

A mathematical elucidation of separation membrane operations and technology of chemical and physical processes: An advanced review

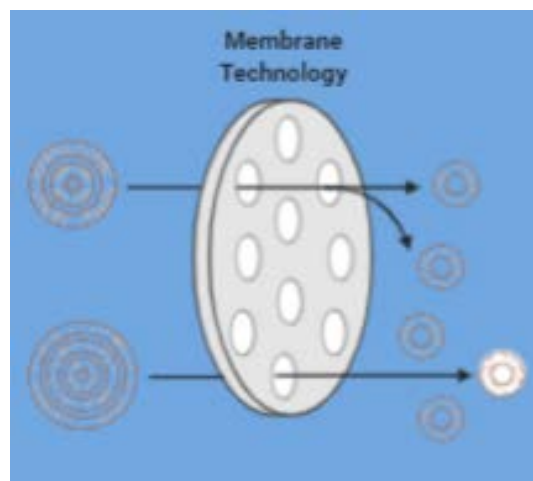
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ABSTRACT

Reviving mathematical elucidation of separation membrane setups, and analyzing actual processes (chemical and physical processes), and illustrating situations that happened during the operations were interpreted distinctly. Mathematical elucidation applies to operations, as well as a broad range of processes used in chemistry and chemical technology concerned with heat, mass and momentum transfer, phase transition, chemical reactions, adsorption, desorption. The strategies were engaged to determine the numerous claims that persisted in the mathematical interpretation of separation membrane operations of chemical and physical processes. The illustrations of mathematical elucidation of various processes help in solving various complications that exist in engineering tasks, process simulation, and designing methodologies, controlling the processing, optimization, determination of parameters, experiment prediction, planning, and diagnosis and troubleshooting. All mathematical elucidation of numerous models were employed to redefine membrane technology. Innovative arenas concerned with membrane technology and engineering were presented as their concerned elucidated equations can be employed for the separation as unit operations. Several efforts have been done and applied to expose the role of membrane engineering in foremost technology such as water desalination or purifications. The authors provide a high grade practical and industry-relevant approach to the subject by highlighting mathematical elucidation of separation membrane technology. This review summarized the poles apart aspects of numerous models such as Schofield's model, Tomaszewska's model, Lawson-Lloyd model, Lagana's model, Yu's model, Hayer's model, Eleiwi's dynamic model, Response surface model, Ali's model, and Cheng's model applied in separation membrane technology along with physical and chemical operations.



Keywords: Mathematical Elucidation, Membrane Technology, Engineering Tasks, Chemistry, and Chemical Technology

INTRODUCTION

In, membrane separation, chemical design, and physical processes involve separating the materials.¹ These separation membrane operations are critical components in balancing the chemical and physical functioning of separation membranes.² The foundations of mathematical elucidation of separation membrane operations covered selection, improvement, and membrane preparation methods. The operative fractionation or separation

technologies are also considered essential for its architecture and in numerous applications.³ Thus, using membrane separation technology is a promising approach to the separation process. The need to achieve a mathematical elucidation of separation membrane operations is nowadays required to develop a framework for sustainable development.⁴ Membrane separation operations differ based on chemical and physical routes, separation mechanisms, and the size of the separated particles.⁵ The applied extensively membrane routes consist of various processes such as ultrafiltration, electrolysis, nanofiltration, microfiltration, reverse osmosis, membrane contactors, dialysis, electrodialysis, pervaporation, gas separation, membrane distillation, and vapor permeation.⁶ Membrane separations can be represented by a mathematical elucidation of separation membrane operations and can be defined as a new type of unit

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operation.⁷ The processes of membrane separation based on the movement of different molecules existed in different phases. These components consist of usually miscible. The separation membrane barrier has the capability to check the hydrodynamic⁸ streams.⁹ The applicability of a mathematical elucidation of separation membrane operations of chemical and physical processes perform under the influence of their thermodynamic potential and pass it because of a driving force exerted, the gradient of the vapor pressure, temperature gradient, term osmosis, dialysis (osmosis, liquid permeation), a gradient in electric potential, and electrodialysis (ion-selective membrane).¹⁰

Membrane distillation processes are mainly applied for wastewater treatment, the separation of water isotopes, desalination the concentration of acid treatment of agro-food, and other applications.¹¹ Here, water is the only main constituent that existed in the supplied solution that is to be separated. The partial pressure existing difference between the feed-membrane interface and permeate-membrane interface represents the driving force of MD.¹² To prevent the penetration of the solution unless the hydrostatic pressure exceeds liquid entry pressure, the aqueous solution on the feed side must be hydrophobic.¹³ Depending on the creation and partial pressure difference between the feed-membrane interface and permeate-membrane interface (which is the driving force in MD)¹⁴, there are various types of membrane distillation, such as direct contact membrane distillation (DCMD)¹⁵ vacuum membrane distillation (VMD) air gap membrane distillation (AGMD) and sweeping gas membrane distillation (SGMD).¹⁶ In DCMD solutions on both feed and permeate sides keep in direct contact with the membrane, and the temperature difference between the two sides create the transmembrane vapor pressure difference that drives the process.¹⁷ DCMD has been successfully applied in desalination, textile wastewater contaminated with dye pharmaceutical wastewater containing taurine wastewater contaminated with heavy metals,¹⁸ and sulfuric acid solutions rich in lanthanide compounds.¹⁹ Besides, DCMD has also been applied successfully to processes where high temperature leads to the degradation of the process fluid. Sakai et al. have used it in practice that is related to the detection of blood concentration. Kimura et al.²⁰ applied DCMD in the concentration of fruit juices.²¹ So far various models have been published to understand and simplify direct contact membrane distillation (DCMD).²² The initial work was published in the 1980s. Since then, 10 models for the DCMD process are developed. In this letter, we are presenting a short description and comparative analysis of the same.²³ The models are compared based on existing parameters i.e. type of variable, use of empirical data, a type of equation employed to describe the process, the probability of this module compartment segmentation, described balances, type of operation process, and type of module geometry.²⁴

However, few membranes exhibited excessive perspective and enhanced environmental performance in many liquid phases.²⁵ Nevertheless, the synthesis, reactions can reduce the need for a complex solvent required during the handling of the operations implemented for chemical and physical processes.²⁶ For example, a high molecular weight molecule transferred from one solvent to

another, concerning the feasibility persisted between two stages during the solvent exchange in complex synthesis, and recycling and use again of homogeneous catalysts.²⁷ During the solvent exchange process, the nanofiltration is illustrated as, fast and effective resources of exchange.²⁸ These exchanges occurred from a high boiling point solvent to a low boiling point solvent.²⁹ A mathematical elucidation of separation membrane operations of chemical and physical processes is a difficult process to define the numerous existing processes.³⁰ The application of a mathematical elucidation of separation membrane operations for chemical and physical processes is as (i) Gas diffusion³¹, The rates of gas diffusion depend on the pore sizes and the molecular weights.³² We may have a molecular, transition, and Knudsen diffusion regions depending on the relative sizes of pore and gas molecules³³ (ii) Microfiltration³⁴ (MF): This refers to membranes that have pore diameters from 0.1 to 10 μm . It is applied to screen deferred particulates and bacteria, from the solution.³⁵ (iii) Ultrafiltration (UF): This process refers to membranes with different pore applied for filtering-dissolved macromolecules.³⁶ This work summarized the different aspects of different models, such as Schofield's model, Tomaszewska's model, Lawson-Lloyd model, Lagana's model, Yu's model, Hayer's model, Eleiwi's dynamic model, Response surface model, Ali's model, and Cheng's model for the evaluation of resistance to filtration due to the cake layer, through physical and chemical operations.³⁷

CLASSIFICATION OF TRANSPORT PROCESSES AND SEPARATION PROCESSES (UNIT OPERATIONS)

In chemical and other physical processing in which the entering feed materials are modified or processed into final products, researchers are trying to derive a mathematical elucidation of separation membrane operations seemingly different from biological processes. Such derivations break them down into a series of separate and distinct steps. These reviving approaches are commonly defined as more descriptive term separation processes common to all types of diverse process industries. For example, the separation process is defined as distillation applied for purifications or separation. The absorption of the oxygen and hydrogen gas occurred during the process of the fermentation and separation that directed the diffusion or mass transfer. Other fundamental mechanisms of the processes such as drying, membrane separation, absorption, distillation, and crystallization also materialized during the aforementioned processes. Heat transfer is the other process that occurred in drying, distillation, and evaporation. The transferor transport processes further classified into different segments such as momentum transfer, heat transfer and mass transfer followed by the process from one phase to another distinct phase.

Therefore, the separation processes covered various processes such as mass transfer include distillation, absorption, liquid-liquid extraction, membrane separation, adsorption, crystallization, and leaching. Therefore, reviving the different aspects of mathematical elucidation of separation membrane operations expresses the chemical and physical processes in the form of questions that will lead the path of innovations.

Classification of Separation Processes

Transfer and change of energy and transforming change of materials are the main components of the separation process primarily by physical-chemical means. The important separation processes, which can be combined in various sequences in a process such as evaporation, drying, distillation, absorption,^{38,39} membrane separation, liquid-liquid extraction, adsorption, ion exchange, liquid-solid leaching,⁴⁰ crystallization, wherein the solute is removed by precipitating and mechanical-physical separation techniques. These processes involve separating different materials of all the states by mechanical processes (filtration, settling, centrifugation). The transport processes covered momentum, heat, mass transfer, and separation processes that can be utilized for mathematical elucidation of separation membrane operations of chemical and physical by applying the concerned principles and techniques for innovations.

MOLECULAR SEPARATION

The mathematical elucidation of basic transport phenomena in separation membrane operations of chemical and physical processes is of a tremendous impact on the separation technique.⁴¹ These mechanisms rely on separation membrane operations of chemical and physical processes, and for selecting the most suitable membrane materials (figure 1).⁴² These approaches also covered the up-gradation of the technique applied for material development. The mathematical elucidation of separation membrane operations should deal with several physical features and phenomena, spanning length scales, thus demanding numerous methodologies.⁴³ The solid frameworks now available mainly rely on the mathematical elucidation of separation membrane operations of chemical and physical process aspects, in which the equation of state models and free volume theories are

applied. This formula is describing thermodynamic and kinetic features, to be united with unfitting transport processes.⁴⁴ Mathematical elucidation of membrane transport henceforth, a distinction is made between the membrane process and a membrane transport model. These specified models are designated to transport across the membrane itself. An accurate membrane transport mathematical elucidation delivers a priori prediction concerning the membrane performance. The elucidation of mathematical separation membrane operations can contribute to a better adoption rate of chemical and physical processes.⁴⁵ These mathematical elucidation tactics are applied in the pharmaceutical industry by enabling the choice of appropriate membranes with a superior foregone conclusion.⁴⁶ Numerous mathematical elucidation models have been anticipated to elucidate the transport of solvent and solutes across membranes. Various examples reported wherein such derivations were applied, for example, one of them is the solution-diffusion model that describes the mathematical description of solution-diffusion models. During the mathematical elucidation of this model, the fluxes of solvents and solutes via the membrane are surmounted.⁴⁷ The membrane permeability coefficients of solvents and solutes were applied during the elucidation of the chemical and physical processes respectively. The mathematical elucidation of the Pore-flow Model⁴⁸ relates membrane transport.⁴⁹ These processes are interrelated to the pressure gradient generated via the membrane. Here, it was noticed that the solvent flow signified the hydrodynamic equation (Hagen-Poiseuille equation) or a modification of it. Solute transport is defined by the "partitioning" equation for measuring the affinity of the solute to the membrane.⁵⁰ It also represents the concentration of the solute the concentration of solute in the pore mathematically. These mathematically elucidated transport equations narrate the rate of solute transport to the membrane pore. The solute-solvent parting procedures occurred because of the difference in the rate of transport of solute and solvent through the membrane pore.⁵¹

The chemical and physical processes happened because of the higher or lower affinity resulting from solute sorption into the membrane pore and then solvent sorption; the Donnan-steric pore model defines by the extended Nernst-Planck equation.⁵² These model equations also describe the hindered transport of ions and solutes that existed just because of the steric and electrostatic hindrance. Donnan-steric pore model assumes that a porous membrane structure with uniform pore sizes pores with tortuosity of unity.⁵³ The negligible concentration of the polarization pores can be charged, and it also depends on the pH and ionic strength of the solution to the membrane.⁵⁴ Generally, the pores have hard walls while the solutes in the model represented by hard spheres. These operations obey the Stokes-Einstein equation.⁵⁵ Here, the solvent performs as a continuum wherein the solvent transport equation accounts that this equation differs slightly from the equation used earlier. The separation membrane operations of chemical and physical processes neglected to consider the direction of pressure drop despite by communicating the pressure drop from the retaining to the saturated side.⁵⁶ In the elucidation of mathematical, the solvent transport equation prescribed only

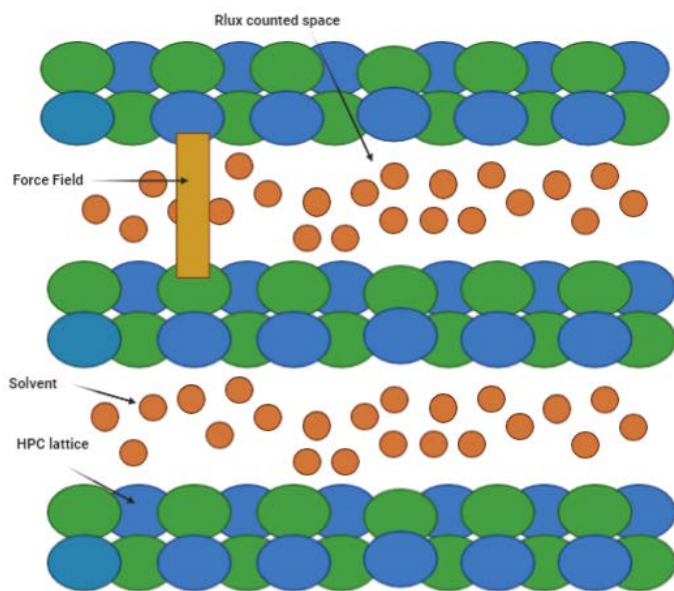


Figure 1. Illustration of the slit pore and solvent molecules in the pore and representing the applied simulation for generating the force field to push the solvent molecules. The number of solvent molecules traversing the reference point to determine the solvent flux through the pore.

straight pores of identical sizes. It is notified here that this derived equation differs slightly from the equation used by Bowen and Welfoot. In this mathematical elucidation of separation membrane operations, the direction of pressure drop is neglected despite expressing the pressure drop from the retaining to the infiltrate side.⁵⁷ The porosity of the membrane has two groups and both of them were neglected while demonstrating in the equation.

The magnitude of water flux fits well interpreted with this Hagen-Poiseuille equation variant; hence and this equation can be recommended as a good model to represent the solvent flow behavior that occurred during the traveling in the membrane pore.⁵⁸ As the quantification of solution viscosity increases, the relative to the viscosity in the bulk solution also increased. The quarantine of solvent molecules in the membrane pore can be defined by the partitioning equation.⁵⁹ It was noticed that the positioning of solvent molecules at the pore wall influenced the dielectric constant. These parameters enhanced the energy barrier of the ion during salvation in the pore. Born model becomes is more significant and can define the mathematical elucidation of separation membrane operations, when an ion is larger, representing the relative difficulty into the pore.⁶⁰ Therefore, the solute transport equation defines solute transport across the pore. As per the hydrodynamic model, the aforementioned mathematical elucidation of separation membrane operations modified to consist of hindered convection.⁶¹ These equations expressed the diffusion within the pores, which was derived from the balance of the chemical potential of a solute. These chemical and physical processes moved along the pore and the drag force on the solute.⁶² The conclusion differs from the outputs of Bowen and Welfoot. The main reason behind it the change in sign resolution for the solvent transference equation used.

REVIEW OF THE MATHEMATICAL MODELING OF THE POPULAR MODELS

Schofield's model in 1987 has first proposed the complete mathematical model for DCMD.⁶³ Using mathematical equations, the model explains mass and heat transfer. The simple structure of the model and the basic mathematical complexity allow its easy and quick use in the simulation of DCMD. The model treats the air trapped in the pores of the membrane as a stationary film and the operation as a steady-state process. But oversimplification, model reliance on empirical correlations, and the use of discrete parameters make this model unfit for process design. However, it can be used for process control and optimization of specific cases and simple DCMD analysis.

The following semi-empirical equation is used to describe the transmembrane⁶⁴ vapor flux⁶⁵;

$$J = \left[\frac{1}{a_{sch} \left(P_M / P_{ref} \right)^{b_{sch}}} + \frac{P_a}{d} \right]^{-1} \Delta P \quad (1)$$

Where a_{sch} is the membrane permeation constant, P_M is the average pressure within the membrane pores, P_{ref} is the reference pressure, b_{sch} is the exponent which defines the influence of

Knudsen diffusion and viscous flow on the vapor flux, P_a is the average pressure of air within the membrane, and d is the membrane molecular diffusion coefficient.

The heat transfer within the membrane can be described as;

If Q_{MC} is the transmembrane conductive heat flux, Q_{MV} is the transmembrane⁶⁴ heat transfer of the vapor, then the transmembrane heat flux Q_M is given by equation⁶⁵;

$$Q_M = Q_{MV} + Q_{MC} \quad (2)$$

$$Q_{MV} = J \Delta H_V = h_V \Delta T_M \quad (3)$$

$$Q_{MC} = \left(k_M^{eff} / \delta_M \right) \Delta T_M = h_C \Delta T_M \quad (4)$$

Where, ΔH_V is the latent heat of vaporization, h_V is the heat transfer coefficient of the vapor, T_M is the membrane temperature, k_M^{eff} is the effective thermal conductivity of the membrane, h_C is the conductive heat transfer coefficient, and δ_M is the membrane thickness.

The heat supplied on the feed side to the interface which supplies both the latent heat associated with vapor flux and the heat loss arising from conduction across the gas-filled membrane can be described by film heat transfer coefficient (h_f). On the permeate side, the heat leaving the membrane can again be described by film heat transfer coefficient (h_p).

$$\text{Therefore, } Q_M = h_f \Delta T_f = h_p \Delta T_p \quad (5)$$

Using the above equations vapor flux simplifies to

$$J = \frac{h_V}{\Delta H_V} \frac{h}{h_V + h_C + h} (T_F - T_P) \quad (6)$$

$$\text{Where, } h_V = \Delta H_V \frac{dP_M}{dT_M} \left[\frac{1}{a_{sch} \left(P_M / P_{ref} \right)^{b_{sch}}} + \frac{P_a}{d} \right]^{-1}$$

$$h = \left(\frac{1}{h_f} + \frac{1}{h_p} \right)^{-1}$$

And

$$h_C = k_M^{eff} / \delta_M$$

The transmembrane vapor flux is affected by viscous flow and diffusion (Ordinary and Knudson diffusion).

In 1994, **Tomaszewska's model** was introduced as 1D Mathematical model for DCMD.⁶⁶ The main distinguishing feature of this model from Schofield's model is the ability to estimate the temperatures and concentrations of the feed and permeates flows along with the DCMD unit. This model is with average mathematical complexity and its equations can be solved numerically. Applications of this model are possible for particular cases such as process design and optimization, where the processes of heat transfer within the DCMD module have been already understood.

In this model, the transmembrane vapour flux is described as follows;⁶⁷

$$J = \frac{\varepsilon_M M D_{VA} P_M}{\tau_M \delta_M R_g T_M} \ln \left(\frac{P_M - P_{VP}}{P_M - P_{VF}} \right) \quad (7)$$

Where, ε_M is membrane porosity, M is molecular weight, D_{VA} is the total diffusion coefficient, τ_M is membrane tortuosity, R_g is universal gas constant, T_M is the average temperature of the membrane, p_{VP} and p_{VF} are the partial pressures of the vapor at the feed-membrane interface and permeate-membrane interface, respectively.⁶⁶

The total diffusion coefficient (D_{VA}) is a result of the combination of the Knudsen diffusion coefficient (D_K) and ordinary diffusion coefficient (say water vapor-air diffusion coefficient, D_{WK}) given as;

$$D_{VA} = \left(\frac{1}{D_K} + \frac{1}{D_{WK}} \right)^{-1}$$

Tomaszewska et al. described the changes in temperature and concentration in the feed and permeate channel.⁶⁷ The equations derived to describe these changes are;

$$dx_{VZ} = \frac{J dA_M (x_{VZ} - 1)}{\dot{m}_Z} \quad (8)$$

$$dT_Z = - \frac{dQ + J dA_M (H_V - C_{HZ} T_Z)}{\dot{m}_Z C_{HZ}} \quad (9)$$

Where, A_M is the surface area of the membrane, x_{VZ} is the mass fraction of water in liquid, \dot{m}_Z is the mass flux of feed or permeate liquid, Q is the total heat, H_V is the enthalpy of vapor, and C_{HZ} is the specific heat of feed or permeate fluid.

These equations can be used to give distributions of temperature and concentration along with the DCMD module. This model is applied for steady-state operations.

In 1996, the Lawson-Lloyd model⁶⁸ was introduced which is based on the dusty gas model (DGM).⁶⁹ One of the basic properties of the DGM is its representation of the solid porous medium as a kind of component of the gas mixture, which consists of giant dust particles (with huge molar weight, motionless under the influence of the virtual external force). This model properly determines the different types of transport modes, which are affecting the transmembrane vapour flux in the steady-state operation of DCMD with the help of DGM. It is static and uses overall integral and algebraic equations with the lumped and discrete parameters. This model is also capable of predicting the effect of the bulk solution temperature difference across the membrane on DCMD performance.⁶⁹ The drawback of the aforementioned model is heat transfer coefficients in the equations which require empirical correlations or experimental data; and cannot determine velocity, concentration, and temperature profiles within the DCMD module. This model is applied for control and process design for specific cases with known conduction of experiments or empirical correlations.

In this model, the viscous flux in porous media has been neglected, and the diffusive vapor flux (for the component i) is given by the following equation⁶⁹;

$$\frac{N_{Di}}{D_{Ki}^{eff}} + \sum_{j \neq i} \frac{p_j N_{Dj} - p_i N_{Di}}{P_M D_{ij}^{eff}} = - \frac{\nabla p_i}{RT_M} \quad (10)$$

Where, N_{Di} and N_{Dj} are i and j component diffusive fluxes respectively, p_i and p_j are i and j component partial pressures respectively, D_{ij}^{eff} is an effective ordinary diffusion coefficient, D_{Ki}^{eff} is a Knudsen diffusion coefficient, and P_M is the pressure of the gas mixture.

In 2000, **Lagana's model** was proposed using the DGM, which is applied for hollow fiber DCMD modules with cylindrical geometry.⁷⁰ In this model, the thickness of the membrane influenced by the difference between the pressures of the liquids and vapour pressure. The penetration within the liquid is assumed as dependent on the transmembrane pressure, which likely to be approached reality. In comparison with the previously mentioned three models (i.e. Schofield's model, Tomaszewska's model, Lawson-Lloyd model), this model was a significant step forward with a more detailed description of the mass and heat balances. All the equations which are being used for transmembrane heat transfer require either empirical correlations or experimental data. Therefore, we can say that this model is kind of empirically dependent model with distributed continuous parameters about the steady-state operation of the DCMD module.

In this model, the transmembrane vapour flux is calculated by applying the DGM⁶⁸;

$$J_{DW} = \left(\frac{1}{D_{KW}^{eff}} + \frac{y_{air} P_M}{D_{WA}^{eff}} \right) \left(\frac{-1}{R_g T_M} \right) \frac{dp_1}{r} \quad (11)$$

Where, y_{air} is the mole fraction of air in the gas mixture, D_{KW}^{eff} is the effective Knudsen diffusion coefficient for the water vapor, D_{WA}^{eff} is the effective ordinary diffusion coefficient for the water vapor and air, r is the radial coordinate, and p_1 is the partial pressure of the water vapor.

And the integral form of the above equation for further calculation is, as;

$$J_{DW} = \frac{D_{WA}^{eff}}{R_g T_{Mavg}} \frac{1}{R \ln \left(1 + \frac{\delta_M}{R} \right)} \ln \left[\frac{y_{W,R+\delta} D_{KW}^{eff} - (D_{KW}^{eff} + D_{WA}^{eff})}{y_{W,R} D_{KW}^{eff} - (D_{KW}^{eff} + D_{WA}^{eff})} \right] \quad (12)$$

Where, $y_{W,R+\delta}$ and $y_{W,R}$ are the mole fractions of the water vapor in the gas mixture at the permeate membrane interface and feed-membrane interface, respectively.

The total transmembrane vapour flow rate for all sizes of pores is calculated using the following equation⁶⁸;

$$F_M = \int_0^\infty J(r_M) \pi r_M^2 f(r_M) dr_M \quad (13)$$

where, r_M is the pore radius.

In 2012, **Yu's model**⁷¹ was introduced based upon the computational fluid dynamics (CFD) approach in the DCM.⁷² In this model heat and mass balance (as in all the previously

mentioned mathematical models of DCMD) are being used, and also describe the momentum balance. This structure allows estimation of the concentration, velocity, and temperature profiles in the feed and permeates domains and overall values for the heat and mass transfer through the membrane. The heat transfer within the membrane depends on heat transfer coefficients which are determined empirically.

In this model, the overall heat transfer coefficient for the hollow fiber module is given by the following expression⁷²;

$$\frac{1}{K_{M+\delta}} = \frac{1}{h_F} + \frac{1}{h_M} + \frac{1}{h_P} \frac{R_{M+\delta}}{R_M} \quad (14)$$

Where $K_{M+\delta}$ is the overall heat transfer coefficient, h_M is the membrane heat transfer coefficient, h_F and h_P are the heat transfer coefficient of the feed membrane interface and permeate membrane interface respectively, R_M is the inner radius of the hollow fiber, and $R_{M+\delta}$ is the outer radius of the hollow fiber.

The membrane heat transfer coefficient is calculated as follows⁷²;

$$h_M = h_{MD} + h_{HL} \frac{R_{M+\delta}}{R_M} = \frac{q_M}{(T_{FM} - T_{PM})} \quad (15)$$

Where, h_{MD} is the heat transfer coefficient due to evaporation and conduction, h_{HL} is the conductive heat transfer coefficient, and q_M is the transmembrane heat flux.

The transmembrane vapour flux is described by the following equation⁷²;

$$J = C_M(P_{MF} - P_{MP}) \quad (16)$$

Where, C_M is the intrinsic mass transfer coefficient, P_{MF} and P_{MP} are pressures at feed membrane interface and permeate membrane interface respectively.

The Yu's CFD model is applied for the steady-state operation. In 2015, **Hayer's model** was proposed based on the CFD approach.⁷³ Some assumptions are established in this model, such as the DCMD process being conducted in a steady-state; the feed liquid is an ideal mixture provided by salty water; the membrane is fully hydrophobic without wetting effects; no air molecules are present in the membrane pores; no solute (salt) is transferred; the no-slip condition is obtained on the membrane surface. In this model, the momentum transfer in both the shell and lumen sides of the membrane is governed by the well-known Navier-Stokes equation jointly with the continuity equation. The most complicated part of this model among all the models is the mathematical structure of this model, considered in this section. The model takes into account the viscous flow, Knudsen diffusion, and ordinary diffusion.

In this model, the following equations describe the transmembrane vapour flux⁷³;

$$N_M = N_V + N_D = u_M C_M - D_{eff} \nabla C_M \quad (17)$$

$$\nabla(D_{eff} \nabla C_M) = 0 \quad (18)$$

$$D_{eff} = \frac{\varepsilon_M}{\tau_M} \left(\frac{1}{D_K} + \frac{1}{D_{WA}} \right)^{-1} \quad (19)$$

Where all symbols and notations are having their usual meanings.

Hayer et al.⁷³ defined and described the momentum, heat, and mass transfer in and through the membrane within the feed and permeate channels⁷³. Therefore, in each point of the DCMD module, the velocity and concentration profiles are calculated, while the temperature profiles are specified for the feed and permeate domains. Despite the promising prospects, this model has major disadvantages (for example), there is no simulation of heat transfer through the membrane, so the temperatures at the membrane surfaces stay the same as in the bulk phases. In particular, it is assumed that only water vapor is within the membrane pores, but it is a rough estimate since air molecules are certainly present within.

In 2016, **Gustafson's stepwise model** was proposed by using a step-wise approach in which the DCMD unit is divided into numerous segments.⁷⁴ For each segment, the mass and heat balances are determined. This model is more useful than one segment model (for example Lawson-Lloyd's model or Schofield's model). Also, the multistep model is more suitable for the optimization of the length of DCMD modules. Hence, this model requires empirical data for an explanation of the heat transfer; but unable to describe the concentration, velocity, and temperature parameters within the DCMD module. Hence, we can say that this model is useful for process design and optimization with well-defined empirical correlations.

The transmembrane mass flux is calculated using the following equation⁷⁴;

$$J = C_M[P_V(T_{FM}, S_{FM}) - P_V(T_{PM}, S_{PM})] \quad (20)$$

Where, C_M is the membrane distillation coefficient, P_V is the water vapor pressure, T_{PM} , T_{FM} are the temperatures of permeate membrane interface and feed membrane interface respectively, S_{PM} and S_{FM} are the salinities of permeate membrane interface and feed membrane interface respectively.

The transmembrane heat flux is described by the following equation⁷⁴;

$$q_M = q_M^V + q_M^C = J \nabla H_V(T_{FM}, S_{FM}) - K_M \frac{T_{FM} - T_{PM}}{\delta_M} \quad (21)$$

Where the symbols and notations are having their usual meanings. The heat and mass transfer coefficients for the feed and permeate channels are calculated from the following correlations⁷⁴;

$$h_{F,P} = Nu_{F,P} \frac{h_{F,D}}{d_h} = (0.023 Re_{F,P}^{0.8} Pr_{F,P}^{1/3}) \frac{k_{F,P}}{d_h} \quad (22)$$

$$K_F = Sh_{F,P} \frac{D_F}{d_h} = (0.023 Re_F^{0.8} Sc_F^{1/3}) \frac{D_F}{d_h} \quad (23)$$

Where, $Nu_{F,P}$ and $Sh_{F,P}$ are the dimensionless Nusselt and Sherwood numbers, respectively, Re is the dimensionless Reynolds number, Sc is the dimensionless Schmidt number, d_h is the hydraulic diameter of the flow channel, D_F is the diffusion coefficient of the solute through the solution, and $k_{F,P}$ is the thermal conductivity of the feed or permeate liquid

Another, **Eleiwi's dynamic model** was proposed based on the dynamic operation of DCMD.⁷⁵ In this model, the 2D advection-

diffusion equations had been used for heat and mass transfer within the DCMD unit. The application of this model in the process design, control, and optimization is limited due to oversimplification and the absence of a description of the mass balances for the feed and permeate side. In this model, the transmembrane vapour flux is described by the equation⁷⁵;

$$J = C_M [P_{MF}(T_{FM}) - P_{MP}(T_{PM})] \quad (24)$$

The membrane transfer coefficient is given by the following equation [31];

$$C_M = 1.064 \frac{\varepsilon_M \tau_M}{\tau_M \delta_M} \left(\frac{M}{R_g T_{Mmean}} \right) \quad (25)$$

And the heat flux through the membrane is given by equation⁷⁵

$$Q_M = \frac{A_M k_M}{\delta_M} (T_{FM} - T_{PM}) + A_M J \Delta H_V (T_{Mean}) \quad (26)$$

Where all symbols and notations are having their usual meanings.

The temperature distribution within the feed and permeate channels is fully described by using this model, however, for the membrane domain, the heat and mass transfer described by the above equations do not fully estimate the temperature and concentration of the water vapor. At the same time, the momentum and mass balances within the feed and permeate channels are not described which makes it impossible to analyze the impact of fluid velocity and concentration on the module efficiency.

Response surface model proposed by Cheng et al. is based on the response surface (RS) methodology.⁷⁶ This model utilizes experimental data between controlled variables and response variables. As valuable factors, the inlet temperatures of the feed and permeate flows, the velocity of the feed fluid, module packing density, and length-diameter ratio were considered as optimization variables. The comprehensive index makes a balance between the permeate flux and thermal energy consumption. This model uses the DCMD process as the “black box” in which the dependence between input and output results is not determined physically. Hence, we can say that it is described numerically based on multiple experiments. It is a fully empirical model that requires experimental data and can be applied only for analysis and optimization of the performance of the already prepared DCMD module in the range of experimental values.

In this model, the transmembrane flux is calculated by the following equation⁷⁶;

$$J = \dot{m}_P / (A_M \tau) \quad (27)$$

Where, A_M is the area of the hollow fiber surface in the lumen side, \dot{m}_P is the mass flow variation on the permeate side over a given period, τ .

The comprehensive index (CI) is calculated by the expression;

$$CI = w_j x_j + w_{prw} x_{prw} + w_{pre} x_{pre} \quad (28)$$

Where, w_j , w_{prw} and w_{pre} are the weight coefficients, x_j , x_{prw} , and x_{pre} are the normalized objectives.

In 2018, **Ali's model was proposed** for the design of DCMD units.⁷⁷ This model is based on a multiple segmentation of the DCMD unit. The numerical procedures use in this model are

similar to Gustafson's model as well as the segmentation method. Ali's model is more suitable for the design and optimization of the DCMD module; than other existing models.

In this model, the transmembrane mass flux⁷⁷ is calculated by the following equation⁷⁸;

$$J = C_M (P_{MF} - P_{MP}) \quad (29)$$

And the transmembrane heat flux is described by the following equation;

$$q_M = K(T_{W,F} - T_{W,P}) = J_M \Delta h_V + \frac{k_M}{\delta_M} (T_{W,F} - T_{W,P}) \quad (30)$$

Where all symbols and notations are having their usual meanings.

MEMBRANE MATERIALS

Nanofiltration (NF) membranes are used for softening of water or hardness removal (Ca^{2+} and Mg^{2+}) from water. NF membranes possess wettability and surface charge as main surface properties.⁷⁹ A high-performance membrane can be acquired on controlling these properties by incorporating nanomaterials into matrices of the host. An increase in surface hydrophilicity by the addition of hydrophilic nanoparticles can lower the fouling of NF membranes.⁸⁰ Integration of carboxylated MWCNTs for modifying polyamide NF membranes has been studied. In a recent study, iron-based nanoparticles significantly retained dye due to strong forces of repulsion between functional groups of nanomaterials and dye.⁸¹ Moreover, these membranes showed better water permeability, hydrophilicity, and antifouling performance. Membrane distillation (MD) is a process for separating mixtures using a microporous hydrophobic membrane (figure 2).⁸² The membrane distillation technique is given preference over conventional methods for separating the mixtures due to their high rejection and their potential in improving energy savings.⁸³

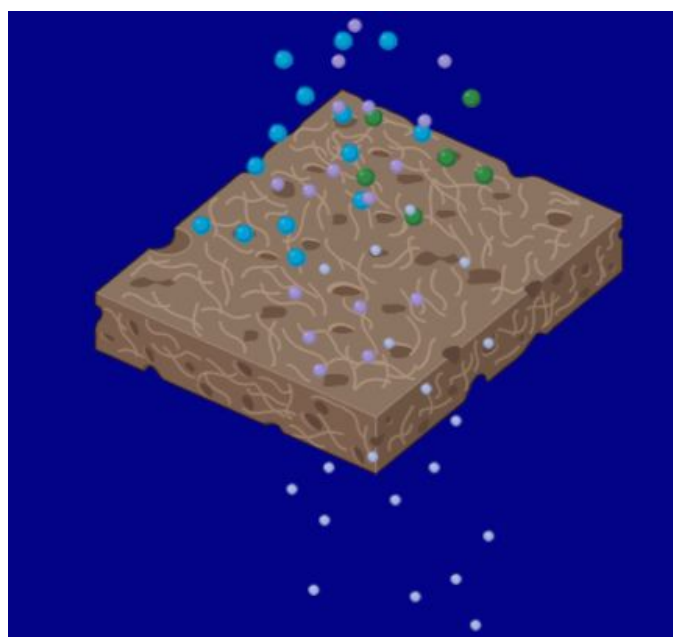


Figure 2. Separation membrane operations of processes.

SURFACTANTS, GRAPHENE-BASED MEMBRANES AND NANOFILTRATION

Pressure-driven membrane separation (PDMS) techniques are used to treat surfactants found in different kinds of wastewaters. Surfactants may affect membrane filtration performance due to their distinct characteristics.⁸⁴ On the treatment of wastewaters having surfactants in PDMS, several studies have been done from the last two decades. The surfactant's effects on the performance of membrane were discussed via two aspects: surfactants' influence on fouling of membrane and increased eradication of pollutants by surfactants.⁸⁵ The characteristics of surfactants were outlined in the solution and at the solid-liquid interface.⁸⁶ In the processes of membrane filtration, the fouling of the membrane is caused by surfactants mostly through concentration polarization, adsorption, the formation of cake, and blocking of the pore. The factors such as properties of the membrane, the composition of feed water, and operation state may influence the degree of fouling.⁸⁷ Moreover, surfactants positively affect the performance of the membrane. In presence of surfactants, increased eradication of different kinds of pollutants by PDMS has been outlined and the mechanism of eradication has been revealed.⁸⁸ More reports were also proposed on membrane fouling by surfactants and increased eradication of pollutants by surfactant aided membrane filtration.

Graphene is a two-dimensional material that exhibits outstanding mechanical, thermal, and electrical properties due to its special one-atom-thick structure.⁸⁹ Graphene and its derivatives (e.g., graphene oxide) are evolving nano-building blocks for separating membranes characterizing different laminar structures and physicochemical properties.⁹⁰ Grapheme-based membranes have attained a special interest from the last few years for purifying gases and water due to their remarkable properties of molecular separation. Graphene constitutes a single layer of carbon atoms organized in an sp^2 -bonded aromatic structure.⁹¹ Delocalized π -orbitals electron clouds occupy the gaps of aromatic rings in a graphene sheet, thus preventing the diffusion of even the smallest molecule, helium. In the pristine state, graphene was therefore tested to be an impermeable material.⁹² However, it was reported that through monolayer graphene protons were able to penetrate. Graphene being impermeable for molecules makes it applicable as a barrier layer for liquids and gases or to protect surfaces of metals against corrosion.⁹³ For molecular separation, a graphene-based membrane has to be organized with nanochannels or nanopores through physical or chemical approaches for the separation of molecules.⁹⁴ In the desalination process, graphene-based materials have outstanding advantages due to their fascinating characteristics, including large surface area, single atomic layer structure, hydrophobic property, richly modified approaches, etc.⁹⁵

Nanofiltration (NF) membranes with ultrahigh permeability and high rejection are the need of the hour to upgrade separation efficacy in desalination and wastewater treatment.⁹⁶ Enhancing the permeability of water despite maintaining the high rejection of the latest and leading-edge thin film composite (TFC) NF membranes

remains a major challenge.⁹⁷ Contamination of water and dearth, due to exasperate by rapid population and economic growth, has evolved to be a global problem. To increase freshwater supply either by seawater/brackish desalination or reuse of wastewater, researchers are steadfast to develop state-of-the-art materials and technologies.⁹⁸ Pressure-driven membrane-based technologies, like nanofiltration (NF) and reverse osmosis (RO), are the most productive and technologically developed among all desalination technologies. Particularly, the non-acceptance of organic molecules and multivalent salts with (MWCO) > 200 Da molecular weight cut-off by NF membrane, makes them an absolute water treatment technology for applications in low energy, high output desalination were monovalent ions with high rejection is not necessary.⁹⁹ Treating industrial process streams, brackish groundwater softening and wastewater decontamination are included in these applications. Thin-film composite (TFC) designs are used to make high developed NF membranes, depositing an active layer of polyamide (PA), made by interfacial polymerization, above a porous support structure likely microfiltration (MF) or an ultrafiltration (UF) membrane.¹⁰⁰ The scalable and cost-effective high-performance membranes with powerful mechanical integrity are produced by such a TFC structure.¹⁰¹ Further increasing the permeability despite managing rate of high-solute rejection can drastically decrease membrane area needed to reach a target water production rate, as a result decreasing NF capital cost and making it economical.

CHARACTERIZATION OF MEMBRANE MORPHOLOGY

The essential part of the research and development of membrane is its characterization. Designing systems and processes of the membrane are dependable on reliable data that relates to the properties of the membrane. It is important to know the properties of the membrane to identify the type of membrane to be used for a certain process.¹⁰² Different membranes demand different techniques for their characterization as their properties and applications vary from one another. The characterization of porous ultra-filtration or microfiltration membranes depends on their pore size, their distribution of pore size, their flux, and the cutoff of their molecular weight.¹⁰³ Membrane material nature (hydrophobic or hydrophilic or having positive or negative charges) and membrane structure contribute other characteristics.¹⁰⁴ Therefore, a horde of research and industrial fields ranging from controlled drug delivery to energy storage is open to appreciate the role of nanoporous materials¹⁰⁵ owing to a comprehensive control on pore size, surface parameters, and their distributions thereby facilitating the enhanced performance of these materials. Pore size, pore distribution, total surface area pore volume significantly channelized the impact of porous material as an efficient catalyst, while also serving as a desirable candidate in the transport phenomenon.¹⁰⁶ The bubble gas phenomenon for the sake of understanding seeks a high interfacial tension parameter γ for gas permeation, which is served better by manipulating the pore size.¹⁰⁷ Techniques such as mercury intrusion porosimetry are employed to analyze and evaluate the pore size distribution and pore volume thereby significantly contributing to the

cataloging of solid and powder materials. Another impactful pore size characterization is done by employing Gas- a liquid equilibrium method, which however has the limitation of characterizing only active pores and recasting the blocked ones.¹⁰⁸ Gas composition and purity oriented techniques play a pivotal role in the applicability part such as pure gas permeation analysis and its interaction with the polymer post equilibrium. Atomic force microscopy (AFM) is a significant characterization tool to study the pore size distribution, surface morphology, and surface chemistry besides also chalking out its electrical properties.¹⁰⁹

The analysis of materials otherwise cryptic to the naked eye is remarkably addressed using the technique of microscopy.¹¹⁰ Microscopy is a technique that has its footing in almost every legion of research from biology to chemical and material sciences. This open-mindedness has almost revolutionized the comparatively novel science called Nanotechnology.¹¹¹ In the section that follows, we take a bird's eye view of various microscopy techniques that are prominently used in the field of nanotechnology.¹¹² Scanning electron microscopy SEM used a highly energetic and target-specific electron beam on the sample under investigation. The interaction between the electrons and particles of the sample read out a specific blueprint that interprets the surface morphology, crystalline size, and orientation.¹¹³ Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate various signals at the surface of solid specimens.¹¹⁴ The signals detected from electron-sample interactions exposed external morphology (texture), chemical composition, and crystalline structure and orientation of materials.¹¹⁵

Transmission electron microscope (TEM) also employs an electron particle interaction rendering a unique imprint of the sample on the fluorescent screen.¹¹⁶ TEM, unlike SEM, exploits the transmittance properties of the sample, hence, giving its internal topology. Atomic force microscopy (AFM) is high-resolution microscopy, resolving to the limit of 1000 times more penetrative than the optical diffraction limit while keeping the working force of the tip constant.¹¹⁷ Ultraviolet-visible spectroscopy presents the absorbance and reflectance characteristics of the sample, giving a detailed wavelength range of absorbing and reflecting peaks in the UV-Vis spectrograph.¹¹⁸ Photoluminescence or PL is principled at excitation and de-excitation accompanied by photon emission.¹¹⁹ It categorizes the sample based on total electron activation energy. Raman spectroscopy relies on inelastic scattering, or Raman scattering of monochromatic light giving out various rotational and vibrational that conform to the materials under survey.¹²⁰ Fourier transform infrared spectroscopy (FTIR)¹²¹ is used to detect different functional groups in the sample.¹²² It gives out the infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas, which corresponds to different attached functional groups.¹²³ X-ray photoelectron spectroscopy (XPS)¹²⁴, also sometimes called electron spectroscopy for chemical analysis (ESCA), is a technique for analyzing the surface chemistry of a material.¹²⁵ It details the elemental composition of the sample. X-ray crystallography is principled at Bragg's law of diffraction. It is a diffraction technique and employed to determine the crystalline

structure of polymers.¹²⁶ Positron annihilation lifetime spectroscopy (PALS), anon-destructive characterization exposed material properties at nanoscale. PALS records the implantation time of the positron on the material and the subsequent emission of annihilation radiation.¹²⁷

CONCLUSION AND FUTURE PROSPECTIVE

There are so many versatility and advantages persisted in the membrane separation techniques which can be used the analysis of configurations and operation modes. Various processes such as food processing, water treatment, pharmaceutical production, biotechnology, energy generation, and many other processes i.e. reverse osmosis, membrane distillation, microfiltration, ultrafiltration, forward osmosis, and nanofiltration can be done only by utilizing membrane separation. The underlying membrane process mechanism is a selective separation accomplished and deals with the physical and chemical differences between a membrane, solute, and a solvent. Various features of the solvent i.e. size, charge, activity, or partial pressure are the other key features that can influence the versatility and advantages of the underlying membrane mechanism. The membrane separation can perform distillation and chemical extraction, with high selectivity, process versatility, and modular design. Therefore, authors presented a mathematical elucidation of separation membrane operations of chemical and physical processes with the latest developments and opportunities concerned to the membrane separation techniques with other details such as (development of membrane separation techniques, optimization methods for improved application of membranes, fabrication and modification of membranes, application of membrane techniques, a case study of membranes applied in industry, characterization of membranes, biofouling of membranes, a novel configuration of membrane processes.

As a conclusion, it is seen that the quality of the models has been improved significantly from the first to the recent studies (Schofield's model, Tomaszewska's model, Lawson-Lloyd model, Lagana's model, Yu's model, Hayer's model, Eleiwi's dynamic model, Response surface model, Ali's model, and Cheng's model) with the increased mathematical complexity and features of the models from 1987 to 2018. Schofield's model is used to evaluate heat flux and transmembrane vapor values and is, therefore, the most evolved models due to its simplicity. The illustration of the transfer of heat and mass is the same in Lawson-Lloyd and Schofield's model. However, the combination of the mass transfer modes in the Lawson-Lloyd model is different from Schofield's model. Unlike Schofield's model and Lawson-Lloyd's model, Tomaszewska's model describes the mass and heat balances within the feed and permeate channels. This model is similar to the Lawson-Lloyd model in terms of the transmembrane mass and heat transfer by using the algebraic equations with lumped distributed parameters. After this, Lagana's model continued the trend in increasing the complexity of the equations for the mass and heat balances. Lagana's model explains transmembrane mass transfer alike the Lawson-Lloyd model by evaluating the integral equation from the DGM. The only model which can be applied for the dynamic operation of the DCMD module is Eleiwi's model.

The model describes the heat transfer in the feed and permeates channels without describing mass and momentum transfer. The type of flow is described by using empirical correlations and coefficients. Among all models, Hayer's model and Yu's model have the highest complexity. These models describe the momentum, mass, and heat transfer in the feed and permeate channels. Ali's model and Gustafson's model use the same approaches which were used in the Lawson-Lloyd model. The segmentation approach is applied by these models when compared to the Lawson-Lloyd model and these models multiply the DCMD module into many linked segments, wherein each segment every compartment is determined in terms of heat and mass balance. In contrast to all the other models, the RS model is an empirical model that is not based on the description of physical phenomena but is using the approximate function to describe the dependence of the results of experiments on the process parameters.

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AUTHOR CONTRIBUTIONS

R.K. conceived the idea and trained the models. R.K. and M.P.C. preprocessed the data. R.K. supervised the project. R.K. and M.P.C. analyzed the results and wrote the manuscript together. M.P.S wrote material and characterization sections. All authors read and approved the manuscript.

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COMPETING INTERESTS

The authors have declared that no competing interest exists.

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