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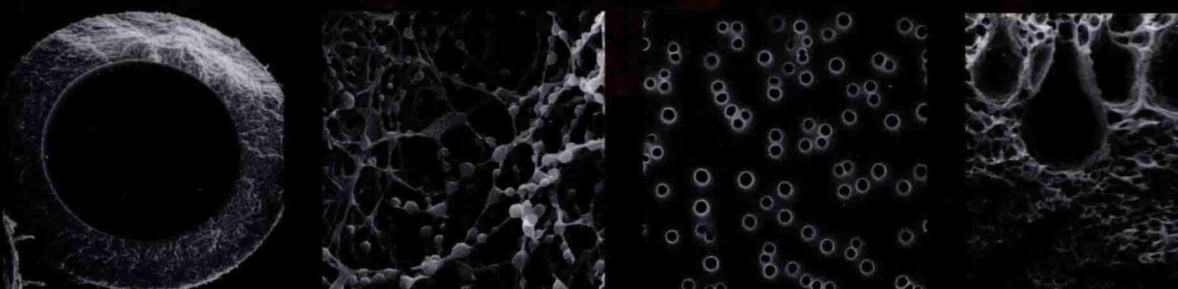
COMPREHENSIVE MEMBRANE SCIENCE AND ENGINEERING



Edited by
Enrico Drioli • Lidietta Giorno

VOLUME

I

Basic Aspects of Membrane Science and Engineering

COMPREHENSIVE MEMBRANE SCIENCE AND ENGINEERING

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Volume 1
BASIC ASPECTS OF MEMBRANE SCIENCE AND ENGINEERING

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COMPREHENSIVE MEMBRANE SCIENCE AND ENGINEERING

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Introduction

The last century has been characterized by a huge resource-intensive industrial development, particularly in some Asian countries, spurred by the growth in the global population level, by a significant elongation of life expectation, and by an overall increase in the standards characterizing the quality of life. These positive aspects of our recent history have been combined however with the emergence of related problems such as water stress, the environmental pollution, and the increase of CO_2 emissions into the atmosphere. These negative aspects of the transformations which have been characterizing our recent progress have been very much related to the momentum at which transformations themselves occurred and to the lack of innovations and introduction of new strategies capable of both controlling and minimizing the relatively obvious negative aspects of industrial development worldwide. A clear example is represented by the wastewater treatment strategy. As illustrated in **Figure 1**, from 1556 until today, the same concept is basically present in various wastewater-treatment systems.

The need to achieve a knowledge-intensive industrial development is nowadays well recognized. This will permit the transition from an industrial system based on quantity to one based on quality. Human capital is increasingly becoming the driving force behind this socio-economical transformation. The challenge of sustainable growth relies on the use of advanced technologies. Membrane technologies are in many fields already recognized as amongst the best-available technologies (BATs) able to contribute to this process (**Figure 2**).

Process engineering is one of the disciplines most involved in the technological innovations necessary to face the new problems characterizing the world today and in the future as well. Recently, the logic of process intensification has been suggested as the best process engineering answer to the situation. It consists of innovative equipment, design, and process development methods that are expected to bring substantial improvements in chemical and any other manufacturing and processing, such as decreasing production costs, equipment size, energy consumption, and waste generation, and improving remote control, information fluxes, and process flexibility (**Figure 3**).

How to implement this strategy is, however, not obvious. An interesting and important case is the continuous growth of modern membrane engineering whose basic aspects satisfy the requirements of process intensification. Membrane operations, with their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, compatibility between different membrane operations in integrated systems, low energetic requirement, good stability under operating conditions and environmental compatibility, easy control and scale-up, and large operational flexibility, represent an interesting answer for the rationalization of chemical and any other industrial productions. Many membrane operations are practically based on the same hardware (materials), only differing in their software (methods). The traditional membrane separation operations (reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF), electrodialysis, pervaporation, etc.), already largely used in many different applications, are today conducted with new membrane systems such as catalytic membrane reactors and membrane contactors. At present, redesigning important industrial production cycles by combining various membrane operations suitable for separation and conversion units, thus realizing highly integrated membrane processes, is an attractive opportunity because of the synergic effects that can be attained.

In various fields, membrane operations are already dominant technologies. Interesting examples are in seawater desalination (**Figure 4**); in wastewater treatment and reuse (**Figure 5**); and in artificial organs (**Figure 6**).

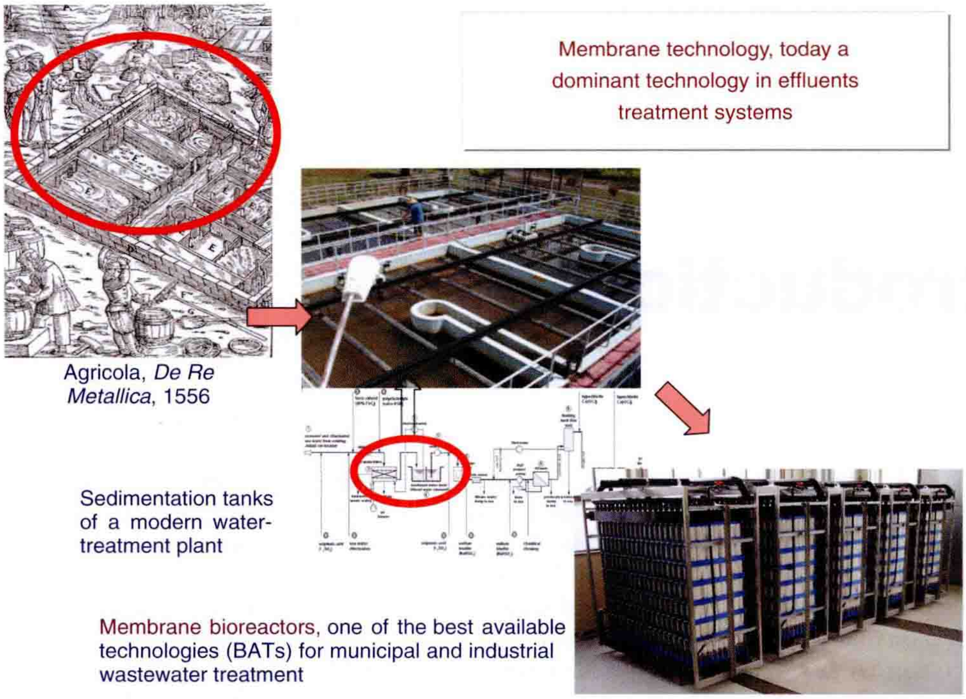

Figure 1 Wastewater-treatment technological approach in the past and today.

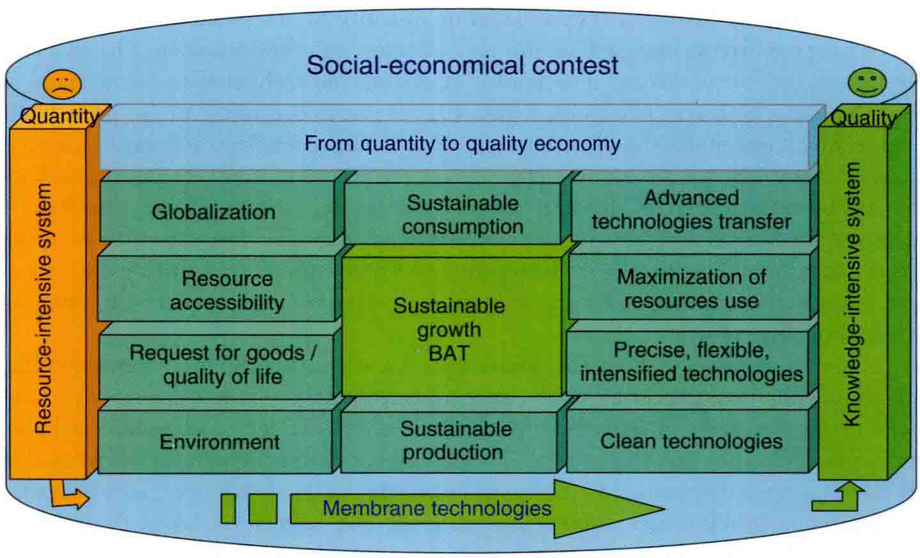

Figure 2 Current social-economical and technological contest driving the transition towards a knowledge-intensive system to guarantee sustainable growth.

It is interesting to consider that a large part of the membrane operations realized today at the industrial level has been in existence in the biological system and in nature ever since life came into being. A major part of biological systems is, in fact, well represented by membranes which operate molecular separations, chemical transformation, molecular recognition, energy, mass and information transfer, etc. (**Figure 7**).

Some of these functions have been transferred at the industrial level with success. We are, however, far away from being able to reproduce the complexity and efficiency of the biological membranes, to integrate the

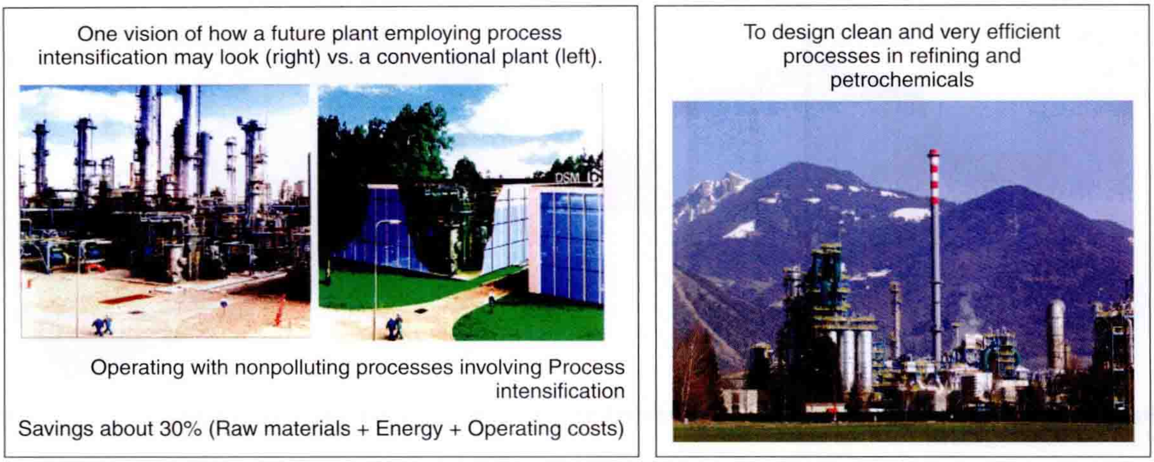

Figure 3 Process intensification strategy. Reproduced from Jean-Claude Charpentier, Modern Chemical Engineering in the Framework of Globalization, Sustainability, and Technical Innovation, Ind. Eng. Chem. Res., Vol. 46, No. 11, 2007.

Figure 4 Membrane desalination plant. RO membrane units from El Paso Desalintion Plant, Texas: the site of the word's largest inland desalination plant (104 000 $m^3\ d^{-1}$). Production costs for water are less than less than 0.36 \$ m^{-3}. From http://www.epwu.org/167080115.

various functionalities, the capability to repair damage, and to maintain for a very long time their specific activities, avoiding fouling problems, degradation of the various functions, and keeping the system alive. Therefore, future generations of membrane scientists and engineers will have to address their attention to understanding and reproducing the astonishing natural systems, which are at the basis of the life with which we are familiar.

In *Comprehensive Membrane Science and Engineering*, we have tried to present and discuss the most relevant results of membrane science and engineering reached during the last years.

Authors from all around the world, senior scientists, and PhD students have contributed to the four volumes covering fundamental aspects of membrane preparations and characterization, their applications in various unit

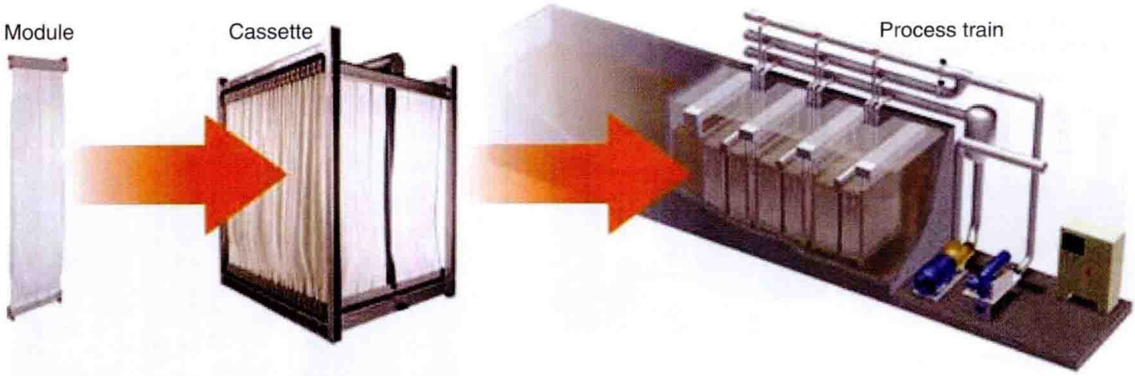

Figure 5 Submerged membrane module for wastewater treatment. From ZeeWeed® Submerged Membrane System, from http://www.gewater.com.

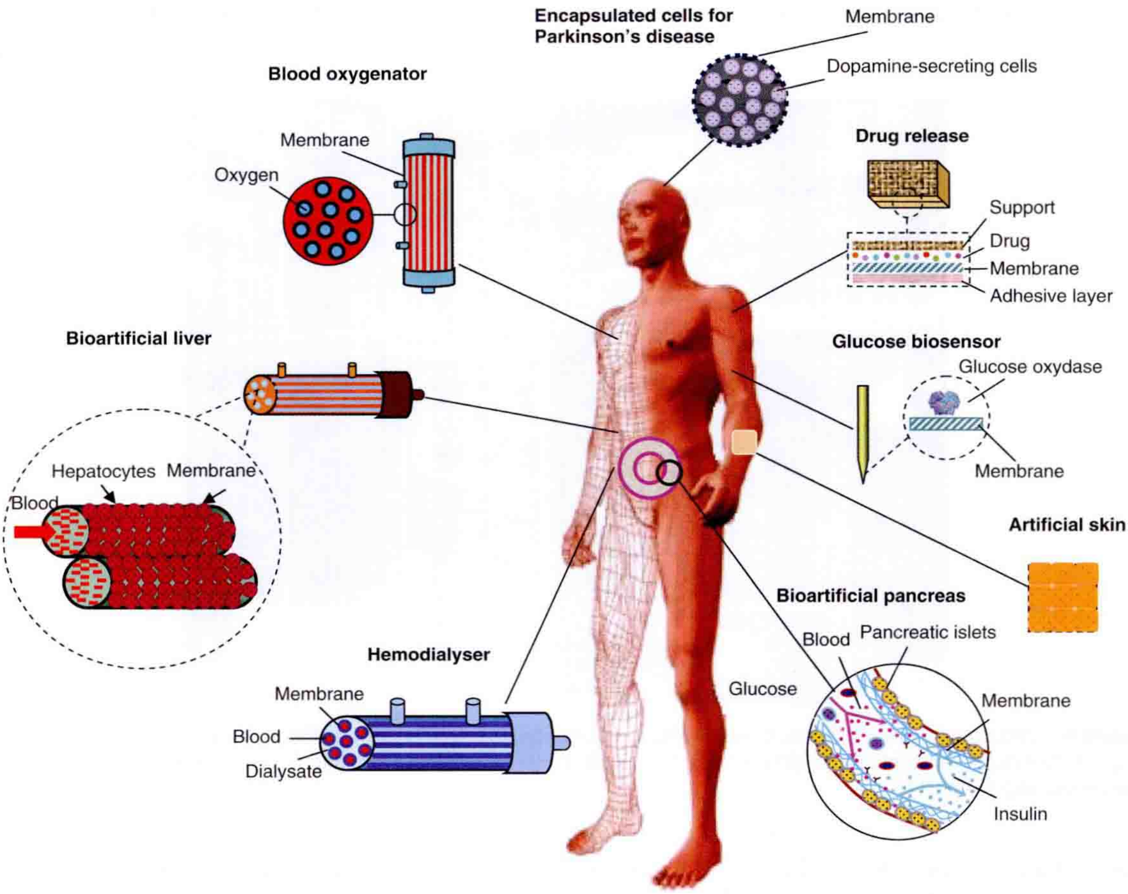

Figure 6 Membranes and membrane devices in biomedical applications. Modified from L. De Bartolo e E. Drioli. "Membranes in artificial organs" In Biomedical and Health Research vol. 16: New Biomedical Materials – Basic and Applied Studies Haris, P.I. and Chapman, D. (Eds.) IOS Press: Amsterdam/Berlin/Tokjo/Washington, (1998) pp. 167–181.

operations, from molecular separation to chemical transformations in membrane reactors, to the optimization of mass and energy transfer in membrane contactors. Their application in strategic fields, including energy, environment, biomedical, biotechnology, agro-food, and chemical manufacturing, has been highlighted.

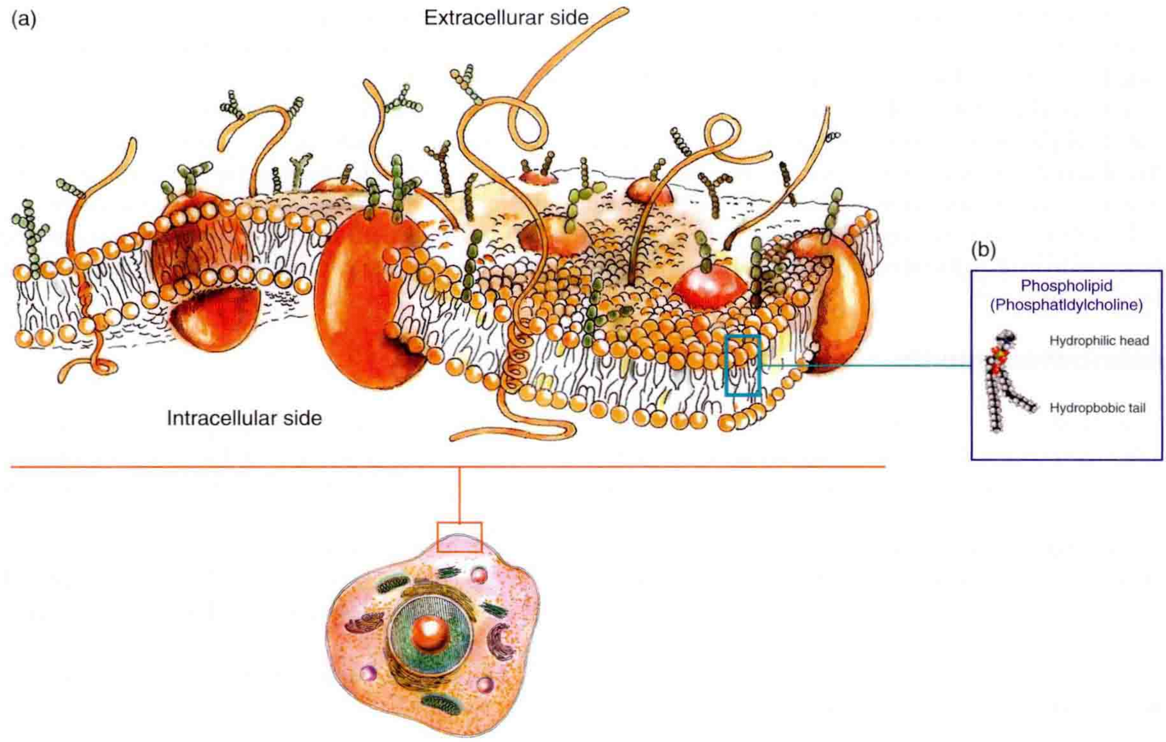

Figure 7 Biological membrane functions. From http://www.mcgraw-hill.it/.

Today, the possibility of redesigning a significant number of membrane operations, introduced via industrial production, is becoming more and more attractive and realistic.

Strong efforts are however necessary for spreading the available knowledge in membrane engineering to the public and for educating the younger generations more and more in the fundamentals and applications of these creative, dynamic, and important disciplines.

With this text we have tried to contribute to these efforts.

In Volume 1, fundamental aspects of the transport phenomena, which characterize permeability and selectivity in molecular separations based on polymeric, inorganic, and mixed-matrix membranes are discussed together with the basic principles for their preparation in various possible configurations (flat sheets, tubular fiber, microcapsules, etc.). The basic methodology generally utilized for their characterization is also discussed.

In Volume 2, the most relevant membrane operations such as the pressure-driven systems in liquid phase (MF, UF, NF, and RO) and in gas phase (gas separation and vapor permeation) together with other separation processes, such as dialysis, pervaporation, and electrochemical membrane systems, are analyzed and discussed in their basic principles and applications.

In Volume 3, the recent interest in the combination of molecular separations with chemical transformations largely present in biological systems is presented. It is important to recall that the industrial development of these membrane reactors and catalytic membrane systems is not yet at the level of the more well-known pressure-driven processes. However, the expectation of a significant fast growth of membrane reactors and membrane bioreactors is very significant. Interesting success, in fact, can already be indicated by the recognition of the submerged membrane reactors such as BAT in municipal wastewater treatment and reuse. The potentialities of this system in the area of bioengineering and biomedical applications are also very attractive, where bioartificial organs, such as bioartificial liver and pancreas, are in some case already at clinical trial level.

Volume 4 is addressed to the description of relatively new membrane operations, where membranes are not required to be selective. Their role is the optimization of the best mass and energy transfer between different phases, acting as membrane contactors. Membrane distillation, membrane crystallizers, membrane emulsifiers,

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1.01 Biological Membranes and Biomimetic Artificial Membranes

L Giorno, R Mazzei, and E Drioli, Institute of Membrane Technology, ITM-CNR, University of Calabria, Rende (CS), Italy

Glossary

Aquaporin Protein system that permits the passage of water through the biological membrane.
Bioartificial synthetic membrane Artificial membrane system that simulates biological membrane.
Biological membrane A complex multifunctional and dynamically structured multicomponent system acting as an enclosing or separating barrier within or around a cell.
Biomembrane Biological membrane.
Biomimetic membrane system Artificial membrane system that biomimics biological membrane.
Integral protein Structural protein of biological membrane.
Phytoalexins Substances used from vegetal cells synthesized in response to pathogen attack.
Phytoanticipin Preformed substances, contained in vegetal cells used for defense against pathogens.

1.01.1 Introduction

The key feature that distinguishes a biological membrane from an artificial membrane is that the biological membrane is extremely selective, precise, and efficient in terms of: recognition properties; regulation of passage of diverse atoms and molecules having diverse physical and chemical properties; signaling and information transmission; response to external physical, chemical, and biochemical stimuli; and self-regulating, self-healing, and self-cleaning properties.

The biological membrane is able to recognize what the cell needs for its survival and accordingly promote the exchange of matter, information, and energy. The cell membrane is able to recognize harmful components and block their passage into the cell or even capture and eliminate them. The cell membrane performs these actions dynamically with the capacity to adapt to new events.

On the other hand, biological membranes would not be able to satisfy industrial production requirements in terms of mechanical stability and productivity, which must be much higher than the ones biomembranes can usually afford. On the contrary, artificial membranes can guarantee sustainable productivity and mechanical stability. In fact, unlike most biological membranes, artificial polymer membranes are very stable and can withstand considerable pressure, essential requirements for practical use, such as industrial production, water purification, and desalination processes. The challenges of man-made membranes are to achieve selective, recognition, and response properties similar to the ones biological membranes can exhibit while maintaining much higher mechanical and production properties.

The biological membrane has evolved through eons and, according to the evolution theory, it represents the most suitable system which adapted to the environment boundary conditions. It can be considered then, basically as the selected result of a long trial-and-error process, which most probably started with much simpler molecules and systems and evolved into the membranes we know today. The ambition is that by a rational approach, one may dare to design and achieve such or better performance and even faster! The challenge is to know how. A holistic systems membrane engineering approach may represent an integrative strategy to advance the current knowledge achieved in the field.

It is worth considering that unlike biological membranes, which are formed on the basis of a very accurate and regulated bottom-up process (able to also correct eventually mistakes that occurred), artificial membranes have been initially developed by very far approach. Nowadays, bottom-up methodologies are being developed, including self-assembling of functional molecules. Still, most industrial applications rely on traditional polymer membranes. However, the advances in knowledge about individual element properties, their resulting functions when assembled in a complex system, as well as about how to prepare complex systems, will aid to move toward biomimetic artificial membranes with advanced efficiency. The term 'biomimetic' is used in the general sense of achieving performance, functions that mimic the biological ones (this can be achieved with the use of biological tools as well as with artificial tools used separately or as integrated hybrid systems).

1.01.2 Biological Membrane

A biological membrane or biomembrane is a complex multifunctional and dynamically structured multicomponent system acting as an enclosing or separating barrier within or around a cell (**Figure 1**). Such a barrier is a selectively permeable structure finely controlling the transport of substances in and out of it, needed for cell survival. The size, the charge, and other chemical properties of atoms and molecules will determine whether they will pass through it. Selective permeability is the essential key feature for effective separation of a cell or organelles from its surrounding. Biological membranes also have certain mechanical and elastic properties. If a particle is too large or otherwise unable to cross the membrane, but it is still needed by the cell, it could either go through one of the protein channels or be taken in by means of endocytosis..

The cell membrane contains a wide variety of biological molecules, primarily proteins and lipids, which are involved in a variety of cellular processes such as cell adhesion, ion channel conductance, cell signaling, and cell signal transduction.

The biological membrane also serves as the attachment point for the intracellular skeleton and,

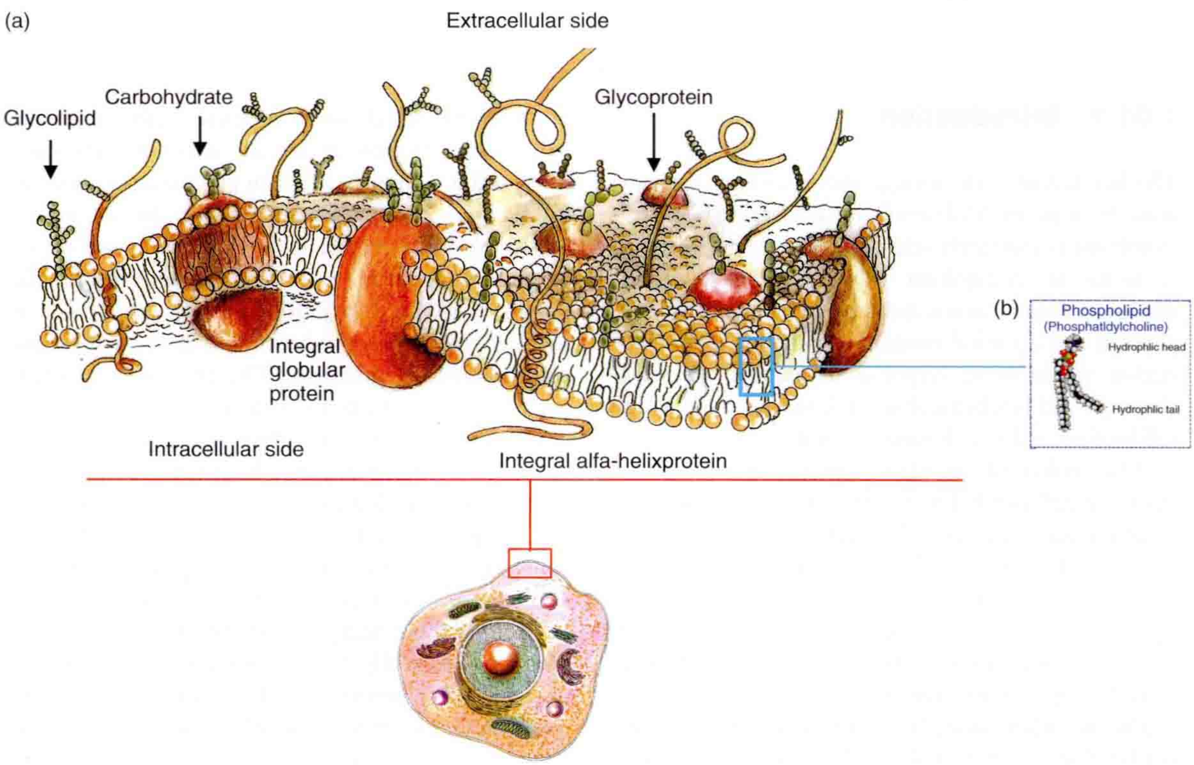

Figure 1 Biological membrane.