.18	2.72	3.63
Total	5.75	1.84	4.29	11.88

The TDS in sea water varies from 30,000 to 50,000 ppm, depending upon site and flow of the varied water quality flows from land through rivers plus the industrial effluent inputs to the sea.

All above data indicates the need for treatment of water and water desalination. There are many toxic elements present as metal ions, dissolved in industrial outgoing streams, injurious to human health. Limits of some of these toxic metallic ions (Table 2) are provided below to make the user aware of their harms. The maximum contaminant level (MCL), allowed in drinking water and maximum contaminant level goal (MCLG) level in drinking water below which there is no known and expected risk to health, according to Environmental Protection Agency (EPA, USA).

Reverse osmosis, Electro dialysis, Micro filtration (MF) and Ultra filtration (UF)

MF and UF processes are used to remove suspended solids. RO is used for removing all the metal ions up to a level of 95-99% of both brackish and sea waters. Electro dialysis is used to remove metal ions as well as anions from brackish water (3,000 to 10,000ppm).

Table 2. Limits of toxic metal ions Concentration in Potable water (EPA standard, USA, Qadeer, 2003)

Ions	MCLG (mg/litre)	MCL (mg/litre)
As(V)	None	0.010
Ba	0.004	0.004
Cd	0.005	0.005
Cr (total)	0.100	0.010
Hg	4.000	4.000
Se (IV)	0.050	0.050
Cu	1.300	1.300
Be	0.004	0.004
Pb	0.000	0.015
Tl	0.0005	0.002

Supported liquid membranes are used to treat industrial effluents to recover metal ions. Emulsion and SLM are used to enrich gold, silver and other metal ions.

RO is the minimum energy consuming process for desalination and is used for small and large scale desalination.

Micro filtration removes suspended species of size 100-0.01µm. For example Pollen (100µm), starch (10µm), blood cells (1µm) and bacteria (1µm).

Ultra filtration removes species of size 0.001 to 0.01µm, i.e., DNA and viruses (0.01µm), albumin (0.01µm) and glucose (0.001µm).

Hyper filtration or reverse osmosis removes all above mentioned species and dissolved salts including NaCl and KCl. Pyrogens are also removed. Reverse osmosis removes all sea and brackish water salts and also some anions. The membrane has a life of 2 to 3 years, depending on quality of feed water.

Membranes with high flux are to be selected. Spiral-wound, hollow fiber membrane modules are used.

UV radiation kills algae, bacteria, protozoa and fungi at 254nm, wavelength. The dead products are also removed by RO.

Electro dialysis (ED) uses electricity to pull ions from high TDS waters and solutions. Cation and anion exchange membranes, allow cations and anions to pass through, leaving feed water desalinated. An ED stack consists of hundreds of membrane pairs. It is applicable to brackish waters only. Membranes are to be used to treat aqueous liquids and gaseous effluents.

Environmental Problems and Solutions

Problems: There are so many problems regarding clean water and air in Pakistan, which are to be addressed and solved in order to supply clean water and air for human consumption and industrial use. Some of these are:

- Water gets contaminated by sewerage and industrial effluents.
- Purification of water by distillation and other processes is expensive.
- Water bodies are being contaminated by industrial effluents.
- Under ground water is brackish and not fit for human consumption.
- Environment is polluted by industrial gaseous effluents.
- Natural gas is contaminated with hydrogen sulphide and carbon dioxide.
- Gaseous fuels are inefficient due to moisture.
- Industrial effluents like the oxides of nitrogen, ammonia, hydrogen sulphide and carbon dioxide contaminate environment.

Solutions to the problems

Air and water are to be treated before their entry to water bodies. Gaseous effluents are to be treated before their release to atmosphere. Membranes processes are an easy way to overcome all these problems. Brackish and sea waters can be desalinated, using membrane processes.

Gaseous Separations and industrial Effluents Treatment

Gases diffuse selectively though membranes and so, when pass through membrane modules, separate the gases. As such, undesired components can be removed. The separation factors of some of the gases combinations are given in Table 3.

Table 3. Separation factors of some gaseous combinations. (Kartz and Narayan, 1986; Chaudry, 1997)

Combination	Separation factor
H_2/CO	40
H_2/Methane	50 to 200
CO_2 /CH_4	10 to 50
H_2 /N_2	50 to 200
O_2/N_2	10 to 30

Supported Liquid Membranes for Removal of Toxic Metal ions and Gaseous Stripping

Supported liquid membranes are made of micro porous supports, which may be of plate shape, tubular or spiral wound structure and configurations (Mckay, 1980). Extracting liquid in these supports is absorbed by soaking the supports in the liquid of choice. The liquid can also be passed through once or twice to hold the same in these supports. The feed and stripping solutions are separated by these supports and are kept in flowing or stirred conditions. The metal ions associate with the extractant molecules to make complexes, which diffuse through the supported liquid under concentration gradients inside the membrane. When brought in contact with the stripping solution on the other side of the membrane break the complex to strip the metal ions. The extractant molecules travel back and repeat the process again. These act as shuttles to transport metal ions from feed to stripping phase and separate the metal ions of choice from the other metal ions. The process can also be used for separation of organic components but in this case, inorganic liquid membranes are to be used (Bhave and Sirkar, 1986). The extraction and stripping steps take place simultaneously. Very small amounts of the extractant are used to compare to the classical solvent extraction systems. The energy used in this process is chemical in nature. Low energy use and less capital and operating costs are the special features of SLM processes (More information is available in Chaudry, 1984). Most of the toxic and other metal ions can be removed by designing the liquid membranes.

For gaseous separations and stripping using membrane techniques, some information is provided in Table 4.

Gaseous emissions from Nuclear Industry

There are the following types of gaseous emissions (Table 5) from nuclear industry and can be dealt with by using liquid membranes systems coupled with some other systems.

Table 4. Supported Liquid Membranes and Gaseous Stripping (Chaudry, 1997; Bhave and Sirkar, 1986)

Gas	Absorbent solution	Absorbent nature
Hydrogen Sulphide	Caustic soda	Inorganic
Ammonia	Sulphuric Acid	Inorganic
Sulphur di oxide	Caustic soda	Inorganic
Carbon di oxide	Caustic soda	Inorganic
Carbon di oxide and H_2S	triethrnolamine	Organic
H_2S/CO_2	Amino-2-methylethanol	Organic

Table 5. Nuclear Industry Gaseous Emissions (McKay, 1986)

	Activation Products		Fission Products	
Radio nuclides	H-3	C-14	Kr-85	I-129
Activity	β, γ	β	β, γ	β, γ
Half life (years)	12.25	5730	10.78	$1.6x10^{6}$
Decay time (to 1% activity)	82	38100	72	$1.7x10^{6}$
Decay time (to 0.1% activity)	122	57100	107	$1.6x10^{5}$
Decay rate (fraction/day	$1.55x10^{-4}$	$3.32x10^{-7}$	$1.77x10^{-4}$	$1.22x10^{-10}$

Short lived species like I and Xe^{133} decay within human life time. C^{14} and I^{129} remain perpetually. Kr^{85} is removed by membranes, cryogenic distillation, absorption by liquids, and charcoal (Chaudry, 1997). C^{14} is trapped by immobilised liquid membranes.

Commercial processes used for the recovery of uranium, silver, gold and many other metal ions

There are two types of supported liquid membranes viz. solid supports-based membranes (SLM) and emulsion liquid membranes (ELM). SLM has been described above. In ELM, an emulsion is made consisting of:

i. an organic extractant plus an organic diluent solution and
ii. a stripping inorganic phase.

Both of these are mixed to form an emulsion. The feed inorganic solution is stirred and mixed with above mentioned emulsion, which is in droplet form. The bubbles or droplets constitute organic layer containing extractant. As the feed phase metal ions come in contact with the extractant molecules, they are extracted to bubble layer and react with the stripping phase inorganic liquid and get stripped there. After a calculated time of stirring together, both the feed and emulsion phases are allowed to settle and are separated from each other. The emulsion is broken and the stripping and extractant phases are separated to get separated the stripped metal ions. The extraction and stripping processes take place simultaneously and the processes are very fast. Many metal ions have been separated by using this SLM technique.

Supported liquid membranes (SLM) have been developed in Pakistan by the author and his co-workers. Metal ions which are separated and recovered are Tl, Rb, Cs, Mn, Ag, Zr, V, Cr, Ni, Co, Tc, Mo, Pd, U (Taj et al., 2010; Gul et al., 2011; Chaudry et al., 2008; Amin et al., 2007; Chaudry et al., 2007a; Chaudry et al., 2007b; Naheed et al., 2006; Yamauchi et al., 2005; Naheed et al., 2004; Chaudry, 2002; Chaudry and Ahmad, 2000; Chaudry, 1999; Chaudry et al., 1997a&b; Chaudry and Ahmad, 1993; Chaudry and Ahmad, 1996; Chaudry et al., 1987; Chaudry et al., 1989) and many other metal ions from Periodic Table. More than 95% of metal ions content was removed in all these cases from aqueous wastes and other industrial effluents like that of

i. Electroplating wastes, Ag, Ni,
ii. Tannery wastes, Cr (III) & Cr (VI).

Recovery of Gold and Silver by supported liquid membranes (SLM**)**

ELM and SLM have been applied for the recovery of Au and Ag. (Meifang, 2012-2; Li Hai-bo et al., 2003-2) from Dalian Institute of Chemical Physics, China, became famous for her profitable work which recovers gold from low concentration of gold solution from a gold mine. We recovered Ag from electroplating and other wastes (Chaudry et al., 2008). The processes are more economical and simple than other processes and recover these metal ions upto 97% or more.

Recovery of Gold

Recovery of gold from low grade minerals and solutions is becoming important, due to the high and inflated price of gold in recent years.

Processes used to recover gold include roasting, pressure oxidation and ultrafine grinding. Grinding is done prior to separation by alloying and amalgamation in pyro-separation techniques.

Leaching may be done by nitric acid, sulphuric acid and also by cyanidation. Extraction is done by SLM or ELM. The processes have been applied to very low concentration leach liquors. NaCN converts Au to NaAu $(CN)_2$ and other impurities or alloying metals to their cyanides. Membrane processes are cheaper and easy to apply after leaching.

Membrane Energy Systems for Clean Energy and Power

Membranes are needed to provide clean energy fuels in preference to classical fossil fuels to avoid emission of polluting gases. Production of fuel gases requires treatment to remove undesired components before marketing in public.

Natural gas stripping is used to remove CO_2 and H_2S components. Membranes processes are used for air enrichment with respect to oxygen to enhance fuel efficiency, as it leads to complete burning of fuel. Membrane systems are also used to remove moisture from welding gases to improve the quality of welding and fuel efficiency. Membrane-based reactors use less energy for production of chemicals.

Membranes are an important component of fuel cell. Proton exchange membranes are an essential component of fuel cell to produce electricity.

Ceramic Membranes for Production of Hydrogen Gas

Pakistan has a lot of coal. Coal gasification is one option to obtain energy. There is a need of enriched air with respect to oxygen to coal gasifier and to separate H_2 from CO_2 or to shift to CO in a membrane reactor. Inorganic ceramic membranes (Chaudry, 2012) do have properties that work at high temperature, 500^{O}C, required in this case. Metal doped silica membranes are used for hydrogen separation. Oxygen can be separated and enriched by membranes systems.

Proton Exchange (PE) Membrane and Fuel Cell

PE membranes are used instead of electrolyte to exchange protons in the inside of fuel cell. The fuel cell is simple and uses less space. Hydrogen is fed to anode and oxidised to protons, which pass through proton exchange membrane (PEM). Oxygen is fed to cathode and at catalyst of electrode to get reduced to -OOH and reacts with protons to form water. 4 electrons per molecule of O_2 are consumed at the cathode. Electrons released at anode travel in external circuit and, as such, flow of electric current takes place in the external circuit. Membranes have less ohomic resistance. Hence, ohomic losses are little.

Fuel cells are devices to produce electricity and have efficiency of 60-80%. Hence work on different types of fuel cells is to be carried out in research and educational institutions. This will be one step forward to overcome electric power crisis. More information about fuel cell technology can be gained from Loyselle and Prokopius, 2011; Unnamed, 2007 and Chaudry, 1984.

Recommendations

- PEM fuel cells are more efficient than other fuel cell systems for conversion of chemical energy to electrical energy. The membranes processes are becoming more and more important, due to their simplicity in China, India, Japan, and in many countries of Europe. It is recommended to put the work on fuel cells and membranes on high priority.
- It is recommended to establish at least one Membrane Research Institute inclusive of bio-membrane systems in Pakistan, preferably in Islamabad, keeping in mind futuristic approach to compete with the world.
- Course about membranes and membrane systems should be introduced in all chemistry and chemical engineering departments of different universities.
- PCST may arrange capacity building project in Islamabad, inviting industrial and university professionals and students for their training in membrane field.
- HEC be requested to earmark at least 25 scholarships for Ph.D and M.Phil students in the membrane processes field.
- Clean energy membrane unit processes be introduced in energy and power sector.
- PCST should take a lead to create collaboration of national and international industrial and research concerns to seek international investment in water and environmental sectors.
- International and national seminars and conferences be arranged to invite international professionals and experts of membranes field.
- The expertise, existing in Pakistan, should be utilised by Ministry of Science, Technology and Ministry of Industry and planning Commission.
- Reverse engineering in the membrane field should be started. Membrane-based industries should be encouraged to save energy.
- Funds to an adequate level should be earmarked by Finance Ministry for each year in the national and provincial budgets to develop membranes and membranes processes.

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